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THE FLUIDITIES AND VOLUMES OF SOME NITROGENOUS ORGANIC COMPOUNDS. XXX[1]

BY EUGENE C. BINGHAM, HENRY S. VAN KLOOSTER,
AND WALTER G. KLEINSPEHN

Introduction

In previous papers[2] the atomic constants have been given for a number of the elements, which enable us to calculate the temperature required to give a compound a certain fluidity. It was a matter for regret that the data at hand did not permit the calculation of the constant for nitrogen. We have now studied the fluidity and density of a number of nitrogen compounds from 0° to 100° C in order that we might get some idea of the value of this constant.

Preparation and Purification of Materials
A Comparison of Densities of Samples

1. *Phenylcyanide.*—The sample was prepared from lead thiocyanate. The densities were determined as follows:

TABLE I

Temp. Deg.	ρ $t/4°$	ρ Perkin[3] p. 1206
0	1.0209	
10	1.0128	1.0138
20	1.0038	1.0048
40	0.9866	
60	0.9687	
80	0.9514	
90	0.9418	
100	0.9319	

Corrected boiling point 190.7°, Kahlbaum 190.6°, Perkin 190.7°.

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[1] Contribution from the Gayley Chemical and Metallurgical Laboratory of Lafayette College.

[2] Am. Chem. Jour., 43, 287 (1910).

[3] Jour. Chem. Soc., 69, 1025 (1896). *Quoted values often obtained by interpolation.*

2. *Orthotoluidine.*—Two samples were used.

A. Kahlbaum's product was purified and distilled.

B. A laboratory sample was repeatedly redistilled.

TABLE II

Temp. Deg.	ρ Sample A	ρ Sample B	ρ Jaeger[1] p. 149	ρ Perkin p. 1210
0	1.0155	1.0153	1.0135	
10	1.0074		1.0055	1.0063
20	0.9989	0.9988	0.9965	0.9980
30	0.9904		0.988	0.9901
40		0.9823	0.980	0.9819
50	0.9735		0.973	0.9734
60		0.9656	0.9653	
70	0.9572		0.9575	
80		0.9489		
90	0.9403			
100	0.9313	0.9313	0.934	

The boiling point of Sample B was determined (with a thermometer reading to fifths of a degree) to be constant at 198.2° corrected. Jaeger[1] gives 197.4° p. 149 and Perkin 199°–200° p. 1210.

3. *Aniline.*—Three samples of aniline were tested. Sample A was from Kahlbaum's aniline sulphate, Sample B was a purified and distilled sample of Kahlbaum's aniline, and Sample C was a laboratory sample purified and distilled. The densities were as follows:

TABLE III

Temp. Deg.	ρ Sample A	ρ Sample B	ρ Sample C	ρ Jaeger p. 144	ρ Perkin p. 1207
0	1.0391		1.0390	1.038	
10	1.0307				1.0291
25			1.0173	1.016	1.0161
30	1.0130			1.012	
50		0.9950	0.9958	0.9945	
60	0.9872				0.9851
70		0.9766		0.976	0.9749
75			0.9735		0.9698
100		0.9513	0.9516	0.949	0.9495

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[1] Zeit. anorg. Chem., 101, 149 (1917).

Sample A boiled constant to 0.01° at 182.7° corrected. Sample B boiled constant at 182.8°. Jaeger p. 144 and Perkin p. 1207 both give 184°.

4. *Diethylaniline.*—A sample from Kahlbaum, containing only traces of water, gave a boiling point which was constant to within 0.1°. It was fractionated four times, however, the final distillate being almost colorless. The boiling point, read on a thermometer reading to single degrees and tested against pure aniline, was found to be 212° corrected. Perkin gives 216–216.5° p. 1208. Ullmann[1] gives 215.5°.

The densities observed are as follows:

TABLE IV

Temp. Deg.	ρ	ρ Perkin p. 1208
5	0.9496	
10	0.9421	0.9422
20	0.9340	0.9340
40	0.9179	
60	0.9017	
80	0.8854	
98	0.8710	

5. *Dimethylaniline.*—Two samples of different origin were used for the determinations of density and viscosity. Sample A was the purest commercial product of Baker and Adamson, while Sample B was a Kahlbaum product. They were similarly purified by drying over lumps of KOH, fractionating twice, freezing out twice in melting ice, m. p. 2.1° which agrees well with Jaeger p. 148, 0.5°, and Ullmann p. 444, 2.5°. An attempt was made to purify still further by transformation of the product into trimethylphenylammonium iodide and then decomposing the iodide by heating in a stream of dry hydrogen chloride, as recommended by Merrill,[2] but there resulted the production of aniline hydrochloride as shown by the aniline reaction with calcium hypochlorite. This confirms the observation of Lauth.[3] The density and

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[1] Encyclop. techn. Chem., **1**, Berlin (1914).

[2] Jour. prakt. Chem., **17**, 286 (1878).

[3] Comptes rendus, **76**, 1209 (1873).

viscosity of this Sample C were also abnormal $\rho\,{}^{0}/_{4} = 0.9830$ instead of 0.9726. The method was therefore abandoned.

The Samples A and B were free from aniline and methylaniline as indicated by calcium hypochlorite and acetic anhydride. The corrected boiling points found were A 192.40°, B 192.37°; f. Jaeger p. 148, 191°, Perkin p. 1207, 193°, Ullmann p. 444, 192.5°. The densities were as follows:

Table V

Temp. Deg.	ρ Sample A	ρ Sample B	ρ Jaeger	ρ Perkin
0	0.9724	0.9729		
10		0.9646		0.9654
20	0.9565	0.9566	0.956	0.9570
30		0.9479	0.948	0.9493
40	0.9398	0.9397	0.940	0.9410
50	0.9318		0.931	0.9327
60	0.9235	0.9235	0.922	0.9245
70		0.9152	0.914	0.9162
80	0.9067		0.905	0.9077
90		0.8982	0.897	0.8991
98		0.8918		

6. *Monoethylaniline.*—A Kahlbaum sample was dried over K_2CO_3 and distilled twice. The sample gave no test for aniline. The corrected boiling point was 203.6°; cf. Perkin p. 1208, 205–206° and Ullmann 204°. The densities observed were:

Table VI

Temp. Deg.	ρ	ρ Perkin
0	0.9782	
10		0.9675
20	0.9616	0.9594
40	0.9450	
60	0.9282	
80	0.9114	
90	0.9026	
100	0.8948	

7. *Monomethylaniline.*—Sample A (Kahlbaum) was dissolved in dilute HCl, and a solution of $NaNO_2$ added to the

aqueous salt solution cooled in ice, as described by Nölting and Boasson.[1] The resulting nitroso compound was taken up in ether, the ether distilled, and the nitroso compound reduced with tin and HCl. The methylaniline, regenerated in this way, was taken up in ether, dried over granulated K_2CO_3, the ether distilled, and the compound fractionated three times. Sample B was the original Kahlbaum product, fractionated three times. The results were identical both in respect to boiling point and density. The boiling points were A 194.7°, B 194.8°; cf. Jaeger p. 146, 195.5° and Perkin p. 1207, 195.5°. The densities were:

TABLE VII

Temp. Deg.	ρ Sample A	ρ Sample B	ρ Jaeger p. 146	ρ Perkin p. 1207
0.3	1.0027		1.015	
10.0	0.9951			0.9943
20.0	0.9868	0.9868		0.9864
30.0		0.9783	0.985	
40.0		0.9703		
50.0		0.9622	0.9644	
60.0	0.9538		0.958	
70.0		0.9456	0.947	
80.0	0.9371		0.937	
100.0	0.9202		0.9195	

8. *Nitrobenzene.*—A laboratory sample was dried and twice distilled. Corrected boiling point 209.3°; cf. Jaeger p. 112, 209° and Perkin p. 1180, 210.8°. The densities were as follows:

TABLE VIII

Temp. Deg.	ρ	ρ Jaeger	ρ Perkin
10	1.2138	1.210	1.2130
20	1.2037		1.2033
30	1.1934	1.194	1.1937
40	1.1836	1.185	1.1838
50	1.1734		1.1739
60	1.1636	1.166	1.1638
70	1.1537	1.155	
90	1.1334		
100	1.1232	1.125	

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[1] Ber. deutsch. chem. Ges., 10, 795 (1877).

Fig. 1

The densities are all determined in the pycnometer illustrated in Fig. 1, which has the advantage that it can be employed satisfactorily at temperatures below the room temperature. It is so compact that it occupies little space and exposes little surface, is not readily broken and is convenient to manipulate. The instrument is filled to the mark between the two bulbs by means of a capillary pipette used in filling the viscometer. While the instrument is suspended in the constant temperature bath any surplus liquid is removed. As the liquid warms up to room temperature, the liquid expands into the smaller bulb, but is prevented from vaporizing by means of the capillary tube above this bulb and the stopper of the instrument, which is not shown in the figure. The instrument is calibrated by weighing the instrument filled with water at the various temperatures. The formula for the density then becomes

$$\rho_{\frac{t^\circ}{4^\circ}} = \frac{w'}{w} \cdot \mathrm{D} - 0.0012 \frac{w' - w}{w}$$

where w' = weight of liquid at t° C
w = weight of water at t° C
D = density of water at t° C

Viscosity Measurements

The viscosities of the samples were determined in duplicate by the method which has been described elsewhere.[1] The results are given in the following tables, in which p is the corrected pressure in grams per square centimeter, P is the pressure used solely in overcoming viscous resistance, η is the viscosity expressed in centipoises, φ is the fluidity in absolute units. The constants of the instrument have already been given and were repeatedly tested during the investigation. The viscosity is given by the equation

$$\eta = \mathrm{C\,P}\,t = 1/\varphi$$

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[1] Bulletin 298, U. S. Bur. of Standards.

and the loss in pressure-head in imparting kinetic energy to the liquid is

$$p - P = \frac{C'}{C} \cdot \frac{p}{t^2}.$$

With more viscous liquids and slower rates of flow it was found necessary to exclude dust particles with great care, otherwise the duplicate measurements would not agree as closely as the method would warrant.

The viscosity of aniline has been determined by Faust,[1] by Thole, Mussell and Dunstan[2] and also by Drapier.[3] These values do not agree well among themselves. Our own values accord with those of Drapier. Our values for nitrobenzene are also in accord with the values obtained by him.

Table IX.—Phenylcyanide

Limb	Temp. Deg.	Time Sec.	p	P	η in cp.	φ
L	0.26	585.1	234.64	234.14	1.957	51.10
R	0.29	584.2	235.04	234.54	1.957	51.09
L	10	482.9	234.64	233.92	1.614	61.97
R	10	482.7	235.02	234.30	1.616	61.90
L	20	287.3	325.57	323.56	1.328	75.30
R	20	288.4	325.97	323.96	1.332	75.08
L	20	287.6	325.57	323.56	1.329	75.22
L	30	245.8	325.57	322.83	1.134	88.22
R	30	245.4	325.99	323.15	1.133	88.27
L	40	214.0	325.56	321.98	0.9843	101.59
R	40	213.5	325.96	322.38	0.9833	101.70
L	50	261.7	233.49	231.12	0.8641	115.73
R	50	261.1	233.88	231.51	0.8635	115.80
L	60	233.1	233.50	230.53	0.7677	130.27
R	60	232.5	233.90	230.93	0.7670	130.38
L	70	209.8	233.50	229.86	0.6889	145.15
R	70	208.6	233.90	230.26	0.6862	145.73
L	80	190.6	233.27	228.91	0.6233	160.44
R	80	189.9	233.67	229.31	0.6221	160.75
L	100	183.5	210.10	196.48	0.5151	194.15
R	100	182.5	201.50	196.88	0.5133	194.81
L	100	183.5	201.10	196.48	0.5151	194.15

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[1] Zeit. phys. Chem., **79**, 97 (1911).

[2] Jour. Chem. Soc., **103**, 1108 (1913).

[3] Bull. Acad. roy. belg., **1**, 621 (1911).

TABLE X.—ORTHOTOLUIDINE

Sample	Limb	Temp. Deg.	Time Sec.	p	P	η in cp.	φ
A	L	0.30	1719.3	412.06	412.00	10.12	9.882
	R	0.32	1712.9	412.48	412.42	10.09	9.909
	L	10	1092.1	412.03	411.89	6.426	15.56
	R	10	1091.7	412.42	412.28	6.430	15.55
	L	20	746.6	411.52	411.22	4.386	22.80
	R	20	744.6	411.86	411.56	4.378	22.84
	L	30	541.7	411.92	411.62	3.185	31.39
	R	30	541.3	412.26	411.96	3.186	31.39
	L	30	542.1	411.92	411.62	3.188	31.37
	L	50	329.0	410.13	408.63	1.920	52.07
	R	50	328.5	410.53	409.03	1.920	52.10
	L	50	328.5	410.13	408.63	1.918	52.15
	L	70	224.2	410.17	407.00	1.304	76.71
	R	70	223.4	410.55	407.38	1.300	76.92
	L	90	165.0	410.16	404.28	0.9529	104.94
	R	90	164.7	410.53	404.65	0.9521	105.04
	R	100	180.5	326.50	321.77	0.8297	120.52
	L	100	181.1	326.90	322.17	0.8335	119.98
	R	100	180.4	326.50	321.77	0.8293	120.60
B	L	20	744.8	414.36	414.06	4.406	22.70
	R	20	743.2	414.70	414.40	4.399	22.73
	L	30	542.4	414.32	414.02	3.208	31.17
	R	30	541.3	414.66	414.36	3.204	31.21
	L	40	412.4	414.08	413.12	2.434	41.09
	R	40	412.7	414.48	413.52	2.438	41.02
	L	60	266.6	414.07	411.85	1.569	63.75
	R	60	270.0	414.45	412.23	1.590	62.89
	L	60	267.9	414.05	411.83	1.576	63.45
	L	80	189.9	413.93	409.55	1.111	90.01
	R	80	189.1	414.33	409.95	1.107	90.30

TABLE XI.—ANILINE

Sample	Limb	Temp. Deg.	Time Sec.	p	P	η in cp.	φ
A	L	0.5	1781.9	394.97	394.92	10.05	9.947
	R	0.5	1777.1	395.85	395.80	10.05	9.952
	L	10	1149.9	395.43	395.30	6.494	15.40
	R	10	1148.6	395.81	395.68	6.493	15.40
	L	20	784.7	395.37	395.10	4.428	22.58
	R	20	784.5	395.70	395.43	4.431	22.57
	L	30	569.6	395.13	394.62	3.211	31.14
	R	30	573.1	395.65	395.14	3.235	30.91
	L	45	383.5	395.03	393.90	2.158	46.34
	R	45	382.9	395.50	394.37	2.157	46.37
	L	60	277.6	395.10	392.98	1.558	64.17
	R	60	277.2	395.50	393.38	1.558	64.20
	L	80	196.2	394.96	390.79	1.094	91.34
	R	80	196.0	395.43	391.26	1.095	91.28
	L	98	164.1	364.22	358.37	0.8403	119.0
	R	98	163.3	364.59	358.74	0.8368	119.5
B	L	5.0	1438.4	399.52	399.44	8.2101	12.18
	R	5.0	1433.6	399.83	399.75	8.1900	12.21
	L	15	943.1	399.43	399.24	5.379	18.59
	R	15	938.9	399.8	399.6	5.360	18.66
	L	25	669.4	399.41	399.04	3.816	26.21
	R	25	661.4	399.81	399.44	3.773	26.50
	L	25	658.7	399.41	399.04	3.755	26.63
	R	35	495.4	399.43	398.88	2.823	35.42
	L	35	496.2	399.79	399.24	2.830	35.34
	R	35	495.9	399.43	398.88	2.826	35.39
C	L	0.5	1739.6	405.18	405.13	1.0068	9.932
	R	0.5	1737.5	405.44	405.39	1.0050	9.950
	L	10	1121.0	405.20	405.06	6.472	15.45
	R	10	1123.5	405.51	405.37	6.506	15.37
	L	30	555.9	406.20	405.66	3.222	31.04
	R	30	556.1	405.52	404.98	3.217	31.08
	L	60	271.6	406.24	404.02	1.568	63.79
	R	60	270.9	405.60	403.38	1.561	64.06

Table XII.—Diethylaniline

Limb	Temp. Deg.	Time Sec.	p	P	η in cp.	φ
L	0.5	666.1	404.62	404.27	3.847	26.00
R	0.5	663.6	405.01	404.66	3.836	26.07
L	10	493.9	404.65	404.01	2.851	35.08
R	10	493.2	405.05	404.41	2.849	35.10
L	20	379.1	404.62	403.54	2.185	45.76
R	20	378.4	405.02	403.94	2.184	45.80
L	40	248.1	404.62	402.14	1.425	70.16
R	40	247.7	405.02	402.54	1.424	70.20
L	60	312.1	230.50	228.97	1.021	97.97
R	60	311.8	230.88	229.35	1.022	97.89
L	80	238.6	230.52	227.93	0.7769	128.71
R	80	238.1	230.96	228.37	0.7768	128.74
L	98	194.8	230.57	226.75	0.6310	158.47
R	98	194.2	230.99	227.17	0.6302	158.67

Table XIII.—Mixture 50 Wt. Percent Aniline and 50 Wt. Percent Dimethylaniline

Limb	Temp. Deg.	Time Sec.	p	P	η in cp.	φ
L	0.5	699.8	399.24	398.90	3.988	25.08
R	0.5	699.1	399.64	399.30	3.988	25.08
L	10	523.4	399.22	398.62	2.980	33.55
R	10	522.8	399.58	398.98	2.980	33.56
L	20	403.4	399.22	398.20	2.295	43.58
R	20	403.1	399.59	398.57	2.295	43.57
L	30	321.7	399.21	397.61	1.827	54.72
R	30	320.8	399.61	398.01	1.824	54.82
L	30	321.8	399.21	397.61	1.828	54.71
L	50	221.0	399.20	395.93	1.250	80.00
R	50	220.8	399.60	395.33	1.247	80.19
L	50	223.9	394.11	390.84	1.250	79.99
R	50	223.8	394.53	391.26	1.254	79.76
L	70	167.3	394.11	390.90	0.9343	10.70
R	70	167.3	394.55	391.28	0.9352	10.69
L	70	166.4	394.15	390.88	0.9292	10.76

TABLE XIV.—DIMETHYLANILINE

Sample	Limb	Temp. Deg.	Time Sec.	p	P	η in cp.	φ
A	L	10	359.2	330.20	329.0	1.688	59.23
	R	10	358.6	330.60	329.36	1.687	59.27
	L	20	300.1	330.11	328.35	1.408	71.04
	R	20	300.0	330.48	328.72	1.409	70.98
	L	20	300.4	330.16	328.40	1.414	70.89
	L	30	255.8	331.13	328.72	1.201	83.25
	R	30	255.4	331.50	329.09	1.201	83.28
	L	40	221.9	330.11	326.89	1.036	96.50
	R	40	221.1	330.51	327.29	1.034	96.73
	L	40	221.7	329.9	326.7	1.035	96.64
	R	40	221.3	330.49	327.27	1.035	96.65
	L	60	172.4	330.25	325.06	0.8006	124.9
	R	60	171.8	330.55	325.36	0.7985	125.2
	L	70	154.6	330.14	323.85	0.7152	139.8
	R	70	154.0	330.54	324.25	0.7134	140.2
	L	90	197.7	209.22	205.37	0.5800	172.4
	R	90	196.5	209.69	205.84	0.5778	173.1
	L	90	197.3	209.30	205.45	0.5791	172.7
	L	98	183.8	209.72	205.22	0.5388	185.6
	R	98	182.8	209.33	204.83	0.5349	187.0
B	L	20	380.2	262.26	261.16	1.418	70.50
	R	20	379.2	262.61	261.51	1.417	70.59
	L	40	279.1	262.06	260.06	1.037	96.44
	R	40	278.8	262.55	260.55	1.038	96.36
	L	50	244.6	262.13	259.55	0.9069	110.3
	R	50	244.1	262.49	259.91	0.9043	110.6
	L	60	216.9	262.16	258.90	0.8022	124.7
	R	60	216.0	262.55	259.29	0.8001	125.0
	L	60	217.2	262.14	258.88	0.8033	124.5
	L	80	175.2	262.51	257.61	0.6448	155.1
	R	80	174.1	262.11	257.21	0.6397	156.3

TABLE XV.—MONOETHYL ANILINE

Limb	Temp. Deg.	Time Sec.	p	P	η in cp.	φ
L	0.27	706.2	408.51	408.19	4.118	24.28
R	0.27	709.1	408.89	408.57	4.139	24.16
L	0.27	705.4	408.50	408.18	4.113	24.31
L	10	511.0	408.55	407.93	2.978	33.58
R	10	510.8	408.97	408.35	2.980	33.56
L	20	386.4	408.54	407.47	2.254	44.36
R	20	385.9	408.93	407.86	2.248	44.48
L	40	247.3	408.54	405.97	1.434	69.72
R	40	246.9	408.94	406.37	1.433	69.72
L	60	176.0	408.48	403.50	1.014	98.57
R	60	175.6	408.88	403.90	1.013	98.70
L	60	175.4	408.48	403.50	1.011	98.91
L	80	189.9	286.27	282.06	0.7652	130.69
R	80	189.3	286.67	282.46	0.7639	130.91
L	90	243.9	196.27	193.74	0.6750	148.14
R	90	242.9	196.80	194.27	0.6741	148.34
L	99.67	219.4	196.37	193.27	0.6058	165.08
R	100	218.4	196.40	193.30	0.6031	165.82
L	100	218.4	196.80	193.70	0.6043	165.48

TABLE XVI.—MONOMETHYLANILINE

Limb	Temp. Deg.	Time Sec.	p	P	η in cp.	φ
L	20	401.7	403.20	402.19	2.308	43.33
R	20	402.0	403.60	402.59	2.312	43.25
L	30	315.8	403.16	401.53	1.812	55.20
R	30	316.2	403.60	401.97	1.816	55.07
L	30	314.7	403.20	401.57	1.806	55.39
L	40	257.2	403.20	400.77	1.473	67.91
R	40	259.0	403.68	401.25	1.485	67.36
L	40	256.3	403.18	400.75	1.467	68.15
L	50	265.1	322.92	320.65	1.214	82.35
R	50	265.4	323.13	320.86	1.216	82.20
L	70	265.7	235.52	234.11	0.886	112.54
R	70	264.6	235.98	234.57	0.8867	112.78
L	0.3	794.0	375.18	374.92	4.253	23.51
R	0.3	799.0	375.62	375.36	4.285	23.34
L	10	575.0	375.25	374.74	3.078	32.49
R	10	569.6	375.63	375.12	3.053	32.76
L	20	428.7	375.23	374.34	2.293	43.62
R	20	428.7	375.63	374.74	2.295	43.57
L	40	273.2	374.18	372.02	1.452	68.88
R	40	272.8	374.68	372.52	1.452	68.88

TABLE XVII.—NITROBENZENE

Limb	Temp. Deg.	Time Sec.	p	P	η in cp.	φ
L	0.30	542.5	399.03	398.34	3.086	32.40
R	0.30	542.8	398.06	397.37	3.080	32.46
L	10	441.5	398.96	397.92	2.509	39.86
R	10	442.6	398.06	397.02	2.509	39.85
L	20	356.0	398.27	396.68	2.017	49.59
R	20	355.9	397.32	395.73	2.011	49.72
L	30	298.2	398.08	395.84	1.686	59.32
R	30	297.6	397.25	395.01	1.679	59.57
L	40	254.8	398.14	395.11	1.438	69.55
L	50	222.6	398.06	394.11	1.253	79.83
R	50	222.4	397.24	393.29	1.249	80.06
L	60	195.4	398.13	393.04	1.097	91.18
R	60	194.7	397.26	392.17	1.091	91.70
L	70	471.4	146.66	145.78	0.9814	101.90
R	70	465.4	145.82	144.94	0.9633	103.80
L	70	467.2	146.78	145.90	0.9735	102.73
R	70	465.2	145.91	145.03	0.9635	103.78
L	90	376.8	146.91	145.58	0.7834	127.65
R	90	375.2	146.01	144.68	0.7752	128.99
L	100.5	340.7	146.90	145.29	0.7069	141.46
R	100.5	339.4	146.00	144.39	0.6999	142.89
L	100.5	341.5	146.90	145.29	0.7086	141.13
R	100.5	340.7	146.00	144.39	0.7025	142.34

The fluidity-temperature curves of the different substances are shown in Figs. 2 and 3 as taken from Tables IX–XVIII.

Discussion

Of the compounds studied phenylcyanide has the highest fluidity and aniline the lowest at the higher temperatures. The slopes of the amino compounds are similar, Figs. 2 and 3, but not identical. Thus orthotoluidine and aniline have nearly the same fluidity but the curves cross, the fluidity of aniline increasing faster as the temperature is raised due, presumably, to its higher association which breaks down as the temperature is raised. Monoethylaniline and diethylaniline show the same phenomenon as aniline and orthotoluidine, the monoethylaniline having the higher temperature coefficient as we should expect, since monoethylaniline would be expected to be the more highly associated of the two. The curve for monomethylaniline is closely parallel to monoethylaniline as we should expect, and it of course crosses the curve of diethylaniline. Were these amino compounds unassociated we should expect them to have not only the same slope but we should expect a different placing of the curves on the diagram, for as we add methylene groups to the homologues we would look for a constant increase in the temperature

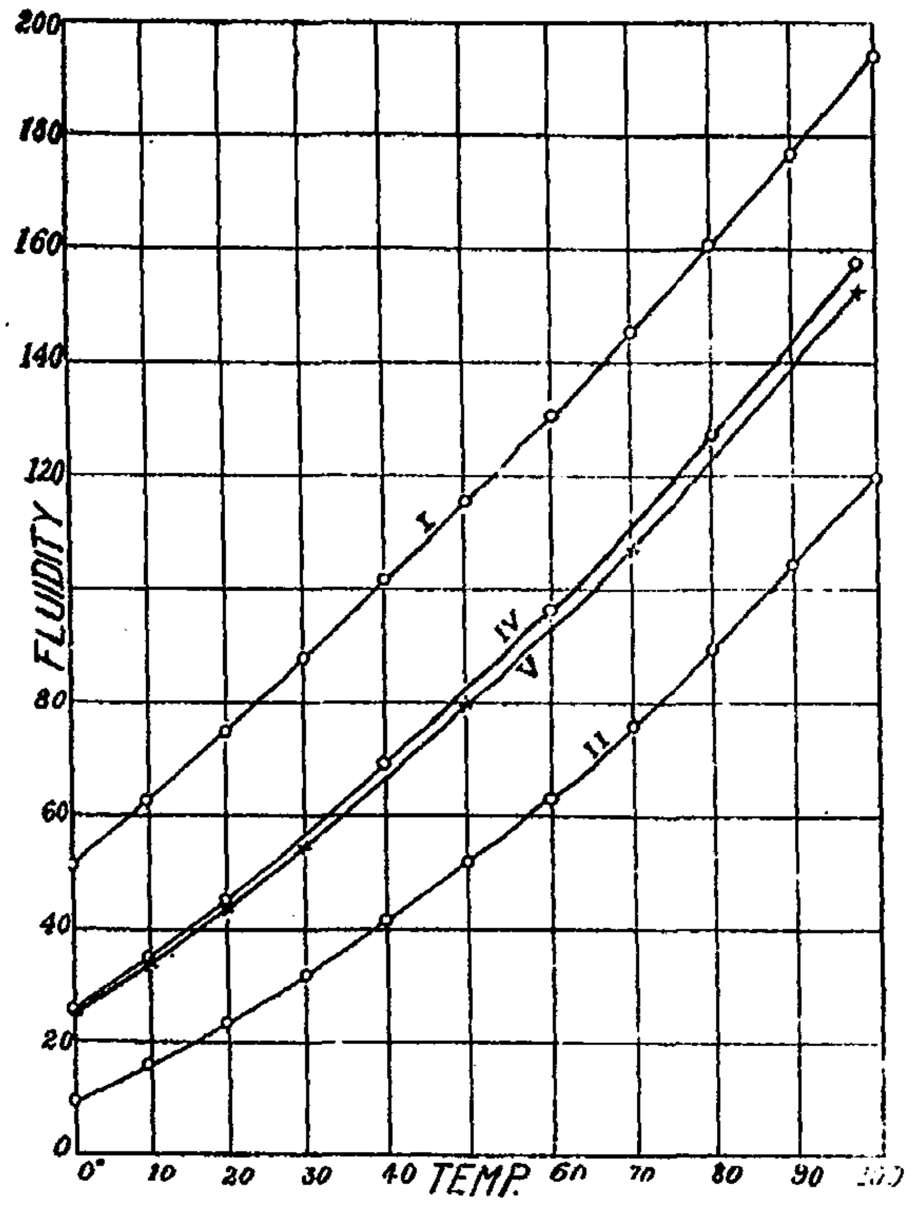

Fig. [illegible]

I Phenylcyanide
II Orthotoluidine
IV Di thylaniline
V Mixture 50 percent by weight aniline with 50 percent dimethylaniline

required to give any given fluidity, as, say, 100 or 200. What we find, however, is that adding a methylene group to the benzene ring in aniline at moderate temperature (55°) is

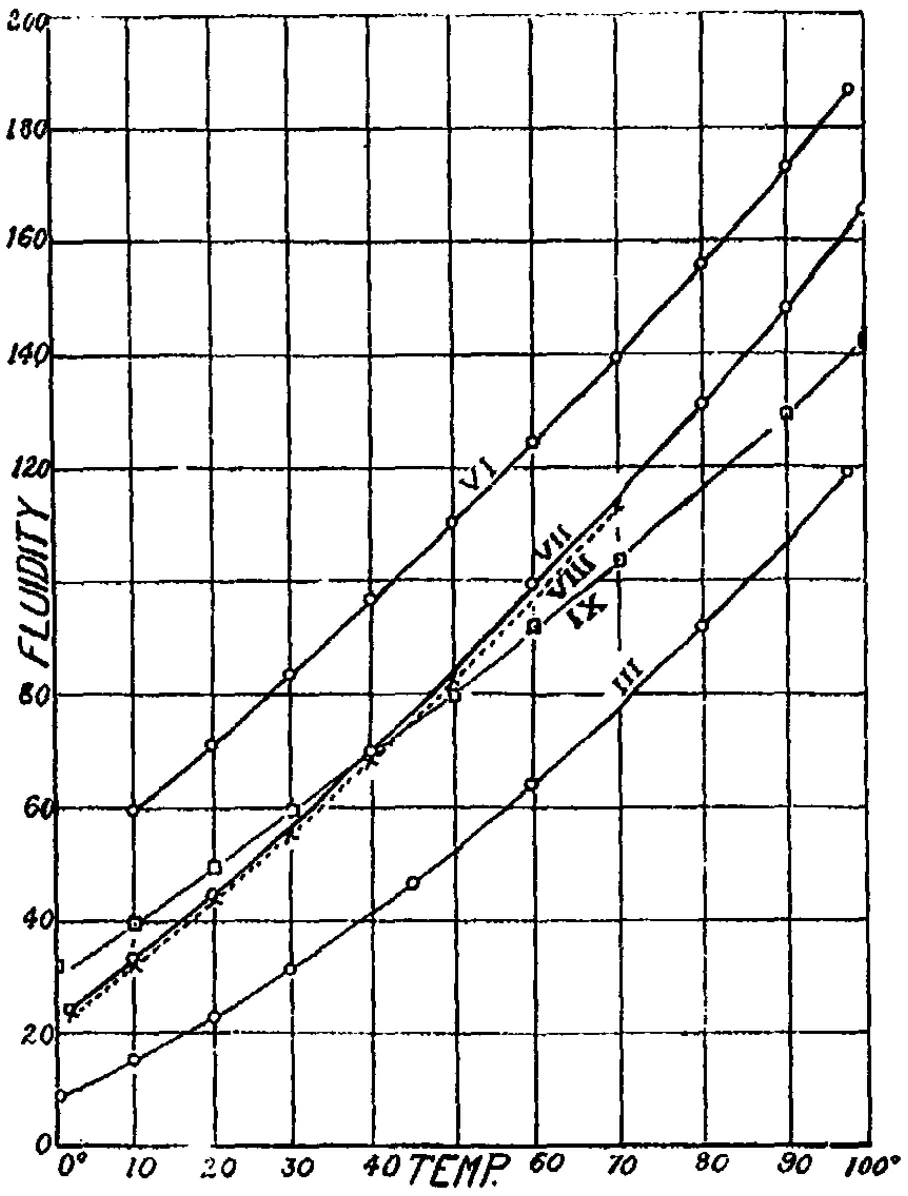

Fig. 3

III	Aniline
VI	Dimethylaniline
VII	Monoethylaniline
VIII	Monomethylaniline
IX	Nitrobenzene

without effect, since the association of the aniline is decreased just sufficiently to make up for the increased size of the molecule. But the decrease in the association is comparatively slight so long as the substitution is in the benzene ring, hence the low fluidity of orthotoluidine. When the methylene group is added to the amino group the effect is much greater, and the fluidity is increased thereby over 50% in monomethylaniline. A more logical way of expressing it is to say that the temperature required to give any fluidity is some 20° less, but this is an unaccustomed mode of expression. Monoethylaniline increases the fluidity a little more, but if this side chain were still further lengthened it is safe to predict that there would be a decrease in the fluidity. Of course dimethyl and diethylaniline still further destroy the character of the highly associated ammonia and, as a result, dimethylaniline shows the highest fluidity of all the amines. The association having been largely destroyed already, the further addition of methylene groups can only cause a decrease in the fluidity, and as a matter of fact diethylaniline and monoethyl aniline have curves which cross each other, the temperature coefficient of diethylaniline necessarily being the smaller of the two because diethylaniline is less associated. Higher homologues of diethylaniline would be expected to show a still lower fluidity in a regular manner as the molecular weight increased.

Phenylcyanide has a fluidity-temperature curve which is closely parallel to the curve for dimethylaniline, the phenylcyanide having the highest fluidity of any of the substances studied. This may be due to lack of association or to some other cause, which would produce a larger "free volume."[1] This cannot be settled by a simple inspection. Nitrobenzene, on the other hand, has a low fluidity and the lowest temperature coefficient of fluidity. This, however, does not necessarily indicate lack of association because we expect the slope of the curve to vary from class to class.

According to Batschinski,[2] when we plot the fluidity against the specific volume, we should get linear curves for substances which are unassociated. Of those shown in Fig. 4, phenyl cyanide gives a linear curve except for the two lowest points. Aniline, orthotoluidine, and diethylaniline give

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[1] Jour. Am. Chem. Soc., **36**, 1393 (1914).

[2] Zeit. phys. Chem., **84**, 643 (1913).

curves which deviate from linearity to a greater or less degree.

By extrapolating the fluidity-temperature curves we have obtained the temperature corresponding to a fluidity of 200. These values are given in Column 2 of Table XVIII. Bingham and Miss Harrison[1] have given the values for the atomic absolute temperatures corresponding to this fluidity as C = —95.7, H = 59.2, O = 24.2. In an unsaturated compound, there is compensation[2] for each pair of hydrogen atoms short of complete saturation to an amount of 114.4 which we refer

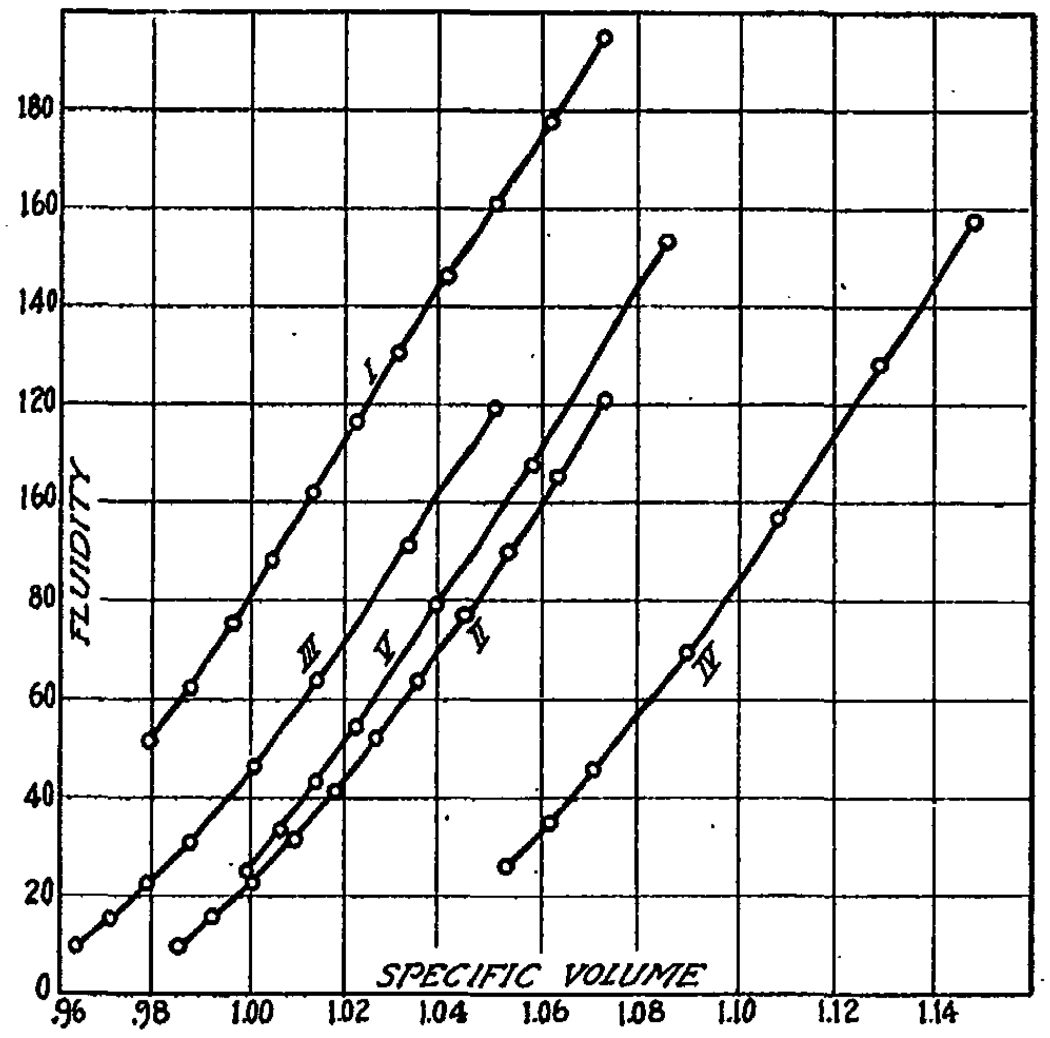

Fig. 4

I Phenylcyanide
II Orthotoluidine
III Aniline
IV Diethylaniline

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[1] Zeit. phys. Chem., 66, 23 (1909).
[2] Am. Chem. Jour., 43, 307 (1910).

to as the value of a double bond, although the term is objectionable. We can now calculate the value of the molecule except for the nitrogen atom as given in the third column of Table XVIII.

TABLE XVIII

THE VALUE OF A NITROGEN ATOM

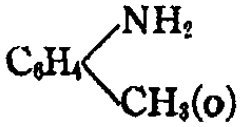
Subst.	Obs. Temp. $\varphi = 200$	Calc. Temp. of residue	Diff.
Phenylcyanide	375.5	312.5	63.0
Orthotoluidine	410.0	320.5	89.5
Aniline	400.0	297.8	102.2
Diethylaniline	392.0	388.6	3.4
Dimethylaniline	378.5	343.2	35.3
Ethylaniline	392.0	343.2	48.8
Methylaniline	394.0	320.5	73.5
Nitrobenzene	412.0	227.8	184.2

We have calculated the values on the assumption that benzene C_6H_6 required 4 pairs of hydrogen atoms to give complete saturation. In phenylcyanide it is necessary to have 2 more pairs.

We find that the difference between the observed temperature and that calculated varies widely, so that it is impracticable at this time to secure a good value for the constant for nitrogen. However, assuming diethylaniline to be non-associated, we may take the value for the nitrogen atom to be 3.4 and then we can calculate the association factors of the other compounds by dividing the observed temperature by the calculated. We get the values which are given in Table IV. Aniline is found to have the highest association of the amines with orthotoluidine coming next in order. Then come in order monomethylaniline and monoethylaniline, followed by dimethylaniline and diethylaniline. This is as we would expect from the known properties of liquid ammonia. Ramsay and Shields, however, have regarded even aniline as non-associated.

The high values for the association of phenylcyanide and nitrobenzene are the most surprising and particularly in

TABLE XIX

Substance	Obs. Temp. $\varphi = 200$	Calc. Temp. $\varphi = 200$	Association Factor
C_6H_5CN	375.5	315.9	1.19
 $C_6H_4(NH_2)(CH_3)(o)$	411.0	323.9	1.27
$C_6H_5NH_2$	400.0	301.1	1.33
$C_6H_5N(C_2H_5)_2$	392.0	392.0	1.00
$C_6H_5N(CH_3)_2$	378.5	346.6	1.09
$C_6H_5N(C_2H_5)$	392.0	346.6	1.13
$C_6H_5NHCH_3$	394.0	323.9	1.22
$C_6H_5NO_2$	412.0	231.2	1.78

the case of the former, one is led to suspect that constitutive influences may be at work which render the value given for the association unreliable. The temperature required to give phenylcyanide a fluidity of 200 is not relatively great and its molecular weight is not small as compared with the other compounds studied. The low calculated value arises from the low constant for nitrogen and the fact that carbon has a constant which is a large negative number. It is possible, therefore, that in cyanides and nitro compounds the constant of nitrogen must be given a special value. Fortunately such constitutive influences have not had to be taken into account heretofore except in the case of the halogens. A much larger amount of experimental material is required to separate completely the effects of association and constitutive influences.

We have measured the fluidity of one mixture of aniline with dimethylaniline over the range of temperature from 0° to 100° C, and we find that at mean temperatures the fluidity lies exactly on the linear fluidity-volume concentration curve. It appears, therefore, that at low temperatures there is a very feeble union between the aniline and dimethylaniline. The union is, however, so very unstable that at higher temperatures it is entirely masked by the dissociation of the aniline, caused by the presence of the dimethylaniline.

Summary

Measurements of the fluidity and densities of various organic compounds containing nitrogen indicate that:

1. Aniline is considerably associated.
2. Substitution of groups in the benzene ring affects the association but slightly.
3. Substitution of groups in the amino group reduces the association progressively.
4. The atomic constant for nitrogen in aniline at a fluidity of 200 is 3.4, but it remains an open question whether it has the same value in nitriles and nitro compounds.
5. Mixtures of aniline and dimethylaniline follow the additive fluidity rule fairly closely.

The authors desire to thank R. B. Karn, M. Marasco, and W. T. Spry for assistance in the experimental part of this investigation.

Easton, Pa.
July 10, 1919

MUTUAL ACTION OF SOLS

BY WILDER D. BANCROFT

If we mix colloidal solutions of two substances, each of which adsorbs the other, the mutual adsorption will have some effect on the adsorption of the peptizing agent. If it causes a decrease in the adsorption of the peptizing agent, this means a decreasing stability of the colloidal solution and may lead to precipitation over some range of relative concentrations. In case this occurs, we shall have colloidal solutions of decreased stability when either colloid predominates sufficiently and precipitation for intermediate relative concentrations. The range over which precipitation occurs may be great or small, depending on the ease with which the peptizing agent is displaced or neutralized. The most familiar case of such precipitation is when we are dealing with two colloids having opposite electrical charges. This point was studied carefully by Biltz[1] and the general statement is to be found in all the text-books on colloid chemistry. The negatively charged colloids studied by Biltz were platinum, gold, selenium, cadmium sulphide, antimony sulphide, arsenic sulphide, stannic oxide, molybdenum blue (Mo_3O_8), tungsten blue (W_2O_3) and vanadium pentoxide. The positive colloids were the oxides of iron, aluminum, chromium, thorium, zirconium, and cerium. Precipitation occurs when each positive colloid is mixed with each negative colloid in proper proportions. Biltz was interested in determining the concentrations at which the most complete precipitation takes place; but he was not especially interested in the rather vague points at which precipitation does not take place. While his data are quite sufficient to show that precipitation is specific,[2] they are hardly adequate to show that the range varies markedly with different substances.

Since a colloid peptized by water may be charged posi-

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[1] Ber. deutsch. chem. Ges., 37, 1095 (1904).

[2] Bancroft: Jour. Phys. Chem., 19, 363 (1915).

tively or negatively, there is no reason why it should not precipitate another colloid under suitable conditions. We usually consider the colloids peptized by water solely as protecting colloids, but this is clearly an inadequate view, as is shown by the experimental data. Years ago Schulze[1] pointed out that small amounts of a gelatine solution were as effective as lime or alum in causing the rapid sedimentation of clay and that addition of minute quantities of gelatine to barium sulphate simplified the question of filtration and washing very much. He, of course, gave no adequate explanation of the phenomenon and the real explanation was given by Billitzer,[2] who called attention to the fact that while gelatine, agar-agar, etc., ordinarily check the precipitation of colloidal solutions by electrolytes, small amounts of these same substances may have a precipitating action. This can be detected even when the gelatine produces no precipitation itself. Billitzer cites the experiments of Neisser and Friedemann in which it was found that a mastic emulsion containing a trace of gelatine was precipitated more readily by sodium chloride than when no gelatine is present. Billitzer finds that gelatine precipitates such negative colloids as antimony sulphide and arsenic sulphide in acid or neutral solution, but does not precipitate positively charged sols such as hydrous ferric oxide. Gelatine in ammoniacal solution precipitates hydrous ferric oxide, though no precipitation occurs if ammonia is added to a mixture of gelatine and ferric oxide. Bismarck brown, which is a positive colloid, is precipitated by an alkaline gelatine solution while eosine is precipitated by an acidified gelatine solution.

Graham[3] points out that "soluble silicic acid forms a peculiar class of compounds, which like itself are colloidal, and differ entirely from the ordinary silicates. The new compounds are interesting from their analogy to organic substances, and from appearing to contain an acid of greatly

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[1] Pogg. Ann., **129**, 369 (1866).

[2] Zeit. phys. Chem., **51**, 145 (1905).

[3] Jour. Chem. Soc., **15**, 246 (1862).

higher atomic weight than ordinary silicic acid. Like gallo-tannic acid, gummic acid, and the other organic colloidal acids, silicic acid combines with gelatine, the last substance appearing to possess basic properties. Silicate of gelatine falls as a flaky, white and opaque substance, when the solution of silicic acid is added gradually to a solution of gelatine in excess. The precipitate is insoluble in water and is not decomposed by washing. Silicate of gelatine, prepared in the manner described, contains 100 silicic acid to about 92 gelatine. This is a greater proportion of gelatine than in the gallo-tannate of gelatine and requires for soluble silicic acid a higher equivalent than that of gallo-tannic acid. In the humid state the gelatine of this compound does not putrefy. When a solution of gelatine was poured into silicic acid in excess, the co-silicate of gelatine formed gave, upon analysis, 100 silicic acid with 56 gelatine, or little more than half the gelatine stated above as found in the compound prepared by reversing the mode of mixing the solutions. The gallo-tannate of gelatine is known to offer the same variability in composition. The gelatine used in the preceding experiments was isinglass, purified by solution in hydrochloric acid and subsequent dialysis. When the acid escapes by diffusion, a jelly is formed in the dialyzer. This jelly is from the earthy matter, amounting to about 0.4 percent in isinglass, and is not liable to putrefaction. Co-cilicic acid also precipitates both albuminic acid and pure caseine."

Lumière and Seyewetz[1] have studied the action of salts of chromium upon gelatine because of its importance for the theory of chrome tanning. If a suitable amount of chrome alum is added to a gelatine sol or if sheets of gelatine are soaked long enough in a chrome alum solution, the gelatine becomes insoluble even in boiling water and does not putrefy on standing as the original gelatine would have done. They found first that gelatine could be rendered insoluble by treatment with almost any salt of the formula Cr_2X_3, sulphate, sulphite, nitrate, chloride, fluoride, acetate, formate, citrate,

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[1] Bull. soc. chim. Paris, (3) 29, 1077 (1903).

or lactate. Since it had been shown by Namias that the power of chrome alum to make gelatine insoluble was increased by addition of alkali up to the point where precipitation of hydrous chromic oxide occurred, experiments were made with the green basic chromic sulphate of Recoura. Gelatine treated with a solution of this salt resisted repeated washing with boiling water better than gelatine which had been treated with a solution which was not basic. On the other hand, gelatine is not made insoluble by treatment with a so-called solution of chromic oxide in potassium hydroxide; but this is probably due to the excess of alkali. If the proper amount of ammonia is added to gelatine and then a chrome alum solution, the gelatine becomes insoluble in boiling water; but this is not the case if ammonia is present in excess.

Experiments on the amount of chrome alum necessary to make gelatine insoluble in boiling water showed that two grams of chrome alum per hundred grams of gelatine is the minimum amount. This ratio is independent of the concentration of the gelatine solution taken; but with gelatine concentrations of less than five percent the time necessary to make the gelatine insoluble increases with increasing dilution and may reach fifty hours with a 2.5 percent gelatine. The maximum amount of chrome alum which can be fixed by gelatine is 21 grams chrome alum per hundred grams of gelatine. When more chrome alum is taken chromium can be washed out of the solidified mass by boiling water. Lumière and Seyewetz formulate their results by saying that "to saturate one hundred grams of gelatine with chromium takes about ten times as much chrome alum as the minimum amount necessary to make the same weight of gelatine insoluble." While there is no serious objection to speaking about saturating the gelatine, they were really measuring the range of relative concentrations over which complete precipitation occurs.

Experiments with chromic sulphate, chloride, nitrate, and acetate showed that approximately the same quantity of chromic oxide was necessary to make the gelatine insoluble irrespective of the nature of the acid. Since this implies that only the chromic oxide counts, experiments were made to see what became of the acid radical. Sheets of gelatine were immersed in a known chromic sulphate solution and the solution analyzed afterwards. The ratio of chromium to sulphate in the solution was practically the same before and after treatment with gelatine which meant apparently that the chromic sulphate was taken up as a whole. It could not be the chromic sulphate as such which made the gelatine insoluble because the same result could be obtained when chrome alum was added to an ammoniacal gelatine. When the gelatine containing chromic sulphate is washed repeatedly with boiling water, acid is extracted very slowly, but after some washings the gelatine swells and a little is carried off in the wash water, leaving the residue relatively richer in chromium, the chromic oxide content running up to 5.4–5.6 grams per hundred grams of gelatine. If the gelatine is treated with dilute alkali, it is possible to remove the acid without causing any swelling or any solution of the gelatine. When the gelatine is treated in this way the maximum amount of chromium found in the gelatine is 3.3–3.5 grams Cr_2O_3 per hundred grams of oxide.

The explanation seems to be that the chromic oxide makes the gelatine insoluble and that the acid is adsorbed strongly by the chromic oxide, the gelatine, or both. When the acid is washed out at high temperatures, it causes a swelling of the gelatine. In fact, an insoluble gelatine, which has been freed from acid, swells rapidly and finally dissolves if boiled with water containing small amounts of acid or alkali. If the acid is adsorbed by the chromic oxide in the gelatine, it would be interesting to know whether there is a time factor and whether after standing for a month it would be easier to wash out the acid.

Coming back to the general problem, if the ratio of gelatine to the other colloid is increased sufficiently, we shall pass through the precipitation range into the range where the colloidal solution is stabilized by gelatine and then behaves more like a water-soluble colloid. Colloidal gold and colloidal silver solutions, when stabilized by gelatine, can be evaporated and redissolved because the gelatine prevents the irreversible agglomeration. When less gelatine is used, it may retard, though not prevent, the change of red colloidal gold to blue. Zsigmondy[1] defines as the gold number the number of milligrams of a protecting colloid which just prevents the color change in a 10 percent red gold solution, containing 0.0053-0.0058 percent gold, when one cubic centimeter of a 10 percent sodium chloride solution is added. Of course a strongly adsorbed non-electrolyte, such as sugar, will act similarly to gelatine; but, in most cases, the adsorption is so much less that these substances are only interesting theoretically as stabilizers.

Even though the gelatine or similar substance may not be present in sufficient amount to prevent precipitation, its presence may make itself known by cutting down the agglomeration of the colloidal precipitate. When caseine is precipitated from cow's milk by acid, it comes down in relatively coarse lumps which is one reason why cow's milk is bad for infants. By adding gelatine[2] to the milk, the growth of the curdy precipitate can be prevented. In human milk a protecting colloid is present and consequently coarse curds are not formed. This property of gelatine and other strongly adsorbed substances of keeping down the size of precipitates is made use of in the preparation of many colloidal solutions. By varying the amount of gelatine one can vary the fineness of the precipitate. The addition of gelatine to ice cream prevents the formation of coarse crystals. In electrolytic refining of metals and in electroplating, addition agents are used to make the deposited metal less coarsely crystalline. An addition agent must not be carried away from the cathode by the current and must be adsorbed by the precipitating metal. Gelatine is used in lead refining and has a great effect in an acidified copper sulphate solution. Many of the essential oils have proved satisfactory.

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[1] Zeit. anal. Chem., 40, 697 (1901).

[2] Alexander: Jour. Soc. Chem. Ind., 28, 280 (1909).

Glucose can also be used in some cases, not because it is a colloid, but because it is adsorbed strongly by the precipitating metal.

In the case of two colloids each peptized by water, the mutual adsorption may cut down the adsorption of water sufficiently to cause precipitation. This seems to be the most plausible explanation for the behavior of gelatine and tannin. The only difficulty is that the adsorption is more marked when the gelatine is positive and the tannin negative, which is more what one would expect if the two were colloids peptized by ions. There seem to be at least two possible ways out of this difficulty. It may be that gelatine is not really peptized by water and that we are dealing with a case of ion peptization where the range of instability is very small. The other possibility is that we get a different adsorption when the colloids are charged oppositely and that the resulting complex is less readily peptized by water under those conditions. This is not an impossibility. Earlier in this paper it was shown that ammoniacal gelatine precipitates colloidal ferric oxide, whereas there is no precipitation if the gelatine and ferric oxide sols are mixed before the ammonia is added. There seems to be no way at present to decide this question.

Tannin and basic dyes give a precipitate, but the range over which this occurs is very limited and in order to make use of this property in dyeing, it is customary to fix the tannin with a salt of antimony. Of course, in so far as the water peptization is cut down the mixture will tend more and more to behave like a colloid peptized by ions.

Tiebackx[1] finds that when a half percent gelatine solution is mixed with a four percent gum arabic solution, the mixture is precipitated readily by acids. If the acid is washed out, the coagulum can readily be dispersed in water. Tiebackx points out that the properties of a gelatine and gum arabic mixture are almost those of a globulin or of caseine. "Caseine is peptized by dilute alkalies and somewhat stronger

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[1] Zeit. Kolloidchemie, 8, 198, 238 (1911).

acids, the precipitation range lying between these two limits. Sulphuric acid is also adsorbed by caseine somewhat more strongly than hydrochloric acid. With globulin and caseine the acids are also displaced by salts as can be shown by methyl orange. The displacement of acid also involves a peptization for van Dam[1] has shown that presence of five percent sodium chloride increases the amount of caseine peptized by a given concentration of acid."

Apparently gelatine and agar-agar are two practically non-miscible liquids for Beijerinck[2] reports that it is impossible to mix a hot ten percent gelatine solution with a hot two percent agar solution, one of the liquids being emulsified in the other when the two are shaken together. The phenomenon is even more marked when ten percent soluble starch is shaken with ten percent gelatine.

Biltz[3] obtained no precipitation upon mixing any two of his positively charged sols and no precipitation on mixing any two of the negatively charged sols except when gold or selenium was mixed with the sulphides and there chemical action probably took place. Biltz concluded that sols of like charge had no effect upon each other; but this does not follow because adsorption of one colloid by the other would not neutralize the electrical charge and therefore would not cause precipitation. In certain cases we know that there is adsorption. In alkaline solutions peptized chromic oxide holds up ferric oxide if the latter is not present in too large amounts[4] and is carried down completely by it if the ferric oxide is present in excess. Other cases of the same type could be cited. The fact that gelatine protects ferric oxide when added before the ammonia shows that it must have been adsorbed by the ferric oxide. Bechhold[5] has shown that an ultra-filter which will stop Prussian blue and will let arsenic

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[1] "Van Bemmelen Gedenkboek," 104 (1910).

[2] Zeit. Kolloidchemie, 7, 16 (1910).

[3] Ber. deutsch. chem. Ges., 37, 1095 (1904).

[4] Northcote and Church: Jour. Chem. Soc., 6, 54 (1854); Nagel: Jour. Phys. Chem., 19, 331 (1915).

[5] Zeit. phys. Chem., 60, 299 (1907).

sulphide pass, holds back the arsenic sulphide when mixed with Prussian blue. Although both are negatively charged sols, it seems evident that there is a mutual adsorption. On the other hand, Bechhold found that hemoglobin can be separated from Prussian blue by filtration through a suitable ultra-filter, the hemoglobin going through the filter. In this case there is no appreciable adsorption.

The general results of this paper are as follows:

1. When positively charged gelatine is mixed with a negatively charged sol or negatively charged gelatine with a positively charged sol, there may be precipitation over a range of relative concentrations.

2. When two water-peptized sols are mixed, the mutual adsorption may decrease the adsorption of water to such an extent that precipitation occurs.

3. There may be, and often is, mutual adsorption when two sols having the same electrical charge are mixed.

4. The mutual adsorption of positively charged ferric oxide and positively charged gelatine gives a different product from the mutual adsorption of positively charged ferric oxide and positively charged gelatine. This probably has a bearing on the mutual adsorption of gelatine and tannin.

Cornell University

ADSORPTION BY PRECIPITATES. II

BY HARRY B. WEISER AND EDMUND B. MIDDLETON

Adsorption by Hydrous Ferric Oxide

Since the precipitation of a colloidal solution by the addition to it of electrolytes is accomplished by the neutralization of the charges on the colloidal particles by the adsorption of ions of opposite charge, it would seem possible to deduce the order of adsorption of ions from the critical concentrations of electrolytes necessary to produce coagulation. In a recent communication[1] on the adsorption of anions by precipitated barium sulphate it was shown, however, that the order determined from coagulation data was not the same as the order determined by direct analysis of the precipitated salt. Thus Kato[2] found that approximately equivalent concentrations of chloride, bromide, iodide, chlorate and nitrate were necessary to effect precipitation of colloidal barium sulphate, which would indicate that these ions tend to be adsorbed to the same degree. By direct analysis of the precipitate obtained by mixing solutions of sodium sulphate with a definite excess of the barium salt of the respective anions, the following order of adsorption was obtained:

nitrate > chlorate > chloride > bromide > iodide.

Moreover, there was a wide variation in the amounts of the different ions carried down. The results obtained by Kato are in exact accord with what one would expect if Schulze's law held, namely, that the power of an active ion to precipitate colloidal solutions is a function of its valence or of the number of electrical charges which it carries. The results obtained by direct analysis indicate that there is a specific factor in addition to the valence factor which causes barium sulphate to adsorb ions of the same valence to widely different degrees. The results obtained by direct analysis are not

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[1] Weiser and Sherrick: Jour. Phys. Chem., **23**, 205 (1919).

[2] Mem. Coll. Sci. Eng. Kyoto Imp. Univ., **2**, 187 (1909–10).

strictly comparable with those deduced from coagulation data since the salt analyzed was not precipitated from a colloidal solution as such. It would seem, however, that the manner of precipitation would affect only the absolute amounts adsorbed and not the order. Colloidal barium sulphate is positively charged as a rule. Precipitation takes place when an anion is adsorbed in sufficient amount to neutralize the positive charge, thereby allowing the finely divided colloidal particles to agglomerate into masses sufficiently large to settle. If the charge on the anion is the only factor that determines the amount adsorbed, coagulation should take place in the presence of equivalent amounts of the various ions and equivalent quantities should be carried down in the precipitate. On the other hand, if barium sulphate shows a specific or selective tendency to adsorb certain ions more than others of the same charge, this tendency must be independent of the charge so that ions of the same valence may be carried down in widely varying amounts. Since this selective tendency will manifest itself during the process of agglomeration and precipitation, one would expect to find the same relative amounts of ions carried down by precipitated barium sulphate whether this precipitation took place from true or colloidal solution. This would seem to be the case particularly with univalent ions which precipitate only in the presence of a relatively large excess. In the previous paper it was pointed out that the method of getting critical coagulation concentrations is open to certain errors and that these were magnified in the case of colloidal barium sulphate. However, this source of error seems inadequate to account for the apparent absence of a specific factor in the above-cited data from Kato's coagulation experiments with colloidal barium sulphate, whereas this factor is distinctly marked as shown by direct analysis of the precipitated salt.

Some quantitative data obtained by Whitney and Ober[1] are frequently referred to[2] as proof that equivalent concen-

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[1] Jour. Am. Chem. Soc., 23, 842 (1901).

[2] Taylor: "Chemistry of Colloids," 104 (1915); Zsigmondy-Spear: "Chemistry of Colloids," 51 (1917); Philip: "Physical Chemistry," 206 (1913).

trations of all precipitating ions are carried down by a precipitated colloid. From a quantitative determination of the amounts of certain ions carried down by colloidal As_2S_3, these investigators conclude that the amount of an ion carried down by a precipitated colloid is independent both of the concentration of the colloid and the electrolyte; and that equivalent amounts of different ions are carried down by the same weight of precipitate. In their experiments 100 cc or 200 cc portions of the colloidal solutions were precipitated with solutions of the chlorides of calcium, strontium, barium and potassium. In each case, the amount of metal in the solution before and after the precipitation was determined gravimetrically, the difference representing the amount adsorbed. Table I was constructed from their results.

TABLE I

Salt	Colloid cc	Electrolyte cc	Metal added g	Metal adsorbed by 100 cc of colloid		Error
				Observed	Calculated	
$CaCl_2$	100[1]	25	0.0724	0.0020	0.0022	11%
$CaCl_2$	200	25	0.0724	0.0019		
$SrCl_2$	200	25	0.1071	0.0036	0.0049	21%
$SrCl_2$	200	25	0.1071	0.0041		
$BaCl_3$	200	30	0.1675	0.0076	0.0076	—
$BaCl_2$	200	30	0.1675	0.0076		
KCl	100	—	2.00	0.0032	0.0043	21%
KCl	200	—	5.00	0.0036		

We should expect to get equivalent quantities adsorbed in the presence of an excess of the precipitant only in case arsenic trisulphide shows no selective tendency to adsorb one ion more than another. The results above tabulated do not show the absence of this factor. Whitney and Ober assumed that the determination of barium ion was probably the most accurate and used the amount of this ion adsorbed as a basis of comparison. In the next to the last column of the table are given the amounts of the various ions equiva-

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[1] Diluted with 100 cc water.

lent to 0.0076 gram of barium; and in the last column the percentage differences between the observed and calculated values. There is a variation of more than 20 percent in certain cases. Furthermore the amounts adsorbed are less than they should be on the assumption that the calculated values are correct. This may be explained by assuming that arsenic trisulphide shows a stronger tendency to adsorb barium ion than the other ions and hence carries down relatively more of it. Because of the small adsorption, it was difficult to determine the amount adsorbed. Thus in the case of potassium, only about one six-hundredth of the amount added was carried down. However, the variation from strict equivalence cannot be attributed to experimental errors since the correction might show greater rather than smaller variation. Whitney and Ober did not carry out the precipitation in equivalent concentrations of electrolyte because the precipitation value for the potassium salt is much greater than that for salts of the divalent metals; and also because they concluded that the concentration of electrolyte had no effect on the amount adsorbed. It may not be possible to detect the effect of small variations in the concentration particularly when the concentrations are all large relative to the amount adsorbed; but the concentration of potassium ion used was approximately one hundred times as great as that of the other ions. It would be interesting to know how much barium ion, say, would be adsorbed from a solution one hundred times as concentrated as that actually employed.

On the basis of Whitney and Ober's experiments and similar data on the adsorption of aniline ion and new magenta cation, Freundlich[1] makes the assumption that in the coagulation of a colloid, equivalent amounts of precipitating ions are carried down by the same weight of colloid. A logical deduction follows, namely, that the most readily adsorbed ion precipitates in the lowest concentration and *vice versa*. In order to account for the marked influence of the valence of inorganic cations, say, on the precipitation of a negative

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[1] Freundlich: Zeit. Kolloidchemie, 1, 321 (1907).

colloid, he further assumes that cations of different valence are equally adsorbed from equimolar solutions which would explain the well-known fact that the precipitation values (which correspond in the first instance to equivalent amounts) are very different. To test his theory, Freundlich[1] extended the work of Whitney and Ober by an investigation of the relationship between the precipitation values of various ions for colloidal arsenic trisulphide and the adsorption of the ions by precipitated arsonic trisulphide. The critical coagulation concentrations of a number of salts were first determined for a colloid containing 1.857 grams per liter. This was followed by direct determination of the amounts of several ions adsorbed by arsenic trisulphide. The following general procedure was used in finding the adsorption values: A colloidal solution was prepared and precipitated with hydrochloric acid. The precipitate obtained was thoroughly washed, dried at 50° to 60°, and ground in a mortar. A weighed amount of this powder was next shaken with a solution containing a given cation and the adsorption calculated from the concentration of the solution before and after shaking.

Although the above-mentioned method of determining adsorption from solution is quite generally employed, Leighton[2] has shown that the results are correct only in case no liquid is taken up by the adsorbent. If the solid adsorbed the solute and solvent in the same ratio in which they occurred in the solution there would be no change in concentration and the apparent adsorption would be zero.

The first point tested by Freundlich was whether organic cations with the largest precipitation values were adsorbed the least and *vice versa*. The adsorption of the following salts with organic cations was studied: aniline chloride, *p*-chloraniline chloride, morphine chloride, strychnine nitrate and new magenta. Since the degree of adsorption was comparatively small and the methods of analysis not all that could be de-

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[1] Zeit. phys. Chem., 73, 385 (1910).

[2] Jour. Phys. Chem., 20, 32, 188 (1916); cf. Weiser and Sherrick: Loc. cit.

sired, and since the sulphide was not obtained absolutely pure, no high degree of accuracy was claimed for the results. By comparing the adsorption isotherms for the different salts with the coagulation data first obtained, considerable variation was noted. Thus, strychnine nitrate showed a high precipitation value and a high degree of adsorption. Also the precipitation concentration for aniline chloride was 2.5 times as great as for *p*-chloraniline chloride and yet the adsorption isotherms almost coincided throughout. A closer investigation of the coagulation with strychnine nitrate showed that there were two critical coagulation concentrations: one low and another relatively high. "In short, in the case of strychnine nitrate, one is confronted with a series of so-called abnormal values such as is recognized for salts of heavy metals and dyes. It results in the case of a negative colloid, when precipitation is accomplished with a salt derived from a difficultly soluble base. This, when added in excess, can surround the colloidal particles and produce a positive colloid which is precipitated again by the anion only at higher concentration. The lower precipitation value corresponds to arsenic trisulphide colloids, and the higher to a positive colloid of the base concerned." In view of this source of error, the precipitation values of all the organic ions were redetermined. A comparison of the revised precipitation values with the adsorption isotherms shows a closer agreement. However, aniline chloride again shows a precipitation value more than twice that of *p*-chloraniline chloride and yet the adsorption isotherms practically coincide, as above mentioned. On the other hand, strychnine nitrate, morphine chloride and new magenta precipitate in almost the same concentrations, 0.39, 0.36 and 0.30 millimol per liter, respectively, and yet the isotherms are quite widely separated compared to those of the aniline chlorides which have markedly different precipitation values. Furthermore, strychnine nitrate precipitates at a higher concentration than morphine chloride and is apparently more strongly adsorbed. However, the isotherm for morphine chloride was drawn from data calculated from a different sample of arsenic trisulphide than that used in the other cases. In the light of these variations, it would seem, therefore, that even the revised data scarcely warrant the conclusion that the "parallelism is satisfactory throughout."

The second point considered was whether metal cations were equally strongly adsorbed from equimolar solutions. This was tested by determining the adsorption of ammonium, uranyl, aluminum and ceric ions. The determinations were carried out in the same manner as above described, but they were rendered particularly difficult on account of the very slight adsorption. Colorimetric methods were used throughout. The methods for cerium and uranium were most satisfactory, but a "half quantitative method" was used for aluminum; and the Nessler method for ammonia was inaccurate on account of the reaction between the mercury of the reagent and the hydrogen sulphide and arsenic trioxide in the solution. "The curves for $UO_2^{\cdot\cdot}$ and $Ce^{\cdot\cdot\cdot}$ coincide within the limits of experimental error. The point for aluminum is quite close. The curve for ammonium is distinctly lower but, as before mentioned, such errors are introduced that the adsorbed amounts are probably too small." On the basis of these data, Freundlich concludes that for the light metal cations, equimolar amounts are adsorbed from equimolar solutions. As a matter of fact, the adsorption value is so small, 0.0001 to 0.0002 mole per gram, that it is questionable whether the data can be regarded as sufficiently accurate to justify the conclusion; particularly, since the actual values show almost twice as much adsorption from cerium nitrate solutions as from ammonium chloride solutions of the same concentration.

Freundlich next precipitated colloidal arsenic trisulphide with solutions of uranyl nitrate and ceric nitrate of known concentrations and analyzed the supernatant liquid colorimetrically for uranyl and ceric ions, respectively. From these data, he found that 0.088 milliequivalent of uranyl ion and 0.069 milliequivalent of ceric ion were adsorbed per gram of arsenic sulphide. The molar concentration of uranyl nitrate at the start was nine times that of the ceric nitrate which is the approximate order of precipitation values. It will be noted also that the amount adsorbed in milliequivalents is about thirty percent more for uranyl ion than for ceric ion. Nevertheless, he concludes that equivalent (not equimolar) amounts of cations are carried down in the precipitation of colloids.

In order to test this last conclusion more fully, Freundlich and Schucht[1] determined the precipitation value for colloidal mercuric sulphide and the amount of adsorption by the precipitate in the region of the precipitation concentration. The adsorption was determined for the metallic cations NH_4, $Ag^{\cdot}$, $Ba^{\cdot\cdot}$, $Cu^{\cdot\cdot}$ and $Ce^{\cdot\cdot\cdot}$ and for the dye cations new magenta, brilliant green, auramine, and methylene blue. The method of determining the adsorption values was as follows: "The experiments were carried out with a definite volume of the colloid (usually about 50 cc) to which was added, as a rule, five cubic centimeters of electrolyte containing the cation whose adsorption it was desired to measure. The mixture was allowed to stand fifteen minutes, the particles centrifuged out, and the clear solution poured off and analyzed. This gave the equilibrium concentration. Since the concentration at the outset and the content of colloid was known, the amount adsorbed per gram of mercuric sulphide could be found. The concentration of the electrolyte must be in the neighborhood of the precipitation value. It could be somewhat smaller as the flocks will still centrifuge out well, but not if the concentrations are very much smaller. In general, it must not be too large, otherwise with a number of cations one gets into a zone of non-precipitation, or if this is not the case, the change in concentration due to adsorption may be too slight.

"The analysis of the end concentration offers considerable difficulty and a number of special methods had to be

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[1] Zeit. phys. Chem., 85, 641 (1913).

used since one is dealing with regions of exceedingly small concentrations, as shown in Table II."

The above method of procedure is open to the same objection referred to in the determination of adsorption by arsenic trisulphide, namely, that it assumes that the precipitate adsorbs none of the solvent. The results follow:

"We first compared the amounts adsorbed in milliequivalents obtained at the precipitation value. The majority of these have been found directly. With the dyes the results are obtained from the precipitation value since the concentration after adsorption is practically zero. It is only necessary to determine how many milliequivalents there are in 55 cc and how many grams of mercuric sulphide there are in 50 cc of the colloid; and divide the one by the other. In order to facilitate this calculation the content of the colloid in grams per liter is given in parenthesis after the precipitation value. Also with copper nitrate, the concentration after adsorption may be regarded as practically zero when one observes from Table VIII that with a concentration somewhat larger than the precipitation value, only a small percentage remains in solution."

The results are reproduced in Table II.

TABLE II

Cation	Adsorption at precipitation value. Milliequivalent	Precipitation value	Concentration of colloid. Grams per liter
NH_4	0.050	10.20	13.74
Ag	0.020	0.28	11.74
New Magenta	0.008	0.097	13.74
Brilliant Green	0.004	0.048	8.38
Auramine	0.011	0.094	10.05
Methylene Blue	0.007	0.097	4.96
Ba	0.044	0.510	8.26
Cu $Cu(NO_3)_2$	0.030	0.150	8.26
Cu $CuSO_4$	0.022	0.260	14.43
Ce	0.012	0.082	10.45

From the second column of the table it will be noted that the adsorption as determined varies continuously all the way from 0.004 to 0.050 milliequivalent per gram. It would seem that the data disprove rather than prove the assumption that equivalent amounts are adsorbed at the precipitation concentration. Freundlich recognizes the lack of uniformity in the results, but attributes the variation to the minute amounts adsorbed and to the difficulties and errors incident to the determinations. Although there are unfortunate difficulties in this particular case, one cannot predict with any degree of certainty whether the same experimental method would show greater or lesser variation with greater adsorption and more quantitative determinations. To quote from Freundlich: "The differences in the second column in the table appear large at the first moment. The absolute differences are, however, not greater than with the arsenic trisulphide colloid, only in the latter case the precipitation values and the adsorbed amounts are much greater and the relative differences are therefore smaller. Also, the values that are the farthest off (NH_4 and Ba) are not easy to determine and are therefore not very certain. Above all, should be considered how difficult are the determinations and how small the amounts. With this understanding the results speak rather for than against equivalence. They indicate with assurance that the great differences in the precipitation values are perhaps not due to great differences in the amount adsorbed but much more to great differences in the adsorbability."

"The following particular points may be emphasized: new magenta and methylene blue have the same precipitation value and their adsorption isotherms almost coincide. From Figure 4 may be seen that barium ion is much less adsorbed than copper ion, at least in the region of the small adsorption values which are necessary for the precipitation of mercury sulphide colloids. The barium ion curve is much steeper than the copper ion curve, therefore the precipitation value of the first is considerably greater than that of the latter. The fact that the curves for copper nitrate and copper sulphate do not coincide need not be attributed to experimental errors. The adsorption of the cation is unquestionably influenced by the nature of the anion as shown by the investigations of Michaelis and Lachs[1] and by Freundlich and v. Elissafoff.[2] Apparently the salt is first adsorbed as a whole and then there is an interchange between the more readily adsorbed ion and the ion already on the colloid. At any rate, what we know is that sulphates are less strongly adsorbed than nitrate, chloride, bromide, etc. This accounts for the greater precipitation value of $CuSO_4$ compared with $Cu(NO_3)_2$."

As Freundlich points out, the precipitation values of new magenta and methylene blue are identical and the adsorption value of the cations are almost the same. It is interesting to note, however, that the precipitation value of auramine is but three percent lower than that of new magenta, but the adsorption value is thirty-seven percent higher. Moreover, the precipitation value of brilliant green is only one-half that of new magenta and the adsorption value at this concentration is in reality but half as much instead of being the same or larger in accord with Freundlich's conclusions from experiments on the adsorption of organic cations by arsenic trisulphide. There is no doubt that the anion has an effect as above explained; but it does not seem likely that this effect alone would account for the precipitation value for $CuSO_4$ being 75 percent higher than that for $Cu(NO_3)_2$; particularly in view of the fact that Freundlich found thallium nitrate and thallium sulphate precipitated colloidal mercuric sulphide in almost the same concentration. The conclusions finally reached show the need of more quantitative data. "These investigations confirm the theory developed concerning the relation between adsorption and coagulation. Even though earlier investigations with arsenic trisulphide show more strikingly the equivalence of the amounts adsorbed and the relationship between the precipitation value and adsorbability or valence, because the observed effects were larger and

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[1] Zeit. Elektrochemie, 17, 1, 917 (1911).

[2] Zeit. phys. Chem., 79, 410 (1912).

easier to measure, the results with mercuric sulphide colloid have the advantage that conclusions from analogy and extrapolation are unnecessary. The adsorption experiments with arsenic trisulphide powder were carried out at a concentration quite different from the critical coagulation concentration of colloidal arsenic trisulphide while with the mercury sulphide colloid, the adsorption was measured directly by the particles of the colloid itself in the region of the precipitation concentrations and the expected relationship confirmed. The necessity of working at very low concentrations and with a limited amount of adsorbent introduced very appreciable difficulties in addition to the instability of the colloid itself which makes it apparent that the numerical relations are in part only half quantitative."

From the above survey of the important available quantitative data on the relationship between precipitation of colloids and adsorption by the precipitates, it would seem that an important point mentioned at the beginning of this paper had not been taken into account. Since the first step in the precipitation of a colloid by an electrolyte is the neutralization of the charge by adsorption of an ion of opposite charge, it follows that two adsorbing media are concerned in the process: the electrically charged particles and the electrically neutral particles. Accordingly, the total amount of a given ion carried down by a precipitated colloid is determined by (1) the adsorption of the charged particles during the process of neutralization, and (2) the adsorption by the electrically neutral particles during the process of agglomeration and settling. Since neutralization is accomplished when equivalent amounts of ions are adsorbed, it might seem to follow that one would find equivalent amounts of ions in the precipitate after the neutralization. This would be true if the electrostatic attraction of the charged particles for ions of opposite charge was the determining factor or if the particles tended to adsorb all ions of the same valence to the same degree. As a matter of fact, such is not the case. There is a tendency to attribute the differences in the precipitating value of salts with cations, say, of the same valence to differences in the degree of ionization,[1] to differences in the mobility of the ions,[2] to different stabilizing effects of different anions, and to errors in determining the critical coagulation concentration. While all these things must have an effect, the importance of which will be considered later on, there are many unmistakable examples of ions of the same valence having an abnormally high or abnormally low precipitating power that can be due only to marked variation in the adsorption tendency.

Since the electrically charged particles show a selective tendency to adsorb certain ions more than others even of the same valence, it is evident that this tendency is independent of the charge and one should expect the neutralized particles to show selective adsorption. Accordingly, although equivalent amounts must be adsorbed to effect neutralization, the amounts actually carried down in a given case will be the sum of (1) the amount necessary to neutralize the charge on the colloid and (2) the amount adsorbed from the solution during the process of agglomeration and settling. The first amount is necessarily constant for ions of the same valence; the second will vary with the nature of the adsorbing medium, the nature of the adsorbed ion, and the concentration. If the amount of adsorption of a series of ions is determined at the precipitation concentration as Freundlich did, it is evident that the agglomeration and precipitation will take place in varying concentrations of solution. With certain electrolytes a considerable excess is necessary to effect precipitation; while with others, notably the dyes, the precipitation concentration may be so low that all the added electrolyte may be removed from solution. In the first case the adsorption may attain approximately to the saturation value for the given ion; while in the latter case, this value would not be reached. Comparisons of the amounts adsorbed at the

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[1] Hardy: Zeit. phys. Chem., 33, 385 (1900).

[2] Freundlich: Ibid., 44, 129 (1903); Pappadà: Gazz. chim. ital., 42, I, 263 (1912).

precipitation concentrations must necessarily show some variation unless the precipitation concentrations are identical. The variations from equivalence in the adsorption values determined by Freundlich are probably due quite as much to the varying concentration and adsorbability of the ions as to errors in the analytical procedures. The adsorption of equivalent amounts of ions effects neutralization but the amounts carried down by the precipitate are not equivalent because of selective adsorption of ions by the neutralized particles.

As above explained, the adsorption values at the precipitation concentration are not comparable because of the variability of the latter and the consequent variability in the degree of saturation of the adsorbent by the adsorbed phase. Accordingly, the adsorption values should be compared above the precipitation concentration, so that one is working in a region of the "flat" of the adsorption isotherm, where the adsorbent is practically saturated. The adsorption values of the sulphides are so small and consequently the errors in analysis so great that our attention was turned to hydrous ferric oxide. The physical character of the latter is such that one should expect to get relatively high adsorption values.

Considerable work has been done on the precipitation of colloidal ferric oxide. For the most part, this has been carried out on the colloid prepared by Graham's[1] method which consists in dissolving freshly precipitated iron oxide in ferric chloride and dialyzing until the colloid gives no test for ferric ion with potassium ferrocyanide.[2] This colloid is highly hydrous, is colored deep brown and the particles are very finely divided. It lacks uniformity, as it does not all precipitate at once on the addition of a certain concentration of nitric acid. "This is because the more hydrous form changes gradually on standing to the less hydrous form which latter precipitates first when nitric acid is added."[3] A num-

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[1] Jour. Chem. Soc., 15, 250 (1862).

[2] Fisher and Kusnitzky: Biochem. Zeit., 27, 311 (1910).

[3] Bancroft: Jour. Phys. Chem., 19, 237 (1915).

ber of investigators have determined the critical coagulation concentration of electrolytes for the Graham colloid. From incomplete data obtained by Hardy, the order of adsorption of anions appears to be

citrate > sulphate > oxalate > nitrate > chloride.

Duclaux,[1] working with a colloid containing 203 × 10^{-6} equivalents of iron and 16 6 × 10^{-6} equivalents of chlorine per liter, found that the critical coagulation concentrations of sodium sulphate, citrate, chromate, carbonate, phosphate hydroxide and ferrocyanide varied from 13 × 10^{-6} in the case of ferrocyanide to 19 × 10^{-6} equivalents in the case of phosphate. From this, he concluded that equivalent amounts of the various ions caused the same effect, and, furthermore, that the amount necessary for precipitation is the same as the chloride content of the colloid within the limits of the experimental errors inherent in the method of determining the coagulation concentration. A marked variation was observed with sodium chloride and sodium nitrate which required 2000 × 10^{-6} and 1880 × 10^{-6} gram equivalents, respectively, to precipitate the same amount of colloid as the seven salts above referred to. From Duclaux's data, the order of adsorption appears to be

ferrocyanide > chromate > hydroxide > citrate > sulphate > carbonate > phosphate > nitrate > chloride.

Freundlich,[2] working with a colloid containing sixteen millimols of iron per liter, found the order of anions to be

dichromate > sulphate > hydroxide > salicylate > benzoate > formate > chloride > nitrate > bromide > iodide.

Pappadà's[3] experiments on coagulation indicate that the order is

citrate > chromate > sulphate > hydroxide.

As will be seen, there is apparently a wide variation in the order of ions as deduced from the coagulation experiments

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[1] Jour. chim. phys., 5, 29 (1907).

[2] "Kapillarchemie", 352, 358 (1909).

[3] Zeit. Kolloidchemie, 9, 233 (1911).

of different investigators. This is particularly evident among the strongly adsorbed ions which precipitate in relatively low concentration. The variation in the results is undoubtedly due to variations in the method of determining the critical coagulation concentrations and the errors inherent in the process.

Péan de St. Gilles prepared colloidal iron oxide having properties somewhat different than the Graham colloid, by continued boiling of a solution of ferric acetate. The colloid so prepared was turbid in reflected light but clear in transmitted. It gave a much more intense light cone than the Graham colloid and hence contained much larger particles. Giolitti[1] made an extended study of the precipitation of the Péan de St. Gilles oxide by a number of electrolytes. He found that considerable amounts of hydrochloric, hydrobromic, hydriodic, nitric, perchloric, and bromic acids must be added to a suspension of the colloid in order to effect precipitation. The oxide came down as a brick-red powder which was peptized by water when the acid was washed out. He found further that traces of sulphurous, selenious, iodic, periodic, boric and phosphoric acids and of salts effected precipitation. Under these conditions he observed that the precipitate was gelatinous and did not redissolve on washing. The precipitation of ferric oxide in two different states by different electrolytes is an interesting and important phenomenon that has been studied in this laboratory and will be reported on in a subsequent communication.

Determination of Precipitation Values

Preparation of the Colloid.—The colloid prepared by the method of Péan de St. Gilles has been used throughout these experiments. This was chosen on account of the relative ease of preparation and the fact that it is apparently more uniform and homogeneous than the Graham colloid which becomes less hydrous with time. The actual procedure employed in the preparation was as follows: Twenty-five grams of ferric

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[1] Gazz. chim. ital., 35 II, 181 (1905); 36 II, 157, 433 (1906).

choride were dissolved and precipitated with a slight excess of a solution of sodium carbonate. The solution in which was suspended the gelatinous precipitate was transferred to 250 cc bottles and centrifuged until the precipitate was thrown down. After pouring off the supernatant liquid, water was added and the matted gel thoroughly stirred up. The solution was again centrifuged and the washing process repeated until the wash water showed no test for chlorides. The gel was then suspended in a solution of acetic acid containing slightly less acid than enough to dissolve the oxide. This was allowed to stand for several days with frequent stirring after which the solution was filtered, highly diluted and boiled vigorously. The boiling was continued from 24 to 36 hours, or until there was no odor of acetic acid in the vapors above the boiling liquid. The red color of the ferric acetate became gradually brick-red as the boiling continued; and the liquid which was clear at the outset became turbid in reflected light, owing to the presence of the suspended particles of ferric oxide.

Since a quantity of the colloid was necessary for the experiments that were planned, several portions were prepared as nearly as possible in the same way and the several solutions mixed. Before starting the experiments, approximately twenty-five liters of the colloid were prepared containing 1.544 grams of iron oxide per liter. The same colloid was used in all the experiments herein described. The experiments were carried out with as much dispatch as possible in order to avoid variations arising from possible variations in the colloid. This precaution was doubtless unnecessary, however, since a portion of the colloid has been standing several months without apparent change. Moreover, the critical coagulation concentration for potassium sulphate has remained constant, indicating that the colloid was very stable in the absence of electrolytes.

Determination of Precipitation Values.—In order to precipitate a colloid by a given electrolyte, it is necessary to exceed a certain definite minimum concentration. As previously pointed out, it is difficult to determine the critical concentration since several factors are involved: such as the rate of addition of the electrolyte,[1] method of strirring, time of standing, etc. Several methods have been used to determine the coagulation concentration. Schulze[2] allowed a drop of the colloid to flow into a large volume of the electrolyte. In this way a series of determinations was made until that concentration of solution was found that just coagulated the drop. Hardy[3] added the electrolyte from a burette a drop at a time to a given amount of the colloid until precipitation just took place. Both of these methods are objectionable since experience has shown that a quantity of salt that will not effect precipitation immediately, will frequently do so on standing; and that the quantity of electrolyte necessary to effect precipitation is different when the electrolyte is added all at once than when it is added in several successive portions. In order to obtain results as nearly comparable as possible, Freundlich[4] used the following procedure: "A constant volume of salt solution was added with constant shaking to a constant amount of colloid (usually 2 cc of the solution to 20 cc of the colloid) in a glass cylinder that had been steamed out a few times. The mixture was set aside for a definite time (two hours), after which a few cubic centimeters were filtered off and analyzed colorimetrically or chemically to determine whether or not any colloidal material remained." Duclaux[5] followed a similar procedure but added sufficient electrolyte to cause immediate coagulation of the colloid.

The method first used in these experiments consisted in placing ten cubic centimeters of the colloid in a large test tube and ten cubic centimeters of the electrolyte in another. The electrolyte was first poured rapidly into the colloid after which the solution was transferred rapidly from one test tube

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[1] See Freundlich: Zeit. phys. Chem., **44**, 129 (1903).

[2] Schulze: Jour. prakt. Chem., [2] **25**, 43 (1882); **22**, 320 (1884).

[3] Zeit. phys. Chem., **33**, 385 (1900); cf. Pappadà: Zeit. Kolloidchemie. **9**, 136, 233 (1911); **10**, 314 (1912).

[4] Zeit. phys. Chem., **44**, 131 (1903).

[5] Loc. cit.

to the other, two or three times. In this way it was hoped to get rapid and uniform mixing. By making a series of determinations in the region of the critical coagulation concentration it was possible to get that concentration which would just cause coagulation. Early in the investigations it was found, however, that results could not be duplicated by this method of procedure; particularly with those electrolytes that precipitate in very low concentration. The method served to determine the approximate coagulation concentration and was used throughout for that purpose only. It was evident that the method of mixing and shaking was in some way at fault and the procedure was modified accordingly.

In order to obtain rapid and uniform mixing, an apparatus was designed and manipulated as follows: A glass tube 4 cm. in diameter and 20 cm. long was fitted with rubber stoppers. A groove was cut around one of these in such a way that a stopper was made for one end of a smaller tube that held it concentric with the first. The small tube was 2.5 cm. in diameter and 7 cm. in length. The apparatus was thoroughly cleaned, rinsed carefully with distilled water and allowed to drain. Into the smaller tube was measured a definite quantity of an electrolyte of known strength which was subsequently made up to twenty cubic centimeters. The stopper was then fitted securely in the larger tube and twenty cubic centimeters of the colloid were run into the space between the two tubes. After stoppering, the tube was inverted with a quick jerk that rapidly and effectively mixed the two solutions. The contents of the tube were then poured into a 50 cc graduate which was stoppered and allowed to stand for twenty-four hours, after which the observations were made. Duclaux's method of adding sufficient electrolyte to cause immediate precipitation was unsatisfactory, particularly with electrolytes that precipitated in high concentration.

In order to determine whether coagulation was complete in a doubtful case after twenty-four hours, the supernatant liquid was poured from the graduate into a tube and centrifuged for five minutes. A portion of the solution was transferred to a test tube and one cubic centimeter of *N*/2 potassium sulphate was added. The absence of a precipitate after standing for an hour indicated that precipitation had been complete. This method of detecting complete precipitation was highly satisfactory since even a trace of the gelatinous red precipitate could be readily detected. The procedure was sufficiently accurate that it was possible to determine the critical concentration to within 0.05 cc of *N*/100 solution in 40 cc, with those electrolytes that precipitated in low concentration. Moreover, no difficulty was experienced in duplicating results with a given electrolyte.

As the colloid is positively charged, the anions are chiefly concerned in the precipitation. In the first series of experiments, potassium salts were used, thus eliminating the effect of the cation in so far as possible. It is obviously impossible to render the effect of the cation constant since the concentration differs in every case. Half-normal solutions of salts with univalent anions were used in all cases except with potassium iodate. Hundredth-normal solutions of other salts were employed. A 10 cc calibrated pipette was used to measure the half-normal solutions and a 2 cc Ostwald pipette to measure the hundredth-normal solutions. As before stated, the quantity of electrolyte taken was diluted to 20 cc before mixing with an equal volume of colloid. It was necessary to determine the approximate coagulation concentration first, after which a series of experiments in the critical region located the value with considerable accuracy. The results are recorded in Table III. In the first column is tabulated the anions; in the second, the number of cubic centimeters of solution in 20 cc that just failed to precipitate completely 20 cc of the colloid; in the third, the number of cubic centimeters in 20 cc that caused complete precipitation; in the fourth, the precipitation concentration in milliequivalents per liter, calculated from the data in column 3.

TABLE III
Precipitation Values of Potassium Salts

Salt	Electrolyte cc	Electrolyte cc	Precipitation value. Milliequivalents per liter
Ferrocyanide	1.05 $N/100$	1.10 $N/100$	0.275
Ferricyanide	1.10 $N/100$	1.15 $N/100$	0.287
Dichromate	1.45 $N/100$	1.50 $N/100$	0.375
Tartrate	1.55 $N/100$	1.60 $N/100$	0.400
Sulphate	1.70 $N/100$	1.75 $N/100$	0.437
Oxalate	1.85 $N/100$	1.90 $N/100$	0.475
Chromate	2.55 $N/100$	2.60 $N/100$	0.650
Iodate	3.55 $N/100$	3.60 $N/100$	0.900
Bromate	2.40 $N/2$	2.50 $N/2$	31.3
Thiocyanate	3.65 $N/2$	3.75 $N/2$	46.9
Chloride	8.00 $N/2$	8.25 $N/2$	103.1
Chlorate	9.00 $N/2$	9.25 $N/2$	115.6
Nitrate	10.25 $N/2$	10.50 $N/2$	131.2
Bromide	10.75 $N/2$	11.00 $N/2$	137.5
Iodide	12.00 $N/2$	12.25 $N/2$	153.6
Formate	13.60 $N/1$	13.80 $N/1$	172.5

From the data tabulated above the order of adsorption of ions appears to be

ferrocyanide > ferricyanide > dichromate > tartrate > sulphate > oxalate > chromate > iodate > bromate > thiocyanate > chloride > chlorate > nitrate > bromide > iodide > formate.

With the exception of formate ion, the order of ions is identical with that deduced from Freundlich's[1] data for those ions that are common to both series. This is what one should expect, since the adsorbing medium is hydrous ferric oxide in both cases, the only difference being the degree of hydration and the relative size of the particles in the two colloids.[2] It will be noted that univalent ions, with the exception of iodate ion, precipitate only in relatively high concentrations, and that the precipitation values differ widely, varying from 31, for bromide ion, to 172 for formate ion. Ions, other than univalent, precipitate in exceedingly low concentrations in every

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[1] Loc. cit.

[2] Bancroft: Jour. Phys. Chem., 19, 232 (1915).

case. The variations in the precipitation values of different multivalent ions are somewhat greater than observed by Duclaux;[1] but it was found, as previously stated, that Duclaux's method of procedure was less satisfactory than our own. Duclaux recognized the difficulties involved, but believed that the variations in his values were due to experimental error. It is believed, however, that a redetermination of precipitation values on the Graham colloid using the method outlined in this paper would show variations as great as we observed with the Péan de St. Gilles colloid. A study of the Graham colloid was not made since the order of variation is relatively unimportant compared with the fact that the precipitation values are not the same, as Duclaux believed. The Graham colloid is stabilized by preferential adsorption of hydrogen ion and probably some ferric ion. The chloride ion present in the solution is a measure of the cations adsorbed. Different concentrations of electrolytes are necessary to neutralize the adsorbed ions and precipitate the colloid. The concentration of anion necessary to effect neutralization will approximate the chloride ion concentration only in so far as its adsorption tendency approaches that of the adsorbed cations.

A series of precipitation values was determined with various acids in the same manner as described for the potassium salts of the anions. The results are tabulated in Table IV.

It will be noted that, as usual, univalent ions precipitate only in relatively high concentrations, while divalent and trivalent ions precipitate in very low concentrations. This is in accord with Giolitti's results above referred to. Iodic and periodic acids behave like sulphuric acid, which would indicate that in these cases we are not dealing with the normal acids HIO_3 and HIO_4, respectively. The evidence indicates that concentrated solutions of iodic acid are associated to form complex molecules like $(HIO_3)_2$ and $(HIO_3)_3$; and that the acid behaves as if it were polybasic.[2] Above one-eighth

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[1] Loc. cit.

[2] See Abegg: "Handbuch der anorg. Chem.," 4, II, 500 (1913).

TABLE IV

Precipitation Values for Acids

Acid	Electrolyte cc	Electrolyte cc	Precipitation values. Milliequivalents per liter
Dichromic	0.75 *N*/100	0.80 *N*/100	0.200
Tartaric	1.85 *N*/100	1.90 *N*/100	0.475
Sulphuric	1.90 *N*/100	1.95 *N*/100	0.485
Citric	1.90 *N*/100	2.00 *N*/100	0.500
Oxalic	2.05 *N*/100	2.10 *N*/100	0.525
Iodic	2.35 *N*/100	2.40 *N*/100	0.600
Phosphoric	3.40 *N*/100	3.50 *N*/100	0.875
Hydrochloric	....	16.0 *N*/2 ?	200.0(?)
Nitric	..	17.0 *N*/2 ?	212.5(?)
Formic	5.25 2 *N*	5.5 2 *N*	275.0
Boric	6.75 3 *N*	7.0 3 *N*	525.0

normal, however, the association of the acid is apparently inappreciable and it behaves like a monobasic acid.[1] Periodic acid, H_3IO_6 or $HIO_4.2H_2O$, is ionized chiefly as a binary electrolyte[2] but it gives some divalent anions,[3] which may account in part for the small precipitation value. Giolitti has included boric acid with sulphuric and phosphoric acids, whereas our observations show that it precipitates only in very high concentration. As a matter of fact, one should expect it to behave as a weak monobasic acid for it ionizes but very slightly, giving only the ions $H^{\cdot}$ and $H_2BO'_3$.

The order of ions would seem to be

dichromate > tartrate > sulphate > citrate > oxalate >
iodate > phosphate > nitrate > chloride >
formate > borate.

Considering the ions common to both series, it will be noted that the order is the same with the acids as with the potassium salts. The precipitation values of the former are somewhat

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[1] Miolati and Mascetti: Gazz. chim. ital., **31**, I, 93 (1901); Atti Accad. Lincei, [5] 14 I, 217 (1905).

[2] Rothmund and Drucker: Zeit. phys. Chem., **46**, 849 (1903).

[3] Miolati and Mascetti: Loc. cit.; cf. Thomsen: Ber. deutsch. chem. Ges., **7**, 71 (1874).

larger since hydrogen ion is more strongly adsorbed than potassium ion.

Determination of Adsorption

Weiser and Sherrick[1] determined the amounts of various ions adsorbed by barium sulphate, by precipitating the salt under definite conditions; washing the precipitate; and analyzing it directly for the adsorbed anion by a suitable method. For two reasons it was decided to adopt a similar process for determining the ions adsorbed by precipitated ferric oxide: in the first place, the analysis of the solution before and after precipitation is not applicable when a high concentration is necessary to effect coagulation since the amount adsorbed is too small compared with the amount added; in the second place, this method probably does not give correct results in any case and it certainly would not with a gelatinous precipitate like ferric oxide, which must adsorb some of the solvent as well as the solute. Giolitti[1] pointed out that acids with a high precipitation value like hydrochloric, hydriodic, hydrobromic and nitric, produce a granular precipitate that redissolves on washing. Accordingly it was decided to use the potassium salts that produce a gelatinous precipitate, which it was thought would not redissolve on washing. Unfortunately such was not the case with those salts that precipitate in high concentration. In the procedure that was adopted, the precipitation was first effected by addition of the electrolyte after which the precipitate was centrifuged out and the supernatant liquid poured off. Distilled water was then added for the purpose of washing; the precipitate stirred up; and again centrifuged. As a rule, enough of the precipitating agent was washed out by the first washing so that a part of the colloid was peptized. Repeated attempts to modify the procedure to enable the precipitate to be washed, failed to give satisfactory results. The precipitate was gelatinous but the adsorption of univalent ions was so slight that they were readily removed.[2] This difficulty was not encountered

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[1] Loc. cit.

[2] Cf. Bancroft: Jour. Phys. Chem., 19, 236 (1913).

with the precipitate obtained with multivalent ions, for the latter were not removed by washing, owing to marked adsorption; and the precipitate did not redissolve. Our attention was accordingly directed to the determination of the adsorption of multivalent ions by the hydrous oxide.

Since the alkali salts of weak acids are hydrolyzed to a greater or lesser extent, it was decided to precipitate the colloid with the acids rather than their salts. From experiments with uranyl nitrate and beryllium sulphate, Freundlich[1] concluded that hydrolysis had no effect on the precipitation value. Since these salts at dilution V = 1024 liters are hydrolyzed to only approximately five percent,[2] the effect may not be very marked; but with a salt like the normal potassium or sodium phosphate, which is 98 percent hydrolyzed,[3] the effect must come in. Moreover it seems altogether probable that the high precipitating power of certain alkali salts with organic anions may be due in part, at least, to the formation by hydrolysis of the strongly adsorbed hydroxyl ion.

General Method of Procedure.—As before explained, if comparable results are to be obtained the amount adsorbed must be determined in the presence of an excess of the precipitating agent. Accordingly, fiftieth normal solutions of the electrolytes were made up and the concentrations accurately determined by a suitable method, which was the same as that used for determining the concentration after adsorption. An amount of the electrolyte equal to 50 cc of $N/50$ solution was used to effect the precipitation. This was carried out as follows: An apparatus was employed similar to that used in determining the critical coagulation concentrations except that it was larger. The outer tube was 5 cm in diameter and 38 cm in length, while the inner tube was 3 cm in diameter and 18 cm in length. The electrolyte was placed in the inner compartment and 200 cc of colloid in

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[1] Zeit. phys. Chem., 44, 129 (1905).
[2] Ibid., 30, 193 (1899).
[3] Shields: Ibid., 43, 71 (1905).

the outer compartment. By inverting the apparatus with a jerk and shaking briskly, rapid and uniform mixing was obtained. This solution was immediately transferred to a 275 cc wide-mouth bottle, taking care to rinse the apparatus three or four times with three to five cubic centimeters of water each time. After standing for five minutes the bottle was placed in the centrifuge and centrifuged for ten minutes at the rate of 2000 r. p. m. By this process, the precipitate was matted firmly in the bottom of the bottle, so that the supernatant solution could be poured off into a glass evaporating dish. In order to remove the electrolyte as completely as possible, the bottle was inverted and rinsed by directing a fine stream of water from a wash bottle against the sides, using particular care to avoid dislodging any of the precipitate. About 20 cc of water was then added to the bottle, which was subsequently shaken by a rotary motion until all the precipitate was completely broken up; after which it was transferred quantitatively to a special thick-walled tube of 60 cc capacity. The total volume of solution was 50 cc. This solution was centrifuged for ten minutes at 3000 r. p. m., the supernatant liquid added to the glass evaporating dish, and the sides of the tube carefully rinsed. Twenty cubic centimeters of water were then poured over the precipitate and a stopper was inserted in the container, which was shaken briskly for several minutes until the precipitate was thoroughly broken up. The stopper was removed and rinsed after which the solution was centrifuged and the wash water added to the rest. The washing was repeated but it was probably unnecessary. This method of washing the precipitate was much more effective and rapid than the usual method of washing on the filter paper, since a gelatinous precipitate is difficult to break up simply with a stream from a wash bottle. The supernatant liquid and washings were either evaporated and analyzed directly or diluted to a definite volume and an aliquot part taken for analysis. This general procedure was followed in determining the adsorption of phosphate, citrate, iodate, sulphate, tartrate, oxalate and dichromate ions. The determination of adsorption of the specific ions will now be considered in detail.

Adsorption of Iodate Ion

Method of Analysis.—An approximately $N/50$ solution of iodic acid was prepared by weighing a calculated amount of pure iodine pentoxide and dissolving in water. Ten cubic centimeters of this solution were placed in a 350 cc Erlenmeyer flask, diluted to 100 cc and the solution rendered alkaline by the addition of a slight excess of standard potassium hydroxide solution. To this solution were then added ten cubic centimeters of five percent KI solution and an excess of acetic acid. The following reaction takes place:

$$KIO_3 + 5KI + 6HAc = 6KAc + 3H_2O + 6I$$

The liberated iodine was titrated with standard thiosulphate solution, using starch as indicator. The thiosulphate solution was approximately fiftieth normal and just before using it was standardized against a weighed amount of purified resublimed iodine. This precaution was necessary on account of the tendency of thiosulphate to undergo slight oxidation on standing. That the method gives concordant results is shown from Table V.

Table V

Standardization of Iodic Acid

Iodic acid taken cc	Thiosulphate taken 0.022227 N cc	Normality of acid	
			Average
10	53.79	0.01993	
10	53.88	0.01996	
10	53.71	0.01990	0.01993

Adsorption of Iodate Ion.—To 200 cc of colloid containing 0.3088 gram of ferric oxide were added 50.18 cc of the standard iodic acid which is equivalent to 50 cc of $N/50$ acid. The procedure was carried out as previously described in detail. The solution containing the unadsorbed iodic acid was diluted quantitatively to 500 cc and 50 cc were taken for analysis. Four determinations were made and the average was taken as the adsorption value. The details are given in Table VI.

Table VI

Adsorption of Iodate Ion

Thiosulphate taken cc			$N/50$ Iodic acid cc			Adsorption value. Milliequivalents		
I	II	Average	Taken	Re-maining	Ad-sorbed		Per g Fe_2O_3	
20.53	20.55	20.54	50.00	38.05	11.95	0.2390	0.7739	Average
20.93	20.93	20.93	50.00	38.76	11.24	0.2248	0.7292	
20.52	20.52	20.52	50.00	38.01	11.99	0.2398	0.7765	
20.92	20.96	20.94	50.00	38.78	11.22	0.2244	0.7266	0.7512

Adsorption of Dichromate Ion

Ostwald[1] has shown that the solution of chromic anhydride in water is not chromic acid, H_2CrO_4, but the dichromic acid, $H_2Cr_2O_7$. An approximately $N/50$ solution of this acid was prepared and analyzed iodometrically, taking advantage of the following reaction:

$$K_2Cr_2O_7 + 6KI + 7H_2SO_4 = 4K_2SO_4 + Cr_2(SO_4)_3 + 7H_2O + 3I_2$$

Seubert and Hinke[2] have made an extended study of the rate of progress of the reaction in the presence of different quantities of the reacting substances. The following proportions were found to be particularly satisfactory for analytical purposes: dichromate, 0.05 g; potassium iodide, 0 5 g; sulphuric acid, 1.8 g; total volume, 100 cc. Under these conditions the reaction is complete in about six minutes. The procedure used in the standardization was as follows: 10 cc of the acid were measured into a 500 cc Erlenmeyer flask, neutralized with potassium hydroxide, and diluted to 65 cc. To the dichromate solution were added 10 cc of five percent potassium iodide solution and 25 cc of eight percent sulphuric acid solution; after which the flask were stoppered and allowed

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[1] Ostwald: Zeit. phys. Chem., 2, 78 (1888).

[2] Zeit. anorg. Chem., 14, 1147 (1902).

to stand for ten minutes. The liberated iodine was titrated with standard thiosulphate solution, using starch as indicator. The green color of the chromic salt did not interfere with the starch-iodide end point and excellent results were obtained.

Table VII
Standardization of Dichromic Acid

Acid taken cc	Thiosulphate taken 0.022227 *N* cc	G acid per liter	Normality	
10.00	26.13	0.21102	0.01936	Average
10.00	26.10	0.21081	0.01934	
10.00	26.13	0.21102	0.01936	
10.00	26.15	0.21124	0.01938	0.01936

Determination of Adsorption.—The solution, after the usual precipitation and washing, was evaporated to about 150 cc and then transferred quantitatively to a 200 cc volumetric flask and diluted to the mark. Fifty cubic centimeters were taken for analysis and the process carried out as above described. Check determinations were made on each sample. The results are given in Table VIII.

Table VIII
Adsorption of Dichromate Ion

Thiosulphate taken 0.022227 *N* cc			*N*/50 Dichromic acid cc			Adsorption value. Milliequivalents		
I	II	Average	Taken	Re-maining	Ad-sorbed		Per g of Fe_2O_3	
30.40	30.41	30.41	50.00	45.06	4.94	0.0988	0.3199	Average
30.58	30.58	30.58	50.00	45.31	4.69	0.0938	0.3037	
30.49	30.53	30.51	50.00	45.21	4.79	0.0958	0.3132	
30.56	30.59	30.57	50.00	45.34	4.66	0.0932	0.3018	0.3119

In order to determine whether the adsorbent was approximately saturated with dichromate ion under the conditions above described, the adsorption value was redetermined using a more dilute solution of dichromic acid. This was possible because of the low precipitation value of the acid. The experiments were carried out as before except that 50 cc of *N*/100 solution were used to effect the precipitation. The solution after the precipitation was evaporated to 200 cc, diluted quantitatively to 250 cc and 80 cc taken for analysis. The results are given in Table IX.

Table IX
Adsorption of Dichromate Ion from *N*/500 Solution

Thiosulphate taken cc			*N*/100 Dichromic acid cc			Adsorption value. *Milliequivalents*		
I	II	Average	Taken	Remaining	Adsorbed		Per g of Fe_2O_3	
17.78	17.77	17.78	50.00	41.61	8.84	0.0884	0.2862	Average
17.63	17.74	17.68	50.00	40.93	9.07	0.0907	0.2937	0.2904

Since the adsorption value obtained from the more dilute solution is but slightly less than was found for the more concentrated solution (0.2904 as compared with 0.3119 milliequivalent anions per gram of ferric oxide) it is evident that the adsorbent is approximately saturated under the conditions chosen; and hence that the adsorption would be increased but slightly by increasing the concentration of solution.

Adsorption of Oxalate Ion

Method of Analysis.—A fiftieth normal solution of oxalic acid was prepared by direct weighing of the required amount of Kahlbaum's oxalic acid "for analysis." This solution was used for the standardization of a permanganate solution that was subsequently used to analyze the solution after precipitation. An approximately *N*/50 solution of potassium permanganate was prepared and allowed to stand several days before standardization. Since the volume of solution to be analyzed was approximately 350 cc, the standardization of the permanganate was made in this volume. Before adding the permanganate, a definite excess of sulphuric acid was added and the solution heated to 60 degrees. By taking the necessary precautions, accurate results were obtained, as shown in Table X.

TABLE X
Standardization of Permanganate

N/50 Oxalic acid cc	Permanganate solution cc	Normality of permanganate	
20.30	25.20	0.024826	Average
20.03	24.95	0.024912	
20.15	25.05	0.024862	
20.15	25.06	0.024862	
20.05	24.95	0.024886	0.02487

Determination of Adsorption.—The precipitation was carried out in the usual way and the entire solution analyzed directly. The results are given in Table XI.

TABLE XI
Adsorption of Oxalate Ion

Permanganate cc	N/50 Oxalic acid cc			Adsorption value. Milliequivalents		
	Taken	Re-maining	Adsorbed		Per g Fe_2O_3	
28.95	50.0	36.00	14.00	0.2800	0.9066	Average
29.00	50.0	36.06	13.94	0.2788	0.9028	
28.90	50.0	35.93	14.07	0.2814	0.9112	
28.65	50.0	35.63	14.37	0.2874	0.9306	0.9128

Adsorption of Tartrate Ion

Method of Analysis.—Since oxalic, tartaric and citric acids can be very readily titrated with sodium hydroxide, using phenolphthalein as indicator, the direct titration of these acids would seem to be the simplest method of analysis. A complication arises from the fact that the colloidal solution is slightly acid with acetic acid which was not completely removed in the boiling process, so that the solution after precipitation can not be analyzed directly. It was found, however, that solutions of citric and tartaric acid, to which has been added a little acetic acid, could be evaporated to dryness and heated in the drying oven to 70 degrees to remove the acetic acid. There was no loss of citric or tartaric acid in this way as the subsequent experiments show. As is well known, oxalic acid can not be subjected to such treatment, as solutions of the acid can not be boiled without loss. A fiftieth-normal solution of tartaric acid was prepared by weighing the calculated amount of Kahlbaum's reagent "for analysis." This was titrated with sodium hydroxide solution, compared with the $N/50$ oxalic and found to be $N/50$ as is evident from Table XII. In order to show that a small amount of acetic acid may be removed without the loss of tartaric acid, 25 cc of the solution were taken, three drops of acetic acid added, and the solution taken about to dryness on a hot plate. It was then placed in the oven at 70 degrees and heated for one or two hours after all the water had been driven off. The acid was then redissolved in 50 cc of water, phenolphthalein added and finally titrated with NaOH which was 0.019304 normal. The results of Experiments 7 and 8 as compared with 4, 5 and 6 show that the acetic acid had been removed without loss of tartaric acid.

TABLE XII

Standardization of Tartaric Acid

No.	Acid	Acid cc	Base cc
1	Oxalic	25	25.90
2	Oxalic	25	25.95
3	Oxalic	25	25.95
4	Tartaric	25	25.95
5	Tartaric	25	25.95
6	Tartaric	25	26.00
7	Tartaric	25	25.93
8	Tartaric	25	25.96

Determination of Adsorption.—As the titration of the acid proved to be entirely satisfactory, the precipitation was carried out in the usual way. The solution after the precipitation was taken almost to dryness on a hot plate and the drying completed in the oven at 70 degrees as previously described. The results are given in Table XIII.

Table XIII
Adsorption of Tartrate Ion

NaOH taken 0.019304 *N* cc	*N*/50 Tartaric acid cc			Adsorption value, Milliequivalents		
	Taken	Remaining	Adsorbed		Per g of Fe_2O_3	
						Average
31.75	50.00	30.65	19.35	0.3870	1.2631	
31.95	50.00	30.85	19.16	0.3832	1.2408	
31.80	50.00	30.79	19.21	0.3842	1.2440	
32.00	50.00	30.89	19.11	0.3822	1.2376	1.2464

Adsorption of Citrate Ion

Method of Analysis.—A fiftieth-normal solution of citric acid was made by direct weighing of the required amount of Kahlbaum's reagent "for analysis." The normality was tested by comparison with the *N*/50 oxalic and found to be correct. (Compare Experiment 1 with 2, 3 and 4, Table XIV.) That the solution could be evaporated to dryness to remove acetic acid was shown in the same manner as above described. (Experiments 5 and 6, Table XIV.)

Table XIV
Standardization of Citric Acid

No.	Acid	Acid cc	Base cc
1	Oxalic	25	25.93
2	Citric	25	25.90
3	Citric	25	25.90
4	Citric	25	25.90
5	Citric	25	25.86
6	Citric	25	25.89

Determination of Adsorption.—The precipitation and washing were carried out in the usual way. It was found, however, that in this case the second washing could not be added to the rest since an appreciable amount of the precipitate went into colloidal solution. The results are given in Table XV.

TABLE XV

Adsorption of Citrate Ion

NaOH taken 0.019304 *N* cc	*N*/50 Citric acid cc			Adsorption value. Milliequivalents		
	Taken	Re-maining	Adsorbed		Per g of Fe_2O_3	
						Average
27.77	50.00	26.80	23.20	0.4640	1.5024	
28.00	50.00	27.02	22.98	0.4596	1.4882	
27.45	50.00	26.48	23.52	0.4704	1.5231	1.5046

Adsorption of Sulphate Ion

Method of Analysis.—An approximately *N*/50 solution of sulphuric acid was prepared and analyzed gravimetrically by the barium sulphate method. 50 cc of the solution were taken for analysis; diluted to 200 cc, 0.2 cc of hydrochloric acid added, and heated to boiling. To the boiling solution was added from a burette a definite slight excess of a solution of barium chloride, the addition being made drop by drop with constant stirring. This solution was then digested on the hot plate for six hours, after which it was filtered through a Gooch crucible and the precipitate washed, dried and ignited in the usual way. See Table XVI.

TABLE XVI

Standardization of Sulphuric Acid

Sulphuric acid taken cc	$BaSO_4$ found g	Normality of acid	
			Average
50.00	0.1164	0.019944	
50.00	0.1166	0.019979	
50.00	0.1162	0.019911	
50.00	0.1162	0.019911	0.019936

Determination of Adsorption.—The solution after precipitation and washing was evaporated to 200 cc and analyzed for sulphate in exactly the same manner as above described. The results were entirely satisfactory, as shown in Table XVII.

TABLE XVII
Adsorption of Sulphate Ion

$BaSO_4$ found g	N/50 Sulphuric acid cc			Adsorption value. Milliequivalents		
	Taken	Remaining	Adsorbed		Per g of Fe_2O_3	
0.0889	50.00	38.08	11.92	0.2384	0.7719	Average
0.0892	50.00	38.21	11.79	0.2358	0.7635	
0.0898	50.00	38.46	11.54	0.2308	0.7473	
0.0893	50.00	38.25	11.75	0.2350	0.7609	0.7609

Adsorption of Phosphate Ion

Method of Analysis.—Analysis of the phosphoric acid solutions were made by the volumetric method of Pemberton[1] which consists in precipitating the phosphate ion as phosphomolybdate, dissolving the latter in standard alkali and titrating back with standard nitric acid. One mole of P_2O_5 requires forty-six moles of KOH. The precipitation was accomplished by ammonium molybdate solution which was prepared in the usual way and allowed to stand for ten days. The solution and back titration were accomplished with tenth normal solutions of NaOH and HNO_3, respectively. The procedure in detail was as follows: 40 cc of an approximately $N/50$ phosphoric acid solution were allowed to run into a 250 cc Erlenmeyer flask supplied with a clean rubber stopper. This solution was heated to forty degrees in a water bath and to it were added 15 cc of ammonium nitrate solution containing 750 grams per liter, and 50 cc of the molybdate solution. The flask was set in the water bath at forty degrees for thirty minutes, after which it was shaken vigorously for five minutes and returned to the water bath for an additional thirty minutes. It was then filtered, the precipitate washed first with two percent nitric acid to free from ammonium

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[1] Jour. Am. Chem. Soc., **16**, 278 (1894).

molybdate and finally with one-tenth percent ammonium nitrate to free from nitric acid. Care was taken to use just as little wash water as possible on account of the slight solubility of the precipitate. The precipitate with the filter paper was transferred to a beaker, dissolved in a measured excess of *N*/10 NaOH and after adding six drops of one percent phenolphthalein the excess alkali was titrated back as rapidly as possible with the standard acid. The results of the standardization are given in Table XVIII.

TABLE XVIII
Standardization of Phosphoric Acid

Acid taken cc	Base required to dissolve phosphomolybdate			Normality of acid	
	Base cc	Acid cc	Difference cc		
40.00	74.18	11.41	62.77	0.02046	Average
40.00	75.25	11.38	63.13	0.02058	
40.00	75.23	11.20	63.29	0.02063	
40.00	72.33	9.02	63.31	0.02060	
40.00	72.47	9.44	63.03	0.02054	0.02056

Determination of Adsorption.—After carrying out the precipitation and washing in the usual way, the solution was evaporated to 50 cc, transferred to a 150 cc Erlenmeyer flask and analyzed as described above. The results are given in Table XIX.

TABLE XIX
Adsorption of Phosphate Ion

N/10 Alkali to dissolve phosphomolybdate cc			*N*/50 Phosphoric acid cc			Adsorption value. Milliequivalents		
Base	Acid	Difference	Taken	Remaining	Adsorbed		Per g Fe_2O_3	
50.68	14.90	35.78	50.00	23.34	26.66	0.5332	1.7265	Average
51.04	14.84	36.20	50.00	23.56	26.44	0.5288	1.7123	
50.40	14.21	36.19	50.00	23.60	26.40	0.5280	1.7097	
50.41	14.68	37.73	50.00	23.31	26.69	0.5338	1.7284	
50.49	14.21	36.18	50.00	23.66	26.34	0.5268	1.7058	1.7165

Discussion of Results

The results of the above series of experiments are summarized in Table XX. In the last two columns are tabulated the degrees of ionization and the ionization constants of the various acids. Since the adsorption values were determined from solutions that were $N/250$ at the outset, the degree of ionization at this dilution was calculated from conductivity data. The numbers (1), (2) and (3) before the ionization constants indicate that the values are for the first, second and third steps.

TABLE XX

Anion	Adsorption value Per gram Fe_2O_3		Precipitation value, Milliequivalents per liter	Ionization of 0.004 *N*. Solutions percent	Ionization constants K × 1000
	Milligram anions	Milliequivalent anions			
Phosphate	0.5721	1.7165	0.875	70	(1) 11.0 (2) 0.002 (3) 0.084
Citrate	0.5018	1.5046	0.500	51	(1) 0.82 (2) 0.03 (3) 0.0007
Tartrate	0.6232	1.2464	0.475	53	(1) 0.97 (2) 0.06
Oxalate	0.4364	0.9128	0.525	88	(1) 100.0 (2) 0.05
Sulphate	0.3804	0.7609	0.485	95	(1) 450.0 (2) 17.0
Iodate	0.7512	0.7512	0.600	96	(1) 190.0
Dichromate	0.1559	0.3119	0.200	98	(1) large (2) large

From the table it will be seen that all the ions are strongly adsorbed by hydrous ferric oxide; the amounts varying in milliequivalents per gram from approximately 0.3 in the case of dichromate to 1.7 in the case of phosphate ion. The average adsorption value in milliequivalents per gram of arsenic trisulphide was found by Whitney and Ober[1] and by

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[1] Loc. cit.

Freundlich[1] to be approximately 0.08; and the average value per gram of mercuric sulphide was but 0.02.[2] The values for hydrous ferric oxide show clearly that the amounts of ions carried down by a precipitated colloid are not equivalent. As a matter of fact, the actual variation in the values is less than noted by Freundlich with mercuric sulphide; but he attributed the variation from equivalence to the analytical difficulties connected with the determination of very small adsorption values. The relatively large adsorption values in the case of hydrous ferric oxide and the accuracy with which they may be determined indicate conclusively that the values are not even approximately the same. As before explained, other conditions remaining the same, equivalent amounts must be adsorbed to neutralize the charge on the colloidal particles; but the adsorption does not stop with neutralization of the charge and the amounts actually carried down by the precipitate will vary with the adsorbability of the ions.

If the ions are arranged in the order of their adsorption values expressed in milliequivalent anions per gram of adsorbent, the following series is obtained:

phosphate > citrate > tartrate > oxalate > sulphate > iodate > dichromate,

the phosphate being adsorbed the most and the dichromate the least. The precipitation values expressed in milliequivalents per liter would indicate the order of adsorption to be

dichromate > tartrate > sulphate > oxalate > citrate > iodate > phosphate.

It is evident that there is a tendency for ions with the lowest precipitation values to be absorbed the least and *vice versa*, which is diametrically opposed to what one should expect. Since the ionization constant for the third step in the ionization of both citric and phosphoric acids is very small it might seem preferable to consider them as dibasic acids rather than

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[1] Zeit. phys. Chem., 73, 385 (1910).

[2] Freundlich and Schucht: Ibid., 85, 641 (1913).

tribasic. The only change that this would make in the series of adsorption values would be to put tartrate ion ahead of citrate and phosphate ions, the series becoming

tartrate > phosphate > citrate > oxalate > sulphate > iodate > dichromate.

Under these conditions the precipitation values would indicate the order to be

dichromate > citrate > tartrate > sulphate > oxalate > phosphate > iodate.

The marked difference between the order of ions as determined by direct analysis and as deduced from precipitation values indicates one of two things: either there is some experimental error in the procedures or the precipitation values do not give a true measure of the order of adsorption. On account of the accuracy of the analytical methods employed in the determination of the relatively large adsorption values and the close agreement among the several determinations for each ion, it would seem that the adsorption values are quite accurate. By carrying out the experiments in the same way each time there was no difficulty in checking the precipitation values. But as previously pointed out, there are certain factors other than the valence of the precipitating ion that can not be maintained constant with a series of electrolytes; and these may have a marked influence on the critical coagulation concentrations. Among these variable factors may be mentioned the degree of ionization of electrolytes; hydrolysis of certain salts; the mobility of the ions which for certain ions decreases with the dilution on account of increased hydration; the stabilizing influence of the ion having the same charge as the colloid; and the rate of coagulation. Moreover the method of determining the critical coagulation concentrations may influence the order of precipitation values for a given colloid. Since these variable factors have an effect in determining the precipitation concentration that is more or less independent of the specific adsorption tendency, it is evident that precipitation values in themselves may not give a true measure of the relative tendency of ions to be adsorbed by a given disperse phase. Accordingly it is not surprising that the order of adsorption determined by direct analysis is markedly different from the order deduced from precipitation data. We should ordinarily expect the deduced order of adsorption to be least accurate in cases where the precipitation values are close together and comparatively small.

At first thought it might seem preferable to determine the adsorption values at the precipitation concentration. But as previously pointed out, in the nature of things comparable values could not be obtained under such conditions. The colloid is neutralized when equivalent amounts of various ions are adsorbed; but the particles after neutralization adsorb the various ions in proportion to their specific adsorbability and their concentration in the solution. Since the precipitation concentrations vary widely, the degree of saturation of the adsorbing medium at the precipitation concentration will necessarily vary so that the results will not be comparable. Accordingly the adsorption values were determined at a constant concentration considerably above the precipitation concentration.

Since the precipitating power of an electrolyte is determined by the precipitating power of the active ion, one might expect to find the electrolyte with the greatest ionization constant having the greatest precipitating power. As a matter of fact, there is apparently little connection between the two, as may be seen from the table. The electrolytes arranged in the order of ionization constants beginning at the largest are

dichromate > iodate > sulphate > oxalate > phosphate > tartrate > citrate;

while the electrolytes in the order of their precipitation values, beginning with the smallest, are

dichromate < sulphate < tartrate < citrate < oxalate < iodate < phosphate.

That there is little connection between the precipitating power and the ionization constants is readily understood when we consider that most of the electrolytes are quite highly ionized in 0.004 normal solutions and are even more strongly ionized at the precipitation concentrations. Accordingly, the differences in the degree of ionization at high dilution may be relatively unimportant compared to the other factors that determine the precipitation value. In line with this we find that the precipitation values of the relatively highly ionized potassium salts of the acids follow the same order as the acids themselves.

Since all the acids are fairly highly ionized at the dilution used in determining adsorption values it is questionable whether differences in the ionization have an effect at all comparable with the differences in the specific adsorbability of the different ions. Thus dichromic and sulphuric acids are practically completely ionized and yet sulphate ion is adsorbed more than twice as strongly as dichromate ion. Moreover, iodic acid is as strongly ionized as sulphuric acid and the univalent iodate ion is adsorbed about as strongly as the divalent dichromate ion. Futhermore, citric and tartaric acids have approximately the same ionization constants; are ionized to approximately the same extent; and have nearly the same precipitation values; and yet the adsorption values are quite different. As before mentioned, it may be that citric and phosphoric acids should be considered as dibasic, but this would not change the order materially.

The series of adsorption values is unfortunately incomplete since the adsorption of but one univalent ion could be determined under the constant experimental conditions which must be maintained if comparable results are to be obtained. However, it will be noted that the trivalent ions have the largest adsorption values and with the exception of dichromate, the univalent iodate ion is least adsorbed. This same tendency for ions of higher valence to be adsorbed most strongly was noted in the case of precipitated barium sulphate. That there are exceptions to this rule and that ions of the same valence are frequently adsorbed in widely varying amounts may be expected since adsorbability is a specific property of ions.

Summary

The results of this investigation may be summarized as follows:

(1) Since the first step in the precipitation of a colloid by an electrolyte is the neutralization of the charge by the adsorption of an ion of opposite charge, it follows that two adsorbing media are concerned in the process: the electrically charged particles and the electrically neutral particles. Accordingly the total amount of a given ion carried down by a precipitated colloid is determined by (*a*) the adsorption by the electrically charged particles during the process of neutralization; and (*b*) the adsorption of the electrically neutral particles during the process of agglomeration and settling. Failure to take (*b*) into account has led to the erroneous conclusion that the amounts of all precipitating ions carried down by a precipitated colloid are equivalent.

(2) The adsorption of equivalent amounts of precipitating ions will neutralize a given amount of colloid, providing the stabilizing effect of the ion having the same charge as the colloid is maintained constant; but the amounts adsorbed by the neutralized particles will vary with the nature of the adsorbing medium, the nature of the adsorbed ion and the concentration of the ion in the solution.

(3) The determination of adsorption values at the precipitation concentration, as a rule will not give comparable results because of the variability in the latter and the consequent variability in the degree of saturation of the adsorbent by the adsorbed phase.

(4) The variation from equivalence in the adsorption values determined by Freundlich are probably due quite as much to the varying concentration and adsorbability of the ions as to the errors in the analytical procedures.

(5) The precipitation concentrations of a number of acids and salts and the adsorption values of phosphate, tartrate, iodate, sulphate, citrate, dichromate and oxalate ions have been determined for colloidal hydrous ferric oxide prepared by the method of Péan de St. Gilles. The relatively

strong adsorption of the above-mentioned ions by the hydrous oxide made possible the accurate determination of the adsorption values.

(6) The adsorption of univalent ions by the hydrous ferric oxide was so weak relatively that the precipitate was readily peptized by washing, owing to removal of the precipitating ions.

(7) The amounts of the ions adsorbed are not even approximately equivalent. The order of adsorption is: phosphate > citrate > tartrate > oxalate > sulphate > iodate > dichromate, the phosphate ion being adsorbed the most and dichromate the least. The order of adsorption determined by direct analysis is entirely different from the order deduced from precipitation values on the assumption that the most strongly adsorbed ion precipitates in the lowest concentration. The latter order is: dichromate > tartrate > sulphate > citrate > oxalate > iodate > phosphate.

(8) In addition to the effect of the valence and the adsorbability of precipitating ions, the precipitation values are influenced by differences in the degree of ionization of electrolytes; the hydrolysis of certain salts; the stabilizing effect of the ion having the same charge as the colloid; the mobility of the ions which in certain cases decreases with dilution owing to increased hydration; the rate of coagulation; and the method of procedure in determining the critical concentrations. Because of these effects the order of adsorption of ions deduced from precipitation values are not trustworthy, particularly in case the ions compared all precipitate in very low concentrations.

(9) The order of precipitation values is the same for the acids as their potassium salts except that the former precipitate in somewhat higher concentration than the latter owing to the stabilizing effect of the strongly adsorbed hydrogen ion. There is apparently no connection between the precipitation values and the ionization constants of the acids investigated, probably because precipitation takes place at such high dilution, 0.0002 to 0.0008 normal.

(10) The order of precipitation values of the potassium salts beginning with the smallest is: ferrocyanide < ferricyanide < dichromate < tartrate < sulphate < oxalate < chromate < iodate < bromate < thiocyanate < chloride < chlorate < nitrate < bromide < iodide < formate. The order is practically the same as Freundlich found for the Graham colloid. This would follow if the only difference between the two colloids is in the size and degree of hydration of the particles.

(11) The precipitation values of salts of polybasic acids are not so close together as Duclaux found for the Graham colloid. This is partly due to differences in the method of determining the critical concentration. The precipitation values are not the same and equivalent to the chloride content of the colloid, as Duclaux supposed. The chloride content of the Graham colloid is a measure of the adsorbed ferric and hydrogen ions by which the colloid is stabilized. Other conditions being the same, the precipitating values of anions will approach equivalence to the chloride ion concentration in so far as their adsorbability approaches that of the stabilizing cations.

(12) There is a tendency for ions of the highest valency to be most strongly adsorbed. That there are exceptions to this rule and that ions of the same valence are frequently adsorbed in widely varying amounts may be expected since adsorbability is a specific property of the ions.

Investigations on adsorption by precipitates are being continued in this laboratory.

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NOTE ON THE LIQUEFACTION OF GELATIN BY SALTS

BY T. R. BRIGGS AND EVELYN M. C. HIEBER

It is a well-known fact that both the velocity with which aqueous gelatin solidifies on cooling and the temperature at which the jelly forms are influenced by the presence of dissolved substances.[1] Alkali sulphates, citrates, tartrates and acetates, as well as glycerin, raise the temperature of gelatinization, while chlorides, bromides, iodides and sulphocyanates lower it, the iodides and sulphocyanates being most active.

The following simple experiments serve well to illustrate the phenomenon and they also show that the salts are without permanent effect upon the gelatin We are unaware of any one having established the latter point experimentally, though Larguier des Bancels hints of having done so.[2]

Commercial gelatin of the highest grade was submitted to long-continued dialysis to remove soluble impurities. Mixtures of gelatin, salt and water were prepared, each containing approximately 5 percent of gelatin. The mixtures were placed in test tubes in a constant temperature bath at 19° C and allowed to stand 36 hours. The data follow:

TABLE I

Added Electrolyte	Concentration of Salt	Condition of Gelatin at 19° C		
		After 30 minutes	After 24 hours	After 36 hours
$ZnCl_2$	33%	Fluid	Fluid	Fluid
KCl	33	Jelly	Jelly	Jelly
NH_4NO_3	33	Fluid	Fluid	Fluid
KSCN	33	Fluid	Fluid	Fluid
$MgCl_2$	33	Fluid	Jelly	Jelly
KNO_3	Saturated (cold)	Fluid	Semi-fluid	Semi-fluid
NH_4Cl	Saturated (cold)	Fluid	Jelly	Jelly

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[1] Cf. Pascheles: Pflüger's Archiv., 71, 333 (1898); Steele: Zeit. phys. Chem., 40, 689 (1902); Levites: Zeit. Kolloidchemie, 2, 162 (1908); Sadikoff: Zeit. phys. Chem., 41, 15 (1904).

[2] Larguier des Bancels: Comptes rendus, 140, 290 (1908).

The contents of the test tubes were then transferred to dialyzing thimbles of collodion. After 24 hours' dialysis at 19° C, the mixtures in *all* the thimbles were found to have set to a firm jelly. The experiments show that removal of $ZnCl_2$, NH_4NO_3, KSCN or KNO_3 permits the gelatin to reassume its normal power of gelatinization.

The three thimbles, containing the solidified gelatin from the experiments with $ZnCl_2$, NH_4NO_3 and KSCN, were next placed in solutions of $ZnCl_2$, NH_4NO_3 and KSCN (33 percent), respectively. After one hour the contents of each thimble were seen again to be completely fluid, showing that the process of liquefaction and gelatinization produced by salts is entirely reversible, being similar in this respect to liquefaction and gelatinization due to changes of temperature.

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NEW BOOKS

Catalysis in Theory and Practice. *By Eric K. Rideal and Hugh S. Taylor. 21 X 15 cm; pp. xv + 496. New York: The Macmillan Co., 1919.*— In the preface the authors say: "In the development of chemical science during the preceding hundred years, the steady progress in importance which catalytic operations have achieved is distinctly remarkable. Their importance emerges alike in the purely theoretical and in the technical aspects of the subject. In the natural order, also, investigation has shown how predominating a part the catalytic phenomenon plays. From the strictly utilitarian point of view, industry was not slow to appreciate the advantages to be derived from the employment of agencies which should facilitate and 'speed up' manufacturing processes, nor was there lacking a body of scientific workers who steadily supplied the investigative and theoretical bases upon which such applications could be reared. As the scientific viewpoint developed, the physiologist and biologist rapidly associated the simpler chemical phenomena with the more complex processes operating in living matter. Today, therefore, catalysis intrudes prominently into all branches of natural science, both pure and applied. The need for an exposition of the fundamental principles involved in this particular field of general chemistry and of the applicability of such principles in modern life has been widely felt and has offered to the authors the necessary inducement to prepare the present volume."

The chapters are entitled: early history; theoretical introduction; the measurement of reaction velocity in catalytic processes; oxidation processes; hydrogen and hydrogenation; dehydrogenation; the fixation of nitrogen; hydration and hydrolysis; dehydration; applications of catalysis to organic chemistry; ferments and enzymes; catalysis in electro-chemistry; catalysis by radiant energy; catalysis in analytical chemistry.

Under oxidation processes are included: contact and chamber sulphuric acid; the Hargreave salt-cake process; the oxidation of ammonia; the Deacon chlorine process; the Weldon chlorine process; the Chance-Claus sulphur process; the removal of hydrogen sulphide from illuminating gas; surface combustion; the Welsbach mantle; the preparation of formaldehyde; the preparation of aniline black; and the drying of oils.

Under hydrogen the authors consider the electrolytic process, the steam-iron process, and the catalytic water-gas process. The last process is considered the best even though the carbon dioxide which must be removed is upwards of thirty precent of the gas mixture. With the new catalytic agents, p. 165, it is possible to oxidize and eliminate traces of carbon monoxide. Hydrogen of high purity can be prepared by exploding acetylene under pressure by means of an electric spark; but the cost is high. It is suggested, p. 174, that a catalytic process should be developed whereby hydrocarbons and carbon dioxide should react to form hydrogen and carbon monoxide. Under hydrogenation the hardening of oils is technically the most important sub-heading.

In the chapter on the fixation of atmospheric nitrogen, the processes considered are the arc process, the Haber ammonia process, the cyanamide process, the nitride process, and the Bucher process. It has been found by the Badische Company that the positive catalytic effect produced by a given substance may be increased considerably by the addition of small quantities of other substances which are called promoters. In regard to this Rideal and Taylor say, p. 31: "The method of activation of a catalyst by addition of small quantities of promoters is being extended rapidly in technical applications, and already in such important industries as ammonia synthesis, ammonia oxidation by non-platinum catalysts and contact sulphuric acid manufacture using base metal contact materials, the use of promoters has been claimed definitely in the patent literature. Thus far no theory put forward to account for the acceleration of reaction by minute quantities of promoters added to the main catalyst material, is completely satisfactory. A possible mechanism, which, however, has received no experimental test, may be advanced by considering the case of ammonia synthesis from mixtures of nitrogen and hydrogen. Reduced iron is an available contact substance, the activity of which may be regarded as due to the simultaneous formation of the compounds, hydride and nitride, with subsequent rearrangement to give ammonia and unchanged iron. Or, maybe, the activity of the iron is due to simultaneous adsorption of the two gases. The particular mechanism of the catalysis is unimportant for the present considerations. Now such bodies as molybdenum, tungsten, and uranium have been proposed, among others, as promoters of the activity of iron. It is conceivable that these act by adjusting the ratio in which the elementary gases are adsorbed by or temporarily combined with the catalytic material to give a ratio of reactive nitrogen and hydrogen more nearly that required for the synthesis, namely, one of nitrogen to three of hydrogen. From the nature of the materials suggested as promoters, it would seem that they are in the main nitride-forming materials, which on the above assumption of mechanism would lead to the conclusion that the original iron tended to adsorb or form an intermediate compound with greater proportion of hydrogen to nitrogen than required by the stoichiometric ratio. The catalytic activity of reduced iron as a hydrogenation agent would tend to confirm this viewpoint."

Under hydration the technically important problems during the war were synthetic acetic acid and acetone. These two processes are apparently on a sound commercial basis which is more than can be said of synthetic alcohol at present. The Canadian process for oxidizing aldehyde to acetic acid involves the use of oxygen under pressure with manganese acetate and other substances as catalytic agents. Care must be taken to prevent the formation of instable per-acids. The Badische Company claims to have got round this difficulty by using combined salts of iron and the alkaline earths, making it possible to oxidize at low temperatures, p. 251.

On page 274 the authors point out that lime acts catalytically in saponifying fats because one need use only one percent of lime. They do not show that the probable reason for this action is the emulsification of water in oil in presence of a calcium soap. Under dehydration the most important process during the war was the conversion of alcohol into ethylene in presence of alumina or kaolin as catalytic agent.

The chapter on ferments and enzyme action is good. Enzymes are classified as inducing coagulation, hydrolysis, and reduction or oxidation. Bertrand considers that enzymes consist essentially of an albuminous organic colloid associated with an inorganic colloid, which latter is the active catalyst, the co-enzyme or co-ferment. He regards the following elements as being the basis of enzyme catalytic activity: manganese in the oxydases and calcium in coagulation processes, while iron is associated with haemoglobin, magnesium with chlorophyll, and iodine in the thyroid gland. The authors say in regard to this, p. 350, that "Bertrand's hypothesis would appear tenable if the various enzymes acting catalytically in the above processes could also be divisible into three groups, and if in each group one enzyme were replaceable by another of the same group. We have already noted that with inorganic catalysts rough groupings may be compiled, such as certain oxides for processes of oxidation, reduced metals for hydrogenation, and irreducible oxides for dehydration and dehydrogenation, and we might postulate an even more rigid classification for the enzymes in each group. But, in actual fact, enzymes are not interchangeable to the extent which would be logically expected from Bertrand's hypothesis. Although the extreme view frequently stated that each chemical action requires its own particular enzyme, which is inoperative for any other reaction, is not entirely correct, yet the specific nature of enzyme action is so marked as to demand an inquiry into the reason."

Under catalysis in electrochemistry we find cathodic and anodic overvoltage, and passivity as the important features. Under catalysis by radiant energy, a good deal of space is of course given to the action of light on the hydrogen-chlorine gas mixture. The authors consider that a preliminary ionization of the chlorine does not occur, p. 419. "The work of Lenard and his pupils forms contributory evidence in opposition to the electronic theory of photo-chemical reaction. These workers showed that ionization, the formation of fogs, and chemical reaction are three quite distinct results of light action which have nothing to do with each other. Thus fog formation in illuminated chlorine is no evidence of ionization, and in the ozonization of oxygen, ionization and chemical reaction are affected by different regions of the spectrum and may be realized separately. The later investigations of Le Blanc and Vollmer also show that ionization is not detectable in a hydrogen-chlorine mixture illuminated by an Osram lamp."

Catalysis in analytical chemistry includes preferential combustion of gases, volumetric analysis involving permanganate, reduction of nitrates and chlorates, the Kjeldahl process for nitrogen determination, etc.

The book is an excellent one and the authors are to be congratulated on their work. The only criticism that the reviewer desires to make is that they have not always differentiated quite clearly enough between technical and laboratory processes. For instance, under dehydrogenation which, if any, are of importance technically at present?

Wilder D. Bancroft

Piezochemie Kondensierter Systeme. *By Ernest Cohen and W. Schut. 26 × 18 cm; pp. x + 449. Leipzig: Akademische Verlagsgesellschaft, 1919.* — This book was nearly printed in July, 1914, just before the war broke out; but was, of course, held up in consequence. The papers which have appeared since that time are given in an appendix; but no attempt has been made to rewrite the text. The reason for writing this book was the excellent one that the data which are here gathered together are scattered through at least fifty different journals, while the subject is treated very briefly in the recognized tables of physical and chemical data. Only those data are included in this volume which deal with sharply defined substances. Those who know the previous books by the senior author will not need to be told that the work has been done well.

The first chapter deals with the production and measurement of high pressures. The authors have devised an automatic regulator which enables them to keep any pressure up to 1500 atm. constant to within one-tenth of a percent for an indefinite period. The second and third chapters are devoted to compressibility, including as sub-heads: definitions and methods; discussion of methods; compressibility of glass, mercury, water, and ice; coefficients of compressibility (of the elements and the solid compounds coefficients of compressibility) of liquids and solutions adiabatic compressibility. The fourth, fifth and sixth chapters are concerned with the effect of pressure on the coefficient of expansion, the surface tension, and the point of maximum density of water and aqueous solutions. The surface tension increases with increasing pressure at the dineric interface for mercury and water mercury and ether, and carbon bisulphide and ether, while it decreases for water and ether or chloroform, the change in all cases being a linear function of the pressure. In the seventh chapter are data in regard to the effect of pressure on melting points and inversion points. Under these latter the author discusses the special cases of ammonium nitrate, ice, silver iodide, carbon dioxide, zinc sulphate, carbon tetrabromide, and dibrompropionic acid.

The eighth chapter deals with the flow of solids under pressure and with permanent changes in density. The authors accept the formula of Johnston and Adams which is based on the assumption that a pressure, which is exerted only on the solid phase, increases the vapor pressure and the solubility of the solid phase and lowers its melting point. While this is unquestionably true, it does not seem to the reviewer to follow necessarily that all flowing of solids under pressure, is preceded by a melting. The authors accept the explanation of Johnston and Adams that in Kahlbaum's experiments on the permanent change of density with high pressure, Kahlbaum was really working with unequal pressures; but they consider that a possible change to an allotropic modification is more probable than the formation of an amorphous film. The reviewer would have welcomed a discussion whether an amorphous film can be formed with a metal even if melting does take place.

The ninth chapter gives data on the viscosity of water and of aqueous solutions as affected by pressure. With pressures up to 900 atm., the viscosity decreases with rising temperature between 0° and 32°. Above 32° there is a decrease up to 400 atm. and an increase of viscosity when the pressures exceed that value. The effect of pressure on the viscosity of sodium chloride solution varies with the temperature and the concentration. At +2° the viscosity of an eight percent solution decreases with increasing pressure, while at 14° it increases.

There are six chapters on the effect of pressure on the electrical conductance, the transference number, the thermoelectric force, the dielectric constant, the Faraday law, and the electromotive force after which comes a chapter on the effect of pressure on solubility and one on the effect of pressure on reaction velocity. The last three chapters deal with diffusion, refractive index and rotation of the plane of polarized light.

This brief outline will show what an amount of ground is covered by the book. The whole subject is presented critically from a single point of view. The American Chemical Society is preparing to publish a series of scientific and technical monographs. If we can turn out anything as good in its way as this volume, we shall have done very well.

Wilder D. Bancroft

Handbook of Chemistry and Physics. *By Charles D. Hodgman, M. T. Coolbaugh, and C. E. Senseman. Seventh edition. 17 × 11 cm; pp. 553. Cleveland: The Chemical Rubber Company, 1918.*—In this seventh edition the chief change is in the introduction of an entirely new and very much enlarged table of the physical constants of organic compounds. The list embraces about two thousand compounds including many which have only recently become of importance. The more common alkaloids and their salts have been included. No absolutely sharp division between the organic and the inorganic tables can be made, certain substances being listed in both tables in deference to their importance in both branches of chemistry. In general, metallic salts formed by the organic acids, such as acetates, citrates, oxalates, etc., are listed under inorganic compounds. It is hoped that the numerous cross references and synonyms given will make the list more valuable to students not familiar with the nomenclature of organic chemistry. The constants, however, will be found in each case under the preferred name: The figures given have been made as accurate and as definite as possible. The molecular weights have been recomputed and the constants are so far as possible checked by reference to two or more authorities.

The reviewer is glad to bear witness that he has found the book helpful on the occasions on which he has had occasion to refer to it. He cannot endorse the statement, however, that tannic acid is soluble twenty parts per 100 cc of water.

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French Educational Ideals of Today. *By Ferdinand Buisson and Frederic E. Farrington. 21 × 14 cm; pp. xii + 326. Yonkers-on-Hudson: World Book Company, 1919. Price: $2.25.*—Recognizing the fact that the American public is quite ignorant of French methods and ideals of education, the authors have compiled this volume of addresses on educational topics by distinguished Frenchmen. There was unquestionably a need for such a book and this volume will be helpful in bringing about a clearer understanding of what is being done in France. On the other hand the title is misleading because the book does not deal with university education or ideals at all. Some of the titles of the papers are: letters to the primary teachers of France; new methods in the Paris primary school; the new program for infants schools; the place of science in secondary education; the teaching of elementary geometry; the modern subjects in secondary education. It is a good book and an interesting one; but it does not help the university teacher with his problems and never was intended to.

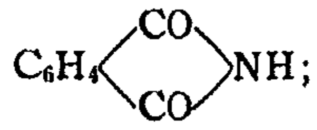
Wilder D. Bancroft

METALLIC SALTS OF PYRROL, INDOL AND CARBAZOL

BY EDWARD C. FRANKLIN

Introduction

The ammono acids, that is to say, the acids of the ammonia system of acids, bases and salts,[1] are derivatives of ammonia in which one or two hydrogen atoms of the ammonia molecule are replaced by negative groups. A number of examples of compounds so related to ammonia are acetamide or acetyl amide, CH_3CONH_2; nitramide or nitrosyl amide, NO_2NH_2; benzenesulfonamide or benzenesulfonylamide, $C_6H_5SO_2NH_2$; phthalimide or phthalyl imide,



$$C_6H_4\begin{matrix}\diagup CO \diagdown \\ \diagdown CO \diagup\end{matrix}NH;$$

benzenesulfonnitramide or nitrosyl benzenesulfonyl imide, $C_6H_5SO_2NHNO_2$; methyl nitramine or methyl nitrosyl imide, CH_3NHNO_2; acetanilide or phenyl acetyl imide, $CH_3CONHC_6H_5$; trinitraniline, $C_6H_2(NO_2)_3NH_2$; urea, $CO(NH_2)_2$; hydrocyanic acid,[2] CNH; cyanamide,[2] $CNNH_2$; etc.

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[1] Am. Chem. Jour., 28, 83 (1902); 47, 285 (1912); Eighth Int. Cong. App. Chem., 6, 119 (1912); Jour. Am. Chem. Soc., 37, 2279 (1915).

[2] Hydrocyanic acid and cyanamide are carbonous and carbonic acids, respectively, of the ammonia system as the following considerations will show.

Esters of ortho carbonic acid, $C(OR)_4$, are known as are also esters and metallic salts of ordinary carbonic acid. Reactions, however, which might be expected to form ortho carbonic acid give instead the final dehydration product, carbon dioxide. This fact is usually explained by assuming that the ortho acid primarily formed loses water in accordance with the scheme $C(OH)_4 \longrightarrow CO(OH)_2 \longrightarrow CO_2$. A similar scheme representing the stepwise deammonation of an hypothetical ortho ammono carbonic acid may be written as follows: $C(NH_2)_4 \longrightarrow NHC(NH_2)_2 \longrightarrow NHCNH$ or $NCNH_2 \longrightarrow (NC)_2NH \longrightarrow C_3N_4$, in which are to be recognized the formulas for guanidine, cyanamide and dicyanimide. The first and last formulas represent no known compounds. The three known compounds are obviously related to ammonia as carbonic acid is related to water. Guanidine, although undoubtedly a very weak one, is an acid to the extent at least that it forms a copper and silver salt. A considerable number of salts of cyanamide are known. The technically important calcium cyanamide is prepared by the nitridation of calcium carbide in a manner anal-

These substances are true acids ranging in acidity from benzenesulfonnitramide, which approaches the ordinary mineral acids in strength, through such compounds as phthalimide and benzenesulfonamide, which are well known to possess weak acid properties, to acetamide and urea which are not ordinarily recognized as acids at all.[1] The acid proper-

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ogous to the formation of calcium carbonate by the oxidation of the same calcium compound. In liquid ammonia solution cyanamide conducts the electric current, discharges the red color of an alkaline solution of phenolphthalein and attacks the more positive metals, with the evolution of hydrogen, to form salts. Cyanamide is certainly an acid, and moreover since it is related to ammonia strictly as aquo carbonic acid is related to water, it is an ammono carbonic acid. Urea, it may be noted here, is a carbonic acid derived at the same time from both ammonia and water. Written NH_2CONH_2 it is an ammono acid; the formula $HNC(OH)(NH_2)$ represents it as a mixed aquo ammono carbonic acid.

A possible tautomeric formula for formic acid is $C(OH)_2$, in which carbon is divalent. The familiar action of carbon monoxide on potassium hydroxide, which might be expected to form potassium carbonite, gives instead potassium formate. An analogous tautomeric formula for formamidine, $HC(NH)NH_2$, formally ammono formic acid, is $C(NH_2)_2$. Loss of a molecule of ammonia from this formula gives CNH which is Nef's formula for hydrocyanic acid. This acid, therefore, appears to be an ammono carbonous acid. The tautomeric formula for hydrocyanic acid, HCN, since it results from the loss of ammonia by the formamidine formula $HCNHNH_2 \longrightarrow HCN$ and also by the loss of water from the formamide formula, represents an acid anammonide. From these considerations it seems reasonable to assume that the acid properties of hydrocyanic acid are due to the presence of the ammono carbonous acid molecules in the tautomeric compound.

[1] Cognizance is, of course, taken of the well-known fact that the acid amides and imides of the oxygen acids are tautomeric compounds. Benzenesulfonnitramide, for example, may be represented by any one of the formulas $C_6H_5SO_2NHNO_2$, $C_6H_5SO_2NNOOH$ or $C_6H_5SOOHNNO_2$, the first of which represents the compound as an ammono acid, the latter two as aquo acids. In all probability the salts of the acid amides are tautomeric compounds just as the free acids are, although there are observations on record which seem to show that in certain metallic derivatives the metal is definitely attached to nitrogen, in others to oxygen. (Hantzsch: Ber. deutsch. chem. Ges., 35, 2717 (1902); Peters: Ibid., 40, 235 (1907).) Assuming for the moment that in such salts as mono potassium urea and potassium benzenesulfonnitramide the metal is in combination with oxygen and that, therefore, the compounds are aquo salts and not ammono salts it is still necessary to conclude that in such compounds as dipotassium urea and dipotassium benzamide one of the potassium atoms must be in combination with nitrogen and, therefore, to this extent an ammono salt. Obviously, there can be no question of tautomerism in connection with those am-

ties of acetamide, urea and other very weak ammono acids, however, show themselves distinctly when in solution in liquid ammonia as has been shown by the writer and his students in earlier papers.

The fact that acids too weak to be recognized as such in aqueous solutions are still capable of showing acid properties when dissolved in liquid ammonia is undoubtedly due to the

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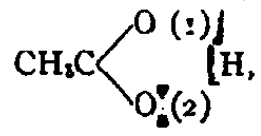
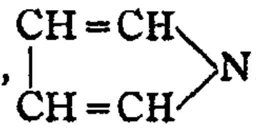
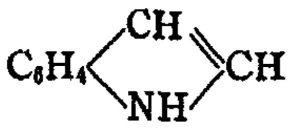
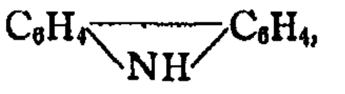
mono acids which contain no oxygen such, for example, as hydrazoic acid or ammono nitric acid, HNNN; cyanamide, $NCNH_2$; ammono titanic acid, $NTiNH_2$; succinimidine, $(CH_2CNH)_2NH$; etc.

Some light seems to be thrown on the tautomeric properties of the acid amides by reviewing the resemblances between the amino and imino groups, on the one hand, and the hydroxyl group on the other, a resemblance which to a considerable extent exists also between the oxides and nitrides. Just as the aquo acids and bases are electrophiles, so also are the ammono acids and bases. The amino group of an ammono base ionizes as such when the base is dissolved in liquid ammonia giving a solution which conducts the electric current, brings about the striking color changes with which we are familiar in connection with the hydroxyl ion, and shows other characteristically alkaline properties. The amino and imino groups present in ammono acids dissociate off hydrogen ions when dissolved in ionizing solvents precisely as hydroxyl groups present in aquo acids do under similar circumstances. As hydroxyl groups give to the alkyl hydroxides the general properties known as alcoholic, so we find the primary and secondary alkyl amines possessing many properties in common with the alcohols. The dehydration of polyhydroxy compounds to oxides is paralleled by the deammonation of amino compounds to form imino compounds and nitrides. As compounds containing two hydroxyl groups in combination with the same carbon atom are rare, so similar diamino compounds are not numerous. Compounds containing an amino group and an hydroxy group in combination with the same carbon atom are known but such substances lose either water or ammonia with greater or less ease just as dihydroxy compounds lose water and diamino compounds lose ammonia. From urea, for example, either water may be removed to form cyanamide, or ammonia to form cyanic (cyanuric) acid, after the manner indicated in the equations $OC(NH_2)_2 = OCNH$ or $NCNH_2$ or $NHCNH + NH_3$ or H_2O and $NHC(NH_2)(OH) = NHCO$ or $NCOH$ or $NHCNH$ or $NCNH_2 + NH_3$ or H_2O.

When now these closely related groups are found in compounds attached to the same carbon atom it certainly is not surprising to find the ionizable hydrogen (or metal) wandering from nitrogen to oxygen and *vice versa*. Enquiring whether CH_3CONH_2 or CH_3CNHOH is the formula for acetamide is something like asking whether the acid hydrogen atom in acetic acid,  $CH_3C\begin{cases} O\ (1) \\ O\ (2) \end{cases} H$, is attached to oxygen atom (1) or (2).

lower solvolytic[1] action of the latter solvent as compared with the former, which in turn results from the very slight autoionization[2] of liquid ammonia.

It follows, therefore, that salts of the weaker ammono acids which, because of the strong hydrolytic action of water are incapable of existence in the presence of this solvent, have been easily prepared from liquid ammonia solutions. Pyrrol,  $\begin{array}{l}CH=CH\diagdown\\ \vert \qquad\qquad\;\; >NH\\ CH=CH\diagup\end{array}$, indol,  $C_6H_4\begin{array}{l}\diagup CH \diagdown\\ \qquad\quad >CH\\ \diagdown NH \diagup\end{array}$, and carbazol,  $C_6H_4\begin{array}{c}\text{———}\\ \diagdown NH \diagup\end{array}C_6H_4$, are obviously derivatives of ammonia in which ammonia hydrogen is replaced by distinctly negative groups. They are therefore to be classed among the ammono acids and as such should react in liquid ammonia with the more electropositive metals and their amides to form salts.

The experiments described below show that these substances react with metallic potassium, sodium, calcium and magnesium and with the amides of sodium, potassium, calcium and silver to form salts after the manner which has been shown to be characteristic of ammono acids, amides and imides in general.[3]

Metallic Salts of Pyrrol

A freshly distilled specimen of pyrrol from Kahlbaum failed to dissolve completely in liquid ammonia. A slightly

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[1] Certain salts in liquid ammonia undergo decomposition which is strictly analogous to hydrolytic decomposition in water. The writer some years ago coined the word ammonolysis to describe such phenomena. Bruni and Manuelli (Z. Elektrochem., 11, 554 (1905)) called the analogous reactions in formamide solution amidolysis. Alcoholysis is a name not unfamiliar. Finally, reactions have been observed in this laboratory in connection with the study of the alkyl amines which are analogous to ammonolytic reactions. The word solvolysis is suggested as a suitable name by which to designate the general phenomenon independently of the particular solvent.

[2] Just to what extent liquid ammonia is ionized has not been determined. Since, however, it is a comparatively easy matter to obtain the liquid with a specific conductance less than one-eighth that of the purest water, its autoionization must be much below that of water.

[3] Cf. Franklin and Stafford: Am. Chem. Jour., 28, 84 (1902); Franklin: Jour. Am. Chem. Soc., 37, 1279 (1915).

soluble impurity, presumably some hydrocarbon, was observed suspended in the pyrrol solution in the form of colorless globules. Before use, therefore, the preparation was purified by the method of Ciamician and Dennstedt.[1] Pure pyrrol dissolves abundantly and completely in liquid ammonia.

Potassium Pyrrol, C_4H_4NK.—This salt has been made by the action of metallic potassium[2] on pyrrol and also by heating pyrrol with fused potassium hydroxide.[3] It is a crystalline solid which hydrolyzes completely in the presence of water.

An attempt was made to prepare potassium pyrrol by bringing together potassium amide and pyrrol in liquid ammonia solution. On evaporating the solution to high concentration and cooling no separation of the salt could be brought about even at temperatures approximating the freezing point of the solution. When the ammonia was evaporated away an amorphous viscous mass was left behind.

When a solution of metallic potassium was added to a solution of pyrrol the blue color of the metal solution was rapidly discharged and at the same time hydrogen gas was set free. The quantity of hydrogen evolved was not determined. The product of the reaction refused to crystallize when the concentrated solution was strongly cooled. Notwithstanding these failures to prepare a crystallized salt there can be scarcely any doubt of its formation in accordance with the reactions represented by the equations

$C_4H_4NH + KNH_2 = C_4H_4NK + NH_3$ and

$C_4H_4NH + K = C_4H_4NK + H,$

which represent the action of an ammono acid on an ammono base and metal, respectively.

Sodium Pyrrol,[4] $C_4H_4NNa.NH_3$ *and* C_4H_4NNa.—Sodium

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[1] Ber. deutsch. chem. Ges., 19, 173 (1886).

[2] Anderson: Trans. Roy. Soc. Edinburgh, 21, IV, 571 (1858).

[3] Ciamician and Dennstedt: Loc. cit.

[4] Metallic sodium acts on pyrrol at high temperatures, Ciamician and Dennstedt: Loc. cit.

amide, which is practically insoluble in liquid ammonia, dissolves readily in a solution of pyrrol. On evaporating a solution made by dissolving the sodium amide formed from 0.105 gm. of metallic sodium in a moderate excess of pyrrol to high concentration and cooling to the temperature of a bath of a carbon dioxide and ether, a crystalline mass was obtained from which a small amount of mother liquor was drained. The salt was redissolved in a small quantity of pure solvent, the solution again cooled to crystallization and the crop of crystals obtained drained of a small quantity of mother liquor. The preparation was then dried in vacuum at —39°. On warming to 20° it lost 0.0395 gm. NH_3. Its weight dried at 20° in vacuum was 0.2134 gm. One-half gave 0.0850 gm. Na_2SO_4. The other half gave 0.0167 gm. N by the method of Kjeldahl.

Calculated for C_4H_4NNa		Found
Na	25.9	25.8
N	15.7	15.7
$1NH_3$	19.1	18.5

The salt separates from solution at low temperatures containing one molecule of ammonia which it loses at laboratory temperature. The salt is vigorously hydrolyzed in the presence of water to pyrrol and sodium hydroxide.

Calcium Pyrrol, $(C_4H_4N)_2Ca.4NH_3$ *and* $(C_4H_4N)_2Ca$.—This salt was made by the action of pyrrol on metallic calcium in liquid ammonia solution in accordance with the equation

$$Ca + 2C_4H_4NH = (C_4H_4N)_2Ca + H_2.$$

The compound containing four molecules of ammonia was obtained well crystallized and quite colorless. The anammonous salt was slightly yellow and had the dull appearance of a salt which had effloresced. It is vigorously attacked by water, giving as products of its hydrolysis, pyrrol, and calcium hydroxide.

For analysis the salt was treated first with water, then with dilute hydrochloric acid and finally with sufficient alcohol to dissolve the pyrrol. Calcium was determined by evaporating an aliquot part of the solution to dryness, treating the residue with sulfuric acid, heating to drive off the excess of sulfuric acid and weighing as calcium sulfate.

Preparation I.—Into the two legs of a reaction tube were introduced, respectively, 0.105 gm. of metallic calcium and 1.2 equivalents of pyrrol. On mixing the liquid ammonia solutions of these two substances the blue color of the metal solution was rapidly discharged, hydrogen was liberated and soon a crop of crystals began to separate from the solution. The product of the reaction was well washed with pure solvent and dried in vacuum at —39°. The specimen on warming to 20° lost 0.0772 gm. NH_3. Its weight, dried at 20°, was 0.2034 gm. Two-fifths gave 0.0647 gm. $CaSO_4$. One-fifth distilled with potassium hydroxide gave a trace of ammonia. Two-fifths heated with sulfuric acid according to the method of Kjeldahl gave 0.00133 gm. N.

Preparation II.—A second crop of crystals obtained by concentrating and cooling the mother liquor from the preceding preparation was washed, then dried in vacuum at —39°. Heating the ammonated salt to 39° entailed a loss of 0.0436 gm. NH_3. The specimen dried at 39° weighed 0.1132 gm. Two-fifths gave 0.0362 gm. $CaSO_4$. Another two-fifths heated with sulfuric acid according to Kjeldahl gave 0.0076 gm. N. One-fifth distilled with potassium hydroxide gave 0.0003 gm. N.

Preparation III.—Surmising that the nascent hydrogen resulting from the action of pyrrol on metallic calcium might bring about the reduction of pyrrol to tetrahydropyrrol the hydrogen evolved in this experiment was collected and measured. The action of 0.129 gm. calcium on 0.433 gm. pyrrol gave 65.0 cc hydrogen, whereas the quantity calculated on the bases of the equation

$$Ca + 2C_4H_4NH = (C_4H_4N)_2Ca + H_2$$

should have been 71 cc. A small portion of the pyrrol was probably reduced.

A portion of the specimen dried at —39° in vacuum weighed 0.1590 gm. Two-fifths gave 0.0360 gm. $CaSO_4$. The remaining three-fifths distilled with potassium hydroxide gave 0.0220 gm. N. The pyrrol nitrogen was not determined.

Calculated for $(C_4H_4N)_2Ca$	Found	
	I	II
Ca 23.3	23.4	23.5
N 16.3	16.4	16.7
$4NH_3$ 39.5	38.0	38.5

Calculated for $(C_4H_4N)_2Ca.4NH_3$	Found III
Ca 16.7	16.7
N 11.7	....
NH_3 23.3	23.1

Magnesium Pyrrol, $(C_4H_4N)_2Mg.2NH_3$.—Pyrrol in solution in liquid ammonia attacks metallic magnesium slowly with the evolution of hydrogen gas and the formation of a colorless, slightly soluble, magnesium salt. The product formed by the action of 0.310 gm. pyrrol on a slight excess of metallic magnesium was transferred from the unchanged magnesium to the second leg of the reaction tube where it was thoroughly washed with successive portions of solvent. Dried in vacuum at 20° the specimen weighed 0.1590 gm. Two-fifths gave 0.0387 gm. $MgSO_4$. Three-fifths gave 0.0327 gm. N by the method of Kjeldahl.

Calculated for $(C_4H_4N)_2Mg.2NH_3$	Found
Mg 12.8	12.3
N 29.5	34.3

In view of the high nitrogen content of this preparation and of the fact that but one specimen was made there is some uncertainty concerning the composition of this salt.

Silver Pyrrol, $C_4H_4NAg.NH_3$.—Silver amide dissolves readily in a liquid ammonia solution of pyrrol to form a clear, colorless solution from which a well-crystallized product of the composition represented by the above formula may be easily obtained. Although almost colorless when first formed, the crystals of the salt rather rapidly become gray and finally black. The solution also, on standing, slowly deposits black metallic silver. The salt is hydrolyzed in the presence of water to silver oxide and pyrrol.

Preparation I.—In this experiment the silver amide resulting from the action of one equivalent of potassium amide on 0.225 gm. of silver nitrate was dissolved in a liquid ammonia solution containing 0.220 gm. of pyrrol. A small quantity of black insoluble residue, partly platinum used in the formation of potassium amide, was allowed to subside after which the clear, colorless solution was decanted into the second leg of the reaction tube, there evaporated to small volume and cooled to the temperature of a liquid ammonia bath. The crop of well-formed crystals obtained was recrystallized once, giving a specimen which, dried in vacuum at —39°, weighed 0.1779 gm. On heating the salt to 35° a colorless liquid, which could have been nothing but pyrrol, was observed condensing in the cooler neck of the tube. The heating was interrupted, the tube cooled and weighed. It had lost 24 gm. in weight. The salt was obviously undergoing ammonolysis into pyrrol and silver amide in them anner represented by the equation

$$C_4H_4NAg + NH_3 = C_4H_4NH + AgNH_2.$$

The specimen gave 0.1321 gm. AgCl.

Preparation II.—The silver amide from 0.340 gm. silver nitrate was treated with a solution of one equivalent of pyrrol, which, however, failed to dissolve all the silver amide. Complete solution followed the addition of a further half equivalent of pyrrol. From the clear, colorless solution, after adjusting the concentration and cooling to —39°, a good crop of crystals was obtained. The product was not recrystallized but simply drained of a relatively large volume of mother liquor. Dried at —39° in vacuum the specimen weighed 0.2418 gm. It gave 0.1765 gm. AgCl and 0.0350 gm. N by the method of Kjeldahl.

Preparation III.—The combined mother liquors from the preceding experiments were evaporated to a proper concentration, then cooled to —39°. The crop of well-formed crystals obtained was drained of mother liquor, then dissolved in pure solvent and recrystallized. The specimen dried in vacuum at 20° weighed 0.1262 gm. It gave 0.0911 gm. AgCl and 0.0178 gm. N by the method of Kjeldahl. The atomic ratio Ag to N is exactly 1 to 2.

Calculated for $C_4H_4NAg.NH_3$		Found		
		I	II	III
Ag	56.5	56.0	55.1	54.4
N	14.7	..	14.7	14.1

Metallic Salts of Indol

Indol is very soluble in liquid ammonia. In contact with ammonia gas at laboratory temperature and atmospheric pressure the substance rapidly absorbs ammonia and deliquesces. On evaporating the solvent away from a solution of indol a thick, viscous residue is left behind.

Sodium Indol.—Sodium amide dissolves readily in a liquid ammonia solution of indol, forming, undoubtedly, the sodium salt. The product of the reaction is, however, so extremely soluble that all attempts to obtain a crystalline product were unsuccessful. The salt is left behind as a viscous, amorphous mass which could not be brought to crystallize even at temperatures approaching the freezing point of the solvent. Pure, dry ether was added to the ammonia solution in the hope that the salt might be brought to crystallize from the mixed solvent. At low temperatures the mixture of ammonia, ether and salt separated into two layers, an upper layer of ether and a lower one consisting of a concentrated solution of the salt in liquid ammonia.

Potassium Indol.—Although, undoubtedly, potassium indol is formed by mixing solutions of potassium amide and indol and also by the action of metallic potassium on indol in liquid ammonia solution, it was not possible to bring about the separation of a crystalline product. When the solvent was evaporated away from these solutions either at high or low temperature a syrupy residue was left behind which, after standing for a long time at very low temperature, solidified to a crystalline mass from which it was not practicable to separate any mother liquor.

Calcium Indol, $(C_8H_6N)_2Ca.4NH_3$.—Metallic calcium dissolves readily in a liquid ammonia solution of indol to form calcium indol which separates, beautifully crystallized, from the moderately concentrated solution.

Preparation I.—Into one leg of a reaction tube 0.245 gm. of indol was introduced and into the other 0.042 gm. metallic calcium, after which ammonia was distilled into the apparatus to dissolve the calcium and indol. On pouring the metal solution into the indol solution the blue color of the metal rapidly disappeared and at the same time a vigorous evolution of hydrogen took place. With proper adjustment of the concentration of the resulting calcium salt solution it was a simple matter to obtain an abundant crop of crystals by cooling the solution to —39°. The crystals were dissolved in pure solvent and recrystallized and then washed several times with small quantities of solvent. Preparatory to analysis the salt was hydrolyzed by treatment with water and then dissolved in a mixture of hydrochloric acid and alcohol. Calcium was weighed as sulfate. Nitrogen was determined by the method of Kjeldahl.[1] The specimen, dried in vacuum at 20°, weighed 0.1655 gm. Seven-tenths gave 0.0467 gm. $CaSO_4$. The remaining three-tenths gave 0.0151 gm. N.

Preparation II.—In this experiment 0.174 gm. of indol with an equivalent quantity of calcium was used. The crop

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[1] After a number of unsatisfactory nitrogen determinations had been made by this method it was discovered that indol escapes with the steam from a solution strongly acid with sulfuric acid.

of crystals obtained was yellow. After pouring off the mother liquor the salt recrystallized from the pure solvent was still yellow in color. After crystallizing a third time the salt was colorless. What the cause of this behavior may have been is unknown. The specimen, dried in vacuum at 20°, weighed 0.1655 gm. After heating a short time at 100° a sublimate was noticed in the upper cooler portion of the container and in the tube connecting with the air pump. Examination of the sublimate showed it to be indol from which it follows that the ammonated salt, when heated, undergoes ammonolysis in accordance with the equation

$$(C_8H_6N)_2Ca + 4NH_3 = 2C_8H_6NH + Ca(NH_2)_2.$$

Ammonated silver pyrrol[1] and the ammonated copper salt of benzenesulfonamide[2] undergo ammonolysis in a similar manner when heated. The residue in the tube gave 0.0666 gm. $CaSO_4$.

Preparation III.—It was surmised that possibly the hydrogen resulting from the action of calcium on indol might attack the latter reducing a portion of it to hydroindol. Accordingly, the hydrogen gas set free by the interaction of 0.035 gm. calcium and 0.279 gm. indol was collected and measured. A little over 11 cc of hydrogen gas was liberated which is somewhat more than half of what should have been evolved had none been used up in reducing the indol. It thus appears that at most one quarter of the indol may have been reduced to dihydroindol. This experiment could not be repeated on a larger scale in order to isolate a possible reduction product of indol for the reason that a total of two grams only of indol was available for the work described in this paper. The colorless crop of crystals obtained was recrystallized, then washed several times with small quantities of solvent for analysis. The specimen, dried at 20° in vacuum, weighed 0.2371 gm. Forty-five hundredths gave 0.0421 gm. $CaSO_4$. Three-tenths gave 0.0166 gm. N.

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[1] Cf. supra, p. 89.

[2] Jour. Am. Chem. Soc., 37, 2291 (1915).

Calculated for $(C_8H_6N)_2Ca.4NH_3$		Found		
		I	II	III
Ca	11.7	11.8	11.8	11.7
N	24.6	30.5	....	23.3

Magnesium Indol, $(C_8H_4N)_2Mg.4NH_3$.—When a solution of indol, contained in one leg of a reaction tube, is poured upon a clean spiral of metallic magnesium in the other, evolution of hydrogen soon begins, the metal surface shows signs of corrosion and after a time well-formed, colorless, needle-like crystals begin to separate from the solution. In contact with an excess of indol the crystals seem to be stable but when recrystallized from fresh solvent or when the mother liquor is replaced by pure solvent they begin to disintegrate after a time, giving a product which is no longer soluble. It is probable that this behavior is due to the ammonolysis of the salt.

Preparation I.—A piece of clean magnesium ribbon weighing 0.027 gm. was treated with a liquid ammonia solution of 0.263 gm. of indol. Evolution of hydrogen began at once. After a few hours all but a very small quantity of the metal had disappeared and the walls and bottom of the reaction tube were covered with beautiful, colorless crystals. The crystals were shaken loose, transferred to the second leg of the reaction tube and washed twice with small quantities of solvent. The specimen, dried in vacuum, weighed 0.2623 gm. Forty-five hundredths gave 0.0453 gm. $MgSO_4$. By the method of Kjeldahl, three-tenths gave 0.0160 gm. N and one-fourth gave 0.0129 gm. N.

Preparation II.—An excess of magnesium metal was covered with a solution containing 0.144 gm. indol. After several days the product of the reaction had separated as an insoluble, poorly crystalline mass which was suspected to be an ammonobasic compound or mixture. The product was washed several times, dried at 20°, and analyzed. It was found to contain 9.5 percent magnesium and 21.7 percent nitrogen, results which are in agreement with the assumption that the preparation was a basic mixture.

Preparation III.—A strip of clean magnesium weighing 0.021 gm. was treated with a solution containing 0.210 gm. indol. The evolution of hydrogen began at once and after a short time a crop of well-formed crystals had separated from the solution. The crystals were simply drained of mother liquor for analysis. Dried in vacuum at 20° the specimen weighed 0.0827 gm. Six-tenths gave 0.0188 gm. $MgSO_4$, the remaining four-tenths gave 0.0053 gm. N when distilled with potassium hydroxide.

Calculated for $(C_8H_6N)_2Mg.4NH_3$		Found	
		I	III
Mg	7.5	7.8	7.6
Total N	25.9	20.3–19.7[1]	. .
N in NH_3	17.3	. .	16.0

Silver Indol, $C_8H_6NAg.NH_3$.—This salt was prepared by dissolving silver amide, made in accordance with a method which has been described elsewhere,[2] in a liquid ammonia solution of slightly more than an equivalent quantity of indol. The salt is extremely soluble in liquid ammonia and can be separated from the solution in crystalline form only at temperatures approaching the freezing point of very concentrated solutions. After once obtaining a crop of crystals subsequent recrystallization takes place easily, provided care is taken to prevent complete solution of the salt. The solution shows the phenomenon of supersaturation to a very marked degree. When the solvent is evaporated from the solution at higher temperatures, around the boiling point of ammonia, the salt fails to crystallize; it remains behind as a viscous mass which after a time changes to a solid crystalline mass from which mother liquor cannot be drained.

Preparation I.—The silver amide resulting from the

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[1] Nitrogen in indol cannot be determined by the method of Kjeldahl.

[2] Jour. Am. Chem. Soc., 27, 833 (1905).

action of one equivalent of potassium amide[1] on 0.170 gm. silver nitrate was dissolved in a solution containing 0.120 gm. indol. From a highly concentrated solution at a temperature of —80° the salt separates as a crop of well-formed crystals. The crystals were drained of a small quantity of mother liquor, dissolved in a fresh portion of solvent and recrystallized. Again they were drained of mother liquor, dissolved in fresh solvent and crystallized a third time. The specimen, dried in vacuum at 20°, weighed 0.1405 gm. It gave 0.0843 gm. AgCl and by the method of Kjeldahl 0.0124 gm. N.

Preparation II.—This experiment was a repetition of the preceding excepting that 0.059 gm. potassium, 0.225 gm. silver nitrate and 0.177 gm. indol were used. The salt was recrystallized twice as in the preceding experiment for analysis. The specimen, dried in vacuum at 20°, weighed 0.1728 gm. and gave 0.1011 gm. AgCl and by the method of Kjeldahl 0.0137 gm. N.

Preparation III.—The mother liquors from the preceding two preparations were united, evaporated to high concentration and cooled to —80°. The crop of crystals obtained was drained of mother liquor, redissolved in pure solvent and again crystallized. Dried in vacuum at 20°, the specimen weighed 0.1385 gm. Forty-five hundredths gave 0.0367 gm. AgCl. An acidified solution of the remaining fifty-five hundredths was boiled until all the pyrrol was removed. Distilled then with excess of potassium hydroxide,

Calculated for: $C_8H_6NAg.NH_3$		Found		
		I	II	III
Ag	44.8	45.1	44.2	44.5
Total N	11.6	8.8[2]	8.0[2]	10.7[1]
N in NH_3	5.8	..	..	5.8

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[1] Prepared by the action of liquid ammonia on 0.039 gm. potassium in the presence of a trace of platinum black.

[2] These results are low for the reason that nitrogen in indol cannot be determined by the method of Kjeldahl.

0.0043 gm. N was obtained. The filtrate from silver chloride treated by the method of Kjeldahl gave 0.0067 gm. N, whereas 0.0072 gm. should have been obtained.

Salts of Carbazol

A specimen of carbazol from Kahlbaum was purified by crystallization from alcohol and dried in vacuum over sulfuric acid. It is moderately soluble in liquid ammonia.

Potassium Carbazol,[1] $C_{12}H_8NK.NH_3$ *and* $C_{12}H_8NK.3NH_3$.—When a liquid ammonia solution of carbazol was treated with an equivalent amount of metallic potassium a strongly colored solution was formed and at the same time only a very small amount of hydrogen was liberated. No attempt was made to isolate a product from the solution.

In a second experiment 0.480 gm. carbazol was treated with an equivalent quantity of potassium amide. From the yellow solution, showing greenish fluorescence, a crop of very soluble crystals was separated when the concentrated solution was cooled to the temperature of a bath of liquid ammonia.

The specimen, dried at —39° in vacuum, lost 0.0437 gm. NH_3 on heating to 20°. Dried at the latter temperature the specimen weighed 0.2561 gm. One half gave 0.0491 gm. K_2SO_4. The other half was lost.

Calculated for $C_{12}H_8NK.NH_3$		Found
K	17.6	17.2
N	12.6	....
$2NH_3$	12.6	14.0

Silver Carbazol, $C_{12}H_8NAg.NH_3$ *and* $C_{12}H_8NAg.2NH_3$.—Silver amide dissolves readily in an ammonia solution of carbazol to form the silver salt which separates from a solution of moderate concentration on cooling to —39° in well-formed crystals of the composition represented by the second

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[1] Potassium carbazol, $C_{12}H_8NK$, has been prepared by heating carbazol with potassium hydroxide to a temperature of 220–40°.

of the above formulas. On warming they lose one molecule of ammonia.

Preparation I.—A liquid ammonia solution of 0.370 gm. carbazol was poured upon nine-tenths of an equivalent of silver amide. A clear, slightly colored solution resulted from which a crop of slightly darkened crystals was obtained on cooling to the temperature of an ammonia bath. The product was not recrystallized. It was simply washed several times with liberal portions of pure solvent. The preparation, dried at —39° in vacuum, lost 0.0221 gm. NH_3 on heating to 40°. Dried at the latter temperature it weighed 0.3728 gm. The specimen was lost during preparation for analysis.

Preparation II.—A repetition of the preceding experiment gave a solution which was evaporated at laboratory temperature until an adequate crop of well-formed yellowish crystals was separated. After washing with four successive portions of pure solvent the crystals were dried in vacuum at —39°. On warming to 40° the lustrous crystals became dull in appearance and lost 0.0170 gm. ammonia. The specimen, dried at 40°, weighed 0.2956 gm. Distillation with potassium hydroxide gave 0.0142 gm. N. Carbazol nitrogen was not determined. The specimen gave 0.1461 gm. AgCl.

Calculated for $C_{12}H_8NAg.NH_3$		Found	
		I	II
Ag	37.2	...	37.2
N in NH_3	4.8	...	4.8
NH_3 lost at 40°	5.8	5.9	5.8

Calcium Carbazol, $(C_{12}H_8N)_2Ca.4NH_3$ *and* $(C_{12}H_8N)_2Ca.7NH_3$.—Into one leg of a reaction tube 0.323 gm. carbazol was introduced and into the other slightly less than one equivalent of metallic calcium together with a minute quantity of platinum black. Within half an hour after distilling ammonia into the reaction tube the calcium was converted into the amide which is insoluble in liquid ammonia. On pouring the solution of carbazol upon the calcium amide the latter dissolved rapidly to a clear, yellow solution from which, after a short time, beautiful, yellow crystals, showing greenish fluorescence, began to separate. The crop of crystals was washed several times with liberal portions of solvent and dried in vacuum at −39°. On heating to 30°, 0.0223 gm. N as ammonia was given off and the specimen weighed 0.2442 gm. One-half gave 0.0348 gm. N when distilled with potassium hydroxide, the other half gave 0.0377 gm. $CaSO_4$.

Preparation II.—On concentrating and cooling the mother liquor from the preceding preparation, a crop of crystals was obtained which was washed and then dried in vacuum at —39°. It lost 0.0125 gm. N as ammonia on heating to 50°. Its weight after heating to the later temperature was 0.1329 gm. One-half of the specimen gave 0.0167 gm. N, the other half gave 0.0206 gm. $CaSO_4$.

Calculated for $(C_{12}H_8N)_2Ca.4NH_3$		Found	
		I	II
Ca	9.1	9.1	9.1
N in 4 NH_3	12.7	14.2	12.8
3 NH_3	9.5	9.1	9.4

Summary

Any compound of nitrogen which may be looked upon as ammonia in which one or two of the hydrogen atoms are replaced by negative groups should show acid properties. Such compounds are ammono acids.

Pyrrol, indol and carbazol should, therefore, in liquid ammonia solution, react with the more positive metals and with metallic amides to form salts.

The following metallic salts of these ammono acids have been prepared:

Sodium pyrrol, C_4H_4NNa and $C_4H_4NNa.NH_3$.

Calcium pyrrol, $(C_4H_4N)_2Ca$ and $(C_4H_4N)_2Ca.4NH_3$.

Magnesium pyrrol, $(C_4H_4N)_2Mg.2NH_3$.

Silver pyrrol, $C_4H_4NAg.NH_3$.
Sodium indol, $C_8H_6NNa.xNH_3$.
Potassium indol, $C_8H_6NK.xNH_3$.
Calcium indol, $(C_8H_6N)_2Ca.4NH_3$.
Magnesium indol, $(C_8H_6N)_2Mg.4NH_3$.
Silver indol, $C_8H_6NAg.NH_3$.
Potassium carbazol, $C_{12}H_8NK.2NH_3$ and $C_{12}H_8NK.NH_3$.
Silver carbazol, $C_{12}H_8NAg.2NH_3$ and $C_{12}H_8NAg.NH_3$.
Calcium carbazol, $(C_{12}H_8N)_2Ca.7NH_3$ and $(C_{12}H_8N)_2Ca.4NH_3$.

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SUPERSATURATION AND CRYSTAL SIZE

BY WILDER D. BANCROFT

Since von Weimarn was the first man to make a systematic study of the form in which substances precipitate from solution under varying conditions, it is necessary to take von Weimarn's theory[1] as a starting point. "The process of condensation [or precipitation] depends on a number of very different factors: on the solubility of the substance, on the latent heat of precipitation, on the concentration at which the precipitation takes place, on the normal pressure at the surface of the solvent, on the viscosity of the solvent, on the dielectric constant of the solvent, and on the molecular weights of the solvent and of the precipitate. It is of course impossible to take into account now the effect of all these complex factors on the precipitation. We will therefore simplify the problem by considering only two of the factors, the solubility of the precipitating substance and the concentration at which the precipitation begins, or, in other words, the initial concentration of the precipitating molecules. The process of condensation can profitably be divided into two parts. In the first stage the molecules condense to invisible crystals or to crystals which can only just be seen in the ultra-microscope under the most favorable conditions—molecular complexes. From a molecular kinetic point of view, the first stage of the condensation process takes place exactly like a reaction in a solution. The velocity at the important first moment of the first stage of the condensation can be formulated as follows:

$$W = K \frac{\text{condensation pressure}}{\text{condensation resistance}} = K \frac{Q - L}{L} = K \frac{P}{L} = KU \quad (1)$$

where W is the rate of precipitation in the first movement, Q is the total concentration of the substance which is to precipitate; L the ordinary solubility of the substance in coarse crystals; Q — L = P the amount of supersaturation. The

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[1] "Grundzüge der Dispersoidchemie," 39 (1911).

ratio of $P/L = U$ may be called the specific supersaturation [percentage supersaturation] at the moment when precipitation begins. One must not forget that this formula applies only to the first stage of the condensation process when the excess molecules and their smallest complexes come in contact in the dispersing medium and condense. It is only under these conditions that the kinetic conceptions have a meaning analogous to those which have proved useful when studying the kinetics of homogeneous systems.

"The second stage in the process of precipitation is concerned with the growth of the particles as a result of diffusion. The rate of this precipitation, according to the Nernst-Noyes theory, is given by the equation

$$V = \frac{D}{\delta} . O . (C - l) \qquad (2)$$

where D is the diffusion coefficient, δ the length of the diffusion path (the thickness of the adherent film), O the surface, C the concentration of the surrounding solution, and l the solubility of the particles of the dispersed phase for a given degree of dispersity. $C - l$ is the absolute supersaturation.[1] These two equations call for some comment. Direct experiment shows that, under otherwise similar conditions, the rate at which precipitation occurs is greater the larger the value of P and that for the same value of P the rate of precipitation is greater the smaller L is. It follows experimentally, therefore, that the rate of precipitation varies directly with $U = P/L$ increasing or decreasing as U becomes larger or smaller. The experiments do not prove that the rate of precipitation is directly proportional to U. The reason for assuming such a proportionality in Equation 1 is that that is the simplest, most natural, and, theoretically, most pobable relation as well as the one which is the easiest to apply in an analysis of the

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[1] Equation 2 is not only the result of the theory of Noyes and Nernst, but has been verified brilliantly by Johann Andrejew in an extensive series of experiments on the rate of growth of crystals of citric acid, orthochrodinitrobenzene (in ether), and sodium chlorate. Jour. russ. chem. Ges., 40, 397; Zeit. Kolloidchemie, 2, 236 (1908).

phenomenon of precipitation. The more characteristic cases of precipitation become quite clear when considered with reference to Equations 1 and 2, and one is able to classify many phenomena of condensation which at first sight seem quite unrelated.

"The equation $V = D.O (C - l)/\delta$ shows that the growth of the particles of the dispersed phase is cut down very much in two cases, when either $C - l$ or D is very small. The first occurs in very dilute solutions of the reacting substances, and the second in very concentrated solutions when the great rate of precipitation W in the first moment causes the formation almost instantaneously at many different points in the dispersing medium of particles which are not molecularly dispersed and which do not diffuse rapidly. These particles agglomerate but slowly....................

"By means of Equation 1, W = K (condensation pressure/condensation resistance) = KP/L = KU, the following phenomena among others may be easily explained and made to seem matters of course. With a condensation pressure of several grams (P) sparingly soluble substances such as $Al_2O_3.3H_2O$ and AgCl are obtained in the form of a very fine jelly or of a curdy precipitate due to the coalescing of very fine crystals, while readily soluble substances such as NaCl are obtained as small crystals. From Equation 1 we see that in the first case the condensation resistance was small and therefore the rate of precipitation of W very large, while the rate of precipitation is very small in the second case because the resistance to condensation is large. From Equation 1, however, we see what conditions must prevail in order to reverse the results previously obtained with $Al_2O_3.3H_2O$ and NaCl. If we carry out the formation of $Al_2O_3.H_2O$ in strongly ammoniacal solution in which this substance is a good deal more soluble than in water, we shall get microcrystals. If we precipitate sodium chloride by letting HCl and NaSCN, or still better sodium alcoholate,[1] react in a mixture of ether and amyl alcohol in which NaCl is practically insoluble, we

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[1] Jour. russ. chem. Ges., 40, 1127 (1908).

get a curdy precipitate very like that of AgCl. These illustrations when taken in connection with Equation 1 are very convincing. Any reasoning man will see that there is no such thing as a specifically amorphous colloidal substance and that one can obtain any substance in large crystals, no matter how insoluble it may be, by making P and consequently W very small. In extreme cases, when L is vanishingly small, it will of course take seas of reacting solutions and centuries of time to produce large crystals; but it would be just as foolish to doubt the possibility of getting large crystals as it would be to say that NaCl does not occur in crystalline form because it can be obtained in a curdy state.

"We must now take into account that the terms 'practically insoluble' and 'practically instantaneous reaction or precipitation' are very flexible. In most cases the rates of precipitation, W, of practically insoluble substances from reactions between solutions cannot be differentiated quantitatively by our senses and appear to be equally instantaneous for 'practically insoluble' substances which, however, have different solubilities. We cannot doubt, however, that some of these rates are really ten-, a hundred- or a thousand-fold some of the others, just as the practically insoluble substances vary very much in solubility. While we cannot of course measure the true reaction velocity, W, in many cases, we can judge its change from the value U which is proportional to it. To bring this out clearly we give a table for U and W at constant P but varying L:

P	L	U	W
10^{-2}	10^{-4}	10^2	$K.10^2$
10^{-2}	10^{-5}	10^3	$K.10^3$
10^{-2}	10^{-6}	10^4	$K.10^4$
10^{-2}	10^{-7}	10^5	$K.10^5$
10^{-2}	10^{-8}	10^6	$K.10^6$
10^{-2}	10^{-9}	10^7	$K.10^7$
10^{-2}	10^{-10}	10^8	$K.10^8$

"From this table it can be seen that with equal P but varying U, such as $U = 10^2$ and $U = 10^6$, we cannot get dispersed systems of identical properties because the rates of precipitation vary markedly, from $W = K.10^2$ to $W = K.10^8$. It must be noted that for an understanding of the formation of suspensoid solutions it is very important to know that the specific concentration C/l is the important thing[1] and not the absolute concentration C. It would be entirely false, however, to say that the absolute concentration is unimportant, for the latter determines whether a jelly or a suspensoid solution is formed. An equal and high value for W can be obtained in two ways, either by increasing P when L is fairly large or by decreasing P when L is very small. In the second case the dispersed particles are far distant one from another and we get a suspensoid solution or suspension, and in the first case we get a curdy or gelatinous precipitate."

Von Weimarn[2] considers that with increasing supersaturation five stages can be distinguished fairly definitely in the case of sparingly soluble substances, though there is, of course, no sharp dividing line between the stages. For slight supersaturations, no precipitation occurs inside of several years. This may be called the stage of colloidal solutions. In the next stage of higher supersaturation perfect crystals are obtained in a relatively short time. In the third stage skeleton crystals and needles are obtained. When the fourth stage is reached, a curdy, apparently amorphous, precipitate is obtained, and in the highest stage of supersaturation a jelly is obtained. It is immaterial whether all these precipitates are crystalline or not. Von Weimarn considers them all crystalline; but he considers a liquid and a gas as crystalline. This may be true, but it is not helpful because we should then have to invent another word to describe what most people mean by crystalline and that would be confusing. It is undoubtedly true that many precipitates are called amorphous when they are really crystalline; but if a liquid is

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[1] Zeit. Kolloidchemie, 5, 157 (1909).

[2] "Zur Lehre von den Zuständen der Materie," 10 (1914).

amorphous, a precipitate consisting of supercooled and very viscous drops is also amorphous.

Von Weimarn[1] has tested his theory on barium sulphate, among other substances, by mixing equivalent solutions of $MnSO_4$ and $Ba(SCN)_2$. When the reacting concentrations were approximately N/20000 — N/7000 no precipitate was formed in the course of several years. With concentrations of about N/7000 — N/600 perfect crystals were obtained, the rate of crystallization being very small with the more dilute solutions. With initial concentrations of about N/600 to 0.75 N skeleton crystals and needles are formed. When the initial concentrations are about 0.75 N — 3 N the precipitate is curdy, becoming gelatinous at the higher concentrations, while jellies are obtained, at least temporarily, when the concentrations are about 3 N — 7 N.

Satisfactory results have been obtained by von Weimarn with an extraordinary number of salts and he claims never to have found an exception. In spite of that the general presentation does not seem to me ideal. While it is apparently true that one can get any salt coming down in a gelatinous form if the concentrations of the reacting solutions are sufficiently high, those are not the conditions under which jellies are usually obtained. Then von Weimarn's conditions hold only for the case where the solutions are not stirred after mixing. He separates the colloidal solutions from the curdy precipitates in spite of the fact that one can often pass directly from one to the other. The effect of a slight excess of one of the reacting substances is not discussed effectively, though the matter receives a perfunctory and formal consideration in the later work,[2] where the effect of viscosity is also discussed.

I have found von Weimarn's views distinctly more helpful if one discards the formulas and restates the whole thing from another point of view. The mean size of the crystals is determined by the total amount of material crystallizing and the number of crystals. The really important thing there-

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[1] "Zur Lehre von den Zuständen der Materie," 21 (1914).

[2] Von Weimarn: *Ibid.*, 6 (1914).

fore is the number of nuclei which are formed under any given conditions and von Weimarn appears to have overlooked this factor entirely. The difference which this may introduce can be seen very clearly from the behavior of very dilute solutions. Von Weimarn has deduced very properly that the condition favorable to the growth of large crystals is the existence of a very slight supersaturation, but he does not lay stress on the fact that the reason for this is that there is then only a very slight tendency for the solution to crystallize spontaneously and consequently the crystallization takes place only on the crystal which is to grow. If one stirs such a solution vigorously, a number of nuclei are formed and we get colloidal solutions because the number of nuclei is so large that the excess material comes out chiefly as nuclei.

There has been no direct experimental study, so far as I know, of the way in which the number of nuclei varies with the increase in supersaturation; but we can deduce it empirically from the observed behavior of supersaturated solutions. For a definite rate of stirring the number of nuclei seems to increase at first less rapidly than the supersaturation and afterwards more rapidly. This means that we get colloidal solutions of lead chromate, for instance, if we mix very dilute solutions of potassium chromate and lead nitrate,[1] because the number of crystals is so great that the total mass of each one is very small. At a little higher concentration we get flocculent or curdy precipitates because of the agglomeration of the crystals. At still higher concentrations, the number of nuclei has apparently not increased proportionally, for the crystals are distinctly larger. With continuously increasing supersaturations the crystals pass through a maximum size and then begin to decrease either because the number of nuclei are increasing more rapidly than the concentration or because the rate of crystallization becomes so high that good crystals are not formed. At very high degrees of supersaturation, gelatinous precipitates are formed. This was known before in isolated cases, as for

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[1] Free: Jour. Phys. Chem., 13, 114 (1909).

instance when concentrated sodium carbonate and calcium chloride solutions are mixed; but von Weimarn was apparently the first to formulate the general statement. I am not certain whether a gelatinous precipitate is a limiting case when the size of the crystals becomes very small. It seems to me quite possible that we are dealing with the appearance of a second liquid phase; but I shall probably discuss this in a later paper.

Empirically we find that the relative number of nuclei decreases with rising temperature because we get more coarsely crystalline precipitates at higher temperatures, a point which is apparently not covered by von Weimarn's theory. The question of adsorption receives very little attention from von Weimarn[1] in spite of the fact that barium sulphate is well known to precipitate more coarsely crystalline in presence of sulphuric acid or hydrochloric acid and very finely divided in presence of barium chloride. This has been discussed in detail by Weiser[2] so I need not go into it.

The general results of this paper are as follows:

1. The theory of von Weimarn as to the relation between degree of supersaturation and size of crystal is inadequate because it does not take into account the number of nuclei formed.
2. With vigorous stirring and increasing supersaturation we get: colloidal solutions, curdy precipitates, fine crystals, coarser crystals, fine crystals, gelatinous precipitates in the case of a salt which normally precipitates anhydrous.
3. Precipitates are normally more coarsely crystalline at higher temperatures than at lower ones.
4. Von Weimarn's theory applies explicitly to solutions which are not stirred. The conditions for forming large crystals are those in which there is no spontaneous formation of nuclei and in which the rate of crystallization is so slow that branched crystals do not form.
5. The effect of adsorption on the growth of crystals is not covered adequately by von Weimarn.

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[1] "Grundzüge der Dispersoidchemie," 59 (1911).

[2] Jour. Phys. Chem., **21**, 314 (1917).

BENZENE SULFONNITRAMIDE, TOLUENE-4-SULFONNITRAMIDE, 2-NITROTOLUENE-4-SULFONNITRAMIDE, AND SOME OF THEIR SALTS[1]

BY BRUCE REID MATHEWS

Introduction

Benzenesulfonnitride is an ammono acid[2] and has the distinction of being one of the strongest, if not quite the strongest acids, of this class known. Baur[3] has shown that it approaches in strength the ordinary mineral acids. A specimen of this acid and its homologue toluene sulfonnitramide were desired for certain purposes in this laboratory so their preparation was undertaken by the author. With the acids at hand it seemed worth while to determine the extent to which they would form metallic salts. The results obtained are given herewith.

Benzene Sulfonnitramide

Benzene sulfonnitramide was prepared by O. Hinsberg[4] by the action of a mixture of colorless nitric acid, sp. gr. 1.48, and ordinary concentrated sulfuric acid on benzene sulfonamide. He recognized the acid properties of the compound to the extent of preparing the potassium and ammonium salts.

Several attempts were made in this laboratory to prepare benzene sulfonnitramide by Hinsberg's method with only partial success. The compound is difficult to prepare because of its instability and extreme solubility in water. Several times, while recovering part of the ether used in extracting the nitramide from water solution, violent decomposition set in and the compound was entirely lost. It was found, however,

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[1] From a thesis submitted to the Department of Chemistry of Stanford University in partial fulfillment of the requirements for the degree of Master of Arts.

[2] Am. Chem. Jour., 47, 285 (1912).

[3] Ziet. phys. Chem., 23, 412 (1897).

[4] Ber. deutsch. chem. Ges., 25, 1093 (1902).

that by adding ammonia quickly when signs of decomposition appeared, the nitramide could be recovered as the ammonium salt. In fact, most of the other salts were prepared from this compound. Water was the only solvent used throughout this investigation, thus all solubilities, when not otherwise indicated, refer to water.

Salts of Benzene Sulfonnitramide

Ammonium benzenesulfonnitramide, $C_6H_5SO_2NNO_2NH_4$, was prepared by neutralizing benzenesulfonnitramide with aqua ammonia. The product is moderately soluble in water and crystallizes in fine, yellow prisms.

Calculated for $C_6H_5SO_2NNH_4NO_2$: S, 14.7; N, 19.2. Found: S, 13.9; N, 19.5.

Sodium benzenesulfonnitramide, $C_6H_5SO_2NNO_2Na$, was prepared by dissolving the ammonium salt in water and adding an equivalent quantity of sodium hydroxide in solution. The ammonia was then boiled off and the product allowed to crystallize. Colorless crystals were formed which were moderately soluble.

Calculated for $C_6H_5SO_2N(Na)NO_2$: Na, 10.3. Found: Na, 10.5, 10.0.

Calcium benzenesulfonnitramide, $(C_6H_5SO_2N.NO_2)_2Ca.3H_2O$, was prepared from a hot aqueous solution of the ammonium salt and milk of lime. The milk of lime was added as long as it would dissolve after which the solution was filtered. The ammonia was boiled off, and the salt allowed to crystallize. Small, colorless crystals were formed which were moderately soluble.

Calculated for $(C_6H_5SO_2N.NO_2)_2Ca.3H_2O$: Ca, 8.1; H_2O, 10.9. Found: Ca, 8.1, 8.0; H_2O, 10.5, ...

Barium benzenesulfonnitramide, $(C_6H_5SO_2N.NO_2)Ba.3H_2O$, was prepared from a hot aqueous solution of the ammonium salt and an equivalent quantity of barium hydroxide in solution. A slight excess of barium hydroxide was added and the ammonia boiled off. The moderately soluble salt crystallized in fine, white, lustrous plates.

Calculated for $(C_6H_5SO_2N.NO_2)_2Ba.3H_2O$: Ba, 23.1; H_2O, 9.1. Found: Ba, 22.8, 22.8, 23.0, 23.1; H_2O, 9.6, 9.6, 8.6, ...

Strontium benzenesulfonnitramide, $(C_6H_5SO_2N.NO_2)_2Sr.3H_2O$, was prepared by adding a hot aqueous solution of strontium hydroxide to an equivalent quantity of the ammonium salt. The ammonia was boiled off and the salt allowed to crystallize. The product formed very soluble, colorless crystals.

Calculated for $(C_6H_5SO_2N.NO_2)_2Sr.3H_2O$: Sr, 16.0; H_2O, 7.9. Found: Sr, 15.7, 15.9; H_2O, 9.8, ...

Lithium benzenesulfonnitramide, $C_6H_5SO_2NNO_2Li$, was prepared by adding small portions of an aqueous solution of lithium hydroxide to a hot aqueous solution of the ammonium salt as long as ammonia was evolved. The product was fine, colorless crystals which were moderately soluble.

Calculated for $C_6H_5SO_2NNO_2Li$: Li, 3.4. Found: Li, 3.3.

Ammonated silver benzenesulfonnitramide, $C_6H_5SO_2NNO_2Ag.NH_3$, was prepared by adding silver oxide to a hot aqueous solution of the ammonium salt. The product was moderately soluble and crystallized readily into small, drab-colored prisms.

Calculated for $C_6H_5SO_2NNO_2Ag.NH_3$: Ag, 33.1; NH_3, 5.2. Found: Ag, 32.8, 32.2; NH_3, 6.3, 6.0.

Hydrated silver benzenesulfonnitramide, $C_6H_5SO_2NNO_2Ag.H_2O$, was prepared by two methods. First, an equivalent quantity of silver nitrate in solution was added to a hot aqueous solution of the ammonium salt. On cooling the silver salt crystallized out. The second specimen was prepared by adding silver oxide to a hot aqueous solution of benzenesulfonnitramide as long as it would dissolve. The product crystallized in small, lustrous plates of a drab color. The salt was moderately soluble.

Calculated for $C_6H_5SO_2NNO_2Ag.H_2O$: Ag, 33.0; H_2O, 5.5. Found: Ag, 32.6, 33.3, 32.7, 32.0, 32.0, 32.5; H_2O, 5.8, 5.9, 6.5, 5.9.

Thallium benzenesulfonnitramide, $C_6H_5SO_2NNO_2Tl$, was prepared from hot aqueous solutions of equivalent quantities of the ammonium salt and thallium nitrate. The product was only slightly soluble in cold water, and crystallized in almost colorless, fine, lustrous plates.

Calculated for $C_6H_5SO_2NNO_2Tl$: Tl, 50.3. Found: Tl, 50.0, 50.1.

Hydrated cupric benzenesulfonnitramide, $(C_6H_5SO_2N.NO_2)_2Cu.2H_2O$, was prepared by neutralizing a portion of the nitramide in hot aqueous solution, with copper carbonate. The excess copper carbonate was filtered off and the salt allowed to crystallize. Beautiful, light blue crystals were formed which were very soluble.

Calculated for $(C_6H_5SO_2N.NO_2)_2Cu.2H_2O$: Cu, 12.7; N, 11.1. Found: Cu, 12.50, 12.5, 12.6; N, 10.7.

Ammonated cupric benzenesulfonnitramide, $(C_6H_4SO_2N.NO_2)_2Cu.4NH_3$, was prepared in two ways. The first specimen was obtained by adding an equivalent quantity of ammonated copper nitrate, $Cu(NO_3)_2.4NH_3$, to a hot aqueous solution of the ammonium salt. The product was fine, deep blue needles, which were only slightly soluble. The second specimen was prepared by adding aqua ammonia to hydrated cupric benzenesulfonnitramide, heating carefully until the salt was dissolved and allowing to crystallize.

Calculated for $(C_6H_4SO_2N.NO_2)_2Cu.4NH_3$: Cu, 11.9; NH_3, 12.8. Found: Cu, 11.2, 11.3, 12.3, 12.0; NH_3, 12.9, 13.0.

Hydrated nickel benzenesulfonnitramide, $(C_6H_5SO_2N.NO_2)_2Ni.6H_2O$, was prepared by adding nickel hydroxide in slight excess to a hot aqueous solution of the nitramide. The excess nickel hydroxide was then filtered off and the salt allowed to crystallize. The crystals were of a green color and very soluble in water.

Calculated for $(C_6H_5SO_2N.NO_2)_2Ni.6H_2O$: Ni, 10.3; H_2O, 19.0. Found: Ni, 10.0; H_2O, 18.3.

Ammonated nickel benzenesulfonnitramide, $(C_6H_5SO_2N.NO_2)_2Ni.6NH_3$, was prepared by adding an equivalent quantity of nickel nitrate in solution to a hot aqueous solution of the ammonium salt. The salt crystallized into light purple, stout needles which were only slightly soluble.

Calculated for $(C_6H_5SO_2N.NO_2)_2Ni.6NH_3$: Ni, 10.3; NH_3, 18.1. Found: Ni, 10.4; NH_3, 18.1.

Strychnine Salt, $C_6H_5SO_2NHNO_2.C_{21}H_{22}N_2O_2$.—Benzenesulfonnitramide unites readily with ammonia to form the ammonium salt. This led us to suspect that it would unite with the alkaloids, which was found to be true.

Strychnine nitrate was prepared from the sulphate. This in solution was added to a hot aqueous solution of the acid. A precipitate was formed immediately which was found to be very slightly soluble in water.

Calculated for $C_6H_5SO_2NHNO_2.C_{21}H_{22}N_2O_2$: N, 10.5. Found: N, 10.9, 11.6.

Several other salts of the acid were prepared but not in sufficient quantity for analyses. Among these were the magnesium, zinc, mercury, manganese, cadmium and cobalt salts. Each one except the mercury salt showed a definite crystalline form and all of them could have easily been prepared in quantity.

Solubility of Salts of Benzene Sulfonnitramide in Liquid Ammonia

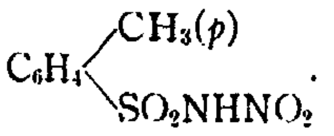
Rough indications of the solubility are indicated by the abbreviations v. e. sol., very easily soluble; v. s., very soluble; m. sol., moderately soluble; etc.

Ammonium salt, v. e. sol., cupric salt, v. sol., barium salt, v. e. sol., potassium salt, v. e. sol., mercurous salt, blackens, nickel salt, sl. sol., calcium salt, v. e. sol., sodium salt, v. sol., silver salt, v. sol., lithium salt, v. sol., thallium salt, v. sol., strontium salt, v. sol.

The Action of Nitric Acid on Paratoluenesulfonamide

The preparation of a toluene compound similar to benzenesulfonnitramide was next attempted. Accordingly, paratoluenesulfonamide was selected for the purpose. This amide was nitrated and the nitration product extracted from the reaction mixture in precisely the same manner described by Hinsberg for the preparation of benzenesulfonnitramide.[1] It was found, however, that by using nitric acid of specific gravities 1.42 and 1.48, two different compounds were formed. These were found, upon investigation, to be paratoluenesulfonnitramide and 2-nitrotoluene-4-sulfonnitramide, respectively.

Paratoluenesulfonnitramide,



$C_6H_4\begin{cases} CH_3(p) \\ SO_2NHNO_2 \end{cases}$.

This compound was prepared by placing 100 grams of colorless nitric acid of sp. gr. 1.42 in a 250 cc Erlenmeyer flask, cooling to 0° in a freezing mixture of salt and ice, and slowly adding 25 grams of paratoluenesulfonamide. Then 60 grams of concentrated, ice-cold sulfuric acid were added in small portions. The mixture was kept near 0° at all times by frequent shaking in the freezing mixture. Before all of the sulfuric acid was added the nitramide separated out as a white crystalline mass. The reaction mixture was poured into a small volume of ice and water and then extracted three times with ether. The ethereal solution of the nitramide was then shaken three times with a small volume of saturated sodium chloride solution to remove the excess nitric acid. Part of the ether was distilled off at 50° and recovered; the last portion was allowed to evaporate in the open. The evaporation was hurried by placing the concentrated ethereal solution on a water bath at 40° to 45°. The yellow, crystalline mass was recrystallized from toluene into a colorless product. The melting point at first was 105°, but after repeated recrystallization from toluene it rose to 110°. The yield ranged from ten to fourteen grams. This compound, like benzene sulfonnitramide, was found to be very soluble in water, ether, alcohol and benzene.

Calculated for $CH_3C_6H_4SO_2NHNO_2$: N, 12.9; S, 14.8. Found: N, 12.6; S, 14.5.

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[1] Loc. cit.

Salts of Paratoluenesulfonnitramide

Ammonium paratoluenesulfonnitramide, $CH_3C_6H_4SO_2NHNO_2.NH_3$, was prepared by neutralizing an aqueous solution of the nitramide with aqua ammonia. The product crystallized in slightly yellow plates which were moderately soluble.

Calculated for $CH_3C_6H_4SO_2NHNO_2.NH_3$: NH_3, 7.3. Found: NH_3, 7.1, 7.0.

Potassium paratoluenesulfonnitramide, $CH_3C_6H_4SO_2NNO_2K$, was prepared by adding an equivalent quantity of potassium hydroxide in solution to a hot aqueous solution of the ammonium salt. The salt crystallized in small, light yellow plates which were moderately soluble.

Calculated for $CH_3C_6H_4SO_2NNO_2K$: K, 15.4. Found: K, 15.1, 15.1, 15.6.

Hydrated barium paratoluenesulfonnitramide, $(CH_3C_6H_4SO_2NNO_2)_2Ba.2H_2O$, was prepared from hot solution of equivalent quantities of the ammonium salt and barium hydroxide. The product crystallized in moderately soluble, yellow plates.

Calculated for $(CH_3C_6H_4SO_2NNO_2)_2Ba.2H_2O$: Ba, 22.8; H_2O, 6.0. Found: Ba, 22.8; H_2O, 5.8.

Silver paratoluenesulfonnitramide, $CH_3C_6H_4SO_2NNO_2Ag$, was prepared by adding an equivalent quantity of silver nitrate in solution to a hot aqueous solution of the ammonium salt. The product crystallized in moderately soluble yellow needles.

Calculated for $CH_3C_6H_4SO_2NNO_2Ag$: Ag, 33.4. Found: Ag, 33.3, 33.9.

Ammonated silver paratoluenesulfonnitramide, $CH_3C_6H_4SO_2NNO_2Ag.2NH_3$, was prepared from a hot aqueous solution of the acid and as much silver oxide as would dissolve. The excess of silver oxide was filtered off and a slight excess of aqua ammonia added. The product crystallized in moderately soluble, gray-colored needles. The low percentage of ammonia could not be accounted for. The specimen was recrystallized and again analyzed but gave the same results as shown by number II below:

Calculated for $CH_3C_6H_4SO_2NNO_2Ag.2NH_3$: Ag, 30.3; NH_3, 9.5. Found: Ag, 30.5, 30.4; NH_3, 7.2, 7.2.

Ammonated cupric paratoluenesulfonnitramide, $(CH_3C_6H_4SO_2NNO_2)_2Cu.4NH_3$, was prepared from hot aqueous solutions of equivalent quantities of the ammonium salt and ammonated copper nitrate with a slight excess of aqua ammonia added. The salt crystallized in slightly soluble, deep blue prisms.

Calculated for $(CH_3C_6H_4SO_2NNO_2)_2Cu.4NH_3$: Cu, 11.3; NH_3, 12.1. Found: Cu, 11.0, 11.4; NH_3, 12.3.

Hydrated cupric paratoluenesulfonnitramide, $(CH_3C_6H_4SO_2NNO_2)_2Cu.3H_2O$, was prepared by adding powdered copper carbonate to a hot aqueous solution of the acid as long as it would dissolve. The excess of copper carbonate was filtered off and the salt allowed to crystallize. The product was very soluble and "seeding" was necessary to start crystallization. Light blue plates were formed.

Calculated for $(CH_3C_6H_4SO_2NNO_2)_2Cu.3H_2O$: Cu, 11.6; N, 10.2. Found: Cu, 11.4, 11.5; N, 10.1.

Ammonated nickel paratoluenesulfonnitramide, $(CH_3C_6H_4SO_2NNO_2)_2Ni.6NH_3$, was prepared by adding an equivalent weight of nickel nitrate in solution to a hot aqueous solution of the ammonium salt. A slight excess of aqua ammonia was added before the salt crystallized. The salt formed in very slightly soluble, bluish purple plates that lost ammonia when heated to 170° and decomposed completely at 290°.

Calculated for $(CH_3C_6H_4SO_2NNO_2)_2Ni.6NH_3$: Ni, 9.9; NH_3, 17.3. Found: Ni, 9.9; NH_3, 16.8.

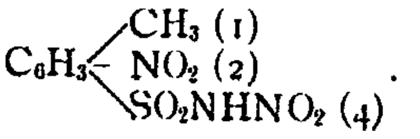
Hydrated calcium paratoluenesulfonnitramide, $(CH_3C_6H_4SO_2NNO_2)_2Ca.H_2O$, was prepared from a hot aqueous solution of the ammonium salt and milk of lime. The excess milk of lime was filtered off and the solution boiled free of ammonia. The salt formed in very soluble, yellow plates.

Calculated for $(CH_3C_6H_4SO_2NNO_2)_2Ca.H_2O$: Ca, 8.2; H_2O, 3.7. Found: Ca, 8.2; H_2O, 3.8.

Solubility of Salts of Paratoluenesulfonnitramide in Liquid Ammonia

The acid is very soluble. Ammonium salt, v. sol., potassium salt, v. sol., nickel salt, sl. sol., calcium salt, sl. sol., copper salt, sl. sol., silver salt, v. sol., barium salt, sl. sol.

2-Nitrotoluene-4-sulfonnitramide,



$$C_6H_3\begin{cases} CH_3\ (1) \\ NO_2\ (2) \\ SO_2NHNO_2\ (4) \end{cases}.$$

This acid was prepared from paratoluenesulfonamide in exactly the same way as paratoluenesulfonnitramide, except that the nitric acid used was of specific gravity 1.48–1.5. It was found that when nitric acid of sp. gr. 1.48 was used, there was no certainty that a second nitro group would be introduced into the benzene ring. It seemed that when nitric acid of sp .gr. 1.48 was used, small variations in the temperature control determined whether a second nitro group was introduced or not. To be sure of preparing 2-nitrotoluene-4-sulfonnitramide, nitric acid of sp. gr. 1.5 was used.

The acid was crystallized from toluene into beautiful, faint yellow needles and when pure melted at 118.5°. A second specimen prepared in the same way as the first melted at 115.5° after repeated recrystallization. From twenty-five grams of paratoluenesulfonamide fourteen grams of the nitramide were obtained.

The nitramide was found to be very soluble in water, absolute alcohol and ether.

One would expect the second NO_2 group to enter the benzene ring in position (2) for the reason that when mono nitrotoluene is prepared, a mixture of the ortho and para compounds is present. In this work, paratoluenesulfonamide was used where the para position was already taken, so one would expect an NO_2 group to go into position (2). Besides this, it is usually difficult to introduce an NO_2 group next to a SO_2OH group which would lead one to expect the NO_2 group to go into position (2). To test the conclusion, the nitramide was decomposed by cautious heating into the corresponding sulfonic acid and the amide of this acid prepared.

The melting point after purification was found to be 142.5°. According to Otto and Gruber,[1] however, 2-nitrotoluene-4-sulfonamide melts at 128°. A second specimen of the nitramide was decomposed by adding acetic anhydride and the amide prepared. This melted at 142°.

Calculated for $CH_3C_6H_3NO_2SO_2NHNO_2$: N, 16.0; S, 12.3. Found: N, 15.8, 16.0; S, 12.1, 12.0.

Salts of 2-Nitrotoluene-4-Sulfonnitramide

Hydrated potassium 2-nitrotoluene-4-sulfonnitramide, $CH_3C_6H_3(NO_2)SO_2NNO_2K.2H_2O$, was prepared from hot aqueous solutions of equivalent quantities of the acid and potassium hydroxide.

Calculated for $C_7H_6O_6N_3SK.2H_2O$: K, 11.7; H_2O, 10.8. Found: K, 11.2; H_2O, 10.8.

Hydrated cupric 2-nitrotoluene-4-sulfonnitramide, $(CH_3C_6H_3(NO_2)SO_2NNO_2)_2Cu.3H_2O$, was prepared by adding a slight excess of copper carbonate to a hot aqueous solution of the nitramide. The salt crystallized in very soluble, greenish blue prisms.

Calculated for $C_{14}H_{12}O_{12}N_6S_2Cu.3H_2O$: Cu, 10.0; H_2O, 8.5. Found: Cu, 10.0; H_2O, 8.3.

Ammonated cupric 2-nitrotoluene-4-sulfonnitramide, $(CH_3C_6H_3(NO_2)SO_2NNO_2)_2Cu.5NH_3$, was prepared from a hot aqueous solution of the nitramide and an equivalent quantity of ammonated copper nitrate in solution. A slight excess of aqua ammonia was added. The salt crystallized in very slightly soluble, fine blue needles.

Calculated for $C_{14}H_{12}O_{12}N_6S_2Cu.5NH_3$: Cu, 9.5; NH_3, 12.7; N, 23.1. Found: Cu, 10.0, 10.3, 10.8, 9.7; NH_3, 12.4, 12.4; N, 23.2. Total nitrogen was determined by the method of Kjeldahl.

Ammonated silver 2-nitrotoluene-4-sulfonnitride, $(CH_3C_6H_3(NO_2)SO_2NNO_2Ag.2NH_3$, was prepared from a hot aqueous solution of the acid and what silver oxide would dissolve. The excess silver oxide was filtered off and a slight excess of aqua

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[1] Liebig's Ann., 145, 23 (1868)

ammonia added. The salt crystallized in slightly soluble, fine, gray plates.

Calculated for $C_7H_6O_6N_3SAg.2NH_3$: Ag, 26.9; NH_3, 8.5. Found: Ag, 27.0; NH_3, 8.0.

Silver 2-nitrotoluene-4-sulfonnitramide, $CH_3C_6H_3(NO_2)SO_2NNO_2Ag$, was prepared from a hot aqueous solution of the nitramide and what silver oxide would dissolve. The excess silver oxide was filtered off and the salt allowed to crystallize. The salt formed in slightly soluble, beautiful, golden colored crystals.

Calculated for $C_7H_6O_6N_3SAg$: Ag, 29.4. Found: Ag, 29.4.

Ammonated nickel 2-nitrotoluene-4-sulfonnitramide, $(CH_3C_6H_3(NO_2)SO_2NNO_2)_2Ni.6NH_3$, was prepared by bringing together equivalent quantities of the nitramide and nickel nitrate in hot aqueous solution and adding a slight excess of aqua ammonia. The crystals formed in very slightly soluble, fine purple plates.

Calculated for $C_{14}H_{12}O_{12}N_6S_2Ni.6NH_3$: Ni, 8.5; NH_3, 15.0. Found: Ni, 9.5, 9.3, 8.9; NH_3, 14.2, 13.4.

Hydrated manganese 2-nitrotoluene-4-sulfonnitramide, $(CH_3C_6H_3(NO_2)SO_2NNO_2)_2Mn.5H_2O$, was prepared from an equivalent quantity of powdered manganese carbonate and a hot aqueous solution of the acid. The product formed in moderately soluble, brownish white prisms.

Calculated for $C_{14}H_{12}H_{12}N_6S_2Mn.5H_2O$: Mn, 8.3; H_2O, 13.5. Found: Mn, 8.3, 8.2; H_2O, 13.2.

Solubilities of the Salts of 2-Nitrotoluene-4-Sulfonnitramide in Liquid Ammonia

Copper salt, m. sol., potassium salt, v. sol., manganese salt, sl. sol., silver salt, v. sol., nickel salt, sl. sol.

This work was done under the direction of Professor E. C. Franklin.

Summary

The sodium, calcium, barium, strontium, lithium, silver, thallium, copper, nickel and strychnine salts of Hinsberg's

benzenesulfonnitramide have been prepared together with the ammonated salts of silver, copper and nickel.

Paratoluenesulfonnitramide and its ammonium, potassium, calcium, barium, silver, copper and nickel salts, together with the ammonated silver, copper and nickel salts, have been prepared.

2-Nitrotoluene-4-sulfonnitramide, the potassium, copper and silver salts, and the ammonated silver, copper and nickel salts have been prepared.

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EXPERIMENTS ON EMULSIONS. III

BY T. R. BRIGGS

Emulsions by Shaking

If one shakes together in a bottle, benzene and aqueous sodium oleate, carrying out the process steadily and without interruption, the time required for complete emulsification increases very rapidly as the ratio of benzene to water grows larger. With uninterrupted shaking, a very long time and the expenditure of much labor are needed to produce an emulsion relatively rich in benzene. Data regarding this point have been submitted in a previous paper[1] of this series. By way of illustration, in one case two hours of violent agitation in a mechanical shaker were required to emulsify completely 96 cc of benzene in 4 cc of one percent solution of sodium oleate. As the machine was producing about 400 oscillations per minute, this time interval represented approximately 48,000 shakes. Had the shaking been performed by hand, some patience and no little endurance would have been demanded. The data follow:

TABLE I

Emulsions by Uninterrupted Shaking. Mechanical Shaker. Benzene and One Percent Solution of Sodium Oleate. Room Temperature

Volume benzene in 100 volumes mixture	Time required to emulsify (Minutes)	Number of shakes (Approx.)
30	less than 1	less than 400
40	1	400
50	3	1,200
60	7	2,800
70	10	4,000
80	15	6,000
90	22	8,800
95	40	16,000
96	125	48,000
99	(incomplete after 8 hours)	?

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[1] Briggs and Schmidt: Jour. Phys. Chem., 19, 478 (1915).

It is well known, however, that little difficulty is met with and comparatively slight labor is required, when emulsions are formed according to the procedure followed in making mayonnaise. In the latter case the total quantity of oil is added little by little and the emulsion is built up gradually but far more easily and quickly than by the method of complete mixing at the start and uninterrupted shaking. Indeed, an emulsion of 96 or even 99 parts of benzene is quite a simple thing to make, provided only that the benzene is added very sparingly at the start and care is taken to emulsify each increment before continuing the additions.

Observation of a rather puzzling phenomenon led me to return to this problem. On one occasion an emulsion was being made by shaking oil and soap solution in a glass bottle. For some reason the shaking was interrupted before the emulsion was complete and the bottle was set aside. The unemulsified portion of oil floated to the top in the usual way. On renewing the shaking after a few minutes, it was observed that three or four shakes (by hand) completed the emulsion, with quite unexpected celerity, for the ratio of oil to water was rather large, and long and tedious shaking would normally be required with uninterrupted agitation. It seemed not unreasonable that the *mode* of performing the shaking might be an important factor; indeed, the fact soon developed that *intermittent* shaking was vastly more effective than the uninterrupted agitation heretofore employed.

The experiments which follow were performed by Messrs. J. C. Ashmead, C. F. Tears and L. H. Clark as part of their senior research. All experiments have been confirmed independently by at least two of the students mentioned above.

Benzene and one percent sodium oleate were mixed in 200 cc bottles. After *five* powerful up and down shakes—necessarily by hand—the bottles were placed upright on the table for 30 seconds, this interval proving sufficient to allow the unemulsified oil to float on the surface of the incomplete emulsion. The shaking was repeated and the bottles allowed to stand for another 30 seconds. Intermittent shaking in this manner was continued until all the benzene was emulsified. The data form Table II.

TABLE II

Emulsions by Intermittent Shaking. Shaking Done by Hand. Two Shakes followed by Interval of 30 Seconds. Benzene in One Percent Sodium Oleate. Room Temperature.

Volume benzene in 100 volumes mixture	Time required to emulsify (Minutes)	Number of shakes
40	less than 1	5
60	less than 1	5
80	less than $4^1/_2$	45
84	5	50
86	7	70
88	$7^1/_2$	75
90	$10^1/_2$	105
92	$12^1/_2$	125
94	21	210
96	42	415

A second series of emulsions was prepared in the way just described, except that only *one* shake was given between the rest intervals of 30 seconds. The results follow.

TABLE III

Emulsions by Intermittent Shaking. Shaking Done by Hand. One Shake followed by Interval of 30 Seconds. Benzene in One Percent Sodium Oleate. Room Temperature

Volume benzene in 100 volumes mixture	Time required to emulsify (Minutes)	Number of shakes
80	$3^1/_2$	7
84	$6^1/_2$	13
86	7	14
88	9	18
90	$12^1/_2$	25
92	$15^1/_2$	31
94	$22^1/_2$	45
96	40	80

To render the comparison more direct, two emulsions were made with uninterrupted shaking by hand, at the rate of approximately 180 shakes per minute. The results were as follows:

TABLE IV

Emulsions by Uninterrupted Shaking. Shaking Done by Hand.

Volume benzene in 100 volumes mixture	Time required to emulsify (Minutes)	Number of shakes
60	4.2	750
80	35.0	6,300

The data recorded in the four tables preceding bring out clearly the extraordinary difference between continuous and intermittent agitation. Intermittent shaking reduced the number of shakes in the case of the 80 percent emulsion from 6,300 to 7 and in the case of the 96 percent emulsion from 48,000 to 80. Intermittent shaking may be six hundred or even a thousand times more effective than uninterrupted but equally violent agitation.

Mr. Clark has carried out some further experiments, as follows:

(*a*) 90 parts by volume of benzene and ten parts by volume of one percent sodium oleate solution were added to a bottle and shaken without interruption for an hour in a shaking machine. The emulsion was still incomplete. At 165 r. p. m. this is equivalent to 9,900 shakes.

(*b*) The same mixture was completely emulsified by means of only 12 shakes by the intermittent method, shaking *once* up and down by hand, and waiting *one* minute between each single shake. Time about 12 minutes.

(*c*) 18 shakes were needed when 30 seconds were allowed to elapse between each shake. Time about 10 minutes.

(*d*) 31 shakes were needed when only 10 seconds were allowed to elapse between shakes. Time about 6 minutes.

(*e*) On employing the method used in (*b*) (intervals of 60 seconds) only 45 shakes were needed to emulsify 95 parts of benzene in 5 parts of soap solution. Such an emulsion could not be obtained by *hours* of continuous shaking.

Mr. Clark's data show that the rest interval is also a factor. As the rest interval increases up to one minute the shakes needed decrease, but the time elapsing increases. Since the time with zero interval (continuous shaking) is very large, the time required to form a complete emulsion passes through a minimum as the rest interval increases.

These experiments as a whole may account for an interesting observation by Lenher and Buell, from whose paper[1] the following paragraph is quoted:

"In order to study this emulsifying action of the soap with water and immiscible liquids, it is noted that, ... simply a uniform shaking, such as is given by a shaking machine, is insufficient. A shaking machine, even when running at high speed, gives unsatisfactory results. In fact a shaking machine does not give as satisfactory results as does the jerky double motion by hand."

When emulsions are prepared by the method employed in making mayonnaise—that is, by adding oil little by little—the mixture in which soap solution is the continuous phase is always large by comparison with the unemulsified layer of benzene. It is true that, for a given mode of shaking, the greater the volume of the soap solution plus the emulsified benzene the easier it is to emulsify a given quantity of fresh benzene. The experiments just described seem to indicate that another factor besides the relative volumes must be considered. The building of a complete emulsion is facilitated by allowing the emulsion complex and the benzene phase to form two distinct layers before each shake. This probably means that emulsions are formed most readily when relatively little oil is agitated briefly while in contact with a relatively large and *unbroken* volume in which soap solution is the continuous phase.

Continuous shaking in a bottle must disintegrate into drops both soap solution and benzene. Since the soap solution in an emulsion is the continuous phase, any process tending to disintegrate soap solution must retard emulsification;

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[1] Jour. Ind. Eng. Chem., 8, 702 (1916).

likewise any process tending to disintegrate benzene must aid emulsification. When benzene is disintegrated into drops in soap solution the soap prevents the drops from coalescing. There is nothing, however, to prevent the rapid coalescence of water drops in benzene, so that it is not difficult to see why shaking produces in due time a complete emulsion of benzene in soap solution. It should be harder to disintegrate all the soap solution and easier to break up the benzene when the volume of the solution is relatively large, hence the emulsion should result quickly. Some time must elapse before maximum disintegration of the soap solution occurs on shaking and during this time it seems reasonable to believe that benzene would be emulsified permanently in greatest amount; hence the first few shakes should be more effective than the subsequent ones. If this be granted, the beneficial action of intermittent shaking follows at once.

In the light of this reasoning, one is justified in expecting rapid and easy emulsification whenever benzene is disintegrated under conditions unfavorable to the simultaneous disintegration of soap solution. Rolling or dragging the benzene layer over the soap solution might fulfill these conditions. One way of doing this experimentally is to employ a mortar and pestle, as is done in the so-called "Continental" method. Rolling a mixture of benzene and soap solution in a cylindrical bottle is another, and this experiment was tried for me by Mr. Tears.

TABLE V

Emulsions by Rolling. One Percent Sodium Oleate.

Volume benzene in 100 volumes mixture	Time required to emulsify (Minutes)	Distance (Feet)
60	1/2	60
70	2/3	80
80	1	140
90	2	276
92	3	420

By adding 30 small glass beads to the 92 percent mixture the time of rolling was reduced to less than 1 1/2 minutes.

A 250-cc cylindrical bottle containing benzene and soap solution was rolled backwards and forwards in a simple apparatus. The total distance travelled by the rolling bottle and the time required for complete emulsification are recorded in Table V.

These data, taken in conjunction with those of Table I and elsewhere, bring out in a striking manner the ease with which benzene emulsions may be made by the method of rolling. They also afford support to the general theory outlined in the preceding paragraphs.

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

1. In making emulsions by direct shaking, intermittent shaking is far more efficient than uninterrupted shaking, even in a shaking machine.

2. The time and the number of shakes required to complete an emulsion both vary with the rest interval between shakes.

3. Emulsions are easily made by rolling or rotating cylindrical bottles containing oil and soap solution. This mode of procedure is similar to the "Continental" method, which will form the subject of a separate paper in this series.

4. The ideal emulsifying process is one causing the benzene to break up into drops with the least disintegration of the aqueous soap solution.

Cornell University

CHARCOAL BEFORE THE WAR. I

BY WILDER D. BANCROFT

When carbonaceous material is heated or otherwise decomposed in the absence of air or in the presence of insufficient air to cause complete combustion, a porous, carbonized or charred product is obtained which is known as charcoal. Charcoal is often called by different names, varying with the material from which it is made. Thus we have wood charcoal, bone charcoal, blood charcoal, sugar charcoal, and gas charcoal. Charcoal made from gaseous material may also be called soot, lamp-black, carbon black, and gas carbon; though this last term is also used to denote carbon from the blast furnace. Charcoal from coal is usually called coke and is ordinarily not considered as charcoal though it comes under the definition. Graphite is usually not classed as charcoal though it is really a limiting case. Another differentiation is into vegetable, animal, and mineral charcoal, where mineral charcoal certainly includes coke and may include the gas charcoals. The two properties of charcoal which interest us are the power of adsorbing or condensing gases in the pores and the power of extracting coloring matter and other substances from solution. This property of wood charcoal was discovered by Löwitz in 1790 and was made use of in the refining of sugar until a pharmacist named Fiquier showed in 1811 that animal charcoal was an even more effective decolorizing agent. In the following year, Derosne employed animal charcoal for the treatment of beet juice in the place of wood charcoal, which had been used for this purpose in France since the beginning of the beet sugar industry there.

Wood charcoal is made by burning or distilling wood in stacks, in pits, in closed chambers of brick or stone, or in iron retorts. The yield of charcoal will vary with the kind of wood, the temperature at which it is charred and the amount of air which is admitted. The yield of charcoal is less, the higher the temperature. Violette[1] obtained yields of 50%

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[1] Comptes rendus, 32, 713 (1851); 38, 107 (1854).

at 250°, 33% at 300°, 20% at 400°, and 15% at 1500°, the highest temperature that could be reached. These temperatures are not to be considered as accurate. At constant temperature the amount of charcoal is greater the longer the time of carbonization. Thus, very slow charring at 400° gave twice as much charcoal as very rapid charring did. At 250° the charcoal contained about 65% carbon, this figure rising to 73% at 300°, 80% at 400°, and about 96% at 1500°. When wood is charred in a completely closed vessel the yield of charcoal is much greater because much of the volatile carbonaceous matter is decomposed. When heated to 300°-400° in an absolutely closed vessel, wood seems to melt and flow, sticking to the walls. When cooled, the mass has no structure and forms a black glistening mass like tar, containing about 67% carbon and 27% oxygen, the unstated balance being probably ash and hydrogen.

Charcoal made in kilns is not homogeneous. It may contain 73% carbon near the outside of the kiln and 85% at the center where it has been heated more. When wood is charred in superheated steam, the product is more uniform and can be controlled better. Thus, it is quite simple to get a reddish charcoal containing 70% carbon or a very black charcoal with 88% carbon. Wood charcoal made at 280° is friable, reddish, and inflammable. When made at 1000°-1500° it is very black, very dense, and very slightly inflammable. When heated to the melting point of platinum, it is hard to break, gives a sonorous ring like a metal when struck, burns with difficulty, and can be heated red-hot in a flame, like iron.

The amount of ash in wood charcoal varies with the nature of the wood; but is ordinarily between one and three percent. Berthelot[1] analyzed one sample containing 1.61% ash and found the ash to consist of SiO_2, 0.083; CaO, 0.679; K_2O, 0.156; iron, alumina, mineral acids, etc., 0.792.

Foster[2] has determined the amount of carbon and hydro-

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[1] Comptes rendus, **141**, 793 (1905).

[2] Proc. Chem. Soc., **1892**, 46.

gen in charcoals obtained by carbonizing sugar and starch, getting the following results:

	C	H	
Sugar	95.0	1.1	High temperature
Sugar	94.1	1.2	Low temperature
Starch	95.0	0.9	

Cross and Bevan[1] lay stress on the fact that charcoal is not, strictly speaking, a form of carbon, and that sulphuric acid does not convert sugar into carbon and water. They propose the term pseudo-carbons for the black substances, containing a more or less high percentage of carbon, which are formed by the charring of carbonaceous compounds either by the action of heat or otherwise.

Carbon black[2] is the soot produced when a flame of natural gas burning with insufficient air impinges against the lower surface of an iron plate. The yield is very low, not over one pound per 1000 cu. ft. of gas. All carbon blacks have a general family resemblance, being very intense in color, and glossy whether rubbed in the dry or in varnish. When pure, they mix readily with water; but traces of oily matter prevent this. It is said that there is a difference in this respect between carbon black and lamp-black which is the soot from oils; but this is not a real distinction. Lamp-black is usually dirtier than carbon black and consequently is wetted less readily; but it is merely a question of degree of purification. Carbon black is an extremely light, fine powder, weighing less than five pounds to the cubic foot and it will sometimes oscillate in waves, almost like water, owing to the large amount of air in the mass. It is easily electrified and flies up in the air if a piece of sealing-wax is rubbed over the sleeve and then passed over the black. To compress carbon black it is necessary to let the air escape without carrying the black with it. This

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[1] Phil. Mag., [5] 13, 325 (1882).

[2] Cabot: Jour. Soc. Chem. Ind., 13, 128 (1894); Int. Congress Applied Chemistry, New York, 12, 18 (1912).

can be done by covering the plunger of the press with a sheepskin, woolly side out. The wool retains the black but lets the air pass through.

It is claimed by Frank[1] that if acetylene is mixed with carbon monoxide or dioxide and decomposed by explosion, the carbon of both gases is deposited in a pure form, free from tarry condensation products, according to the equation $C_2H_2 + CO = 3C + H_2O$. The carbon black so obtained is said to be superior to the best American carbon black in color and covering power. If carbon monoxide or carbon dioxide be allowed to act on carbides of the alkalies or alkaline earths at a high temperature, the carbon comes out as graphite, the reaction being represented by the equation $CaC_2 + CO = 3C + CaO$.

Morehead[2] has patented the preparation of carbon black from a gaseous mixture of acetylene and oxygen or air, the proportion of air being above 1 percent, and preferably about 4.5 percent. The mixture is compressed, passed into a vacuous explosion vessel, and exploded, the minimum pressure required to effect dissociation being used, namely, about 60 lbs. per square inch. The resulting carbon is removed from the explosion vessel by an air-blast.

Mixter[3] has studied the carbon which separates when acetylene under pressure is exploded. As it comes from the bomb it is a grayish black, lusterless, and very bulky, porous mass. When compressed it has a brilliant black luster, but not the metallic appearance of graphite. It is not graphite and does not contain graphite and yet the heat of combustion of 12 grams is 94,728 calories which is fairly close to the value of 94,000 calories for graphite and considerably less than the value of 96,500 calories for sugar charcoal and gas-retort carbon. Mixter considers that this is a special allotropic form of carbon; but it is quite possible that it is a very pure form of carbon be-

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[1] Jour. Soc. Chem. Ind., 24, 1117 (1905).

[2] U. S. Pat. 779,728 (1905).

[3] Am. Jour. Sci., [4] 19, 434 (1905).

cause Mixter gives its composition as 99.95% carbon and 0.03% hydrogen.

When pure acetylene[1] is passed over copper foil at 250° or over reduced, pulverulent copper at about 180°, the gas is absorbed at first without apparent change in the structure of the copper, while hydrocarbons of the ethylene series condense in the cooler parts of the tube. After absorption is nearly complete, the copper begins to swell very considerably in bulk, the color becoming lighter, and the condensing liquids changing to a mixture of ethylene and aromatic hydrocarbons, while the escaping gas consists chiefly of a mixture of ethylene hydrocarbons with some ethane and hydrogen, and a little acetylene. The solid finally becomes a soft, light or dark yellow, substance, composed of matted filaments. When compressed gently, it resembles touch-wood. It burns in air with a smoky flame and an aromatic odor, and leaves a slight residue of copper oxide. It is a hydrocarbon of unknown molecular weight and apparently having the empirical formula C_7H_6, corresponding to about 92.3% carbon. The name "cuprene" has been suggested for it.

Moissan[2] points out that amorphous charcoals always contain hydrogen and are likely to contain traces of iodine, lead, zinc, iron, etc., depending on the way in which they are made. They retain water quite firmly and the true density varies apparently between 1.76 and 1.87. The higher the temperature at which the charcoal has been prepared, or to which it has been heated, the less readily does it burn in oxygen, the ignition temperatures as determined varying from 370° to 506°. It also becomes less readily attacked by a mixture of potassium bichromate and sulphuric acid. The changes take place slowly at each temperature. The amorphous charcoals prepared by Moissan usually contained about 93% carbon, the remainder being presumably ash, hydrogen, and water. The lower the temperature at which the charcoal is prepared, the more nearly brown the color is rather than black.

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[1] Sabatier and Senderens: Comptes rendus, 130, 250 (1900).

[2] Ann. Chim. Phys., [7] 8, 289 (1896).

Black, amorphous carbon, prepared from any form of organic matter by destructive distillation or imperfect combustion, always retains small amounts of hydrogen, oxygen, or nitrogen (if nitrogenous matter be used). One of Mallet's students,[1] therefore, attempted to prepare charcoal from material absolutely free from these elements. Metallic sodium was freed very carefully from any traces of naphtha and was placed in a hard-glass tube from which all the air was driven by carbon tetrachloride vapor, after which the sodium was heated in presence of a current of carbon tetrachloride. In order to protect the glass, the sodium was placed at first on a layer of pure, well-burned lime. The violence of the reaction caused some volatilization of the sodium, however, and the upper part of the glass tube was attacked, introducing silicon into the product. To avoid this the lime was placed later in a loose inner tube of copper foil, platinum having proved unsatisfactory. The carbon always contained some calcium and some copper, which had to be removed by prolonged treatment with nitric and hydrochloric acids, followed by washing with water. After much difficulty a specimen was obtained finally which was almost free from ash. To drive off gases so far as possible the carbon was heated to a temperature not much below that at which it would have begun to burn and was then burned in a little platinum boat in a stream of carefully purified and well-dried oxygen. One specimen gave absolutely no water, showing the absence both of water vapor and of combined hydrogen. Unfortunately, these experiments were not carried further, so we know nothing about the properties of this charcoal.

Mixter[2] calls attention to the fact that the difficulty in obtaining amorphous charcoal fairly pure is a serious obstacle in a study of its properties. It is usually stated that the hydrogen may be removed by heating charcoal in chlorine; but Mixter was unable to find out who was the authority for this statement or what analytical tests have been used to show

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[1] Porcher: Chem. News, 44, 203 (1881).

[2] Am. Jour. Sci., [3] 45, 363 (1893).

whether the resulting product was free from chlorine. Berthelot and Petit[1] treated wood charcoal with hydrofluoric and hydrochloric acids, then with chlorine at a red heat, and finally calcined it in a Perrot furnace, which probably removed all the chlorine. When Weber[2] was determining the specific heat of carbon, he prepared amorphous carbon by heating wood charcoal to bright redness for fifteen minutes in a stream of chlorine in order to remove hydrogen; but he does not say how he proved the absence of chlorine. Wright and Luff[3] heated sugar charcoal for two hours in chlorine and then ignited it for six hours in platinum over a blow-pipe to remove chlorine. Two analyses gave the following results:

Carbon	96.17	95.13
Hydrogen	0.84	0.75
Ash	1.56	1.68
Oxygen (by difference)	1.43	2.44

These analyses are interesting as showing how tenaciously charcoal retains hydrogen even after ignition in chlorine.

While attempting to prepare amorphous carbon free from hydrogen, Mixter observed that charcoal retains some chlorine even at high temperatures. He worked with carbon black, sugar charcoal, and gas carbon. The sugar charcoal contained 0.13% hydrogen and 0.04% ash. It burned with difficulty in oxygen, was hard enough to scratch glass, and was a good conductor of electricity. The carbon black was made from natural gas;[4] it contained 1.0% hydrogen, and 0.04% ash. An air-dry specimen showed 0.23% nitrogen by the absolute method. After the carbon black had been ignited for two hours in dry nitrogen and then allowed to cool in the gas, no nitrogen was obtained on burning with copper oxide. This kind of carbon black conducts electricity when pressed into compact pieces. When heated in a vacuum it yields a

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[1] Bull. Soc. chim. Paris, [3] 2, 90 (1889).
[2] Phil. Mag., [4] 49, 161, 276 (1875).
[3] Jour. Chem. Soc., 33, 17 (1878).
[4] Mallet: Chem. News, 38, 94 (1878).

small sublimate. The gas carbon was the inner portion of a thick piece. It contained 0.035% hydrogen and 0.88% ash.

The gas carbon did not take up chlorine when heated with it, whereas the sugar charcoal and the carbon black, which contain more hydrogen, retain some chlorine persistently, apparently because the chlorine has reacted with the hydrocarbons in the charcoal. While carbon black does not retain nitrogen when heated with this gas, it does when heated with ammonia or with oxides of nitrogen. Mixter assumes that these gases decompose and that the nascent nitrogen reacts with the charcoal. It is not known what the product is, but it cannot be paracyanogen because this would be converted into cyanogen at high temperatures.

Since charcoals may contain graphite, it is necessary to have some definition and test of this substance. Berthelot defines as graphite any sort of carbon which yield graphitic oxide on oxidation.[1] The best oxidizing medium is a mixture of potassium chlorate and nitric acid. The higher the temperature at which the graphite has been formed, the less readily it is attacked by the mixture. Certain graphites swell when oxidized. This is due apparently to the sudden evolution of gas between the plates. While the characteristic reaction of graphitic oxide is extraordinarily sharp with lamellar, natural graphite,[2] it is difficult to apply with the very fine, pulverulent charcoal obtained by certain reactions in the laboratory. Graphitic oxide is absolutely insoluble and keeps the special form of the oxidized carbon. With natural graphite one gets yellow plates of fair size which settle rapidly in water and in salt solutions. It can be recognized easily. With very finely divided charcoals, it comes down as an inpalpable dust, scarcely yellowish, which stays suspended for a long time in liquids. Precipitation and washing by decantation require many precautions and much time. The graphitic oxide thus obtained can be recognized by its property of deflagrating

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[1] Moissan: Ann. Chim. Phys., [7] 8, 306 (1896).

[2] Le Chatelier and Wologdine: Comptes rendus, 146, 49 (1908); 148, 1715 (1909).

when heated, forming a black, voluminous mass of pyrographitic oxide.

The densities of graphites, as determined by flotation in mixed liquids vary from 1.62 to 2.44, depending on the source of the graphite. When purified carefully, the values all come out practically 2.255, 15°/4°. There is, therefore, only one graphite. Le Chatelier and Wologdine consider that there is also only one amorphous carbon with a density of about 1.8. Mixter found 1.919 for the carbon obtained by the explosion of acetylene under pressure; but this probably contained some graphite because Le Chatelier and Wologdine state that acetylene black containing graphite will give 2.05–2.15.

The so-called graphitite from Wunsiedel in the Fichtelgebirge, has always been looked upon as amorphous,[1] and Luzi has made further examination as to whether this is really correct. He finds that the mineral consists of pure carbon containing neither hydrogen nor nitrogen; microscopic examination shows no signs whatever of the substance being of crystalline nature. The conclusion arrived at is that this form of carbon is amorphous, but that it differs considerably from wood charcoal, for ordinary amorphous charcoal has a sp. gr. 1.57–1.88 while the graphitite in question has the sp. gr. 2.21–2.26 (Ceylon graphite according to Brodie has the sp. gr. 2.25–2.26); again, ordinary amorphous carbon is completely oxidized by potassium chlorate and red fuming nitric acid, without formation of the slightest trace of insoluble graphitic acid, while amorphous graphitite gives an insoluble crystalline oxidation product perfectly analogous to or identical with that obtained from crystalline graphite. Schungite occurring in Russia cannot well be compared with the above, since it contains 0.5 percent of hydrogen and 0.5 percent of nitrogen, but it agrees well with ordinary amorphous carbon in that it has about the same specific gravity and in that on oxidation it yields no graphitic acid.

Animal charcoal is usually bone charcoal though it may

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[1] Luzi: Ber. deutsch. chem. Ges., **25**, 1378 (1892).

be made from dried blood, flesh, horns or leather. It should be made from well-selected clean bones of compact structure.[1] These are crushed and then treated with a solvent such as petroleum naphtha to remove the fat and they are then carbonized in cast-iron retorts. Charring for 10–12 hours at a red heat gives better results than charring at a higher temperature for 6–8 hours. A cherry-red heat is the best for producing a black charcoal. At lower temperatures the decomposition of the organic matter is not complete and the product has a characteristic reddish brown color. Too high a temperature gives rise to a vitreous charcoal which generally has a bluish tinge. It is important that the temperature should be kept low in the initial stage of the process, until all of the water has been drawn off, after which it is raised gradually to a cherry-red glow. The charcoal is removed from the retorts and cooled in closed iron vessels. When the charcoal is cold, it is crushed to the desired size. In Austria charcoal is used in lumps the size of a walnut; in Germany the lumps are no larger than a hazel nut, while the French crush to granules of the size of linseed, and in England and America millet seed is the standard.[2]

In new charcoal the carbon should range from 9 to 11.5 percent, the siliceous matter should not exceed 0.5 percent, the ferric oxide 0.15 percent, and the calcium sulphate 0.2 percent. The balance is chiefly calcium phosphate. The color should be black or dark brown. The charcoal should be hard but also porous and should adhere strongly to the tongue. Charcoal made from dried blood, etc., is usually too friable for use in sugar refining; but is used to some extent in bleaching oils, fats, glycerine, etc. Unless dried, bone black may easily contain ten percent water. Bone black always contains nitrogen; but this is not usually given in the analyses. Wallace[3] found 1.55 percent in a total of 8.5 of so-called carbonaceous matter in char made from home-collected bones, but in another

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[1] Newlands and Newlands: Jour. Soc. Chem. Ind., 7, 419 (1886).

[2] Zapiski: Jour. Soc. Chem. Ind., 12, 532 (1893).

[3] Chem. News, 17, 249 (1868).

sample made from foreign bones it was 1.08 out of 9 parts of carbonaceous matter. It diminishes in quantity as the char is used. Two samples of moderately old charcoal gave, respectively, 0.3 and 0.55 percent nitrogen, while the carbon was reported at 15 and 17 percent, respectively.

When the fatty matter in uncharred bones is extracted with ether and the mineral matter with hydrochloric acid, there remains a semi-transparent substance of somewhat variable composition—called ossein. When treated with hot water it is converted into gelatin. The mean value of the analyses of all the bones comprising the skeleton of an ox are ossein 24 percent and ash 66 percent. The large bones such as the femur are the richest in ossein and, therefore, the best for the manufacture of charcoal. Bones which have been exposed to the atmosphere or to moisture lose their ossein and yield a charcoal of little value, which may be recognized by its gray color.

Glassner and Suida[1] give the following analyses of various charcoals.

Water content refers to air-dried charcoal, the other figures to charcoals dried to constant weight at 110°.

	Water	C	H	N	O (S) about	Ash
Animal charcoal	8.29	78.03	0.4	3.02	5.34	13.21
Blood charcoal	25.99	69.98	1.72	7.19	14.71	6.4
Bone charcoal	17.95	67.12	1.24	6.9	20.58	4.16
Glue charcoal	4.86	63.61	2.25	12.21	9.43	12.5
Soot	3.87	92.06	0.73	—	7.21	—
Soot I	—	91.70	0.71	—	75.9	—
Soot II	—	93.67	0.51	—	5.82	—
Wood charcoal	3.83	61.17	2.55	Trace	34.05	2.23
Sugar charcoal	3.99	78.91	0.79	—	20.30	—
Acetylene black	—	98.98	0.11	—	0.91	—

Patterson[2] gives analyses of a series of typical charcoals used in sugar refining.

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[1] Liebig's Ann., 357, 101 (1907); 361, 354 (1908).

[2] Jour. Soc. Chem. Ind., 22, 612 (1903).

ANALYSES OF CHARCOALS

	I	II	III	IV
Carbonaceous matter	18.22	14.47	8.84	9.72
Organic matter soluble in H_2SO_4	1.97	2.09	1.90	1.70
Organic matter soluble in HCl	1.37	1.59	1.33	1.46
Organic matter soluble in water	0.44	0.43	0.12	0.28
CO_2 lost on ignition	2.00	2.96	3.02	2.98
Ash	76.00	78.46	84.79	83.86
	100.00	100.00	100.00	100.00
Total CO_2	2.48	3.50	3.53	3.16
N in carbonaceous and H_2SO_4 organic matter	1.85	1.75	0.99	0.84
N in HCl and H_2O organic matter	0.51	0.33	0.10	0.26
Total nitrogen	2.36	2.08	1.09	1.10

	V	VI	VII	VIII	IX
Carbonaceous matter	10.13	11.36	16.25	5.05	17.05
Organic matter soluble in H_2SO_4	0.27	0.29	0.40	0.02	0.04
Organic matter soluble in HCl	0.55	1.06	0.97	—	—
Organic matter soluble in water	0.56	—	—	—	—
CO_2 lost on ignition	2.12	1.77	1.11	—	0.07
Ash	86.37	85.52	81.27	95.03	82.82
	100.00	100.00	100.00	100.00	100.00
Total CO_2	2.45	2.07	1.61	0.09	0.25
N in carbonaceous and H_2SO_4 organic matter	0.55	0.67	0.71	—	—
N in HCl and H_2O organic matter	—	0.18	0.07	—	—
Total nitrogen	—	0.85	0.78	0.15	0.66

No. I is the dust from new charcoal. Nos. II, III, IV, and V are new charcoals. No. VI is refinery stock charcoal which has been 8 weeks in use. No. VII is refinery stock charcoal which has been in use for 35 weeks. Nos. VIII and IX are spent charcoals turned out of refineries as useless.'

A great difference is noticeable in the percentage of carbonaceous matter in these charcoals. I and II have been made from bones from which little, if any, of the gelatine was boiled out before charring, like III, IV, and V. VI and VII are stock charcoals from one refinery where the carbonaceous matter increases with use, by the charring of vegetable matter absorbed from the sugar solutions in the process of revivification. In VIII the carbonaceous matter had been reduced to about half that in new charcoal by air leakages in the same process; and No. IX, like No. VII, has accumulated carbon, to the extent of about 7½ percent in the course of long use.

The organic matter soluble in water is a trifling quantity, but it is present in all new charcoals. Of course the first washing removes it.

The organic matter soluble in sulphuric acid is a significant constituent of animal charcoal. Together with the carbonaceous matter it forms the residue obtained on treatment with hydrochloric acid, usually called carbon. No. V, which only contains 0.27 percent, has been charred at a higher temperature, and probably for a longer period than the other four new charcoals. The refinery stock charcoals, VI and VII, have lost a large portion of this organic matter, and the spent charcoals, VIII and IX, contain little more than a trace. This organic matter probably plays an important part in the life of the charcoal. The organic matter soluble in hydrochloric acid, although a different quantity and probably containing a little water, is also a significant constituent.

Bone black is used to remove coloring matter and lime salts from sugar. It also takes out gummy matters and, unfortunately, adsorbs a certain amount of sugar.[1]

"In refining sugar, a hot solution of a density of about 50° Brix is passed through filter presses or bag filters, and then

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[1] Clark: Jour. Soc. Chem. Ind., 32, 262 (1913).

slowly run on to animal charcoal, contained in cisterns about 20 ft. high and 8 ft. in diameter and holding about 30 tons. For 20 to 40 hours the liquid percolates through the charcoal, after which hot water is turned on to wash out all the sweet matters. The absorbent properties of the successive layers of charcoal brought into play, the upper portions becoming soon saturated with impurities, while the lower portions only become charged after a considerable time. The liquor which runs off at first, is quite colorless and serves for the manufacture of the highest quality of white sugar. In the course of a few hours it becomes slightly yellowish, and as filtration proceeds, there is a gradual increase in color intensity, until at the end of the operation, it is of a more or less brownish yellow color and can only be utilized for making lower qualities of refined sugars. About one ton of charcoal is used per ton of sugar. Without a well-purified sugar liquor, a large yield of the best quality of white sugar cannot be obtained from the massecuite, owing to the loss of sugar cyrstals in the centrifugal machines from the subsequent excessive washing with water which is necessary to remove adhering colored syrup. The decolorizing power of the charcoal is more or less affected by the nature of the impurities present in raw cane sugars, and it is a matter of common experience that sugars having practically the same polarizations are not equally serviceable from a refining point of view. This may be due to the variety of sugar cane crushed, the soil on which the cane has been grown, or to the process of manufacture of the raw sugar."

Given two sugar solutions of the same color intensity but one containing more salts and more invert sugar, bone black will decolorize the solution with the lesser quantity of salts and invert sugar more effectively than the other. A solution of raw sugar, having a certain color intensity but with a low content of invert sugar and salts may have 95% of its color abstracted by boneblack while another raw sugar solution of approximately the same color but containing more invert sugar and salts may show no more than 85% decolorization after contact with charcoal.

In time the bone black ceases to be active, owing to the accumulation of lime salts and of organic matter. It can be revivified by igniting and treating with acid or in other ways. The general question of revivification will be discussed in detail later; but now it is necessary to consider what factors affect the adsorption by bone black.

As has been pointed out, the so-called carbon in animal charcoal is not pure carbon but consists of a series of complex organic compounds containing a large percentage of nitrogen. The calcium phosphate is not the important ingredient in the decolorizing because the char loses practically all power of removing coloring matter[1] if it is burned perfectly white. If the calcium phosphate be removed,[2] the residual char decolorizes more effectively than the original char. Thus it was found by experiment that the decolorizing effect of the carbon from 1000 grams of old char was greater than that of the entire weight of the char from which it was obtained. It is not practicable, however, to use in sugar refining a charcoal from which the calcium phosphate has been removed because the product is too soft and because it sinters too much when reburned. It is apparently agreed that the main part played by the calcium phosphate is to give the proper structure and rigidity to the charcoal. This does not mean that calcium phosphate has no adsorbing powers. Stenhouse[3] found that the decolorizing power of wood charcoal was increased by impregnation with calcium phosphate and it seems probable from his data that this is a specific effect. It is worth noting, however, that the maximum beneficial effect was obtained with only 7.5 percent calcium phosphate which is a very different value from that for bone black. This point will be discussed later.

In view of the fact that ordinary wood charcoals, which contain no nitrogenous compounds, are very poor decolorizers,

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[1] Wallace: Chem. News, 17, 249 (1868).

[2] Newlands and Newlands: Jour. Soc. Chem. Ind., 7, 429 (1888).

[3] Liebig's Ann., 101, 243 (1856).

Patterson[1] believes that the efficiency of bone black is due in large part to the presence of nitrogenous compounds and he attempts to prove it by extracting this material with hydrochloric acid and sulphuric acid, and observing its properties. The organic compounds extracted by boiling sulphuric acid were precipitated with water and tested against a standard caramel solution. Weight for weight their decolorizing action was 16–40 times as much as that of a good bone black. The substance extracted by cold sulphuric acid was sixteen times as effective as equal weight of bone black. There is, therefore, no question but that the nitrogenous compounds may be the effective decolorizing agents though it does not follow that they must always be.

In order to get more information as to these organic compounds, Patterson[2] treated a large portion of charcoal dust with hydrochloric acid solution, washed by decantation, and dried thoroughly. "The dried carbonaceous residue from the hydrochloric acid treatment was further digested with cold sulphuric acid to separate the organic matter. The acid filtrate was poured into water, and the precipitated organic matter washed by decantation, and finally collected on a filter, scraped into a porcelain basin, and dried. The operation is tedious, but 2 to 3 grams of the organic body were finally obtained. In the process of washing to obtain the pure body it was noticed that after five washings by decantation the precipitate would not settle, but remained in suspension or in colloidal solution in the next washing water and sulphuric acid had to be added to throw it down again. Washing with water on the filter does not dissolve the precipitate when the acid is removed, although it carries it through mechanically if stirred up in doing so; but the organic matter separated by sulphuric acid at 100° C goes freely into colloidal solution on the filter as the acid is washed out and separates again after long standing.

"In the dry condition the organic body presents a horny

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[1] Jour. Soc. Chem. Ind., 22, 608 (1903).

[2] Ibid., 22, 610 (1903).

appearance with conchoidal fracture. Heated in a test-tube it chars very easily, giving off whitish yellow vapors with a strong smell of burnt bones. Thrown into water it does not again assume the hydrated condition. It is insoluble in water, cold or hot; and insoluble in alcohol, ether, benzene, and chloroform. It dissolves freely in sulphuric acid, from which it is thrown down by water in the gelatinous condition, but the acid solution has a reddish color, not yellow like the dilute acid filtrate from the first sulphuric acid separation, which indicates some slight change due to the treatment. Concentrated hydrochloric acid dissolves the hydrated body in the cold to a brown solution. Boiling makes little difference. Dilution with water throws it down again, from which a filtrate is obtained with a very slight yellow color. Boiled with concentrated nitric acid, free from nitrous acid, the body dissolves with liberation of a little nitrous acid, to a brown solution. On dilution with water a portion of the substance precipitates, leaving the solution yellow. The addition of ammonia does not increase the color of the filtrate, as it would if proteids were present. Neither does Millon's test give any reaction for these bodies. Glacial acetic and citric acids have very little action. Tannin does not produce any precipitate in the colloidal solution referred to above, but aluminium, iron, copper, mercury, and magnesium salts do. They do not precipitate the dilute sulphuric acid solution, perhaps because so little substance is present. Strong ammonia dissolves the hydrate freely and dilution does not precipitate it, but it falls out partially on heating, leaving a yellow solution which deposits a few yellow needle-like crystals when evaporated to dryness. This reaction points to the body having the properties of an acid in very dilute solution, while it has those of a base in the original charcoal.

"The dried organic body is only very slightly soluble in strong ammonia, but ammonia does not separate any of it from the carbonaceous residue of charcoal. It is insoluble in soda solution. It neither contains sulphur nor ash. A 50 percent solution of sugar shaken with the dried organic body dissolves a very little to a brownish color which remains brownish when diluted.

"The following results were obtained on analysis of the organic body: I. 0.2262 g gave 0.5217 g CO_2 and 0.0861 g H_2O. II. 0.2024 g gave 0.4738 g CO_2 and 0.0797 g H_2O; and by the Kjeldahl process: I. 0.5262 g gave NH_3 = 4.485 cc normal H_2SO_4 solution. II. 0.4866 g gave NH_3 = 4.160 cc normal H_2SO_4 solution. Worked out, these figures give the following percentages:

	Experiment		Ox-bone Cartilage
	I	II	
Carbon	62.90	63.26	49.81
Hydrogen	4.23	4.37	7.14
Nitrogen	11.98	11.97	17.32
Oxygen	20.89	20.40	25.67
	100.00	100.00	99.94

"These results correspond with the empirical formula $C_{25}H_{20}N_4O_6$. The decomposition and oxidation products have not yet been studied. But since we know the body itself to be a decomposition product of bone cartilage, I have put alongside an analysis of the latter by Frémy[1] for comparison. It is apparent from this analysis that decomposition has not proceeded far, or at any rate so far as we might expect, when we recollect that the bones must have been submitted to a red heat for at least 12 hours in reducing them to charcoal. The large percentage of oxygen, which with its equivalent of hydrogen from the elements of 23 percent of water, might lead us to infer that this substance is a product of the action of the sulphuric acid on the carbonaceous matter, or that it is due to the organic body holding added water so tenaciously that a temperature of 100° C is incapable of drying it. Had the action been the result of oxidation or hydrolysis the weight of the organic body would have been considerably increased,

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[1] Watt's Dictionary, 1, 620.

and the analysis of the carbonaceous residue from hydrochloric acid, given above, would have shown this. But the three constituents of that residue were estimated directly, and they total rather under 100. We have seen that no heat is developed and no gas liberated when this residue is treated with sulphuric acid, as would have been the case had the acid acted chemically on it, and had it contained uncombined water. Much heat is liberated when the residue is not dry from the combination of the acid with the water present. The action seems to be a simple case of dissolution on the part of the acid. We must, therefore, conclude that the oxygen is a constituent element of the organic body, and that it exists in the charcoal itself, as it does in the bone cartilage. I am not aware that oxygen has previously been observed as a constituent of charcoal, but its presence accounts for the fact that water can be driven off at all temperatures up to 300° C. Clark[1] objects to the theory that the decolorizing power of bone black is due chiefly to nitrogenous organic compounds or to "complex nitrogenous carbon" because bone black reaches its maximum decolorizing power only after repeated washings and reburnings, when much of the nitrogen combined with organic matter disappears. It seems to him that the maximum decolorizing power should be exerted when nitrogenous organic compounds were present in large excess. This objection would be sound if it were a question of solution; but the state of the surface is very important in the case of adsorption and it is probable that a given bone black will give the best results with a definite amount of nitrogenous matter, and this concentration need not necessarily be that which occurs fortuitously in freshly-burned charcoal. On the other hand there seems to be good reason to believe that a wood charcoal can be made having a higher decolorizing power than most animal charcoals and perhaps higher than any animal charcoal, so that nitrogenous compounds are not necessary though they may be desirable. Since adsorption is specific, we must distinguish two factors, the nature and the structure of the sur-

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[1] Jour. Soc. Chem. Ind., 32, 262 (1913).

face. If a given surface will not take up a dissolved or dispersed substance, we can get results by impregnating with a third substance which is adsorbed strongly by the surface and adsorbs the dissolved or dispersed substance. Cotton adsorbs certain coloring matters so slightly that it cannot be dyed with them. Dyeing can be effected by mordanting cotton with alumina or tannin as the case may be. The adsorption by wool is so much greater in many cases that a mordant is not necessary though one may be used. The difference between wool and cotton may be realized in charcoal by unspecified changes in the structure. We can consider the nitrogenous compounds as mordants for the coloring matter in sugar. If we have a charcoal of low adsorbing power, the presence of the nitrogenous matter in suitable amount will increase the adsorption very much. If we have a charcoal with just the right structure for adsorbing a particular coloring matter, the addition of nitrogenous matter may clog the pores or disturb things otherwise so as to be positively detrimental. On this hypothesis it is easy to see why people working with different charcoals may get apparently contradictory results. There has been no way of making quantitative comparisons between structures and consequently this factor has only been recognized to a minor extent. People have realized that the porosity of the charcoal was important; but they have not asked themselves what was the proper size or shape of pores to give the best results.

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EXPERIMENTS ON EMULSIONS. IV

BY T. R. BRIGGS, F. R. DuCASSÉ AND L. H. CLARK

PHARMACEUTICAL EMULSIONS

Introduction

Pharmaceutical emulsions are prepared on a small scale most satisfactorily by the so-called "Continental" method, which consists in making what is termed an "emulsion nucleus" with more or less definite quantities of oil, water and gum and subsequently diluting this nucleus with water, as desired. The making of a suitable nucleus is looked upon as something of an art in which success follows only upon strict adherence to an arbitrary method of procedure.[1] The best practice is to place the oil (4 parts) in a dry mortar of sufficient capacity, add acacia (2 parts) and triturate until a smooth paste is formed. Water (3 parts) is then added *all at once*, with trituration, whereupon a creamy nucleus results almost immediately. This nucleus, of course, is an emulsion of oil in water, containing relatively large quantities of oil and gum, the latter acting as the peptizing or "emulsifying" agent. The nucleus is viscous and very sticky, both of which properties may account for the characteristic "crackling" sound which is emitted whenever the completed nucleus is stirred. Being an emulsion of the oil-in-water type[2] it is miscible with water and can be diluted without difficulty.

Roon and Oesper, in the paper cited, have published some interesting studies on pharmaceutical emulsions. They believe that their results confirm Fischer's hypothesis,[3] "that their production [i. e., the production of emulsions] is always associated with the discovery of a method whereby the water (or other medium) which is to act as the dispersing agent is

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[1] Cf. Bancroft: Jour. Phys. Chem., **16**, 747 (1912); Roon and Oesper: Jour. Ind. Eng. Chem., **9**, 156 (1917).

[2] Cf Newman: Jour. Phys. Chem., **18**, 34 (1914); Briggs and Schmidt: Ibid., **19**, 493 (1915).

[3] "Fats and Fatty Degeneration," 5 (1917).

all used in the formation of a colloid hydration (solvation) compound. In other words, when it is said that the addition of soap favors the formation and stabilization of a division of oil in water, it really means that soap is a hydrophilic colloid which, with water, forms a colloid hydrate with certain physical characteristics, and that the oil is divided in this. The resulting mixture cannot, therefore, be looked upon as a subdivision of oil in water, but rather as one of oil in a hydrated colloid."

Roon and Oesper go even farther than Fischer and conclude[1] "(1) that the presence of a hydration compound is necessary for emulsification; (2) that this hydration compound is most efficiently used if formed at the moment of dispersion of the internal phase—in other words, the three constituents, the internal phase, emulsifier and water, in critical proportions, must all be mixed at one time in order to form a properly hydrated nucleus; (3) slight variations from the proper procedure or from the critical proportions yield either less stable emulsions or none at all; (4) no emulsion results if the emulsifier is diluted (hydrated) before dispersion of the internal phase."

The most striking part of the hypothesis of Roon and Oesper is that emulsions are formed only when the "hydration compound" is produced at the moment of trituration or agitation with the oil. Later on, we shall return to review this hypothesis in the light of what our own experiments indicate.

Emulsions by the Continental Method

Experiment 1.—4 grams of powdered gum arabic (acacia) were added to 9 cc of olive oil contained in a large porcelain mortar (diameter 20 cm) and the mixture was thoroughly triturated. Microscopic examination of the product resulting showed that it consisted of a coarse suspension of gum in oil, stabilized more or less by the viscous nature of the oil. Without discontinuing the grinding, 6 cc of water were now added, when in about 20 seconds a creamy emulsion (nucleus) resulted; the latter, owing to its viscous, sticky nature, emitted the characteristic "crackling" sound. The nucleus prepared in

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[1] Jour. Ind. Eng. Chem., 9, 161 (1917).

this way was perfectly miscible with distilled water to form a milky liquid containing globules of oil whose size varied between 2 and 4 microns in diameter. No free oil floated to the top of the diluted nucleus on standing in a closed tube, even after several days, nor did the concentrated nucleus separate into layers. This experiment illustrates the standard "Continental" method of making an emulsion.

Experiment 2.—Instead of adding dry gum to the oil and adding water subsequently, a *solution* of gum arabic containing 4 grams of gum plus 6 cc of water was added to the oil with grinding. No emulsion nucleus resulted. The oil was only slightly emulsified, much free oil remained undispersed and the oily mixture in the mortar gave no "crackling" sound.

Experiment 3.—The procedure of Experiment 1 was followed except that the water was added a few drops at a time instead of at once. No useful nucleus resulted; the emulsion was very incomplete. After the addition of the first few drops of water the gum in suspension throughout the oil coalesced into sticky lumps which adhered to the mortar and prevented proper mixing of the oil and water.

Experiment 4.—No satisfactory nucleus resulted when gum arabic solution was placed in the mortar and oil was added subsequently and all at once, with grinding.

These four experiments bring out the importance of the order and manner of mixing the various components of the emulsion nucleus. They confirm the results of Roon and Oesper. Apparently, unless one "hydrates" the gum at the moment of trituration in the presence of oil and unless this hydration is carried out in one step, no satisfactory nucleus results. As a matter of fact, the oil is *completely* emulsified only under these limiting conditions; in all those experiments which failed to produce a satisfactory nucleus, some, though little, of the oil was actually emulsified.

Unfortunately, the hydration hypothesis of Roon and Oesper cannot be correct for it is easy enough to emulsify olive oil in a *solution* of gum arabic by shaking oil and solution in a bottle. Such an emulsion can be improved and the globules of oil made smaller by subsequent treatment in a homogenizer. One does not "hydrate" the gum in the presence of the oil and yet one gets an emulsion. The experiments which follow will serve to demonstrate that simultaneous hydration is not essential when forming emulsions in a mortar.

The Effect of Finely Divided Solids

Experiment 5.—9 cc of oil were placed in the mortar and rubbed with 3 or 4 grams of sand (finer than 100 mesh). Gum arabic solution (4 grams of gum plus 6 cc of water) was added and, on triturating, there resulted a satisfactory nucleus, very nearly the equal of the nucleus obtained in Experiment 1. Time—15 seconds. Oil globules—4 to 12 microns. No emulsion was formed when water instead of gum solution was added to the oil and sand, showing that we were not dealing with sand as the peptizing agent (cf. Pickering's emulsions).

Experiment 6.—Experiment 5 was repeated using 6 grams of cane sugar in place of the sand. On grinding for 10 minutes a paste resulted containing irregular fragments of sugar averaging about 10 microns in diameter. On adding gum solution and triturating, a perfect nucleus resulted. Time—12 to 15 seconds. Oil globules—2 to 4 microns, maximum 8 microns.

Experiment 7.—6 grams of sodium chloride were used instead of sand; otherwise same as 5. Perfect nucleus. Time — 15 to 20 seconds. Oil globules—2 to 4 microns.

As control experiment a nucleus was made by the standard "Continental" method (cf. Experiment 1). Time—20 seconds. Oil globules—2 to 4 microns. Experiments 5, 6 and 7 were checked by performing them in duplicate.

This second series of experiments proves that it is possible to prepare a normal nucleus, even by the use of gum arabic *solution*, i. e., with previously "hydrated" gum, provided a finely divided solid is present in the oil. Powders soluble in water and powders insoluble in water seem more or less equally effective. Complete nucleus emulsions were obtained with sand, ground quartz, pulverized glass and several other finely divided solids, with gum as the peptizing colloid.

The Surface Factor

Experiment 8. Varying the Size of Mortar and Pestle.—Three mortars and three pestles were used in making standard "Continental" emulsions as in Experiment 1. Large mortar—20 cm in diameter; 7.3 cm deep. Medium mortar—9 cm in diameter; 4.2 cm deep. Small mortar—6.5 cm in diameter; 3.5 cm deep. Width of pestles at base—large, 5.8 cm; medium, 3.2 cm; small, 3.0 cm. Mortar and pestles of porcelain.

(*a*) Large mortar, large pestle. Time—25–30 seconds. Oil globules—1 to 2 microns. Exceedingly uniform emulsion.

(*b*) Medium mortar, medium pestle. Time—25–30 seconds. Globules—2 to 6 microns. Fairly uniform.

(*c*) Small mortar, small pestle. Time—35 seconds. Globules—4 to 10 microns. Non-uniform (many large drops of oil).

This experiment shows that the best results are obtained when the largest rubbing surface is made available. A mortar with a slightly roughened surface seems better than a smooth one.

Experiment 9. Varying the Fineness of Sand.—Following the procedure of Experiment 5, one gram samples of sand (SiO_2) were ground gently with 9 cc of oil and gum solution was added. The data follow:

Fineness of Sand	Remarks
60–100 mesh	Unsatisfactory nucleus; incomplete emulsion
100–200 mesh	Satisfactory nucleus; complete emulsion; 5 to 10 microns
200–350 mesh	Satisfactory nucleus; complete emulsion; 3 to 10 microns
Through 350 mesh	Excellent nucleus; complete emulsion; 2 to 5 microns

In each of these individual experiments the nucleus was diluted by adding 25 cc of distilled water and set aside in order that the permanence of the emulsion might be tested. The emulsions made with sand finer than 100 mesh were fully as permanent as similar emulsions made by the standard "Continental" method. It is evident that the finer the sand, i. e., the greater the specific surface—the better the nucleus emulsion. The sand employed in this work was a pure white material used in the manufacture of high grade carborundum.

Control Experiment.—Oil, 350 mesh sand and water (without gum arabic) did not give a satisfactory nucleus. The results of Experiment 9 cannot therefore be due, save possibly very slightly, to the sand as peptizing agent.

Experiment 10. Varying the Quantity of Sand.—These tests were carried out according to the procedure of Experiment 9, using sand of 100 to 200 mesh and varying the quantity of sand added. The results follow:

Weight of Sand (Grams)	Remarks
0.5	Poor nucleus; some unemulsified (free) oil
1.0	Good nucleus; no free oil; 5 to 10 microns
1.5	Good nucleus; no free oil; 3 to 10 microns
2.0	Very good nucleus; no free oil; 4 microns
2.5	Excellent nucleus; no free oil; less than 4 microns

These data show that increasing the quantity of solid results in a more satisfactory nucleus containing smaller globules of oil. Taken in connection with Experiment 9, they also indicate that the larger the surface of solid exposed to the mixture of oil and solution, the more perfect is the resultant nucleus.

Experiment 11. Varying the Nature of the Finely Divided Solid.—In order to keep the surface factor under control and as nearly constant as possible, all the powdered solids were roughly of equal fineness and were used in equal volumes.

Powdered Solid	Grams	Remarks
Sand—SiO_2	2.5	Good nucleus, uniform; 2–4 microns
Chalk—$CaCO_3$	2.2	Good nucleus, uniform; 3–6 microns
Galena—PbS	7.5	Poor nucleus, non-uniform; 3–25 microns
Zinc blende—ZnS	4.0	Poor nucleus, non-uniform; 3–20 microns
Aluminum	2.7	Poor nucleus, non-uniform; 3–30 microns

To realize the latter condition experimentally, weights in grams were taken equal to the density of the solid. Care was taken not to grind unduly the powdered solid when suspending it in the oil.

These experiments indicate that there are distinct and specific effects due to the nature of the finely powdered solid. Apparently solids easily wetted by water (sand and chalk) are more satisfactory than solids less readily wetted by water[1] (galena, blende, and aluminum) so far as the production of small globules and uniform emulsions is concerned. The influence of the wetting factor will be brought out clearly in later experiments.

Emulsions with Sodium Oleate

Experiment 12.—4 grams of powdered sodium oleate were ground in the mortar with 9 cc of olive oil. On adding 6 cc of water and grinding, a perfect nucleus resulted. Other experiments, similar to Nos. 2, 3 and 4 showed that all the results obtained with gum arabic could be duplicated with sodium oleate. The diluted nucleus made by the standard "Continental" method contained globules averaging 2 to 3 microns in diameter.

Experiment 13.—2.6 grams of sand (350 mesh) were added to 9 cc of oil, whereupon a solution of sodium oleate (4 grams soap plus 6 cc of water) was added with grinding. Although the soap solution was in the form of a paste the nucleus emulsion was obtained after sufficient grinding. Globules—2 microns. This nucleus was even more perfect than the one made by the standard method.

This group of experiments shows that sodium oleate and gum arabic behave in essentially the same way. The effect of finely divided solid is the same in both cases.

Emulsions with Other Oils

Experiments with different oils and gum arabic carried out according to the standard "Continental" method, showed

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[1] Cf. Hofmann: Zeit. phys. Chem., 83, 385 (1913); Bancroft: Jour. Phys. Chem., 19, 294 (1915).

fairly conclusively that the more viscous oils, such as olive oil, linseed oil and pine oil, are much more readily emulsified than are the less viscous oils, such as benzene, toluene, chloroform, and aniline.

Discussion of Results

In view of the foregoing experiments, it is evident that "hydration" of the emulsifying agent—gum arabic or soap—need not be carried out at the moment of disintegrating the oil. It is possible to prepare a perfect emulsion of oil in water with previously "hydrated" gum or soap by using a solution instead of the dry material, provided one follows a suitable procedure. One way to succeed is to use a fairly viscous oil, mix the latter with finely divided solid, such as sand or sugar, and finally to add the solution of acacia or soap with energetic trituration.

It is known that the "Continental" method of the pharmacist gives emulsions of olive oil whose globules are much smaller on the average than they are when oil and previously hydrated gum are mixed and shaken by hand in a bottle. One might argue from this that simultaneous "hydration" produces a far better emulsion. Opposed to such a point of view, however, are the experiments with sand and sugar, in which previously hydrated colloids (solutions of gum and soap) afforded emulsions fully equal to the "Continental" ones. Of course, one might say that sand or sugar are "hydrated" by gum solutions, but this is certainly stretching the theory beyond its elastic limit, at least so far as sand is concerned. It seems better to abandon the hypothesis suggested by Roon and Oesper, and to substitute a new one.

Our own experiments indicate that the presence of finely divided solid in the oil is the *sine qua non* of the "Continental" method. Finely divided solid was present in every experiment which resulted in a satisfactory nucleus emulsion. In the standard "Continental" method powdered gum or soap play the part that sand or sugar do in the subsequent experiments. *Finely divided solids serve to increase the area of the interface between oil and water or between oil and solution.*

Anything which increases the interface between oil and water, assists in the production of an emulsion.

We may consider the mechanism of the "Continental" method to be somewhat as follows: Gum arabic is suspended in a viscous oil by grinding. Water is added and the grinding is continued. Gum being soluble in water (it is really peptized by water) it is probably much more readily wetted by water than it is by oil. Water, therefore, tends to displace the oil from the gum so that each particle becomes coated with an aqueous film. The interface between oil and water is thus enormously increased. The gum soon dissolves, leaving drops of solution scattered momentarily throughout the oil. The triturating action flattens out these drops and in the process oil is disintegrated and emulsified in the solution. The drops of gum solution, as they are stirred around in the mixture, exert an interfacial tearing effect upon the oil and aid in its dispersion. The large drops of gum solution, each drop bearing its load of emulsified oil, soon coalesce to a uniform mass of emulsion (the nucleus). In the standard "Continental" method the powdered gum plays a double rôle (1) that of finely divided solid, (2) that of emulsifying and stabilizing colloid.

The part played by finely divided solids needs no further elucidation. The solid relieves the gum of one of its functions in the standard method so that the gum solution may now be used. The experiments with soluble powders, such as sugar and sodium chloride, show that insolubility is not a necessary requirement.

There are, however, some other interesting possibilities. One might suggest, for example, that when water is added to sodium oleate suspended in oil, the sudden change (decrease) in the surface tension, produced by soap dissolving, might account for the disintegration of oil, much as changes of surface tension at the interface are said to account for Gad's so-called spontaneous emulsions.[1] That the change of sur-

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[1] Cf. Bancroft: Jour. Phys. Chem., 16, 348 (1912).

face tension is actually not an important factor was shown in the following manner.

Experiment 14.—Powdered sodium oleate (4 grams) was suspended in olive oil (9 cc) by triturating in a mortar. Instead of pure water, 6 cc of a two percent solution of sodium oleate were added. An excellent nucleus emulsion made its appearance after a few seconds' grinding. Globules—2 to 3 microns. It was found by experiment that the surface tension of a two percent solution of sodium oleate is very slightly changed by further additions of sodium oleate. Thus a 2 percent solution of sodium oleate rose 15 mm in a given capillary tube; an 8 percent solution rose 16 mm and pure water rose 40 mm.

It is not at all improbable, however, that the process of wetting the suspended solid with water or solution, entailing as it does a displacement of oil from the surface, may help to disintegrate the oil and form the necessary globules. We should, therefore, expect to find such substances as are easily wetted by water[1] assisting most ably in the emulsion forming process, *provided they are suspended in the oil.* The experiments which follow were designed to test this point.

Experiment 15.—Part a. 2.6 grams of sand (350 mesh) were suspended in 9 cc of olive oil, whereupon 10 cc of gum arabic solution were added. A nucleus emulsion resulted after grinding for 35 seconds. Globules—1 to 4 microns.

Part b. 7.5 grams of galena (350 mesh) were suspended in 9 cc of olive oil and gum solution (10 cc) was subsequently added. It required no less than 5 minutes of vigorous trituration to produce a complete emulsion. Globules 1 to 4 microns. Note that 2.6 grams of sand occupy about the sam volume as 7.5 grams of galena.

Experiment 15 may be regarded as strongly supporting the hypothesis. Oil will be displaced by solution more rapidly from sand than from galena. It should therefore be easier to form the emulsion with sand than with galena, and such proved to be the case.

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[1] Cf. Hofmann: Zeit. phys. Chem., 83, 385 (1913).

It follows, as a further necessary consequence of the theory, that sand will be most effective when present originally in the oil and least effective when added with the solution of gum arabic, for under the latter circumstances the displacement of oil does not take place and the solid serves only to increase the interface. Experiment supports this deduction.

Experiment 16.—Part a. 2.6 grams of sand (350 mesh) were added to 10 cc of gum arabic solution in the mortar. Vigorous grinding for 5 minutes was required to emulsify 9 cc of oil in this mixture. Globules—1 to 4 microns. Compare with Experiment 15, Part a.

Part b. 7.5 grams of galena (350 mesh) were added to 10 cc of gum solution in the mortar. Vigorous grinding for nearly 8 minutes was needed to complete the emulsion. Globules—1 to 4 microns. Compare with Experiment 15, Part b.

Experiment 17.—Part a. 2.6 grams of sand (350 mesh) were added to 9 cc of oil in the mortar and 10 cc of gum solution were subsequently added. An emulsion resulted in 1 minute. Globules—1 to 2 microns.

Part b. 2.6 grams of sand were added to 10 cc. of gum solution. Nine minutes of grinding were needed to emulsify 9 cc of oil on placing the oil in the mortar and adding the mixture of sand and solution. Globules—2 to 4 microns.

All of these experiments were checked by tests in duplicate. It is evident that a longer time and more work are needed to make an emulsion when the solid is first wetted by the aqueous solution.

It is now quite definitely established that finely divided solids, whether soluble or insoluble in the aqueous phase, serve greatly to facilitate the formation of emulsions in the mortar. The same is also true of finely divided solids added in the bottle when emulsions are made by shaking. On grinding sodium oleate in benzene and shaking the mixture with water in a bottle an excellent emulsion resulted. A still better emulsion was obtained when a more perfect suspension of soap was made by adding to benzene a small amount of a fifty percent solution of sodium oleate in ethyl alcohol (Squibb's soft soap). Experiment seemed to show that the finer the particles suspended in the oil the more important and beneficial becomes the process of displacing the oil by the aqueous liquid.

When the oil contains particles readily peptized in water —such as gum arabic or soap—the act of peptization may be looked upon as an extreme case of wetting by water. Peptization should therefore entail rapid displacement of oil. Rapid displacement produces maximum disintegration, and might if rapid enough, give rise to so-called "spontaneous" emulsions—emulsions formed merely by contact with water and hence with a minimum of mechanical effort. If one were to produce a *colloidal* solution of sodium oleate in benzene an emulsion should form exceedingly easily on adding water, and might conceivably develop practically spontaneously, wherever water and benzene come in contact. Indeed, certain oily mixtures are known to give spontaneous emulsions in water, for example, lysol and the creosote emulsions. In both these instances, the oil contains the hydrophile[1] colloid in some form of suspension and the act of peptization into the water phase gives rise to an extremely perfect emulsion, almost entirely without externally applied mechanical effort. We have surprisingly little information available concerning spontaneous emulsions, though mixtures giving them are common and some are commercially important.

An effort was next made to apply the theory to the case of water-in-oil emulsions.[2] Linseed oil was heated with rosin, some of which dissolved. Six cc of water were placed in a mortar and ground with various powdered solids. The linseed oil-rosin mixture was then added, following the procedure of Experiment 5. With galena or mercuric iodide emulsions of water in linseed oil were formed in the mortar. These emulsions were analogous to the oil-in-water ones, they could be diluted with linseed oil, but they were very unstable. With water, galena and pure linseed oil no emulsion could be made; nor could one

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[1] Cf. Bancroft's definition: Jour. Phys. Chem., 19, 275 (1915).

[2] Cf. Briggs and Schmidt: Ibid., 19, 478 (1915).

be made with water, sand and linseed oil-rosin. The failure with sand might be attributed to the non-wetting of sand by linseed oil and the absence of the displacement factor. White lead plus water in the mortar, with linseed oil-rosin added afterward, gave a water-in-oil nucleus, exactly what one should expect from the behavior of white lead, water and linseed oil.[1]

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

1. The hypothesis of Roon and Oesper that hydration of the emulsifying colloid must take place at the moment of disintegrating the oil has been shown not to be in accordance with the results of experiment.
2. Even in a mortar, emulsions may be made with previously "hydrated" colloids, provided one modifies the "Continental" procedure.
3. Emulsions are easily produced by the method of trituration in a mortar if the area of the interface between oil and water is made sufficiently large. One way of doing this is to suspend in the oil finely divided solids which are readily wetted by water.
4. The effectiveness of the solid is increased by decreasing the average size of the particles.
5. Up to a certain limit, the readiness with which an emulsion forms increases as the quantity of finely divided solid grows larger.
6. It is better to suspend the finely divided solid in the liquid to be emulsified, before adding the dispersing solution.
7. The most effective solids are those readily wetted by the dispersion medium.
8. In the "Continental" method, gum arabic (acacia) plays the part both of finely divided solid and emulsifying colloid.
9. The finely divided solid serves to increase the area of the interface between oil and water.

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[1] Cf. Bancroft: Met. Chem. Eng., 14, 631 (1916).

10. Wetting phenomena may also cause the displacement of one liquid by the other and consequently give rise to disintegration of the displaced liquid. It is not known to what extent the action depends *per se* upon the emulsifying power of the finely divided solid.

11. Emulsions of water in oil may be made in a mortar in the presence of finely divided solids easily wetted by oil.

Cornell University

NEW BOOKS

The Metals of the Rare Earths. *By J. F. Spencer. 23 × 15 cm; pp. x + 279. New York: Longmans, Green and Co., 1919. Price: $4.50.*—In the preface the author points out that "since the rare earths have attained a commercial and economic importance, and since their scientific importance is so very great and will probably become greater, it would seem essential that a student, before leaving his college career behind him, should possess some knowledge of these substances. Consequently, it has been deemed advisable to add this work to the series of monographs on Inorganic and Physical Chemistry."

The titles of the chapters are: history of the discovery of the rare earths; occurrence of the rare earths in nature; separation of the rare earths; methods of controlling the fractionation of the rare earths; the cerium group of rare earths; the yttrium group of rare earths; thorium; atomic weight determinations; rare earths and the periodic system; uses of the rare earths.

In addition to the regular chemistry, there are a number of items of especial interest to the physical chemist. *The possibility of separating the rare* earths by shaking with phosphate-free charcoal is discussed, p. 52. "Hofmann and Krüss placed a solution of the earths of equivalent weight $B^{III} = 116.8$, in a bottle together with charcoal and shook for some time. The solution was then filtered and the equivalent weight of the earths contained in the charcoal determined, and found to be $R^{III} = 134.4$. Obviously, therefore, a decided separation had been effected. It must be noted, however, that the amount of material absorbed by the charcoal is small; in the case mentioned 0.5 gram was adsorbed by 8 grams of charcoal from 2 grams of the mixture. The weaker bases are adsorbed first by the charcoal. In the case of a mixture of yttrium earths ($R^{III} = 93.03$), a mixture of earths was adsorbed by the charcoal in a single operation, which gave $R^{III} = 96.0$. This is a far more efficient separation than is possible in one operation by means of the aniline fractionation."

On pp. 95 240, and 78, it is pointed out that "many of the compounds of cerium exhibit strong catalytic properties in connection with many types of chemical reactions. Cerium chloride, and indeed the chlorides of all the rare earths, exhibit an oxydase action and accelerate the absorption of oxygen by hydroquinone. Fouard has shown that when a quantity of hydroquinone is sealed in a series of tubes, together with equivalent quantities of chlorides of the rare earths and a measured quantity of air, larger quantities of oxygen are absorbed than would be the case in the absence of rare-earth chlorides. Thus the following percentages of the oxygen present are absorbed in the different cases: with samarium chloride, 75.8 percent; thorium chloride, 63.1 percent; cerous chloride, 57.7 percent; neodymium chloride, 54.2 percent; praseodymium chloride, 53.3 percent; and lanthanum chloride, 22.6 percent. When sodium chloride was used, the percentage of oxygen absorbed was only 17.8 percent. The velocity of oxidation of oxalic acid by nitric acid is greatly accelerated by the presence of cerous sulphate, whereas the sulphates of yttrium, lanthanum, praseodymium, and neodymium have no such action. Oxalic acid is oxidized rapidly by potassium permanganate in the cold in the presence of cerous salts, thus showing that cerium is akin to manganese in this respect. A layer of cerium dioxide serves as a catalytic agent in the burning of organic substances in the Dennstedt method of combustion; it is not poisoned by arsenious oxide or sulphur dioxide. Ammonia is oxidized at 650° when passed over a layer of cerium dioxide; the oxides of lanthanum, praseodymium and neodymium have the same action. Nitrogen and hydrogen, when passed over cerium nitride at 200°, combine to form ammonia to the extent of about one percent."

"Crude cerium earths constitute an efficient catalyst in the contact process for the manufacture of sulphuric acid; the catalytic material is prepared by soaking pumice in a solution of the mixed sulphates and igniting strongly. Cerium sulphate is the active medium in this action but the presence of the other rare-earth sulphates increases its activity. The copper chloride catalyst used in the Deacon process may be replaced by the cerium earth chlorides. With these substances the reaction takes place most efficiently at 350°-480°. Double alkali sulphates of cerium are the best catalysts for the production of aniline black by the action of potassium chlorate or chromate on aniline. According to Lipski and Whitehouse, cerium hydride and nitride act as catalysts in the combination of nitrogen and hydrogen to form ammonia; but the catalyst very soon loses its activity.

"When cerium is heated in hydrogen to 250°-270°, combination takes place with incandescence and the formation of the hydride. It is somewhat doubtful whether this compound is cerous hydride or ceric hydride since the percentage of hydrogen contained in it is found to vary between the amounts required for the two compounds. It is a non-crystalline, dark blue or black powder which takes fire spontaneously in the air. It is decomposed rapidly by moist air, water, and alkalies with the evolution of hydrogen; acids decompose it with the evolution of hydrogen and the formation of cerous salts. When heated in the air it decomposes with a slight explosion and forms a mixture of oxide and nitride, ammonia also being produced. When heated to 800°-900° in nitrogen it is converted into nitride. When cerous hydride is shaken in a closed glass tube, it emits light."

The cerium earths find a certain use in the glass and porcelain industries as coloring materials, p. 239. "When one percent of ceria is added to potash glass a bright yellow color is produced, while larger quantities give shades down to brown. Lime-soda glass in which a portion of the lime is replaced by cerium oxide not only has the colors stated above but also the properties of a potash glass. Neodymium compounds added in small quantities to glass produce blue optical glasses. Such glass exhibits, without any special apparatus, the characteristic neodymium absorption spectrum. If an excess of cerium dioxide is fused with an opaque glass melt a beautiful yellow enamel is produced.

"Many derivatives of the cerium earths possess fire-stable colors which may be used for coloring porcelain. Among these may be noted neodymium phosphate and praseodymium phosphate which give an amethyst-red and a bright green color, respectively. Suitable mixtures of these salts produce many intermediate shades which are very useful in decorating porcelain. Ceric titanate produces a shining yellow color, ceric molybdate a beautiful bright blue, ceric tungstate a bluish green, cerium mangani-titanate an orange-yellow color; neodymium tungstate produces a bluish red color."

Since lanthanum acetate acts as an oxygen carrier in the oxidation of hydroquinone, the author considers that this points to the possibility of lanthanum existing in a higher state of oxidation, p. 104. When lanthanum acetate is precipitated with ammonia, a slimy semi-transparent precipitate is produced. When this precipitate is well washed and treated with a little iodine solution, it takes on a deep blue which spreads slowly through the whole mass. The reaction occurs only when the acetate is used and when the precipitate is slimy, p. 105. If the precipitation is effected from hot solution, the basic acetate is granular and does not adsorb iodine. The reaction is indeterminate and useless in the presence of other cerium earths, praseodymium giving the same color, for instance, p. 113. The catalytic action of thoria receives a brief mention, p. 170. Of course the important use for thoria is in the Welsbach mantles, p. 234. "Cotton fibre was originally used in the manufacture of mantles but this was supplanted by ramie fibre and artificial silk (viscose or nitrocellulose silk). The fibre is woven into tubes of the required size and then washed to remove fatty material and to reduce the ash. The process differs in the various cases. Ramie fibre web is soaked for about twelve hours in two percent nitric acid, centrifuged to remove excess of acid, and then washed with distilled water. Cotton web is washed first in 3-5 percent sodium hyrdoxide, and then in 1-3 percent hydrocholric acid at about 50°. Silk web requires no preliminary water washing. The web is then dried in a current of hot air. Cotton and ramie webs are cut into the requisite size at this stage. The web is then soaked for two minutes in the case of cotton and ramie, and for five hours in the case of silk, in a solution consisting of 100 g thorium nitrate, 10 g cerium nitrate, 5 g beryllium nitrate and 1.5 g magnesium nitrate in two kilos of water. Cotton and ramie webs are now passed between rollers to remove the excess of solution; the silk web is centrifuged. The web is then dried at 30°, cotton and ramie stretched on glass cylinders, silk on wooden rollers. After drying, the mantles are formed, fitted with asbestos loops and other supports, and strengthened by coating the top and bottom with thorium solution containing salts of calcium, aluminum, and magnesium. At this stage the mantle may be branded by stamping with a paste of 1 kg didymium nitrate, 200 g glycerine, 25 g methylene blue, 300 g 96 percent alcohol and 300 g distilled water. The mantle is now shaped on a wooden form and burnt off with a Bunsen flame starting at the top.

"The next process is that of hardening which is carried out by raising the mantle to a high temperature for a few minutes. The mantle is now finished but so fragile that any movement is likely to break it. Consequently, before it can be put on the market it must be strengthened. This is done by immersing it in a solution of 100 g 4 percent collodion, 40 g ether, 6.5 g camphor, and 3.5 g castor oil, and then drying it at 50°-60°.

"A few modifications in the above process are made when nitrocellulose is used. In this case the fibre must be denitrated before burning off; with viscose this is unnecessary. Silk web after being washed in ether containing a little carbon disulphide is impregnated in the usual way, and, after drying, the mantle is denitrated by immersion in 95 percent alcohol containing a little hydrofluoric acid. The other points are in general much like those in the case of ramie and cotton mantles."

There are some other uses for thorium salts, p. 236. "Thorium compounds find use in several devices for intense illumination. Thus, small cylinders, after the nature of the 'limes' used in lime-light lanterns, made of thoria mixed with a little ceria are used for the headlights of motor cars and also for searchlights. Thorium tungstate, chromate, and other salts are mixed with powdered magnesium in the production of flashlight powders. These powders when fired do not emit so much smoke as the simple magnesium powders, and are to be preferred on that account. The filaments of the later forms of the Nernst lamp are composed of mixtures of thoria, yttria, and zirconia, to which small quantities of ceria are sometimes added. Alloys of thorium [?] and tungsten are used in the production of filaments for electric lamps. The filaments are obtained by squirting a colloidal mixture of the two metals. Finally, thorium compounds have a considerable use in radiology."

The chapter on rare earths and the pe riodic systemis excellent and the book is extremely valuable as a whole. The reviewer does not sympathize entirely with the practice of saying more strongly and less strongly basic when one means more sparingly and less sparingly soluble. It is a pity that no reference is made to Loewenstein's work on the continuously varying vapor pressures of the oxalates of cerium, lanthanum, erbium, yttrium, and thorium.

Wilder D. Bancroft

Organic Chemistry. *By Victor von Richter. Translated and revised by Percy E. Spielmann. Vol. 1. Second (revised) edition. 23 × 17 cm; pp. xvi + 719. Philadelphia: P. Blackiston's Sons and Co., 1919. Price: $5.00.*—The first English translation as distinct from the American translations, appeared in 1915. In spite of the scarcity of chemical students in England during the war a new edition has been called for.

The general form of Richter's organic chemistry is perfectly familiar to students of organic chemistry in this country. This volume is devoted to the fatty compounds, aliphatic substances or methane derivatives, chain or acyclic derivatives, the chapters being entitled: hydrocarbons; halogen derivatives of the hydrocarbons; the monohydric alcohols and their oxidation products; dihydric alcohols or glycols and their oxidation products; trihydric alcohols and their oxidation products; tetrahydric alcohols and their oxidation products; the pentahydric alcohols and their oxidation products; hexa- and poly-hydric alcohols and their oxidation products.

There are one or two statements which physical chemists cannot approve. The molecular lowering of the freezing point is not 0.62° for all substances and solvents, p. 16. That was an inaccurate generalization by Raoult and was given up years ago. Nobody uses Rudolphi's dilution formula nowadays, p. 60. On p. 50 it would have been a good thing to refer to mixtures with constant boiling points; and, on p. 47 substances with varying melting points like acetaldoxime should be mentioned. On p. 64 students are likely to get the idea that carbides are made at 3000° whereas this temperature reference is a purely irrelevant and inaccurate one as to what can be done with an electric furnace.

Wilder D. Bancroft

THE NATURE OF PROTOPLASMIC AND NERVOUS TRANSMISSION[1]

BY RALPH S. LILLIE[2]

One of the many remarkable peculiarities of the living system—perhaps the one that impresses us as the most distinctively *vital*—is the regular and rapid transmission of metabolic and functional influence between its different parts. In all higher animals tissues and organs which are widely separated and apparently unconnected except by narrow tracks and strands of protoplasm are observed to exert a profound influence upon one another's activity; and it is a familiar fact that slight changes in the surroundings may, by acting as "stimuli," instantly alter the whole behavior of the organism. Thus we poke or stir an apparently dead animal to see if it is alive. Such facts show at once that the transmissive agency,. whatever its essential nature, is independent of the transport of material between the regions affected; in this general respect the transmission of physiological influence in living matter resembles the transmission of sound, light, wave-motion or electricity. And since all vital processes are dependent on chemical reactions, we may say that living matter exhibits in a high degree the power of chemical action at a distance.[3] This property is not confined to special organisms, tissues or cells; apparently all forms of protoplasm transmit influence in this manner, though in varying degrees and at different rates. Its fundamental biological significance is apparent, since it is the chief means of controlling and coördinating the various separate functions and activities of the organism—a necessary condition of continued life. Transmission of this kind reaches its highest development in the nerves of higher animals; the conduction of states of nervous excitation has been the most fully studied

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[1] Lecture delivered before the Research Laboratory of the General Electric Company, Schenectady, N. Y., December 11, 1919.

[2] Biological Laboratory, Clark University, Worcester, Mass.

[3] Ostwald: "Chemische Fernewirkung," Zeit. phys. Chem., 9, 540 (1891).

phenomenon of this class, and the nature of the nerve-impulse has long been one of the traditional problems of physiology.

Nervous transmission, however, is only one specialized case of the more general process—which is perhaps best called "protoplasmic transmission." This process is illustrated whenever the organism or one of its parts, or even a single cell, responds as a whole to a localized stimulus; some "physiological" influence is transmitted from the original point of stimulation to more or less distant regions of the living system, and either arouses these into activity or changes their already existing activity. Thus, to give a familiar illustration, if we touch or otherwise stimulate a Paramecium at one point, there follows instantly a temporary reversal of the ciliary stroke over the whole surface, as a result of which the animal stops and swims backward; it then turns and swims forward again in a different direction; the whole sequence of movements constituting a well-defined normal feature of its behavior, the so-called "motor reaction." This is a typical case of stimulation; evidently the direct action of the stimulating agent is to cause some local alteration in the surface-layer of protoplasm, and in some manner this initiates a disturbance which is propagated rapidly over the whole surface and alters everywhere the activity of the motile surface-structures or cilia.

It is especially significant that this effect follows a slight change in the *surface* of the cell; since there is much evidence that alteration of the protoplasmic surface-layer forms the essential condition of many if not all cases of protoplasmic transmission. Chambers has found that when a red blood-corpuscle is touched locally by a capillary needle, the whole cell undergoes rapid dissolution; the first visible effect is the diffusion of haemoglobin into the surroundings, not only at the point of contact with the needle, but over the whole surface.[1] Evidently some physical alteration of the surface-

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[1] R. Chambers: Proc. Am. Assoc. Anatomists, 1915 (abstract in Anat. Record, 10, 190 (1916); cf. also Science, 40, 625, 824; and 41, 290 for other observations.

film, associated with loss of semi-permeability, is transmitted over the cell-surface. Similarly, a leucocyte locally punctured or cut undergoes rapid disintegration. These experiments well illustrate the remarkable structural instability of many forms of protoplasm. Blood-corpuscles especially are often extremely sensitive to mechanical contact or other local change of condition; and this property is so highly developed in certain blood-cells (*e. g.*, of Crustacea), that they have received the name of "explosive corpuscles" from the suddenness and completeness of their breakdown; the platelets of mammals exhibit a similar behavior. Changes of activity produced by local physical or chemical alteration in irritable cells have also a marked tendency to spread and to involve the entire cell, so that it reacts as a whole; and there is undoubtedly a common basis for the transmission in all of these cases, although normally stimulation, unless carried to excess, has no evident destructive effects. A muscle-cell stimulated at one end undergoes contraction as a whole; it is impossible in a normal cell to localize the contractile activity, which is instantly transmitted from one end to the other. Hence such a cell exhibits the peculiar type of response called "all or none," responding either completely or not at all—a form of behavior which (we may note in passing), although highly characteristic of irritable living elements, is by no means confined to these but is found also in many inorganic systems which readily conduct chemical disturbances, *e. g.*, explosive mixtures or compounds. Another interesting instance is the transmission of a peculiar structural and chemical change over the surface of the eggs of many animals during fertilization, starting from the point of entrance of the spermatozoon. This phenomenon has recently been demonstrated with great clearness by Just in the sand-dollar egg.[1]

Finally, many of the processes of so-called "physiological correlation" in animals and plants, by which growth or physiological activity in one region influences or controls similar processes in other and often distant regions, appear

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[1] Just: Biological Bulletin, 36, 1 (1919).

to be based upon transmissions of the same essential kind. Cases of form-regulation or other structural changes due to transmitted influences are often attributed to the transport of special material substances or hormones; but this form of explanation, while it has been shown experimentally to hold true in certain cases, by no means applies to all. For example, the effect of severing a nerve-trunk near its origin is to produce highly characteristic metabolic and structural changes at the periphery; these so-called "degenerative" changes occur too rapidly to be accounted for as due to the transport of substances along the axone. Apparently the maintenance of normal structure and functional capacity in this tissue are dependent upon some influence transmitted from the nerve cells in the central nervous system; this influence is comparable with that seen in the dependence of the normal tone and nutrition of a muscle upon its innervation. The alteration in the structure of a gland-cell, following stimulation of its innervating nerve, is another instance of a similar kind. Other related cases are seen in lower animals like planarians and hydroids, where growth and formative processes in development and regeneration are normally carried out under the control or dominance of the most rapidly growing parts of the organism, usually the anterior or apical regions. Many such instances have recently been brought forward by Child, who has referred the transmission of this peculiar "trophic" influence not primarily to a transport of material between the regions concerned, but to some kind of transmitted effect or activity comparable with the nervous.[1] But evidently reference to a nervous or "neuroid" influence does not "explain" phenomena of this kind; it merely places them in the same class with the phenomenon of nervous activity which, familiar as it is, is only one special instance of a more fundamental property or mode of action which is universal in living protoplasm. There is little doubt that all of these different forms of transmission are to be regarded from the same general

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[1] Cf. C. M. Child: "Individuality in Organisms," University of Chicago Press, 1915.

point of view, as examples of protoplasmic transmission, *i. e.*, transmission of physiological influence without accompanying transport of material—what may be called "physiological distance-action."

It is interesting to note that inhibitory as well as excitatory influence may be thus transmitted; for example, growth in one region of an animal or plant frequently inhibits or prevents growth in adjacent regions; this influence is of great importance in the correlation of development or other morphogenetic processes, and undoubtedly plays a great part in the control and regulation of normal ontogeny and regeneration. Similarly, functional activity in one region of an organ may inhibit or prevent activity in another region of the same or a different organ; this is notably the case in the central nervous system, where the neurones innervating antagonistic muscle groups have a reciprocally inhibitory influence on one another's activity. The same kind of reciprocal influence is seen in other tissues, *e. g.*, in peristaltic movement ("myenteric law"), and apparently is usual in conducting elements like nerve-fibers.

Now it seems unlikely that a phenomenon so universal in organisms—one on which so many of their most characteristic activities depend, especially in animals—should be entirely confined to living matter; it is rather to be assumed that processes of the same essential nature are present also in non-living matter. Such a conclusion is implied by evolutionary theory, and if it is granted the question becomes: what is the general type of physico-chemical process to which protoplasmic transmission belongs, as a particular and highly specialized instance? The essential or general basis for conduction-processes of the protoplasmic type must exist in some form in inorganic processes, and our problem is to determine what type of inorganic system presents phenomena of the same fundamental kind, and under what conditions they are manifested.

In considering the physico-chemical nature of the physiological conduction-process it seems desirable to dissociate it as completely as possible from associated and dependent processes of other kinds; and accordingly the special conducting tissue, nerve, in which this dissociation has apparently been accomplished by nature, is the one upon which most of the exact studies of protoplasmic transmission have been made. I shall therefore discuss more especially the conditions in this tissue. These conducting protoplasmic strands, which everywhere pervade the organism in higher animals, transmit excitatory, inhibitory and controlling influences with extraordinary quickness, regularity and dependability. They arise in development as outgrowths from nerve-cells, and in accordance with this mode of origin they must be regarded as possessing the general properties of irritable living protoplasm in addition to—or in correlation with—their own specialized peculiarities as conducting elements. Hence we may consider the conditions under which a nerve is stimulated and conducts stimuli as representing the fundamental conditions of protoplasmic excitation and transmission in general; and these conditions, as well as the constant features of the changes undergone by the nerve itself during transmission, have been determined in great detail by the labors of a long series of investigators. The essential generalizations established by this work may be stated thus briefly: (1) The excitation-state may be aroused or initiated by a variety of means, including mechanical, chemical, thermal, and especially electrical; a high degree of electrical sensitivity is universal in conducting tissues. (2) Once aroused the excitation-state is transmitted automatically from one region of the tissue to the next adjoining; in this manner the active state is propagated continuously along the tissue to any distance without evidence of decrease in intensity. This implies that some process associated with the local activity has the effect of initiating similar activity in adjacent regions. (3) The local process ceases when stimulation ceases, *i. e.*, it is automatically self-limiting, the tissue returning quickly to the resting state; after a brief interval of lowered excitability (refractory period) it may be again stimulated as before.

(4) The rate of transmission exhibits a wide range of variation in different tissues and organisms—from a few centimeters per second to 100 meters or more per second. Under normal conditions and at a definite temperature the rate is constant and specific for each tissue and each organism. (5) This velocity is in any single case dependent on temperature, showing a temperature-coefficient like that of most chemical reactions at ordinary temperatures (Q_{10} = 2 to 3); *e. g.*, in the frog's sciatic nerve the rate at 10° is *ca.* 15 meters per second, at 20° *ca.* 30, and at 30° *ca.* 60 meters per second. This fact implies a dependence of the whole transmission-process on some kind of chemical or metabolic change in the tissue. (6) Transmission may also be influenced reversibly by chemical substances; in particular it is readily decreased in rate or prevented by lipoid-solvent or lipoid-soluble substances and certain salts (especially K, Mg, Ca, Sr, etc.); also by electrically polarizing the conducting elements by an externally applied current (electrotonus). (7) It is unaccompanied by change of form, by evident change of temperature, or by optical change; but is invariably associated with a change of electrical potential in the conducting tissue, the active area becoming temporarily negative (to the galvanometer) by a P. D. of *ca.* 30 to 50 millivolts relatively to the inactive areas. This variation of potential travels at the same rate as the activation-wave, and undoubtedly forms an integral part of the latter.

The question now arises as to the general physico-chemical nature of a transmitted activity having these characteristics. Can we characterize it more definitely than as a "molecular change"—a once favorite expression in the text-books? First of all it is important to note that the excitation-wave on reaching the terminal organ, *e. g.*, muscle, affects the latter in a manner which can be closely simulated artificially only by stimulation with the electric current, especially the interrupted current. This fact in itself suggests that what is really transmitted to the muscle is some form of electrical influence and that the stimulating effect is essentially an electrical effect. There are various reasons for attaching chief importance to the electrical factor in the transmission-process. Sensitivity to electric currents is a universal property of living protoplasm. We find also that in its normal activity living matter gives rise to electric currents in the surroundings. Both of these fundamental discoveries date from the time of Volta and Galvani. It is therefore not surprising to find the suggestion made at different times in the history of physiology that the active region in a conducting nerve may stimulate the adjacent resting region *electrically* by means of the bioelectric current formed at the boundary between the two regions, and that transmission is due to this local electrical stimulation. The active region is negative relatively to the adjacent resting region, so that a circuit is formed between the two. Just as the action-current of one muscle may stimulate another muscle to contract, so the local action-current produced when one region of a nerve enters activity may be sufficiently intense to excite the adjacent resting regions. It is readily conceivable that in this way the excitation-state might be transmitted from active to resting regions. We know that the nerve is sensitive to weak electric currents, and also that such currents arise whenever the tissue becomes active. This general hypothesis thus seems a consistent one, and recently it has again been brought forward and attempts to test it experimentally have been made by several physiologists, including especially the late Keith Lucas, perhaps the most ingenious and exact of recent experimenters in this field. In his Croonian Lecture of 1912[1] Lucas points out that since the electric disturbance is an invariable concomitant of the excitation-wave, it is possible that the two are in reality identical, and that the disturbance of electric potential at one point in a nerve may be the actual and direct cause of the same phenomenon in a neighboring part; and he has brought forward various facts favoring this hypothesis. The majority of physiologists, however, have apparently continued to regard the electric variation as a mere by-product of the

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[1] Keith Lucas: "Croonian Lecture," Proc. Roy. Soc., 85B, 507 (1912).

excitation-process and not as playing in itself any essential rôle in transmission.

Let us now briefly review the chief general facts indicating that the local bioelectric current accompanying local stimulation is the essential factor in the spread of stimulation to adjoining regions of the irritable tissue. On examining the electric current accompanying activity in a conducting tissue like nerve we find that its direction of flow and other chief characteristics—intensity, duration, rate of development—are such that the above hypothesis receives decided support. A current flows between the active region of the tissue (AA) and the adjoining regions (BB) which at the time under consideration are still in a state of rest (see Fig. 1).

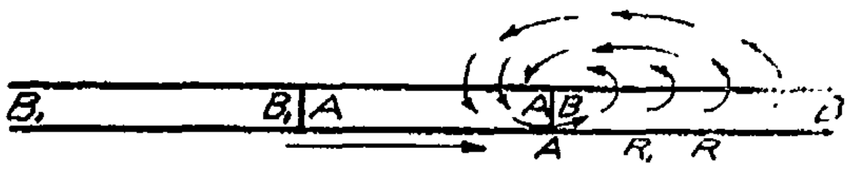

Fig. 1

In this diagram the area AA represents the region of the nerve-axone which is active, or occupied by the excitation-wave, at the instant under consideration; its length in a frog's motor nerve at 20° is about 6 cm. The wave is regarded as moving in the direction of the large arrow. The region now undergoing secondary electrical stimulation by the local action-current between regions A and B extends to the distance AR(*ca.* 3 cm) beyond the wave-front. The direction of the current (positive stream) in part of the local circuit is indicated by the small arrows. The region (B_1B_1) immediately behind the excitation-wave is temporarily in a refractory state.

This current is the so-called action-current; the local bioelectric circuit between regions A and B may be called the "active-resting circuit." Observation shows that the current (positive stream) of this circuit invariably *leaves* the tissue at the inactive or resting regions and *enters* it at the active region; this is what is meant by the usual statement that the active region is *negative*, or that a "negative variation" accompanies activity. Now when we study the conditions under which an external electric current led into the tissue from a battery causes stimulation, we find that stimulation always originates at the region where the positive stream of the stimulating current leaves the tissue, *i. e.*, at the negative electrode; while at the positive electrode, where the current enters the tissue, there is the reverse effect of inhibition or decrease of irritability. This characteristic "polar" condition is found in the great majority of irritable tissues, and is known as the "law of polar stimulation;" in general, anode and cathode have opposite physiological effects upon irritable and other living systems. It is clear, therefore, that wherever in the resting region (B) the current of the bioelectric circuit has sufficient local intensity, it will have a stimulating effect, *i. e.*, will initiate a new state of activity, while at the active region itself (A) its influence will be inhibitory or will tend to cut short activity. Now the very fact which we are trying to explain is that whenever any local region (A) of a conducting tissue like nerve is made to enter excitation—by whatever means, normal or artificial—a similar state of excitation, after a brief interval, appears in the resting area (B) adjoining A and disappears from A itself; *i. e.*, a wave of excitation appears to be transmitted from A to B; B upon thus becoming active repeats this effect upon regions beyond; and in this manner a wave of activity travels along the tissue. All of the characteristics of the activity thus transmitted are those which we should expect to find if the bioelectric current were in fact the condition of transmission. It is a well-established fact that the action current of a tissue like muscle or nerve is amply capable of stimulating another portion of the same tissue. The stimulation of one muscle by the action-current of another is a simple and frequently performed experiment; if the two muscles are in close contact and one is stimulated through its nerve the other contracts, and a similar experiment can be performed, though less readily, with nerve. Thus both the observed intensity and the direction of the action-current are consistent with the hypothesis that the local bioelectric current, when it is brought into existence by stimulating one region of the conducting tissue, itself stimulates the adjoining regions. By a repetition of this effect at each active-resting boundary as soon as it is formed the state of excitation may be transmitted along the tissue for a distance which may be indefinitely great if the tissue is normal in its condition and uniform in its properties throughout its length.

The question now arises whether this hypothesis explains the other characteristic features of the excitation-wave, and especially the high velocity which it attains in the motor nerves of warm-blooded animals. Evidently if we are to have rapid transmission by the above means the local bioelectric current must rise quickly to an effective strength and its stimulating influence must extend for a sufficient distance beyond the region immediately active. The fact is, however, that in rapidly conducting tissues like nerve the rise of the bioelectric current to its maximum at any point is very rapid, occupying about 0.001 second in the frog's motor nerve at 20°. Moreover the tissue is extremely sensitive to weak electric currents; two platinum electrodes differing in potential by 20 millivolts and placed three centimeters apart or even more will stimulate; this P. D. is less than that normally existing between the active and the resting areas of the nerve. The intensity of the normal action-current where it traverses the nerve at a point 3 centimeters distant from the active-resting boundary must be about the same as at a stimulating electrode in the above experiment, since the P. D. and the resistance of the two circuits are similar. Now it is evident that the current of the active-resting circuit is most intense near the boundary between the active and the inactive regions, for the simple reason that the local intensity of the current is determined (in accordance with Ohm's law) by the P. D. and the total resistance of the circuit, and this resistance is directly proportional to the distance between the two areas of unequal potential. Hence near the active-resting boundary the current will be relatively intense, and beyond a certain critical distance from this boundary (AR in diagram) it will be too weak to stimulate. But if the stimulating influence extends for only 3 centimeters beyond the boundary, the speed of development of the bioelectric current is great enough (and the latent period of stimulation brief enough) to account for the actually observed rate of transmission in nerve. In the frog's sciatic nerve the time occupied by the rising phase of the bioelectric variation (*i. e.*, from zero to its full intensity of 30 to 40 millivolts) is about 0.001 second at 20°, the whole variation lasting about 0.002 second; if the current on reaching its full intensity stimulates the adjoining resting region at all points up to a distance of 3 centimeters from the active-resting boundary, stimulation will be initiated at a point 3 centimeters in advance of the active area at a time 0.001 second later than at the active area itself. The local response thus secondarily evoked is of full intensity—*i. e.*, is the same qualitatively and quantitatively as at the original active area, since the tissue reacts on the "all-or-none" principle—hence there is no change in the intensity or other characters of the excitation-wave as it progresses by a repetition of this process at each new active-resting boundary. But a transmission of 3 centimeters in 0.001 second is 30 meters in one second. This is the observed velocity of transmission at this temperature. Observations on the influence of temperature on both processes confirm this interpretation. Raising the temperature 10° doubles the rate of the bioelectric variation; at the same time it doubles the rate of propagation of the nerve-impulse. Lucas has found a constant proportionality between the rate of the local change of potential in muscle and the speed of the contraction-wave at different temperatures.[1] With a temperature-coefficient (Q_{10}) of 2, a velocity of 30 meters per second at 20° would be equivalent to one of 120 meters per second at 40°.

In general we find a close correlation between the local rate of development of the action-current in different conducting tissues and the speed of propagation of the excitation-wave.[2] Further it is remarkable that tissues with rapidly

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[1] K. Lucas: Jour. Physiol., 39, 207 (1909).

[2] In Am. Jour. Physiol., 34, 484 (1914) I have given a table showing the relation between speed of transmission and local rate of development of the bioelectric variation in a large number of different tissues and organisms.

developing action currents and rapid conduction are readily stimulated by *rapidly developing* electric currents which are led into the tissue from outside, but not by slowly developing currents. Such tissues also require only a brief duration in the stimulating current of threshold intensity; the latent period of stimulation is also brief. Quickness of response is characteristic of rapidly conducting tissues, and *vice versa*. Each irritable tissue has its own characteristic "time-factor" of electrical stimulation, called "chronaxie" by Lapicque; this is best measured by the minimal duration of the stimulating current of threshold intensity, which is brief in rapidly responding and rapidly conducting tissues; and correspondingly such tissues are found to be responsive to rapidly changing but not to slowly changing currents. This correspondence between the time relations of the stimulating current and of the tissue's own action-current is highly characteristic; a rapidly conducting tissue always has a brief and rapidly developing action-current, and responds to (or is stimulated by) rapidly developing currents of brief duration. It is as if the tissue were "timed" or adapted to respond to electric currents having the special peculiarities of its own action-currents.[1] The hypothesis that transmission is due to the stimulating effects of the local action-current appears thus consistent with all of the observed characteristics both of the normal response of the tissue to electric stimulation and of its own normal electrical behavior.

Further support of this hypothesis has recently come from a quite different direction. It will be seen on reference to the diagram that any definite velocity of transmission implies that the local bioelectric current has an intensity sufficient to stimulate the resting tissue for only a certain limited distance (AR) in advance of the region already active. Beyond this limit the current will necessarily be too weak for excitation. Everywhere up to the critical point R there will be full and complete stimulation in a normal nerve, since

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[1] Cf. Lapicque: Jour. de Physiol. et de Pathol. gén., 10, 601 (1908), for an account of the time-factor in electrical excitation.

under normal conditions this tissue exhibits the "all-or-none" type of response, and if it responds at all responds with full intensity. But if by any means we lower the intensity of the current traversing the nerve at the point R, *e. g.*, by decreasing the electrical conductivity of the local circuit, then activity in the area A will no longer cause stimulation at R, but the limit of the secondarily stimulated area will be shifted nearer to the active-resting boundary line (*e. g.*, to R_1). In other words, the immediate stimulating effect of any active area will then be exerted through a shorter distance; this implies that the propagation-velocity will be lowered. According to our hypothesis, this velocity should be proportional to the electrical conductivity of the circuit. Recently Mayor has shown in experiments on the nerve-ring of the marine medusa Cassiopea that the velocity of nervous transmission when the tissue is immersed in sea-water of different dilutions runs closely parallel with the electrical conductivity of the medium.[1] This is precisely what we should expect to find on the theory of transmission through stimulation by the local bioelectric current. The existence of such a relation is difficult to explain unless electric currents passing through the medium are an essential factor in the transmission of excitation. The further fact, which has been demonstrated in a number of instances, that stretching the nerve leaves its rate of conduction essentially unaltered,[2] confirms this interpretation, since it implies that stimulation is always being initiated at a certain linear distance in advance of the already active area. In any solution electrical resistance is proportional to linear distance.

If transmission is thus essentially a case of secondary electrical stimulation, the problem of transmission resolves itself into the more fundamental problem of how the electric current produces its stimulating effects in protoplasm. The

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[1] A. G. Mayor: Am. Jour. Physiol., 42, 469 (1917) and 44, 591 (1917).

[2] Cf. Carlson: "Evidence of the Fluidity of the Conducting Substance in Nerve," Am. Jour. Physiol., 13, 351 (1905), and 27, 323 (1911); also McClendon: Proc. Nat. Acad. Sci., 3, 703 (1917).

primary effect of the current must be a chemical one, since vital processes are chemical processes; and, if so, protoplasmic transmission must be referred to the chemical effects produced in the irritable element by the local bioelectric current, especially at its points of exit and entrance, since it is here that the stimulating effects originate. Now there is much evidence that the bioelectric current itself is primarily the index or expression of some change in the physical and chemical state of the *surface-layer* of protoplasm. As we have seen, a change in the physical properties and permeability of the protoplasmic surface-film appears to be a general accompaniment of stimulation; and there is clear evidence that the electromotor variation also accompanying stimulation is a direct consequence of this surface-change. Any change in the chemical composition or physical properties of the cell-surface will necessarily alter the potential-difference of the double electrical layer between protoplasm and medium; and we find in fact that any injurious modification of the surface-layer of the living protoplasm (like poisoning or mechanical injury) alters its electrical potential in the same manner and to the same degree as the normal process of stimulation; *i. e.*, it produces a characteristic local change of potential, the altered region becoming negative relatively to the unaltered regions by a P. D. of 40 or 50 millivolts. The local current arising between stimulated and resting areas appears to be the index or result of a similar local change of potential, due to a temporary alteration of the surface-film at the active area; and this current, by means of the chemical changes which it produces in the adjoining portions of the film, produces there an alteration of a similar kind, and so the effect spreads. Since there is evidence of a temporary loss of semi-permeability in many irritable tissues during stimulation,[1] it seems probable that this alteration consists in a more or less complete temporary disruption or disintegration of the surface-film. The precise nature of the critical or initiatory chemical change

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[1] I have summarized this evidence in several places: cf. Am. Jour. Physiol., **28**, 197 (1911) and **37**, 356 (1915)

induced where the current passes from cell-surface to medium (the region where stimulation originates) is not definitely known at present; but the general evidence already available indicates clearly that stimulation is primarily the result of the chemical and structural changes which the current there induces in the surface-film. Nernst has shown that electrical stimulation depends upon the polarization-effects produced by the current at the semi-permeable surfaces of the irritable tissue;[1] and the chemical effects immediately following this change of polarization appear to form the first step in the stimulation-process proper. The next succeeding step in the process is apparently an extensive alteration or dissolution of the film, followed by its reconstitution as the tissue returns to the resting state.

We return now to the question whether transmission-effects of this general type—through the chemical effects produced by the currents of local electrical circuits—exist also in inorganic systems, and, if so, in what respects such systems resemble living systems.

In point of fact, self-propagating chemical effects due to local circuits are a frequent phenomenon in certain types of inorganic system which, though apparently widely different from protoplasm, are in certain fundamental respects closely related, namely, metals in contact with electrolyte solutions. The most familiar instance is the rusting of iron in water or a salt solution. According to the "local action" theory of corrosion, original with Faraday and de la Rive and now generally accepted, the chemical effect is due to local electric currents formed between adjoining areas of the metallic surface which differ in composition or physical state. Processes of electrolysis at the electrode-areas of these local circuits are the direct cause of the chemical change. The surface of ordinary iron is typically non-homogeneous, with areas of greater and less solution-tension; the regions of higher solution-tension form local anodes where the iron cations enter solution; there they react with carbonate and hydroxyl ions

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[1] Cf. Nernst: Arch. ges. Physiol., 122, 275 (1908).

to form a rust deposit. This local deposit spreads or grows because when once formed it acts as a local cathode and promotes the solution of iron from the unrusted areas in its vicinity. This effect is greatest at the boundary of the rusted area because there the intensity of the local current is greatest. There is in fact a kind of autocatalytic action, the rate of rust-formation increasing as the periphery of the rust spot extends.

The spread of chemical influence over the surface of the metal is in this case a gradual one, and can scarcely be regarded as an adequate model for the rapid chemical transmissions found in living protoplasm. We can, however, easily conceive of possible conditions under which the spread might be rapid. If we could find a metallic surface covered with a thin film of unstable material which is readily and rapidly altered or removed by local electrolysis, we should expect it to show chemical transmission-phenomena which would be rapid in rate and would extend wherever the film extended. Take, for example, a metal (*e. g.*, iron) covered by a thin continuous film of readily reduced oxide; wherever such a film were locally interrupted we should have side by side a free metallic area and an oxide-covered area; in any electrolyte solution these areas would form a local electrical couple with the metallic area anode and the film-covered area cathode. But since the chemical influence at the cathode is of a reducing nature, the film would be at once removed by reduction wherever the intensity of the local circuit was sufficient. The free metallic area would thus be automatically and rapidly extended, since the same conditions would be repeated at every boundary-region between film-covered and metallic areas. Now this is precisely the situation found in passive iron immersed in an electrolyte solution and also in many other cases which I shall not now consider, of which mercury in hydrogen peroxide is perhaps the most interesting; and it can hardly be an accident that this system shows phenomena of activation and transmission which in a surprising number of particulars resemble closely the conditions found in irritable protoplasmic systems like nerve. In both cases we are dealing with film-covered systems which are susceptible to the polar influence of the electric current, as well as to mechanical and other influences. And since the changes occurring during the transmission of activation in passive iron are relatively simple and well understood, we may expect that their study will throw light upon the general physico-chemical nature of the changes underlying transmission in living protoplasm.[1]

It has long been known that iron exposed temporarily to strong nitric acid or other favorable oxidizing agent assumes the so-called passive state, in which it is remarkably resistant to chemical change; *e. g.*, such iron will no longer react with dilute nitric acid, in which ordinary iron dissolves rapidly. But if a piece of passive iron, *e. g.*, a wire, immersed in dilute nitric acid be touched with a piece of ordinary or active iron or a base metal like zinc, or if it be bent or scratched with a piece of glass, or made the cathode in an electric current of moderate intensity, it is at once rendered active and reacts vigorously with the acid until dissolved. The whole metal is not activated simultaneously, but the active state is observed to spread rapidly from the original point of activation over the whole metal; this process of spreading can best be observed in a wire dipped in acid and held suspended in the air and then touched below with a piece of active iron or zinc; the passage of the active state along the metal can be readily followed by the eye, each successive region as it becomes active turning dark (from formation of lower oxide) and effervescing in the adhering acid. Under these conditions the rate of transmission is only a few centimeters per second; but if the wire is activated while it is completely immersed in the acid, the transmission over its whole length is so rapid as to appear almost instantaneous, the rate being often some hundred centimeters per second. This difference of velocity depends on the difference in the electrical resistance of the

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[1] For a more detailed account of this and other parallels with living irritable elements, cf. Science, **48**, 51 (1918); **50**, 259, 416 (1919).

circuit between the passive and active areas under the two conditions, this resistance being high when the metal is in air, with only a thin layer of electrolyte adhering; the intensity of the local current then falls off rapidly with increase of distance from the active-passive boundary line, and is sufficient to reduce the film only in its immediate neighborhood. But when the wire is immersed in a large volume of electrolyte the conductivity is high and the transmission correspondingly rapid. There is thus a relation between the electrical conductivity of the circuit and the speed of transmission, just as in protoplasmic transmission.

I shall now describe briefly the more important resemblances between the conditions of activation and transmission in the two systems under comparison; the case of protoplasmic transmission will then appear in a clearer light and its specific peculiarities can be considered to better advantage.

In the first place, both systems may be activated either mechanically, chemically or electrically, and both give the same kind of transmitted effect whatever the method employed for activation. A passive wire is activated by jarring, bending or scraping, by contact with reducing substances, or by being made the cathode in an electrical circuit; similarly an irritable tissue is activated or stimulated by mechanical treatment, by various chemical substances, and by an electric current at one of its poles (the cathode). The electric current is most effective in activating either protoplasm or passive iron when it rises suddenly or rapidly to its full strength; when its intensity is increased gradually, *i. e.*, from zero or subliminal to a strength more than sufficient for activation with a sudden closure, no effect follows, the system apparently undergoing under these conditions some compensatory change which keeps it inactive. In both cases a single "stimulus" may be ineffective, while a succession of stimuli will call forth activation; this phenomenon of "summation" is especially characteristic of living irritable systems. Again, the character and intensity of the response in any instance are typically constant and independent of the nature of the activating agent; *i. e.*, activation is either complete or absent, a type of behavior called "all-or-none" in physiology, where it is well known to be highly characteristic of irritable and rapidly conducting elements like muscle-cells or nerve-fibers. In both the inorganic and the living systems the activation-wave travels at a velocity which varies under different conditions and has a high temperature-coefficient; in the motor nerves of the more active animals it is usually several hundred centimeters per second, reaching in warm-blooded animals velocities of more than a hundred meters per second; in passive iron velocities of some hundred centimeters per second are usual, although exact measurements under different conditions still remain to be made. The passage of the activation-wave may be blocked in both systems by locally altering the electrical polarization of the surface (a phenomenon known in living tissues as electrotonus), or by certain other means like mechanical constriction or aneasthetization in nerve, or by the contact of a noble metal in passive iron; in these cases also the local change in electrical conditions is probably the essential factor in the effect. A fundamental resemblance is that in both systems the passage of the activation-wave is associated with a local variation of electrical potential, which is readily demonstrated as the active-inactive circuit accompanying the wave passes the electrodes of a galvanometer connected with the conducting tissue or wire. The so-called "positive after-variation" in nerve, in which the active region of the tissue becomes temporarily more positive than normally on returning to the resting state, is also simulated by the passive wire, which is more positive (cathodal) immediately after spontaneous repassivation than later. And finally, what is perhaps the most striking resemblance of all, both tissue and metal on returning to the resting or passive state after temporary activation always exhibit a certain period of delay (called the "refractory period" in irritable tissues) before they recover their former condition of sensitivity and conductivity.

This last phenomenon should be described more fully, since it is perhaps the clearest indication of all that the fundamental conditions of activation and transmission are the same in the protoplasmic system and its metallic model. In every irritable tissue excitation is immediately followed by a brief period of inexcitability, the so-called refractory period; the duration of this is brief in rapidly responding tissues like nerve and voluntary muscle (where it lasts only a few thousandths of a second), and relatively prolonged in "slow" tissues like heart-muscle (about one-third of a second), or involuntary muscle and certain special sensory elements (*e. g.*, photoreceptors in mollusca), where it may last for several seconds or even minutes. Each nerve-impulse as it passes along a nerve is thus followed by a trail or wake of temporary inexcitability. The refractory period evidently represents an interval during which certain processes of restoration or recovery (probably associated with chemical and structural resynthesis) are at work; it has a number of features in common with fatigue and may be regarded as a temporary or evanescent instance of this phenomenon.[1]

Normally a nerve or muscle returns automatically to the resting state after stimulation, and after the refractory interval can be again stimulated as before. Now in a passive wire immersed in strong HNO_3 there is a similar automatic return of passivity, so that the activation-reaction which sweeps over the surface when the wire is touched with zinc is only local and temporary, like the excitation-wave in nerve or muscle. The remarkable fact from the physiological point of view is that the metal immediately after the return of passivity is entirely refractory to reactivation as a whole, and recovers its full power of transmission only by degrees, and the more slowly the stronger the acid. In acid of 60 volumes percent (of HNO_3 sp. gr. 1.42) complete recovery usually requires one or two minutes (varying somewhat with temperature and other conditions); at first the activation-wave is transmitted slowly and for only a short distance, like

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[1] An account of the refractory period in nerve is contained in the recent book by Keith Lucas: "Conduction of the Nervous Impulse," London, 1917.

the transmission-wave in a fatigued or anaesthetized nerve which conducts with a "decrement;" by degrees the distance through which it travels (as well as its speed) becomes greater and greater, until eventually rapid transmission through an indefinite distance becomes again possible.

Now passivity in iron is almost certainly due to the presence of a thin film of oxide or oxygen compound which adheres closely to the surface of the metal; this film gives the passive iron the properties of a cathodal or noble metal, with a potential about 0.7 volt higher (in dilute HNO_3) than the normal or active iron. The spontaneous return of passivity in strong acid indicates therefore the deposition of a fresh film of oxide, and this must occur first at the local anodal regions of the metal, since, as is well known, making an active metal anodal has a strong passivating influence. Each region traversed by the activation-wave becomes temporarily anodal as it becomes active, and is therefore subject to the oxidizing influence resident at every anode; this influence, added to that of the HNO_3, at once reinduces passivity. We thus understand why the local activation is temporary and is at once transmitted to the adjoining passive areas of the metal, which, as already pointed out, are cathodal; being cathodal they are immediately activated by reduction and then at once become anodal, upon which they are automatically repassivated in the manner just indicated. The refractory or non-transmissive condition just described indicates that the newly formed passivating film is in a different physical or chemical condition from an older film; it is less readily removed by cathodic reduction; hence transmission is imperfect or absent. Possibly the film is too thick when first formed—the reflecting power of the surface is then less than later—or its physical condition is otherwise unfavorable to rapid change. The essential condition for transmission is that the film should be readily and rapidly removed by cathodic reduction; and from general considerations it seems probable that the condition which it reaches eventually, when sensitivity is completely restored, is one in which its molecules are closely packed, similarly oriented, and in a layer of about one molecule in thickness. The film is in fact similar to an adsorption-film, which, as the work of Langmuir and others has shown, is in many cases of this order of thickness.[1] On this view, the period of recovery represents a period during which all of the surface oxide molecules, except those directly attached to the metallic iron, are dissolved away by the outer acid, and the remaining molecules are uniformly distributed over the surface in a layer one molecule thick. The film is then in a condition favorable for rapid transmission.

Now in the irritable protoplasmic system (*e. g.*, nerve axone) it seems probable that closely analogous conditions exist. During activation the surface-film (which apparently consists largely of some unstable readily reducible material) is rapidly altered, possibly in large part disintegrated or removed; during the succeeding refractory period it is restored and recovers its original constitution and physical properties.[2] I am inclined to believe—and in this I acknowledge my obligations to Langmuir's work—that the material which is thus altered and replaced during protoplasmic excitation is spread out in a very thin layer, possibly not more than one molecule thick, separating the protoplasm from the surrounding medium. This film consists of some chemically reactive water-insoluble material, probably chiefly lipoid. Just what chemical changes it undergoes during excitation is difficult to say at present. In its reconstitution or redisposition during the recovery phase oxidation-processes appear to be especially important, since all processes of recovery and reconstruction in protoplasm are favored by the presence of oxygen.

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[1] I. Langmuir: Jour. Am. Chem. Soc., 39, 1848 (1917).

[2] These processes occur under the influence of the local bioelectric circuit between the active and the adjoining inactive areas of the nerve. Immediately before becoming active any given area (which is at this time a resting, *i. e.*, positive, area) is traversed by a bioelectric current passing in the direction *from protoplasm to medium* (positive stream); when the area becomes active (and hence negative) this direction is immediately reversed. To this reversal in its direction (shown in the "diphasic" character of the galvanometer curve) corresponds a reversal in the chemical effect of the current at the area in question.

We have assumed throughout our comparison that the electric current can effect chemical changes, especially oxidations and reductions, at the cell-surface in essentially the same manner as at the surface of a metallic electrode, and in fact we have ascribed to the protoplasmic surface-film all of the essential properties of an electrode. Can such a point of view be justified? Usually it is assumed that electrolysis is a phenomenon confined to the region of contact between a metallic electrode and the electrolyte solution adjoining, and that a combination of metallic and electrolytic conductors is necessary both for electrolysis and for the production of electric currents by chemical action.

There must, however, be something insufficient about this manner of regarding the phenomena in question. The conditions in living matter prove that metallic conductors are not essential either to the production of chemical change by the current, or to the production of a current by chemical change, since it is a fact that the electric current alters profoundly the chemical processes in the living system, and also that the living system during its activity produces electric currents which traverse the surroundings. We have seen that different areas of the protoplasmic surface, *e. g.*, of a nerve-fiber, give rise to local circuits whenever they differ in their activity or in their physiological state, just as do two differently constituted areas of a metallic surface; and we have also seen that these currents are intense enough to stimulate other irritable systems of the same kind.

Now it is well known that the electric current produces no chemical change in the interior of an electrolyte solution during its flow; the chemical changes which occur are confined to the region where electricity passes between electrode and solution, *i. e.*, to the surface-layer of the electrode and the adjacent layer of solution. When, however, a current is passed through living matter the case is entirely different; chemical effects are produced not only at the electrodes but throughout the entire mass of protoplasm. In its general physico-chemical constitution protoplasm is essentially a colloidal or emulsion system containing electrolytes and freely partitioned by semi-permeable membranes and other thin films; and we must conclude that the chemical effects produced by the current depend upon this partitioned or film-pervaded structure of the system, since they are absent in homogeneous solutions. We know further that the passage of a current changes the electrical polarization between the opposite faces of any partition which interferes with ionic movement; and the case of electrolysis at metallic electrodes shows that when the P. D. across a boundary-surface reaches a critical value there is a transfer of electricity associated with chemical change. Apparently what is essential to produce this latter effect is that there should be a sufficient fall of potential across a short distance. The thin surface-films in living protoplasm, not only at the general cell-surface but also within the interior of the protoplasmic system, may be assumed to act in a similar manner. Any change in the P. D. across such a partition must effect displacements of electrons in the chemical substances forming the film or in immediate contact with it, and these displacements will, if sufficient, lead to chemical reactions which secondarily alter the character of the film. Chemical and structural changes in these films may thus occur comparable with those induced in the surface-films of passive iron when the metal is made cathode; and if such changes are accompanied by increased permeability or breakdown (like the changes in the passivating films) they may lead to self-propagating waves of chemical and structural alteration similar to those occurring in the metallic system. It thus seems probable, judging from the far-reaching nature of the chemical changes produced in a highly irritable cell, *e. g.*, a muscle-cell, by a slight local stimulus, that in such a case an extensive system of colloidal films or partitions pervading the entire protoplasm is broken down or altered by the rapid propagation of a wave of decomposition originating at the cell-surface. It is as if a heap of passive iron filings immersed in nitric acid were activated; at every film-covered surface a chemical decomposition occurs resulting in the temporary destruction of the film; the film is then reconstituted and the system resumes its previous condition.

Presumably in muscle the accompanying changes of surface-tension in the colloidal structural elements composing the fibrils form the direct mechanical condition of the contraction. We may thus understand why conditions that stabilize the protoplasmic surface-films, like cold, anaesthetics, and certain salts, prevent the propagation of these waves of alteration and hence render the living system irresponsive to stimulation.[1]

There can be little doubt that the electrically controlled chemical reactions in protoplasm are surface-reactions; and, as in other instances of such control, what is needed to initiate these reactions is the conveyance of electricity (positive or negative, according to conditions) into the surface-layer of reactive material from the adjacent electrolyte solution or the other phase contiguous to the reacting layer. In the ordinary case of electrolysis at a platinum electrode this electricity is furnished to the reacting molecules in the surface-layer from the metal, which is connected with some external source of potential. In the case of a chemically alterable colloidal surface-film in a protoplasmic system the electricity is presumably derived from the molecules of chemical substances, *e. g.*, oxygen combined as peroxide, which are in contact with the film. In principle the two cases are not different, as we can readily see if we imagine (for example) the length of metal connecting the oxidizing and reducing surfaces (or electrode-areas) in an oxidation-reduction cell to be progressively reduced until it becomes zero; in such a case the substances whose reaction gives the current would be in direct contact; the reaction and the accompanying electrical transfer would occur as before, although there would be no external evidence of the latter. Similarly two chemical reactions with oppositely directed electron-transfers may occur at different areas of a thin surface-film separating adjacent solutions, in such a manner as to create an electrical circuit between the two areas, provided the potential is sufficient and the electrical resistance not too high. In a system

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[1] In a recent article on the theory of anaesthesia, Biological Bulletin, 30, 311 (1916); I have reviewed the evidence indicating that anaesthetics act in this manner (cf. pp. 352 *seq.*).

of the structure of protoplasm, pervaded by thin films of reactive material, the electrical transmission of chemical influence to a distance is thus theoretically possible, just as it is in a system consisting of a solution containing reactive substances at different regions which are connected through a metallic conductor so as to form a circuit.

There is no difficulty about the conduction of electricity through the general mass of protoplasm or through the surrounding medium; both contain salts and are good conductors of the second class. The critical question is: can conduction take place across the protoplasmic surface-films in association with processes of electrolysis, *i. e.*, chemical change depending on electrical transfer between the interacting molecules under the influence of an externally imposed E. M. F? The foregoing considerations show that if this is possible in the layer of molecules in contact with the surface of a metallic electrode, there is no theoretical reason for denying its possibility at a sufficiently thin layer of chemically reactive material interposed between two electrolyte solutions.

Physiological distance-action thus becomes a special case of chemical distance-action in a system where the reaction-surfaces, instead of being metallic surfaces, consist of thin films of chemically alterable organic material. We must assume this material to be water-insoluble, if we are to account for the characteristic immiscibility of living protoplasm with water and the general stability of protoplasmic structures in their predominantly aqueous media; and since all forms of protoplasm are rich in water-insoluble constituents, the lipoids, we are led to ascribe a physiological rôle of fundamental importance to these substances. They apparently furnish the essential material for the alterable surface-films whose properties we have been considering. The properties of proteins seem less adapted than those of lipoids to fulfil this rôle. The investigation of the properties and the conditions of formation and disintegration of surface-films in general and of lipoid films in particular becomes thus a matter of fundamental physiological interest.[1]

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[1] For a discussion of the parallels between the behavior of protoplasmic surface-films and the surface-film of passive iron, cf. Science, 50, 259, 416 (1919).

THE CONCENTRATION OF RADIUM AND MESOTHORIUM BY FRACTIONAL CRYSTALLIZATION*

BY JOHN L. NIERMAN

Introduction

Markwald[10] and Soddy[11] have shown independently that mesothorium is absolutely identical in chemical nature with radium and cannot be separated therefrom.** In consequence all radium separated from uranium minerals containing thorium, contains also the mesothorium in the mineral, and all preparations of mesothorium contain the radium that is present in the mineral from which the thorium is derived.

In the extraction and recovery of the minute quantities of mesothorium and radium present in radioactive minerals, these elements become associated with barium and follow the barium throughout the process. The refining of mesothorium and radium then consists in separating these elements from barium, the method generally followed being fractional crystallization of the barium solution, first as chloride, and later as bromide. The mesothorium and radium continue to be enriched in the crystal fractions, and reduced in the successive mother liquors.†

In practice,[12] a fair concentration of acid is maintained throughout the chloride and bromide systems, for the reason that the factor of enrichment of mesothorium radium chloride from barium chloride and also of mesothorium radium bromide from barium bromide is regarded as more favorable in acid than in neutral solutions. While it has been shown[3] that the crystallization factor is higher for bromides than for chlorides, the effect of the acidity of the solutions on the progress of

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* Abstract of a thesis submitted in partial fulfilment of the requirements for the degree of Master of Arts in the Graduate School of the University of Missouri, August, 1919.

** The reference numbers refer to the appended bibliography.

† The method is fully described in Bulletin No. 104, U. S. Bureau of Mines (1915).

concentration has not been clearly established. This investigation is confined to the effect of hydrobromic acid on the crystallization factor in bromide solutions of barium, mesothorium and radium. Our experiments show definitely that the crystallization factor is independent of the acid concentration. In other words, the enrichment of mesothorium and radium is the same in neutral as in acid solution when equal fractions of crystals are separated.

The terms "crystallization factor," "concentration factor," "factor of enrichment," "fractionation coefficient" appear to be used synonymously in the refining of radium and mesothorium, but not aways with the same meaning. Evidently these terms always refer to a ratio, but the ratio may be expressed in several related ways, as (1) the concentration of mesothorium in the crystals separated to the concentration of mesothorium in original crystals, used in preparing the solution, concentrations being given as milligrams of mesothorium (expressed in terms of radium) per gram or kilogram of anhydrous crystals; (2) total mesothorium in crystals to total mesothorium in mother liquors; (3) concentration of mesothorium in crystals separated to concentration of mesothorium in crystals from mother liquor, where the ratio is used in the sense of a partition or distribution coefficient. Throughout this paper the term crystallization factor will be used with the first meaning: the ratio, concentration of mesothorium in crystals separated to concentration of mesothorium in original crystals. This factor serves directly in computing the radium or mesothorium content of the head crystals in "stepping up" as this factor raised to the *n*th power, *n* being the number of crystallizations, gives the desired multiplier.

Since mesothorium has never been obtained pure, its amount is expressed by its activity compared with radium. One milligram of mesothorium is the quantity of mesothorium-one, with its equilibrium amount of mesothorium-two, whose gamma ray activity is equal to that of one milligram of radium containing the equilibrium amounts of its short-lived products.

The radioactive bromides used in these experiments were loaned by the Welsbach Company through the courtesy of Dr. H. S. Miner. Before beginning determinations of the crystallization factor, two lots of high grade bromides each containing mesothorium and radium equivalent to about 150 mg of radium in 50 grams were refined by fractional crystallization so as to gain familiarity with the technique of fractionation in acid and neutral solutions.

Purification of Bromides

Before undertaking the determination of crystallization factors the bromides selected for the single fractionations were purified. The three samples of anhydrous bromides weighed approximately 5.7, 3.6, and 9.8 g and contained, respectively, about 2.1, 0.5, and 0.2 mg of mesothorium per g. The crude bromides were fused with a fusion mixture consisting of equal molecular weights of sodium and potassium carbonates and thus converted into carbonates. These carbonates, after being well washed, were converted into bromides by dissolving in pure hydrobromic acid. After adding about 5 mg of thorium bromide, the solutions were made barely alkaline with ammonia, thus removing radiothorium, the isotope of thorium, in the precipitate of thorium hydroxide. The radiothorium was removed in order to have solutions practically free from thorium X and its final product thorium D, which emits a powerful gamma radiation which would interfere with our measurement of activity by the gamma ray method. Hydrogen sulfide was then passed into the solution to precipitate lead and any other heavy metals as sulfides. After filtering the solutions were evaporated to dryness in silica dishes and the ammonium salts smoked off. The dry salts were then dissolved in water and the solution filtered. They are now ready for crystallization and addition of hydrobromic acid.

Crystallization of Bromides

The bromides were concentrated to the desired point by evaporation on an electrically heated water bath. Upon cooling groups of compact crystals form from both neutral and acid solutions. The formation of soft, mushy crystals from neutral solutions appears to be due to the presence of ammonium salts. The liquor was then decanted, and the crystals thoroughly dried, dehydrated, and finally sealed in weighed glass tubes, and their weight determined. The degree of acidity of the liquor from which the crystals separated was now determined by pipetting one cc of the liquor into a flask, diluting and titrating with a standard solution of ammonia, methyl orange being used as the indicator. After returning the titrated portion to the liquor originally poured off the crystals, the solution was evaporated to dryness, the ammonium bromide smoked off, and the anhydrous bromides sealed in a glass tube of the same dimensions as the one containing the crystals.

All crystallizations were made in flat-bottomed silica dishes with nearly straight sides, and the same dishes were used as much as possible. After the activity of the crystals and the bromide obtained from mother liquor had been measured, the salts were combined and brought into solution. Other crystallizations were then made with the view of finally obtaining a series of different quantities of crystals separated ranging from 25 to 70 percent of the bromides in the solution. Working first in neutral solutions the work was then extended to acid liquors. Different quantities of crystals were separated from solutions of different acidities ranging from normal to approximately six times normal. After each crystallization the entire procedure of separating crystals and mother liquor, titrating, drying, sealing, and measuring was repeated. In this way crystallization factors were obtained corresponding to different quantities of crystals from liquors whose acidity ranged from neutral to six times normal.

The graphs obtained by plotting the crystallization factors on one axis and the corresponding percentages of crystals on the other axis of the ordinary system of rectangular co-ordinates are coincident within the limits of experimental error, and therefore show that the presence of acid has no effect on the value of crystallization factor. The experimental data upon which this conclusion is based are summarized in the tables below.

About one-fifth of the total gamma ray activity of the bromides is due to radium. The values given are expressed in terms of a radium standard. After each crystallization the activity of the crystals and of the salt obtained from the mother liquor was determined with a Lind[2] lead-lined electroscope. The glass tubing used in sealing the bromides was of uniform bore and thickness. At first the tubes were measured directly after sealing and every twelve hours thereafter up to 108 hours from the time of sealing. After a number of measurements had been made in this manner, it was found that after sixty hours the activity became practically constant, the equilibrium amount of mesothorium-two having accumulated, so that the activity at the time of sixty hours after sealing was taken as a measure of the mesothorium-radium content of the sample.

Attention should be directed to some sources of error in the experiments. In the first place, as the anhydrous bromides are very hygroscopic it is difficult to keep out traces of moisture in sealing. Again, as a small amount of organic matter always enters the material from brushes used, filtering is necessary which results in small losses in the course of many crystallizations. As the bromides are finally ignited, small quantities are apt to adhere to the dish. Then too, as all crystallizations were made in open dishes, small losses sometimes result from "crawling."

In the following table several complete sets of results are given for each sample of bromides used in the experiments.

The crystallization factor, Cc/Co, is given in the fifth column. Similar tabulations were made for all crystallizations made, but inasmuch as we are concerned chiefly with but two items in Table I, namely crystallization factor and percentage of crystals corresponding thereto, the other results have not been included in the tables that follow.

TABLE I—SELECTED SINGLE FRACTIONATIONS

Wt. of Original Salt	Conc., Co, Mesth. per g	Crystals				Mother Liquor		
		Weight	Conc. Mesth. Cc, per g	$\frac{Cc}{Co}$	Percent of Crystals	Weight of Salt	Concentration of Mesothorium per g of Salt	Percent of Mesothorium
5.735	2.11	1.916	5.01	2.35	33.4	3.819	0.69	21.4
5.785	2.11	2.641	4.08	1.95	46.6	3.143	0.46	11.8
5.738	2.13	3.269	3.45	1.56	61.9	2.469	0.30	7.7
9.710	0.19	2.804	0.52	2.64	28.8	6.906	0.06	23.9
9.833	0.19	3.804	0.43	2.26	38.7	6.029	0.048	14.9
3.634	0.54	1.579	1.06	1.96	43.4	2.054	0.14	15.1
3.643	0.54	1.759	0.99	1.83	48.2	1.883	0.12	12.1

TABLE II—CRYSTALLIZATION FACTORS FOR NEUTRAL SOLUTIONS

Percent of Salt as Crystals	Crystallization Factor	Percent of Salt as Crystals	Crystallization Factor
24.3	2.57	44.8	1.98
27.9	2.62	46.6	1.96
33.4	2.35	48.9	1.83
35.1	2.34	53.6	1.71
38.3	2.23	56.9	1.62
38.7	2.26	62.3	1.47
43.4	1.96	69.0	1.44

TABLE III—CRYSTALLIZATIONS FROM ACID SOLUTIONS

Percent of Salt, Crystals	Crystallization Factor	Normality of Acid in Mother Liquor	Percent of Salt, Crystals	Crystallization Factor	Normality of Acid in Mother Liquor
28.0	2.79	1.33	55.3	1.68	2.93
28.8	2.64	1.16	29.0	2.60	4.12
29.6	2.66	1.44	34.2	2.34	4.23
36.4	2.19	1.56	48.8	1.81	4.32
38.8	2.22	1.75	52.8	1.70	4.58
56.9	1.59	1.14	61.7	1.56	4.34
66.3	1.36	1.14	68.2	1.35	4.10
32.2	2.45	2.31	51.5	1.74	6.91
37.1	2.19	2.36	65.8	1.41	5.52
43.4	2.00	2.55	83.6	1.16	6.88

Having shown that the crystallization factor is independent of the acid concentration of the solution it is of interest to point out that the enrichment is apparently not influenced by the differences in concentration of mesothorium of our solutions. In the course of the crystallizations with the three samples of mesothorium-bearing bromides almost the same percentage of crystals separated out. As shown in the following table the crystallization factor remains constant.

TABLE IV

Conc. Mesth. per gram	Acidity of Solution	Conc. of Crystals	Percent of Crystals	Crystallization Factor
0.19	Neutral	0.43	38.7	2.26
0.55	Neutral	1.23	38.3	2.23
2.23	1.75 N.HBr	4.96	38.8	2.22

An Application to Practice

Assume we have 1000 grams of barium bromide containing one mg of mesothorium per gram to be concentrated by fractional crystallization, the desired product to contain 180 mg of mesothorium per gram. When 40 percent of the salt crystallizes out the factor of enrichment is 2.1. The number of series of fractionations, n, necessary to obtain head crystals whose mesothorium content is 180 times that of the original bromides will be given by the relation —$(2.1)^n = 180$. Solving we have $n = 7$. Since 84 percent of the total mesothorium in the head dish passes up in successive fractionations, the amount of mesothorium in the first head crystals removed from the crystallizing system after seven series of fractionations will be given by —$1000 \times 0.84,^7$ or 294.5 mg. The weight of the first head crystals is expressed by $1000 \times (0.4)^7 = 1.636$ g. If mother liquors are removed from the crystallizing system when their total mesothorium content is reduced to 0.1 mg, about 35 individual crystallizations will be included in the seven series of fractionations.

When 60 percent of the salt is allowed to crystallize out the factor is 1.52. Similar calculations for this case will show that 12 series of fractionations involving about 80 single crystallizations will have to be made to obtain head crystals containing 180 mg of mesothorium per gram. Since 91.2 percent of the total mesothorium in the head dish passes forward with successive fractionations the first head crystals will contain 331 mg of mesothorium and will weigh 2.178 g.

By extending computations of this kind to include the second and third crops of head crystals of the desired mesothorium content, it can be shown that in 10 series of fractionations embracing about 65 single crystallizations 534 mg of mesothorium will be obtained as high grade crystals weighing 2.97 g, when 40 percent of the salt is allowed to crystallize out in each dish. To obtain an equal quantity of high grade crystals, containing 180 mg of mesothorium per g, when 60 percent of salt crystallizes out, will involve more than twice as many individual crystallizations and about 17 series of fractionations. In making these computations, the crystals moving forward are combined with mother liquors backwards from dishes two places apart from each other in the system.[12]

Since the solubility of barium bromide falls off very rapidly with increase of hydrobromic acid in the solution, the tendency in crystallizing from solutions of fair acid concentration is to separate larger crops of crystals than from nearly neutral solutions. As we have found in this work that the crystallization factor is independent of the acid concentration we conclude that the concentration of radium and mesothorium is effected more rapidly in very dilute acid or neutral solutions of the bromides. One advantage gained, as Mme. Curie pointed out,[1] in crystallizing from acid solutions of fair concentration consists in increasing the volume of the solution when the quantity of high grade crystals becomes relatively small.

Summary

(1) The crystallization factor of mesothorium and radium in bromide solutions was found to be independent of the concentration of hydrobromic acid.

(2) The crystallization factors corresponding to different percentages of crystals separating were determined.

(3) For concentrations of mesothorium up to 2 mg per g of salt, the crystallization factor remains constant.

(4) The separation of mesothorium and radium from barium can be conducted advantageously in neutral or dilute acid solutions of the bromides.

This work was suggested by Dr. Herman Schlundt and was carried out under his direction. To him the writer is indebted for much valuable advice, assistance, and encouragement.

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CHARCOAL BEFORE THE WAR. II

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When spent bone-black is burned the charcoal diminishes markedly in bulk.[1] According to Wallace, a ton of new and dry char fills a space of about 48–50 cubic feet, while a ton of old char will occupy no more than 40, 35, 30, or even 28 cubic feet, the apparent density of the dry charcoal thus increasing sometimes nearly to double the original value. There is very little change, however, in the absolute specific gravity of the charcoal, which means that the change in apparent density must be due to a decrease in the amount of pore space. Wallace found that a specimen of new char lost as much of its porosity by being heated in a covered crucible for eleven hours as it would have lost by reburning about one hundred times in a sugar-house. This experiment is not helpful, because we do not know whether the charcoal in the crucible was heated higher and therefore sintered more or whether there was more charring of otherwise volatile matter in the covered crucible, thus clogging the pores. In the regular burning there might easily be some oxidation of carbon, which would increase the porosity. Wallace believes that the change in porosity is due primarily to a sintering of the calcium phosphate, which is not unreasonable. He states that new charcoal will hold 80–100 percent of water and is made perceptibly wet by 20 percent, while old charcoal (two or three years in use) will hold only 30–45 percent and is made perceptibly wet by 5 percent of water.

There is some evidence that part of the change in porosity is due to precipitation of carbon because the percentage of carbon may increase from 8–9 percent up to 14–15 or even to 19 percent, the carbon coming from the organic impurities in the sugar. The carbon from these impurities is deposited partly on the outer surface of the charcoal and partly in the pores. It is possible to prevent this, because the per-

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[1] Wallace: Chem. News, 17, 249 (1868).

centage of carbon does not increase in some refineries and even decreases if the burning is done carelessly. When the retorts are quite tight and the temperature is kept low, the carbon is certain to increase unless the charcoal has been washed sufficiently thoroughly to remove nearly all the organic matter adsorbed from the sugar liquor. This necessitates washing with boiling water and one of the most advanced of the Clyde sugar refiners insists that the charcoal should be boiled with the water.

Newlands and Newlands[1] point out that burning at a high temperature means a waste of fuel and causes serious injury to the char by contracting its pores and thus rendering it less active. When working char was heated in an oil bath to 285–290° for one hour, it acquired the same decolorizing power as the same char re-burned in a pipe kiln; when heated in a bath of melted lead at 325° for one hour, it showed rather more decolorizing power than similar charcoal re-burned in the kiln. They believe that a very short and intimate contact with heat not exceeding 390° is all that is necessary to obtain good results. It is impossible to work at so low a temperature in a pipe kiln of the best design and with the most careful management. Even if the pipes in the kiln revolve, they are sure to be heated unequally, the row nearest to the fire being heated more than the others. In order to get round the difficulty experienced in re-burning charcoal evenly, the use of superheated steam and of various gases has been recommended. While this gives a uniform heating, there is danger of destroying the carbon by the action of the steam or the gas if the temperature is too high. However, this loss can be reduced to an insignificant amount. An ingenious apparatus was patented in 1885 by Poulton, Perrett and Newlands[2] (English Patent 15,897). By means of a fan the steam or gas was caused to circulate through two vessels on chambers, one containing fire-bricks arranged as in the case of regenerators, and capable of being heated by means of a fire or by

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[1] Jour. Soc. Chem. Ind., 7, 421 (1888).

[2] Ibid., 7, 423 (1888).

gas, and the other chamber containing the charcoal to be revivified. The second chamber is provided with sets of movable shelves, one above the other, so arranged that the charcoal can be let down by inclining the shelves from one set to another, the charcoal coming in contact in every movement with more and more superheated steam on its way to the bottom, and finally falling into cooling pipes. Working charcoal containing 18.94 percent carbon was passed through the apparatus fifty times, being moistened with water between each re-burning, this number of re-burnings being about equivalent to six months' work in the refinery. The carbon was determined at intervals to see whether there was any loss.

	% C
Original char	18.94
After re-burning 20 times	17.83
After re-burning 30 times	17.32
After re-burning 40 times	17.20
After re-burning 50 times	17.22

To find out whether prolonged heating was necessary, the charcoal was left for 5, 7.5, 10, 12.5, and 15 minutes on each of the six shelves, or 30, 45, 60, 75, and 90 minutes in the kiln. The temperature of the bottom shelf was 345° and of the top shelf 177°. The best results were obtained with the charcoal which stayed in the kiln the shortest time. The thirty-minute charcoal was better than that which had been re-burned in a pipe kiln.

Newlands and Newlands consider that in those refineries where the carbon in the char is kept as nearly as possible at the same percentage as when new, this is accomplished partly as a result of thorough washing but chiefly by the accidental introduction of air into the pipes of the kiln. The carbon destroyed in the kilns is partly bone carbon and partly sugar carbon; and consequently they believe that a slight regular increase in carbon content is a lesser evil than changing to some extent from bone carbon to sugar carbon. This conclusion seems to rest on the proved assumption that some of the bone carbon burns before the last of the sugar carbon.

The inorganic compounds taken up by the char may cause the latter to deteriorate.[1] In ordinary cane sugars there is 0.5–1.0 percent of soluble mineral matter, consisting of salts of potash, soda, lime, and magnesia; and in beet sugars there is much more—1.5–3.0 percent, and sometimes as much as 6 or 7 percent. The highly soluble salts, such as the salts of potash, do not affect the charcoal, because they accumulate in the syrups; but calcium sulphate is detrimental, owing to its comparative insolubility, and to the fact that it is readily adsorbed from the sugar liquor by the charcoal. It may be removed, however, by copious washing and boiling, and it is even removed in solution by washing with weak sugar liquors. Such charcoal is sure to have its calcium sulphate increased if it be washed with water naturally containing that substance in large quantity. Some charcoals contain 2.5 percent of the salt, and the usual amount in old char is 0.5–0.75 percent. In extreme cases it may be present in Clyde charcoal to the extent of one percent. The calcium carbonate present in some hard waters is also adsorbed by the charcoal.

While too much calcium carbonate is objectionable, Wallace claims that there should always be some present. It is of use in neutralizing the small proportion of free acid present in almost all sugars except beet; and it is still more important in neutralizing the lactic and other acids formed in the weak liquors, by a process of fermentation which it is difficult to prevent. Hence charcoal deprived of its carbonate of lime is objectionable, and its use is certain to produce sour liquors and give rise to the presence of iron in the low-class sugars. As the water of Greenock and Glasgow contains only traces of carbonate of lime, the quantity of that salt naturally in charcoal lessens gradually, until in pretty old char it is sometimes reduced to about 1.5 percent. In refineries conducted on scientific principles the amount is

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[1] Wallace: Chem. News, 17, 249 (1868).

never suffered to fall so low. If it falls below 2.5 percent, sour liquors are sure to follow. When very hard water is used the carbonate of lime either decreases very slightly or it increases, and sometimes even to an alarming extent, as in the continental beet refineries, where the evil is a very serious one.

Various means have been devised to remove the excess of calcium carbonate.[1] Treatment with dilute hydrochloric acid to convert the calcium carbonate into calcium chloride is the ordinary mode adopted on the continent in the beet-sugar factories; but this plan is open to the objection that a certain quantity of calcium phosphate is sure also to be decomposed, and that the framework of the charcoal will consequently be injured. To obviate this to some extent it has been proposed to exhaust the air previous to the introduction of the acid, so as to bring the latter instantaneously in contact with every particle of the charcoal, and in this way equalize its action. As another way of overcoming this difficulty, Beanes used dry hydrochloric acid gas, which is said to have no action on calcium phosphate. Stenhouse and Duncan proposed to use dilute nitric acid in place of hydrochloric acid, and there is little doubt but that it possesses advantages over the latter. Cook has suggested treating the charcoal with a solution of ammonium chloride, and then re-burning so as to produce ammonium carbonate which goes off, and calcium carbonate, which is afterwards dissolved out. Cook also patented the use of phosphoric acid to decompose the calcium carbonate. Patrick, Beanes, and others have proposed to dissolve out the calcium carbonate by means of a saturated solution of carbonic acid. In English refineries the calcium carbonate in all cases decreases during use, and this appears to be due to the employment of cane sugar, which is generally slightly acid.

It has been proposed by Eisfeldt and also by Phillips to digest the charcoal after use in a solution of caustic ammonia, potash or soda in water or alcohol, the ammonia and alcohol

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[1] Newlands and Newlands: Jour. Soc. Chem. Ind., 7, 423 (1888).

being recovered by distillation. In this way the coloring matter and a large portion of other organic and mineral matters can be removed without having to re-burn the char.

Clark[1] takes a somewhat different view. "By repeated revivifications charcoal loses much of its porosity; and organic matters, other than carbon, are reduced to a small amount. Calcium carbonate, which usually amounts to 9 percent in new charcoal, may amount to no more than 3 percent in a working char. Provided the charcoal is well washed before revivification, its decolorizing power lasts for a long time and the falling off in decolorization is very gradual. It has been assumed that the lowering of the efficiency of charcoal is due to the deposition of vegetable carbon on the surfaces of the particles of animal carbon of a complex nature, and while that, no doubt, is true to a large extent, it does not afford a complete explanation of the matter in question. Treatment of the charcoal in the cold with dilute hydrochloric acid improves its decolorizing power considerably, and the effect of this treatment is to dissolve out some lime and phosphoric acid and raise the carbon content slightly. The following experiment shows this plainly: 100 grams of charcoal were treated in the cold with 500 cc of 1 percent hydrochloric acid and the solution tested for calcium and phosphoric pentoxide. It contained 2.8 g calcium and 3.0 g phosphorus pentoxide. By this treatment the carbon in the char was raised approximately 20 percent. A low refinery syrup containing 50 percent solid matters was then heated with treated and untreated charcoal on the water bath in closed bottles for 2 hours and the amount of decolorization ascertained. Quantities of liquor and charcoal taken from the tests were exactly the same in both cases, so that the results are strictly comparable. The untreated charcoal removed 69.8 percent of the color, and the charcoal after treatment with acid, and subsequent washing with water to neutrality, removed 84.6 percent of the color from the solution. If the carbon were the only agent taking part in removing color,

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[1] Jour. Soc. Chem. Ind., 32, 262 (1913).

it is difficult to understand why treatment with dilute acid should have improved its power of decolorization so markedly. Calcium carbonate in the charcoal taken for the experiment amounted to 3.5 percent and the total calcium present was approximately the same as that in new charcoal. It is evident that some of the other constituents of the charcoal have an important influence on the decolorizing efficiency. With repeated revivification, calcium carbonate, as has already been stated, becomes reduced from 9 percent to about 3 percent, and the rest of the calcium is found as calcium oxide in stable combination with phosphate of lime, so that it cannot be converted into calcium carbonate by simply moistening with ammonium carbonate. Attention has been drawn to this compound by different experimenters. Treatment with dilute acid partly decomposes this basic phosphate of lime, and as it is after removal of this compound that the decolorizing power of the charcoal is improved, there is a strong presumption that this substance, as well as vegetable carbon, has a considerable influence in reducing the efficiency of animal charcoal."

Clark's reasoning does not seem to be sound. Presence of adsorbed calcium carbonate would be expected to cut down the adsorption of coloring matter. He is apparently making the unnecessary and tacit assumption that the only thing that counts is the total amount of carbon, whereas a charcoal coated with calcium carbonate would be quite inefficient and would be improved by treatment with hydrochloric acid. The statement that hydrochloric acid removes some of the calcium phosphate is a matter which is in dispute, the discrepancy perhaps being due to differences in the bone-black. Stammer[1] reports that, "experiments with bone charcoal showed that hydrochloric acid does not remove the theoretical amount of lime. In one case the removal of calcium carbonate was 1.26 percent instead of 2.08; in another experiment it was 2.8 instead of 6.2. The finer the charcoal is the better the removal of calcium carbonate. Calcium phosphate is

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[1] Chem. Centralblatt, [2] 13, 1002 (1868).

not dissolved under these circumstances. Special experiments showed that equal volumes of fine charcoal, containing less lime, decolorized better than coarser charcoal containing more lime. Since the decolorizing power did not increase proportionately to the removal of lime it is probable that the increased decolorizing is due to the state of the grains. In one set of experiments equal weights of finely divided charcoal decolorized better than coarser charcoal and in another set the reverse is true. If ignited charcoal is washed with slightly acidified water very little lime is removed, but the charcoal becomes a deeper duller black and its decolorizing power increases distinctly. The conclusion is drawn that the removal of lime from a charcoal has very little effect on its decolorizing power and that this property depends jointly on the aggregation of the charcoal and the condition of the surface."

In a second paper Stammer[1] goes one step farther. "When used bone-black is treated with hydrochloric acid, it often happens that the calcium carbonate is not removed so completely as one would expect from the amount of acid added; that however the acid is neutralized completely by the lime; and yet the phosphates in the charcoal do not go into solution. These apparent contradictions can only be explained on the assumption that lime is present in bone-black in some other form than as carbonate or phosphate. Direct analyses show that in old bone-black 0.7 to 3.9 percent lime is present which is not combined with carbon dioxide, phosphoric acid or sulphuric acid, and must therefore be present in combination with organic substances. The nature of these organic lime compounds is not known." It is possible that we are dealing with marked adsorption rather than with unknown organic compounds.

On the other hand Knapp[1] found that hydrochloric acid did dissolve appreciable amounts of calcium phosphate. "Chemically pure hydrochloric acid and acetic acid of 2

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[1] Chem. Centralblatt, [3] 3, 393 (1872).

percent concentration were added to quite fresh, half-used, and completely exhausted bone-black, and were allowed to stay in contact with them for three days. After determining the amount of lime removed, it was calculated how much acid should have been added to convert the lime to calcium chloride or acetate. The hydrochloric acid was too effective and not only dissolved the lime on the surface of the charcoal but took out some calcium phosphate and sulphate. After treatment, the solution contained nearly all the lime from the sugar solution and $^1/_3$ to $^1/_4$ of the calcium phosphate. Acetic acid did not remove all of the lime. While dilute acetic acid removed only 63 percent of the lime in three days a concentrated acetic acid took out between 95 and 98 percent. It is pointed out by Scheibler that one objection to acetic acid is that it does not dissolve iron phosphate; and iron oxide consequently accumulates in the pores of the bone-black. On the other hand the presence of acetic acid in the charcoal is less damaging than the presence of hydrochloric acid. If the charcoal is ignited, any calcium acetate in the pores is converted into calcium carbonate and acetone while calcium chloride is easily fusible and apparently glazes the charcoal, cutting down its decolorizing and adsorbing power to an amazing extent."

Pfleger and Divis[1] use a dilute ammonium chloride solution for purifying bone-black. This acts chiefly by removing the adsorbed lime or calcium carbonate. The ammonia which is set free acts on the organic substances which have been deposited in the bone-black and the apparatus is so constructed that the ammonia vapors going from one vessel pass into a second, third, and finally a fourth one. To reduce the cost of revivification to a minimum the ammonia is condensed and converted back into ammonium chloride.

Eisfeldt and Thumb[2] subject bone-black to fermentation, then boil with sodium carbonate or hydroxide solution, and wash. It is then treated with ammonia. "The lime taken

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[1] Chem. Centralblatt, [3] 4, 543 (1873).

[2] Ibid., [3] 4, 41 (1873).

out by the bone-black is present partly as calcium sulphate and partly as calcium salts of organic acids which have been formed during fermentation. The calcium sulphate is said to be decomposed by the ammonia into ammonium sulphate and calcium hydroxide and a similar decomposition is assumed to take place with the calcium compounds of the organic acids. It is very probable, however, that double compounds are formed. In the evaporation residue of the ammonia which has been used to purify bone-black, varying amounts of calcium sulphate and calcium hydroxide are found, but only traces of phosphate. A concentrated ammonia solution is much more effective than a more diluted one. 1000 grams of 2 percent ammonia contain 0.742 gram of inorganic substance while 1000 grams of a $^3/_4$ percent solution contain only 0.186 gram. The advantages of purification by ammonia are as follows: Saving of almost all the hydrochloric acid hitherto used and, when fermentation is employed, a complete saving of soda with only a slight loss of ammonia; saving in the wear of the bone-black because it is not attacked by ammonia; saving in the igniting and the consequent disadvantages."

A number of years later Lewicki[1] obtained a patent for regenerating bone-black after fermentation. "The organic impurities, which collect in filtering media, such as the bone-char of sugar refineries, are destroyed by fermentation by means of artificial cultures of bacteria suitable for the purpose. It is not necessary to remove the char from the filtering vessels; fermentation is started *in situ* by running into the filter some diffusion liquor in which the desired organisms are in active growth. Where possible it is desirable to employ aerobic bacteria and to inject air into the filter during fermentation. Purification is effected in a few hours, and the filtering medium may then be washed and sterilized if necessary."

Pampe[2] regenerates charcoal by heating in a current of

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[1] English Pat. 20,303 (1902).

[2] Jour. Soc. Chem. Ind., **6**, 829 (1887).

steam at a temperature of 600–700°. He states, however, that the charcoal must not be very finely divided but should be as large as peas in order that the steam may penetrate readily between the particles.

Blachier and Rouillon[1] claim that hydrogen can be used for revivification of bone-black, the coloring matters adsorbed by the charcoal being destroyed by the hydrogen. This does not seem to be a very encouraging method as it is extremely improbable that the hydrogen would make much of the adsorbed material soluble enough so that it could be washed out readily.

A number of attempts have been made to prepare a synthetic bone-black and these are interesting theoretically though they seem not to have found favor commercially. Meyer[2] states that the decolorizing power of bone-black is usually inversely proportional to the density and that the amount of gelatine in the raw material is important. Too much gelatine closes the pores and gives a brilliant charcoal, while too little gelatine gives a brownish black charcoal. He finds that when gelatine is removed before charring, by heating with water vapor at 160–170° for 22 hours, the charcoal is brown on the surface and gray to yellowish white inside. Since the charcoal prepared from this material had the same decolorizing power as charcoal made from the original material, Meyer concludes that the only value of the charcoal is to give pores of the right size. While this conclusion is true in part, it does not seem to follow from this experiment. Meyer tried to prove his point by making a clay charcoal containing no carbon. The material proved a better decolorizer than the best bone-black from the Waghausel factory. On the other hand, this clay charcoal, containing no carbon, took out almost no lime from the sugar solution which seems to show that the carbon is the substance which adsorbs the lime.

Pilter[3] has started from the opposite point of view, "The

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[1] Jour. Soc. Chem. Ind., 21, 602 (1902).

[2] Chem. Centralblatt, [3] 5, 270 (1874).

[3] Ber. deutsch. chem. Ges., 11, 354 (1878).

organic substance in bones is ossein which is isomeric with gelatine. In order to duplicate bone-black dicalcium phosphate and magnesium phosphate are mixed with gelatine, the mass is compressed under hydraulic pressure, dried and calcined. The charcoal thus obtained is identical in physical qualities with bone-black and is more effective in certain respects. The relative amounts of the two solids and of gelatine can be varied. For disinfection a charcoal is made which contains only magnesium phosphate."

These experiments of Pilter are in accord with what we have previously seen, that a nitrogen content is desirable in bone-black. On the other hand, Stenhouse has tried to prepare a substitute for bone-black from wood charcoal. He states that a good bone-black can be obtained by heating wood charcoal impregnated with aluminum sulphate. The charcoal was black and worked best when containing 7.5 percent alumina. It proved an excellent decolorizing agent for tartaric and citric acid solutions. He also made a synthetic bone-black by treating wood charcoal with calcium phosphate dissolved in hydrochloric acid. In this case, a concentration of 7.5 percent calcium phosphate was the best. The action of the mineral substances may be two-fold. They may decrease the size of the pores and thereby make the wood charcoal more active, or they may act as mordants. This second explanation is the one adopted by Stenhouse and it seems the more probable, because he found that these two charcoals behave entirely differently as against gases, which would not be the case if one were dealing with a matter of the size of the pores alone. The two charcoals behave differently when treated with campeachy wood extract. After such a solution is decolorized and the charcoal is then washed with dilute aqueous ammonia, the filtrate is straw-yellow from the alumina charcoal, a little darker from the bone-black, and as dark as ink from a bone-black which has had the calcium phosphate removed. This is fairly conclusive evidence that the adsorption of the coloring matter is due at any rate in part to the alumina and the calcium phosphate. This is confirmed by some experiments by Glassner and Suida[1] on lamp-black. "When lamp-black is extracted with hot water there is a distinct smell of camphor; but the residue on evaporation does not adsorb dyes. The same is true in regard to the alcoholic extract. On the other hand, benzene extracts from lamp-black an oil which is partially volatile with water vapor and which smells something like camphor. The dry residue removes from aqueous solution the distinctly basic dyes like crystal violet and fuchsine but does not take up acid dyes. This seems to prove that lamp-black contains substances which give rise to the decolorizing action of this charcoal towards basic dyes. The dyes are held very weakly by the lamp-black and go into solution readily in presence of dilute acids or alkalies, alcohol, or dilute acetic acid."

It seems very desirable that further experiments should be made on the decolorizing action of suitably prepared calcium phosphate and alumina. Since these substances are apparently acting as mordants in Stenhouse's charcoal, there is no reason why the optimum concentration should be the same as in bone-black, where the calcium phosphate acts primarily to give structure to the carbon. Instead of adding a calcium phosphate solution to wood charcoal, it can be added before the wood is charred. Melsens[2] claims that a good decolorizing charcoal can be made by impregnating wood with calcium phosphate dissolved in hydrochloric acid and then charred. He does not give any details and consequently it is hard to tell whether he has made any advance over the results of Stenhouse obtained 18 years before.

Lotz[3] claims that a decolorizing charcoal can be made from a mineral charcoal or bituminous mass by treating with ammonia or an alkali carbonate and then with sulphuric acid before igniting. If preferred, the acid treatment may precede the alkali treatment. This looks like a crude method for impregnating the mass with ammonium or potassium

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[1] Liebig's Ann., 361, 353 (1908).

[2] Comptes rendus, 79, 375 (1874).

[3] German Pat. 248,571 (1912).

sulphate, and is probably a method for getting a charcoal with suitable pores. If the statements are to be trusted, it means that a good decolorizing charcoal can be made which will contain little or no nitrogen.

Ostrejko[1] treats "substances containing carbon with aqueous solutions of calcium or magnesium chloride, and then submits the product to dry distillation without access of air, washing the charcoal thus obtained with water, treating it with hydrochloric acid solution, and then again washing it repeatedly with water, and finally drying it or heating to a red heat a second time without access of air." The charcoal thus obtained is claimed to be excellent for decolorizing acids, as well as for ordinary industrial applications. It is stated that charcoal obtained as described from birch wood is from 10–12 times more efficient than ordinary bone-black, and from 50–60 times better than birch-wood charcoal as usually prepared.

Richter and Richter[2] find that a finely divided charcoal can be improved by treating with oxygen and then igniting in absence of air. They also claim that the best way to treat with oxygen is to moisten the charcoal with water. These two cases are cited merely to show that many people claim that a good decolorizing carbon can be prepared from other substances than bone-black. The theory of these two treatments will be discussed later.

The apparent density and the properties of carbon can be varied enormously by precipitating carbon in the pores. Sidot[3] states that when any sort of wood is heated in a porcelain tube in the presence of carbon bisulphide vapor a metallic, elastic carbon is obtained which is as sonorous as steel. The carbon bisulphide decomposes, precipitating carbon in the pores of the wood charcoal. Methyl alcohol, hydrocarbons, etc., act similarly. If methyl alcohol is passed through a white-hot porcelain tube, filaments of carbon are

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[1] Jour. Soc. Chem. Ind., 19, 1099 (1900).

[2] German Pat. 250,399 (1912).

[3] Comptes rendus, 70, 605 (1870).

obtained one centimeter long and silvery white, apparently formed of coalescing balls. Jacquelain[1] purified gas carbon by heating it white-hot and treating it with chlorine. He then filled the voids by passing in hydrocarbons which cracked at that temperature. By decomposing a purified tar in a closed vessel he obtained a brilliant sonorous charcoal having the grain of melted steel. Schenck[2] has patented a method for increasing the density of charcoal by introducing into the heating chamber gases or vapors containing carbon, which will crack at that temperature.

Since charcoal is not ordinarily pure carbon, its apparent properties will vary with its composition and this has an important bearing on the question as to the molecular formula of solid carbon. Verneuil[3] has shown that when strong sulphuric acid reacts with wood charcoal, three of the products formed are mellitic acid, $C_6(CO_2H)_6$, benzene-pentacarboxylic acid, $C_6H(CO_2H)_5.5H_2O$, and pyromellitic acid, $C_6H_2(CO_2H)_4.2H_2O$, all of which are benzene derivatives. The charcoal used by Verneuil was dried at 130° and then had the composition carbon 87.62, hydrogen 2.55, oxygen 8.38, and ash 1.43. If the charcoal was heated white-hot before being exposed to sulphuric acid, the attack by the acid was very slow, the acid was not discolored, the charcoal did not disintegrate, and there was practically no yield of the benzene derivatives. This rather implies that mellitic acid is not necessarily an oxidation product of pure carbon. This conclusion is confirmed by the work of Meyer[4] who showed that the yield of mellitic acid from different wood charcoals may vary between zero and 40 percent. If wood charcoal is heated to white heat before being oxidized, the yield drops almost to nothing. No mellitic acid can be obtained from graphite, or only traces, though mellitic acid can be obtained from graphitic acid. Meyer concludes that mellitic acid is

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[1] Comptes rendus, 94, 873 (1882).

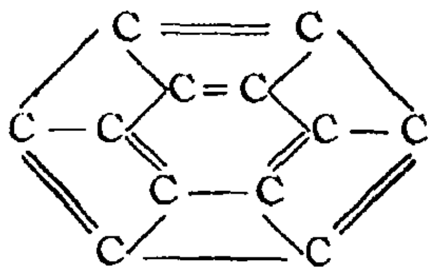
[2] English Pat. 23,085 (1899).

[3] Comptes rendus, 132, 340 (1901).

[4] Monatsheft für Chemie, 35, 163 (1914).

not an oxidation product of pure carbon and that it comes from the oxidation of some hydrocarbon. Consequently no conclusion as to the structure of the carbon molecule can be deduced from the alleged oxidation to mellitic acid.

The occurrence of hydrogen as an integral part of the charcoal has been ignored pretty generally up to recently and a number of people have based their reasoning on the formation of mellitic acid. Thus Dewar[1] says: "Much investigation is still necessary to clear up the nature of the various charcoals and their properties. One chemical character they possess, and that is that, by powerful oxidizing agents like concentrated nitric acid or permanganate of potash, they seem all capable of giving a greater or less yield of an acid called mellitic acid, which occurs in nature as the aluminium salt commonly called honeystone. This acid, we know, is a derivative of benzene, and its production from charcoal suggests that the latter has a structure of double benzene rings, each containing twelve atoms of carbon, as shown. This gives a fundamental molecule containing a large number of latent valences available for chemical or physical combination, and this structure may have something to do with the general absorptive power of charcoal."



Armstrong and Colgate[2] state that carbon should be represented by expressions such as C_x, C_y, etc., in which x and y are high unknown values. Each element in these carbon complexes may be thought of as undergoing oxidation separately and the simple oxide which is obtained eventually may be regarded as formed by the breakdown of the more or less completely oxidized complex. "The only definitive

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[1] Chem. News, 97, 19 (1908).

[2] Jour. Soc. Chem. Ind., 24, 478 (1905).

evidence, available at present, as to the nature of the carbon complex is that afforded by the production of mellitic or benzene-hexacarboxylic acid, $C_6(CO_2H)_6$, on oxidation of charcoal. The formation of such an acid may be regarded as proof of the existence of at least one C_6 benzene (phene) nucleus. Bearing in mind the marked tendency of carbon atoms to become grouped in sixes—revealed in the formation of complex benzenoid hydrocarbons at high temperatures—it may be postulated as probable that the carboxyl groups in the mellitic acid are severally formed by the breaking down of C_6 groups in the charcoal, much in the way that phthalic or benzene-dicarboxylic acid is formed from naphthalene or diphene. Assuming that a tetraphene complex is fundamental to the carbon molecule, to account for the absence of hydrogen it must be further supposed that at least two such systems are superposed or united. On such an assumption the molecule of amorphous carbon would contain at least 36 atoms."

Dimroth and Kerkovius[1] oxidized wood charcoal with nitric acid and decided that the carbon molecule is very large. Aschan[2] writes a structure formula for carbon and Copissarow[3] has published some rather indefinite speculations as to the carbon molecule. Vaubel[4] has approached the subject from a different but more faulty point of view. From a so-called gravity affinity constant and the heats of adsorption he deduces that four atoms of carbon combine with one molecular weight of SO_2, NH_4Cl, CH_3Cl or HCl, or with two molecular weights of CO_2 or N_2O. Consequently the carbon molecule is some multiple of C_4 and he believes that the true value is C_{24}. Della Croce[5] considers that the molecular weight of carbon vapor is probably represented by the formula C_2.

There are also difficulties in connection with the oxygen

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[1] Liebig's Ann., 399, 120 (1913).

[2] Chem. Ztg., 29, 529 (1905).

[3] Mem. Manchester Lit. Phil. Soc., 58, No. 10 (1914).

[4] Jour. prakt. Chem., [2] 57, 342 (1898); 74, 232 (1908); Zeit. angew. Chem., 13, 60, 520 (1900).

[5] Mon. Sci., [5] 5, 25 (1915).

content of carbon. Rhead and Wheeler[1] discuss the adsorption of oxygen by carbon.

"The experiments show that carbon, at all temperatures up to 900° and probably above that temperature, has the power of pertinaciously retaining oxygen. This oxygen cannot be removed by exhaustion alone, but only by increasing the temperature of the carbon during exhaustion. When quickly released in this manner it appears, not as oxygen, but as carbon dioxide and carbon monoxide. The proportions in which it appears in these two oxides when completely removed depend on the temperature at which the carbon has been heated during oxygen fixation. No physical explanation alone can account for this fixation of oxygen; but, in all probability, it is the outcome of a physico-chemical attraction between oxygen and carbon. Physical, inasmuch as it seems hardly possible to assign any definite molecular formula to the complex formed, which, indeed, shows progressive variation in composition; chemical, in that no isolation of the complex can be effected by physical means. Decomposition of the complex by heat produces carbon dioxide and carbon monoxide. At a given temperature of decomposition these oxides make their appearance in a given ratio. Further, when a rapid stream of air at a given temperature is passed over carbon (which has previously been 'saturated' with oxygen at that temperature) carbon dioxide and carbon monoxide appear in the products of combustion in nearly the same ratio as they do in the products of decomposition of the complex at that temperature. Our hypothesis is that the first product of combustion of carbon is a loosely formed physico-chemical complex, which can be regarded as an unstable compound of carbon and oxygen of an at present unknown formula, C_xO_y. It is probable that no definite formula can be assigned to this complex.

"For the present it is sufficient to assume that several carbon molecules hold one oxygen molecule, in bond as it were, and do not allow it to escape in conjunction with one

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[1] Jour. Chem. Soc., 103, 462 (1913).

of their atoms. A considerable evolution of heat takes place during this attachment of oxygen molecules, so much so that some of them eventually acquire sufficient energy to seize hold of a carbon atom and depart with it as carbon dioxide. Some of them become torn apart in the process—become atomized—and leave the carbon molecule as carbon monoxide. This formation of a complex, and partial decomposition as fresh oxygen molecules become attached, goes on until the carbon becomes 'saturated,' the products of combustion during this period (a comparatively short one) being C_xO_y, CO_2, and CO. After the carbon has become saturated there is an alternate formation and decomposition of the complex. Each molecule that impinges on the carbon is at once seized hold of to form the complex formed from previous oxygen molecules. So that, finally, when air is passed over saturated carbon maintained at a constant temperature by the application of an external source of heat, carbon dioxide and carbon monoxide appear in the products of combustion in volume sufficient to account for the total volume of oxygen in the air originally passed."

Armstrong and Colgate[1] believe that the compound is probably the suboxide $C_{12}O_9$ which Meyer and Steiner[2] obtained by dehydrating mellitic acid. While this may be true, this would not account for the compound breaking down gradually as the temperature rises, giving a different ratio of carbon monoxide and carbon dioxide at each temperature. We can postulate one of four things in order to account for the gradual decomposition with rising temperature. There may be a succession of definite compounds of carbon and oxygen, similar to the hydrocarbons. This seems very improbable. There may be several definite compounds which form a series of solid solutions. This also seems improbable. On either of these two hypotheses, one ought to be able to prepare these compounds in a pure state and they should show the same properties in the absence of charcoal. The

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[1] Jour. Soc. Chem. Ind., **32**, 396 (1913).

[2] Ber. deutsch. chem. Ges., **46**, 813 (1913).

third possibility is that there is a definite compound which forms a series of solid solutions with carbon. This again seems improbable. The fourth possibility is that there is a definite compound which is adsorbed by the charcoal and which therefore has a decomposition pressure which varies with varying temperature. This is not impossible because we know that the vapor pressure of adsorbed water does the same thing.[1] When charcoal dried at 150° or 200° is moistened and again dried at 100° it retains the portion of the water which was lost the first time after heating above 100°. In the table are given the data for four different bone-blacks. The data are expressed in percentages and show the amounts lost when heated from 100° to the given temperature, and regained when moistened and heated only to 100°.

	I		II		VI		VIII	
	Lost	Re-gained	Lost	Re-gained	Lost	Re-gained	Lost	Re-gained
°C								
At 150	1.05	1.16	0.97	1.00	0.72	0.68	0.10	0.13
At 200	1.59	1.59	1.48	1.49	1.13	1.08	0.10	0.14
At 250	2.76	2.06	2.39	1.89	1.95	1.43	0.20	0.23
At 300	4.20	2.22	3.54	1.97	3.05	1.60	0.28	0.23

At 150° the new charcoals, Nos. I and II, lose about 1 percent of their weight, but on moistening with water and drying at 100° they regain that 1 percent. The stock and spent charcoals, Nos. VI and VIII, lose less, but they too recover in weight all that was lost on moistening and drying at 100°. The same remark applies to the charcoals heated at 200°, only in this case they lose and recover more weight under the same conditions. When the temperature is raised to 250° the loss is much greater and the charcoals, except in the case of VIII which is spent, are unable to regain all the weight lost at the high temperature. The difference is one-

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[1] Patterson: Jour. Soc. Chem. Ind., 22, 612 (1903); Milne: Chem. News, 28, 13 (1873).

half percent to three-quarters percent on all the charcoals except VIII. This inability to regain lost weight is still more apparent in charcoals heated to 300°, in which case only about one-half of the loss is recovered at 100°. The carbonaceous matter in VIII has been so thoroughly carbonized by the repeated re-burnings of several years that heating, even to 300°, makes very little difference on it. At all temperatures except 300° it regains rather more weight at 100° than the fraction which is lost at the high temperature.

On this hypothesis the pure compound, possibly $C_{12}O_9$ or a decomposition product,[1] would behave in one way when heated by itself and quite differently if heated when adsorbed by charcoal. This experiment should be tried with the suboxide $C_{12}O_9$ and with any other compound which might conceivably break down to form a compound having the properties described by Rhead and Wheeler. It is not necessary to assume that this compound must break down in different ways at different temperatures. There is always an excess of carbon present and on slow heating one would probably always come very close to the equilibrium ratio for carbon dioxide, carbon monoxide, and carbon for the temperature in question.

Charcoal which has been freshly burned and cooled in a vessel from which air is excluded gives out a considerable amount of heat on being exposed to air, owing to adsorption of the latter.[2] If conditions are right, the charcoal may take fire spontaneously as a result of adsorbing oxygen. Bühler[3] points out that after any distillation of wood there is less danger of spontaneous combustion, the more rapidly the charcoal is cooled. This is merely another way of saying that the lower the temperature at which the oxygen is taken up, the less the danger of the charcoal being heated to the temperature at which it ignites. The previous history of the

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[1] Diels and Wolf: Ber. deutsch. chem. Ges., 39, 689 (1906); Diels and Meyerheim: Ibid., 40, 355 (1907).

[2] Newlands and Newlands: Jour. Soc. Chem. Ind., 7, 421 (1888).

[3] Zeit. angew. Chem., 1900, 155.

charcoal is also a factor in determining whether ignition will occur.[1] Dogwood, willow, and alder are said by Hargreaves to make the best charcoal for sporting powders. If they are heated too high, they are less hygroscopic but they also burn less readily when used as powder, so it is necessary to strike a happy mean. If these charcoals are ground one day after they have been burned, they take fire spontaneously; but not if they are ground two days after burning. By that time they have taken up about all the oxygen they are going to, together with some moisture, and the only evolution of heat is that resulting from the grinding. Hargreaves found that in forty-eight hours some of these charcoals absorbed 2.16 percent oxygen. In two weeks they took up 6.9 percent water under the unspecified conditions of the experiment, after which there was not much change.

Ernst[2] passed air slowly over heated coal and found that the percentage of carbon as carbon dioxide was about 95 at 650° and practically zero at 1000°, the carbon being present entirely as carbon monoxide. Boudouard[3] made equilibrium experiments on carbon, carbon monoxide, and carbon dioxide, finding 89.3 percent CO_2 at 550°, 61 percent at 650°, and 7 percent at 800°. By extrapolation he calculates that the equilibrium values are 98 percent CO_2 at 450° and 0.7 percent at 1000°. The two sets of experiments were done in a different way, with a different gas mixture, and with a different so-called carbon, so that the discrepancies at the lower temperatures are perhaps not surprising.

In presence of water vapor the carbon dioxide ratio does not change much. Theoretically it should not change at all at constant volume. Long[4] treated wood charcoal with boiling hydrochloric acid and then with boiling nitric acid. He washed the purified charcoal with distilled water, dried, and

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[1] Hargreaves: Jour. Chem. Soc., 12, 420 (1874).

[2] Jour. prakt. Chem., [2] 48, 31 (1893); Naumann: Zeit. angew. Chem., 1896, 200.

[3] Boudouard: Ann. Chim. Phys., [7] 24, 5 (1901).

[4] Liebig's Ann., 192, 288 (1878).

heated in a Hessian crucible, passing in water vapor when the charcoal was at a red heat. The approximate yields were: hydrogen 64.2 percent, carbon dioxide 30.7 percent, carbon monoxide 4.8 percent, and nitrogen 0.3 percent, or nearly 83.7 percent for carbon dioxide in a mixture of dioxide and monoxide. The temperature at which Long worked is not known; but if we call it 600°, the value of 83.7 agrees fairly well with that of 89.3 percent found by Boudouard at 550°. The two equations are $C + CO_2 = 2CO$ and $CO_2 + H_2 = CO + H_2$. Both can hold simultaneously when the concentration of the carbon monoxide is proportional to the ratio of the water concentration to the hydrogen concentration.

$$KC_{CO} = \frac{C_{H_2O}}{C_{H_2}}.$$

The amount of hydrogen in Long's experiments is rather less than it should be relatively to the carbon dioxide and carbon monoxide. Long shows that this is due to the presence of oxygen in some form in the charcoal.

By working at temperatures at which the water gas equilibrium is not reached in measurable time all sorts of queer results can be obtained. Mond[1] passes carbon monoxide over pulverulent nickel at 350–400°. This catalyzes the reaction $2CO = C + CO_2$, and we get the equilibrium concentration which is practically 100 percent CO_2. If steam is passed in, this oxidizes the precipitated carbon, forming carbon dioxide and hydrogen. When carbon monoxide and steam are led over pulverulent nickel at 350–400°, the final products are carbon dioxide and hydrogen, which is not what one would expect.

Farup[2] has studied the rate of oxidation of purified electric light carbons by oxygen, carbon dioxide, and water. At 850° carbon dioxide and water vapor react at the same speed, while oxygen reacts at this same speed at about 450°. In the case of carbon dioxide the reaction velocity is ap-

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[1] Jour. Soc. Chem. Ind., 8, 767 (1889).

[2] Zeit. anorg. Chem., 50, 276 (1906).

proximately proportionate to the square of the gas concentration. The author concludes that we are not dealing with a surface reaction because the presence of carbon monoxide would cut down the rate enormously. The only explanation that he can offer is that carbon dioxide dissolves as such in solid charcoal and dissociates there to carbon monoxide and oxygen which later reacts with the charcoal. He has not considered the possibility of a marked selective adsorption of carbon dioxide.

Cornell University

A COMPARATIVE METHOD FOR DETERMINING VAPOUR DENSITIES[1]

BY PHILIP BLACKMAN

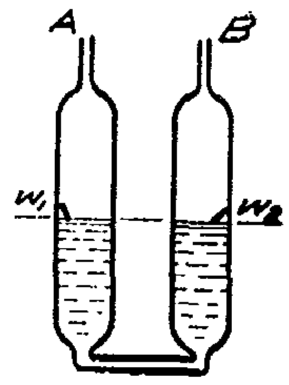

Fig. 1

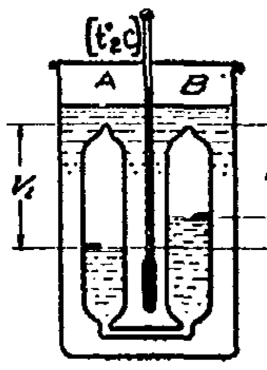

Fig. 2

Method.—Two glass bulbs, best made from some graduated tubing (*e. g.*, disused burette tubing), about 4 inches (10 cm) in length, are joined together by a short piece of capillary-tubing, and their free ends are drawn off sufficiently wide to admit a narrow glass "weighing" tube, Fig. 1. The graduations are merely to permit observing and noting the heights to which the mercury used in the apparatus rises. The apparatus is placed upright and half filled with pure mercury. The substances whose vapor-densities are to be compared are weighed out (weights w_1 and w_2, respectively) in very small quantities in narrow glass tubes and placed one in each bulb. The atmospheric pressure P is observed. One of the bulbs, for example A that containing the substance of weight w_1, is sealed off, and when it has cooled to room-temperature $t°$ the difference in height m between the mercury levels is measured, and the positions of the mercury levels on the graduations noted so that later on the enclosed volume of air V in the bulb A may be determined, Fig. 2. The other bulb B is now sealed off, and when it has cooled to room-temperature $t_1°$, the difference m_1 in height between the mercury levels is measured, and the positions of the mercury levels on the graduations noted so that the volumes V_1 and V_2 of the enclosed air in the bulbs A and B, respectively, may be subsequently determined, Fig. 3. The apparatus is now placed vertically in a deep beaker and completely covered with some suitable

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[1] Read before a meeting of the (London) Chemical Society, 1915, and continued from the Journal of the Chemical Society, 107, 1500 (1915).

medium which is heated to a temperature t_2° sufficiently high to vaporize completely the two substances. The positions of the mercury levels in the two bulbs are noted so that afterwards the enclosed respective volumes v_1 and v_2 of the gases in A and B may be measured; and the difference m_2 in height between the mercury levels is also determined later on, Fig. 4. The bulbs are now cut off from the connecting tube and the mercury is removed. Mercury is poured into them from a burette reading correctly to $^1/_{20}$ cc to reach the positions occupied by the mercury in order to determine the volumes V, V_1, V_2, v_1 and v_2. The vapor-densities d_1 and d_2 can then be compared by the aid of the formula given below, and if one be known the other can be calculated.

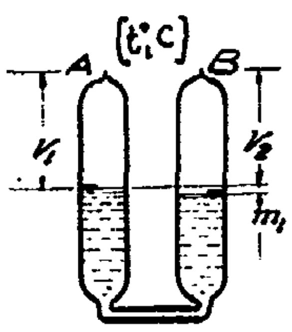

Fig. 3

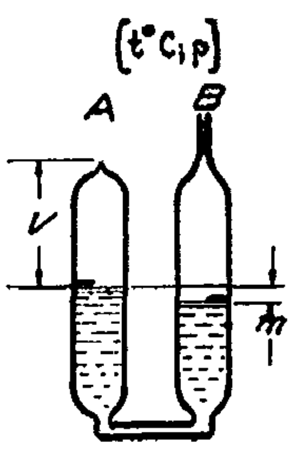

Fig. 4

All measurements are made with the bulbs in a vertical position.

Strictly speaking V, V_1 and V_2 should represent the respective air-volumes *less*, respectively, the volumes of the substances w_1, w_1, w_2.

The method cannot of course be used with substances which react with mercury.

If the results are to be trustworthy a substance which is used for the comparison, and hence whose vapor-density is known, must be pure.

Theory.—It is assumed that at 0° C and 760 mm 1 gram of hydrogen occupies 11160 cc.

As the vapor-pressure of the mercury is equal in both bulbs it is unnecessary to make allowance for it.

(*a*) In A (before sealing B) at t°, air-pressure $= p - m$ (always $-m$, because when A is being sealed up the air in it is heated and because of its expansion it is ultimately on cooling at a lower pressure than the outside air).

(*b*) In A (after sealing B) at t_1°,

$$\text{air-pressure} = \frac{(p - m)V(273 + t_1)}{V_1(273 + t)} \pm m_1$$

= air-pressure also in B at $t_1°$ ($+ m_1$ when the mercury in A is on a lower level than in B, and $-m_1$ when the mercury in A is on a higher level than in B).

(*c*) In A, at $t_2°$, air-pressure

$$= \left[\frac{(p-m)V(273+t_1)}{V_1(273+t)} \pm m_1\right]\left[\frac{V_1(273+t_2)}{v_1(273+t_1)}\right] \pm m_2 \ldots (1)$$

and vapor-pressure

$$= \frac{11160 \times 760(273+t_2)w_1}{273\, d_1v_1} \ldots\ldots\ldots\ldots\ldots\ldots (2)$$

(*d*) In B, at $t_2°$, air-pressure

$$= \left[\frac{(p-m)V(273+t_1)}{V_1(273+t)} \pm m_1\right]\left[\frac{V_2(273+t_2)}{v_2(273+t_1)}\right] \ldots\ldots (3)$$

and vapor-pressure

$$= \frac{11160 \times 760(273+t_2)w_2}{273\, d_2v_2} \ldots\ldots\ldots\ldots\ldots\ldots (4)$$

Now (1) + (2) = (3) + (4), whence

$$\left\{\frac{(p-m)V(273+t_1)}{V_1(273+t)} \pm m_1\right\}\left\{\frac{1}{273+t_1}\right\}\left\{\frac{V_1}{v_1} - \frac{V_2}{v_2}\right\}$$
$$\pm \frac{m_2}{273+t_2} + \frac{31068\, w_1}{d_1v_1} = \frac{31068\, w_2}{d_2v_2}$$

($+ m_2$ or $- m_2$ when the mercury in A is on a lower or higher level, respectively, than in B). Now in general $t° = t_1°$ if the bulbs be both sealed within a short interval of each other, so the formula reduces to

$$\left\{\frac{(p-\;)V}{V_1} \pm m_1\right\}\left\{\frac{1}{273+t_1}\right\}\left\{\frac{V_1}{v_1} - \frac{V_2}{v_2}\right\} + \frac{31068\, w_1}{d_1v_1}$$
$$\pm \frac{m_2}{273+t_2} = \frac{31068\, w_2}{d_2v_2} \ldots\ldots\ldots\ldots (I)$$

$\frac{m_2}{273+t_2}$ is small in comparison with any of the other quantities and may be left out of account unless a very great degree of accuracy is required, and the formula then becomes

$$\left\{\frac{(p-m)V}{V_1} \pm m_1\right\}\left\{\frac{1}{273+t_1}\right\}\left\{\frac{V_1}{v_1} - \frac{V_2}{v_2}\right\}$$
$$+ \frac{31068\, w_1}{d_1v_1} = \frac{31068\, w_2}{d_2v_2} \ldots\ldots\ldots\ldots (II)$$

RESULTS

	p mm	t_1	t_2	m mm	m_1 mm	m_2 mm	V cc	V_1 V_2 cc	v_1 v_2 cc	w_1 w_2 gram	s_1 s_2	$\frac{d_1}{d_2}$ I	II	III	IV	Theory
Ether (diethyl)	757	15	137	4	3	1	3.45	3.80	3.45	0.1133	0.731	37.0	37.0	37.0	37.0	37.0
Acetone								3.95	3.65	0.1001	0.793	30.9	30.9	30.9	30.9	30.9
Chloroform	763	15	150	11	0	—13	3.90	4.75	2.85	0.0811	1.501	59.7	59.7	59.7	59.7	59.7
Diethyl ether								4.35	5.95	0.1190	0.731	36.7	36.8	36.8	36.8	36.4
Diethyl ether	760	16	149	6	7	0	3.05	3.25	3.30	0.0770	0.725	37.0	37.0	37.0	37.0	37.0
Chloroform								3.85	3.60	0.1343	1.498	59.8	59.8	59.8	59.8	59.8
Acetone	749	20	169	9	—18	—4	2.80	2.90	3.80	0.0818	0.792	29.0	29.0	29.0	29.0	29.0
Ethyl alcohol								4.20	3.05	0.0469	0.789	22.6	22.9	22.7	22.8	23.0
Ethyl alcohol	765	18	136	10	10	2	4.75	4.95	4.30	0.0651	0.802	23.0	23.0	23.0	23.0	23.0
Chloroform								2.80	2.25	0.0876	1.495	59.8	59.8	60.0	60.0	59.7
Acetone	765	15	126	7	—2	—6	2.65	2.75	2.40	0.0289	0.793	29.0	29.0	29.0	29.0	29.0
Chloroform								3.10	3.10	0.0798	1.501	60.4	60.3	59.7	59.6	59.7

It would be more accurate to substitute $V - w_1/s_1$, $V_1 - w_1/s_1$ and $^1/_2 - w_2/s_2$ (s_1 and s_2 being the respective specific-gravities of w_1 and w_2 as measured at $t_1°$) for V, V_1 and V_2, respectively, and the formula will then read

$$\left\{\frac{(p-m)(V-w_1/s_1)}{V_1-w_1/s_1} \pm m_1\right\}\left\{\frac{1}{273+t_1}\right\}\left\{\frac{V_1-w_1/s_1}{v_1}-\frac{V_2-w_2/s_2}{v_2}\right\}$$

$$\pm \frac{m_2}{273+t_2}+\frac{31068\,w_1}{d_1v_1}=\frac{31068\,w_2}{d_2v_2}\ldots\ldots\ldots\ldots(\text{III})$$

or without the negligibly small quantity $\pm m_2/(273 + t_2)$

$$\left\{\frac{(p-m)(V-w_1/s_1)}{V_1-w_1/s_1} \pm m_1\right\}\left\{\frac{1}{273+t_1}\right\}\left\{\frac{V_1-w_1/s_1}{v_1}-\frac{V_2-w_2/s_2}{v_2}\right\}$$

$$+\frac{31068\,w_1}{d_1v_1}=\frac{31068\,u_2}{d_2v_2}\ldots\ldots\ldots\ldots\ldots\ldots(\text{IV})$$

The comparative values of these four formulae are shown in table on page 228. Corrections made for the following are of theoretical interest only and of no practical importance: (1) the expansion of the glass bulbs between $t_1°$ and $t_2°$; (2) the expansion of the mercury between $t_1°$ and $t_2°$; (3) the volumes occupied by the glass of the weighing tubes.

It is assumed in each case that the first substance gives the theoretical vapor-density and that the second is the calculated value.

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THE ELECTROLYTIC PREPARATION OF POTASSIUM FERRICYANIDE

BY O. W. BROWN, C. O. HENKE AND I. L. MILLER

The electrolytic oxidation of potassium ferrocyanide to potassium ferricyanide has been investigated by several men, including Hayek,[1] Brochet and Petit,[2] and Grube.[3] The results obtained by these men, as reported in the literature, seem to be somewhat at variance. All of them used a cell with a diaphragm, the oxidation being effected in the anode chamber. In each case the electrolyte in the anode chamber was agitated with a mechanical stirrer.

Brochet and Petit state that the oxidation of potassium ferrocyanide to potassium ferricyanide takes place according to the following reaction:

$$3K_4Fe(CN)_6 + Fe(CN)_6^{IV} = 4K_3Fe(CN)_6.$$

Near the end, when the solution is poor in ferrocyanide, oxygen is evolved. To account for this reaction, Brochet and Petit give the equation

$$Fe(CN)_6^{IV} + 2H_2O = H_4Fe(CN)_6 + O_2.$$

Hayek claims that a current yield of 100% can be obtained. He also states that, with too high a current density, the current efficiency is decreased through the decomposition of water by the ferrocyanide ion, whereby free alkali at the anode is neutralized, and through the electrolytic decomposition of potassium hydroxide.

Grube gives the following table to show the effect of current density on current efficiency:

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[1] Hayek: Zeit. anorg. Chem., **39**, 240 (1904); Jour. Chem. Soc., **86**, 479 (1904).

[2] Brochet and Petit: Comptes rendus, **139**, 855 (1904); Zeit. Elektrochemie, **11**, 104 (1905).

[3] Grube: Zeit. Elektrochemie, **20**, 334 (1914).

TABLE I

Influence of current density on current efficiency.

Anode solution—0.5 molar $K_4Fe(CN)_6.3H_2O$ (46.76 grams of the salt in anode chamber at start).

Cathode solution—0.1 normal KOH.

Temperature—18° C.

Electrodes—Nickel.

No.	Amperes per sq. dcm.	$K_4Fe(CN)_6.3H_2O$ when O appeared Grams	Percent oxidized when O appeared	Current efficiency for complete oxidation
1	2.0	7.62	83.70	80.57
2	1.5	5.70	87.81	83.06
3	1.0	3.48	92.56	90.49
4	0.5	2.05	95.62	94.51

Until bubbles of oxygen began to appear, Grube claims a current efficiency of 100%. The table shows that with a lowering of current density the current efficiency is increased, a fact which one would expect.

The effect of temperature on current efficiency was also investigated by Grube. His results are given in the following table:

TABLE II

Influence of temperature on current efficiency.

Anode—Platinum.

2.0 amperes per sq. dcm.

No.	Temperature centigrade	$K_4Fe(CN)_6.3H_2O$ at start Grams	Percent oxidized when O appeared	Current efficiency
12	18°	41.97	84.08	78.03
13	40	41.97	91.14	83.39
14	50	42.24	92.97	86.46
15	60	42.24	84.54	74.68
16	70	41.15	77.88	70.38

Thus the current efficiency according to Grube increases with temperature up to 50° C after which it decreases with increase in temperature. He accounts for the decrease above 50° C by assuming a chemical decomposition of the potassium ferricyanide according to the following equation:

$$13K_3Fe(CN)_6 + 6H_2O + 9KOH = Fe(OH)_3 + 6NH_3 + 6CO_2 + 12K_4Fe(CN)_6.$$

In our first experiments we tried to effect the oxidation without the use of a diaphragm. This was attempted both with and without a stirrer, also with the electrodes in various positions and shapes; but in all of our attempts without a diaphragm the highest yield obtained was about 50%.

In all of our following experiments a diaphragm was used. The apparatus used in the next four experiments consisted of a beaker 11 cm in diameter and 21 cm high with a capacity of about 2000 cc. The cathode chamber consisted of a porous clay cup, inside of which was placed a cylindrical iron wire gauze cathode. The anode was a 20-mesh copper wire gauze 8 cm by 8 cm, and was held in a horizontal position about 2 inches from the bottom of the beaker. Just above the anode there was a glass stirrer which was rotated by a small electric motor. An ammeter was used to indicate the current. Although this would introduce an error due to the variation in current, this error was small as the variation was slight and the ammeter was read quite frequently.

TABLE III

Experiment 1

To determine the amount of KOH formed.

Anode solution—1400 cc of saturated solution of $K_4Fe(CN)_6.3H_2O$.

Cathode solution—175 cc of saturated solution of $K_4Fe(CN)_6.3H_2O$.

Current—1.05 amperes (0.90 ampere per sq. dcm.).

Bath tension—2.5 volts.

Time after starting Hours	Total KOH formed Grams	KOH in anode chamber Grams	Percent of total in anode chamber	KOH in cathode chamber Grams	Percent of total in cathode chamber
6	14.91	6.43	43.2	8.48	56.8
11	24.76	13.21	53.4	11.54	46.6
16	35.38	20.08	56.7	15.31	43.3
21	42.16	24.09	57.1	18.07	42.9

These results compare favorably with those of Grube. Thus he secured from 39 to 41 where we have 42.9% of total KOH in cathode chamber, and from 61 to 59 where we have 57.1% of total in anode chamber. To account for the potassium hydroxide in the anode chamber Grube gives the equation

$$2K_4Fe(CN)_6 + O + H_2O = 2K_3Fe(CN)_6 + 2KOH.$$

The object of the next three experiments was to determine the effect of potassium hydroxide on current efficiency. The apparatus used was the same as in Experiment No. 1. The current used in Experiments 2, 3 and 4 was 1.25, 1.15 and 1.10 amperes, respectively.

TABLE IV

Experiments 2, 3 and 4

No.	$K_4Fe(CN)_6.3H_2O$ Gm per liter	Grams KOH added to anode chamber	Amperes per sq. dcm.	Voltage		Percent oxidized when O appeared	Current efficiency
				Start	End		
2	234.47	20	0.99	2.5	—	96.8	99.5
3	286.84	40	0.91	2.1	2.0	98.8	99.0
4	276.66	60	0.86	2.0	2.0	98.0	100.0

The current efficiency was calculated up to the time when bubbles of oxygen began to appear. This was 15, 20.33 and 20.33 hours for Experiments 2, 3 and 4, respectively.

The results show that potassium hydroxide does not decrease the current efficiency but rather increases it slightly. Also the potassium hydroxide decreases the voltage required which is a distinct gain.

The apparatus used in the following six experiments was like the one used in the preceding four, except that a rectangular glass battery jar $7^1/_2$ cm by 12 cm by $17^1/_2$ cm high was used instead of the tall beaker.

Experiment 5

The object of this experiment was to titrate with both potassium permanganate and sodium thiosulfate and to see whether or not all of the potassium ferrocyanide that is decomposed is converted into potassium ferricyanide.

The electrolyte in the anode chamber consisted of 1000 cc of a solution of potassium ferrocyanide containing 192.46 grams of $K_4Fe(CN)_6.3H_2O$ per liter. To this 30 grams of potassium hydroxide were added. The cathode chamber contained 110 cc of a 5% solution of potassium hydroxide. The anode was a 7 1/2 by 11 1/2 cm copper wire gauze. The bath tension was 2.0 volts both at the start and at the end. The current varied from 0.92 to 0.95 ampere, the slight variations being noted.

Bubbles of oxygen began to appear at the end of 12.92 hours. At this time titrations with potassium permanganate and sodium thiosulfate gave the following:

$KMnO_4$—2.78 grams $K_4Fe(CN)_6.3H_2O$ per liter.
147.85 grams $K_3Fe(CN)_6$ per liter (by difference).
Current efficiency 99.6%.

$Na_2S_2O_3$—143.19 grams $K_3Fe(CN)_6$ per liter.
Current efficiency 96.5%.

This goes to show that a part of the potassium ferrocyanide which is decomposed is not converted into potassium ferricyanide. This fact leads us to believe that the efficiencies in Experiments 2, 3 and 4 should be decreased by about 3%, as the permanganate method was used. In all the following experiments the thiosulfate method was used.

The permanganate determination was made in the following manner: 5 or 10 cc portions were pipetted out, diluted with water, acidified with dilute sulfuric acid and then titrated with decinormal potassium permanganate. The difference in the permanganate titrations, before and after a run, was taken to indicate the amount of ferrocyanide that had been oxidized to ferricyanide.

The sodium thiosulfate determination is carried out thus: To 5 cc of the bath add about 20 cc of water, potassium iodide solution[1] in excess (the iodine is liberated by the ferricyanide which is converted to ferrocyanide) and then about 10 cc of concentrated HCl. Shake well, add an excess of zinc sulfate

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[1] 10 grams of potassium iodide in 400 cc water.

solution,[1] mix thoroughly and let stand for 15 to 30 minutes. After standing slightly overneutralize with sodium bicarbonate and titrate with decinormal thiosulfate using starch indicator.

The permanganate method determines the ferricyanide indirectly, by assuming that all the ferrocyanide that is decomposed is converted into ferricyanide. The thiosulfate method determines the ferricyanide directly, that is, by the amount of iodine it sets free from potassium iodide.

Brochet and Petit determined ferrocyanide with permanganate, then reduced the ferricyanide and again titrated with permanganate, the difference in the titrations representing the amount of ferricyanide. Grube does not state how he determined the amount of ferricyanide.

The apparatus used in the next five experiments was the same as that used in Experiment 5. The object was to determine the effect of anode material on current efficiency.

TABLE V

Experiments 6, 7, 8, 9 and 10

Anode chamber—1000 cc. of potassium ferrocyanide solution.

Cathode chamber—110 cc of 5% potassium hydroxide solution.

Size of anode—7½ cm by 11½ cm.

Current varied from 0.90 to 0.95 ampere, the variations being noted.

Temperature—18° C.

No.	Anode	Voltage		$K_4Fe(CN)_6.3H_2O$ Gm per liter at start	Current efficiency			
		Start	End		First period	Second period	Third period	Average
6	Copper	2.4	2.1	179.51	91.3	95.3	96.3	94.3
7	Nickel	2.7	—	179.51	95.1	96.1	97.7	96.3
8	Platinum	2.9	2.5	182.28	94.6	94.9	96.6	95.4
9	Graphite	3.0	—	177.66	92.7	95.9	99.7	96.1
10	Pb covered with PbO_2	—	2.3	166.55	95.5	96.0	93.0	94.9

The anodes in Nos. 6 and 7 were wire gauzes while those in Nos. 8, 9 and 10 were perforated plates.

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[1] 40 grams of crystallized zinc sulfate in 400 cc of water.

The electrolysis was divided into periods as follows:

First period—from start to end of two hours.

Second period—from end 2 hours to end 3 1/2 hours.

Third period—from end 3 1/2 hours to end 5 hours.

These results are quite interesting. Thus with the exception of the lead peroxide anode the efficiency in each case is the highest in the third period. This is especially true of the graphite anode, the efficiency being 7% higher in the third period than in the first period. Also graphite is 2% higher in the third period than the second highest which is nickel. The efficiency of the graphite anode is almost theoretical in the third period, being 99.7%.

These results seem to be at variance with those secured by Brochet and Petit, who give graphite a current efficiency of but 33.2%. However, they used a larger current density and their results are for 60 minutes and it will be noted that for the first two hours our efficiency was but 92.7%. It is not unusual for the efficiency of a graphite electrode to increase after being used. Thus in making sodium hypochlorite by electrolysis, if a graphite electrode is used, the efficiency is low at first but the efficiency increases with use, probably until the graphite is saturated with chlorine, when the efficiency is quite high. For nickel, lead, iron and platinum similarly low efficiencies are given by Brochet and Petit.

On the other hand Hayek says that 100% efficiency can be obtained. Likewise Grube claims that he secured 100% efficiency with nickel, platinum, copper, iron and lead peroxide anodes up to the time when bubbles of oxygen began to appear on the anode; however, he does not state how he determined the amount of ferricyanide formed. We never secured 100% efficiency, the nearest being with the graphite electrode in the third period which gave 99.7% efficiency.

In the next experiment the apparatus used was the same as that used in Experiment 1. The anode solution was kept saturated with ferrocyanide by the continued addition of this salt during electrolysis. The potassium ferricyanide separated out in crystals along with a little insoluble matter.

Grube states that the ferricyanide separated out on the anode, increasing the voltage and decreasing the current efficiency. We had no trouble with this latter point. The voltage was rather constant at about 2.6. The stirrer was just above the anode and continually forced the electrolyte through the gauze anode, so that the potassium ferricyanide separated out in the space below the anode instead of on the gauze.

Summary of Results

1. We were unable to secure high current efficiencies in the electrolytic oxidation of potassium ferrocyanide to potassium ferricyanide without the use of a diaphragm.
2. By leaving a space below the anode and forcing the electrolyte through it, the ferricyanide can be made to crystallize out in the space below instead of on the anode which would cause voltage losses.
3. Potassium hydroxide is found in both chambers after electrolysis.
4. Potassium hydroxide does not decrease current efficiency but rather increases it slightly and decreases the voltage.
5. All the ferrocyanide that is decomposed is not converted to ferricyanide.
6. Different current efficiencies are obtained with different electrode material and is usually greatest after the electrode has been used for about four hours. The highest current efficiency in the electrolytic oxidation of potassium ferrocyanide to potassium ferricyanide is obtained with Acheson Graphite anodes.

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NEW BOOKS

Catalysis in Industrial Chemistry. *By G. G. Henderson. 22 × 15 cm; pp. ix + 202. New York: Longmans, Green and Co., 1919. Price: $3.00.* The first chapter begins with generalities in regard to catalysis and catalytic agents, including a discussion of autocatalysis, negative catalysis, catalyst poisons, and promoters. The latter part of the chapter deals with the preparation of active materials. The second chapter is devoted to hydrogen; chlorine and chlorine compounds; graphite; carbon tetrachloride and phosgene; removal of carbon disulphide from coal gas; sulphur, sulphuric acid, sulphuryl chloride, persulphates; regeneration of chromic acid. The third chapter deals with ammonia, nitric acid and other compounds of nitrogen, while the fourth chapter has to do with hydrogenation. Dehydrogenation and oxidation are the subjects of the fifth chapter, while hydration and hydrolysis, dehydration, polymerization and condensation are discussed in chapter six. The last chapter includes such things as: preparation of hydrocarbons, halogen derivatives, amine derivatives, diazo compounds, aldehydes and ketones, and sulphur compounds; intramolecular rearrangement; enzymes; surface combustion. In an appendix is a list of catalysts.

There is only a slight attempt made to consider the theoretical side of the subject. On p. 3 the author says: "The theories which have been advanced to explain the mechanism of catalysis fall into two classes, the chemical and the physical. The former asserts that the effect of the catalyst is to be attributed to the continuous formation and decomposition of unstable intermediate products; while the physical theory explains the phenomena as being due to the condensation, or increase in concentration, of the reacting substances at the surface of the catalyst, such increase in concentration being brought about by capillary forces. Here it must suffice to state that beyond doubt many catalytic reactions, and probably all which take place in homogeneous systems, depend upon the formation of unstable intermediate compounds, and that it is difficult to understand how the physical theory can afford an explanation of the specific action of catalysts and of the diversity of the effects which they produce. In many cases of heterogeneous catalysis the possibility of the formation of intermediate products is by no means excluded. The effect of metals as catalysts of hydrogenation may be explained on the assumption that metallic hydrides are formed, which under the conditions of the experiment give up their hydrogen to the substance undergoing hydrogenation. The catalytic action of metals in promoting the combination of nitrogen and hydrogen to form ammonia may be attributed to the formation of metallic nitrides which interact with the hydrogen; and in fact nitrides, such as uranium nitride, are excellent catalysts of the reaction. The dehydrating action of alumina on alcohols may be the result of the formation and subsequent decomposition of aluminum alkyl oxides, which, in fact, are known to exist and to break down under the influence of heat; for example, the formation of ethylene from ethyl alcohol may be represented by the following equations:

$$(1)\quad Al_2O_3 + 2C_2H_5.OH = H_2O + Al_2O_2(OC_2H_5)_2$$

$$(2)\quad Al_2O_2(OC_2H_5)_2 = H_2O + Al_2O_3 + 2C_2H_4$$

Many other examples might be quoted, but at the same time it must be admitted that in at least some cases of heterogeneous catalysis the physical theory appears to offer the only explanation of the action of the catalyst."

It is interesting to read, p. 9, that "the behavior of a nickel catalyst toward poisons is said to differ considerably according to its method of preparation. A catalyst prepared by distributing basic nickel carbonate on an inorganic carrier and reducing it at a temperature of 450° was found to be remarkably resistant to poisoning by anticatalysts such as hydrocyanic acid, sulphuretted hydrogen, and carbon disulphide, and, for hydrogenation at the ordinary temperature, to have an activity much greater than that of nickel prepared by reduction at much lower temperatures."

Under hydrogenation, p. 93, there are a couple of paragraphs which certainly call for more study. "In discharging a number of dyes employed in pattern printing on textile fabrics, the addition of a catalyst to the reducing agent has been found to increase its efficiency in a very marked manner. Naphthylamine Bordeaux, Paranitraniline Red, Chloroanisidine Orange, *o*-Nitrotoluidine Yellow, Dianisidine Black, Chrysoidine Bistre and analogous compounds are discharged by means of neutral or slightly alkaline pastes containing sodium formaldehyde sulphoxylate along with a metal, metallic oxide, or metallic salt, which either itself is a reducing agent or is capable of acting as a carrier of the reducing power of the sulphoxylate; the salts of iron, *e. g.*, ferrous sulphate or ferric chloride, are preferred as catalysts.

"Somewhat later the remarkable discovery was made that the effect of the color-discharging agent is much intensified by the addition to it of small quantities of certain dyes themselves. For example, sodium hydrosulphite employed in a neutral medium, *e. g.*, in the presence of dextrin and glycerol, gives an imperfect discharge on tissues dyed with *o*-Naphthylamine Claret, but complete discharge takes place readily when certain basic dyes, for instance, Thionine Blue, Auramine, or Rhodamine 6 G, are added to the mixture. With sodium formaldehyde sulphoxylate also some dyes appear to have a catalytic effect in promoting the discharge of colors; those which have been found to act most powerfully in this direction are Setopaline and Nitroalizarine. Rhodamine G and Acridine Yellow act in a similar manner but their effect is not so marked."

On p. 160 the author says: "The rubbers obtained synthetically from isoprene and other similar hydrocarbons correspond not only to the supposed constitution of Para rubber but also to various analogues of that substance, and exhibit differences in properties which depend upon the constitution of the hydrocarbon from which they are prepared by polymerization and the method by which this change is brought about. Harries classifies synthetic rubbers in one or other of two groups: The first comprising the 'normal' rubbers which are obtained by the polymerization of the unsaturated hydrocarbons brought about by heating them alone or along with acetic acid, the second including the 'sodium' rubbers obtained by the action of the alkali metals, especially sodium, on the hydrocarbons. The two series are not identical, but exhibit various differences. Ostromisslenski, in the course of a discussion of the different synthetic rubbers, claims that the product obtained by the polymerization of β-myrcene differs from all previous synthetic caoutchoucs, being perfectly identical with natural Para rubber."

When discussing the organic accelerators of the vulcanization of rubber, p. 187, the author says: "The organic accelerators differ from such substances as magnesia or oxide of lead in so far that exceedingly small quantities are effective; their action is apparently catalytic in character. In this connection it should be noted that certain organic compounds possess the property of retarding vulcanization, that is to say, appear to act as anticatalysts; among such are phenylhydrazine, methylene blue and glucose.

"As already indicated, most of the effective organic catalysts are basic in character, and their activity is roughly proportional to their alkalinity, a relatively feeble base like aniline having little influence on the rate of vulcanization. The inorganic accelerators in common use are also basic in character. Bearing these facts in mind Twiss was led to attribute the relative advantage attaching to the use of organic bases chiefly to the fact that these substances are soluble in rubber, whereas the inorganic catalysts, being sparingly soluble, are not so uniformly distributed through the mass. He therefore concluded that the alkali hydroxides would prove to be excellent accelerators if a solvent for these compounds could be found which would itself dissolve in rubber. He finally patented the use of glycerol which dissolves approximately 25 percent of potassium hydroxide and a smaller proportion of sodium hydroxide. If from 1 to 2 percent of this solution is added to a rubber-sulphur mixture the vulcanization process is strongly accelerated, the effect being comparable with that of the strongest organic accelerator." *Wilder D. Bancroft*

Chemical Engineering Catalog. *By Francis M. Turner, Jr. Fourth edition. 31 × 25 cm; pp. 1200. The Chemical Catalog Company, Inc., 1919. Price: $5.00.*—The fourth annual edition is an improvement over the preceding three. It presents an enormous mass of information in an easily accessible form and is consequently of great value to all who purchase equipment and materials in the various industries using chemical processes of manufacture. As the publishers point out, the field of the Chemical Industries is a broad and vital one, embracing such lines of manufacture as sugar making and refining, fertilizer, cement, paints and varnishes, prepared foods, leather, textile bleaching and dyeing, paper and pulp, rubber, metals, oils, soaps, extracts, glass and many others in addition to chemicals and acids. It is worth noting how many on this list involve colloid chemistry.

The technical and scientific books section has been expanded very much, 1061 books being listed as against 325 in the 1918 edition. The increase in space from twenty-two to sixty pages has made it possible to include a subject index which simplifies the problem of finding references in regard to a particular topic. In most cases the date of publication of the book is given. This is distinctly valuable because the individual publishers of scientific books are very apt to omit that information from their catalogs.

The fact that the number of firms using space has increased from 132 in 1916 to 604 in 1919 shows that the catalog was needed and that consumers are making use of it. *Wilder D. Bancroft*

PROMOTER ACTION IN CATALYSIS

BY ROBERT NORTON PEASE AND HUGH STOTT TAYLOR

It was recognized early in the development of the field of catalysis that catalysts were very susceptible to inhibition or "poisoning" by impurities originally present in the catalyst or absorbed from the reactants. Thus, Faraday found that the catalytic combination of hydrogen and oxygen in presence of clean platinum voltameter electrodes was markedly inhibited by such diverse substances as carbon monoxide and tap-grease. The fact was further emphasized by the early difficulties experienced in the technical application of the contact sulphuric acid process due to the poisoning of the platinum catalyst by As, Sb, P and Pb compounds present in the converter gases. On the other hand, it has more recently been shown that in certain instances, a foreign substance is able to render the catalyst considerably more active. Such substances are called "promoters" in the patents of the Badische Anilin und Soda Fabrik. The term "promoter action" may be assigned to the corresponding phenomenon. An extract from a Badische patent specification, on improvements in the preparation of hydrogen-rich gases from water-gas and steam, which deals with the function of promoters, may be of interest. The extract runs as follows:

"In the researches on the production of hydrogen from mixtures of carbon monoxide and steam, according to the equation:

$$CO + H_2O \rightleftharpoons CO_2 + H_2$$

we have found that the power of catalytic agents generally can be improved by the presence of certain bodies which may be termed PROMOTERS. We have found, for instance, that the activity of the catalytic agents, especially those consisting of or containing iron, or cobalt, or oxides thereof, and also the catalytic activity of other metals or oxides even such as, by themselves, are less active, can be greatly increased by the addition of certain compounds or bodies to which, as aforesaid, may be given the name, promoters. Thus, the activity of catalytic agents consisting of or containing iron, nickel or cobalt, or oxides thereof, can be greatly increased by the addition of oxygen compounds of chromium, thorium, uranium, beryllium, antimony and the like. Further, a catalytic agent consisting of or containing iron in admixture with less than its weight of nickel, particularly after working for a long time, yields better results than does either iron or nickel when employed by itself..... In many cases, particularly when using catalysts of weak activity, we prefer to employ as promoter a compound which differs considerably from the catalytic agent, in particular with respect to valency, chemical basicity and capability of reduction..... The contact masses containing iron as catalytic agent, and a smaller quantity of nickel, as above described as promoter, bring about rapid and far-reaching conversion without the simultaneous formation of methane, even when a comparatively low temperature is employed, and, as compared with pure nickel, are further characterized (especially when suitable oxides or oxy-compounds are employed as binding agents, or as promoters) by possessing greater stability and less sensitiveness to deleterious influences such as, for instance, fortuitous increase of temperature and impurities in the gas mixture."

In attempting a definition of promoter action at this time, it seems best to make the term rather more comprehensive than the above quotation would suggest and to include under it *all those cases in which a mixture of two or more substances is capable of producing a greater catalytic effect than can be accounted for on the supposition that each substance in the mixture* acts independently and in proportion to the amount present. As far as the study of the literature has revealed, the term "promoter" was first applied in the patents of the Badische Anilin und Soda Fabrik on ammonia synthesis,[1] to substances, themselves inert catalytically, which are able to increase the activity of a moderately good catalyst by admixture with it. Cases of promoter action, however, as here understood, were

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[1] Brit. patent 19,249, 8/16/10, C. A., 6, 1346.

well known prior to this time, as will emerge in the following discussion. Among such, many cases are known in which a mixture of two or more substances—each by itself a moderately good catalyst—is unusually active. It is to such cases that the definition given above more directly applies. Nevertheless, it is reasonable to regard examples in which one or more of the components of the catalyst are by themselves relatively inert as limiting cases of the general rule, particularly, as in many cases to be cited later the efficiency of the promoter by itself as catalyst is at present unknown. When more than one of the components are themselves catalysts a difficulty presents itself in choosing between "promoter" and "promoted" analogous to the difficulty in distinguishing between solvent and solute in liquid mixtures. On the basis of the available data, it is not possible to designate one component as catalyst and the others as promoters even though that may be legitimate particularly in cases in which one component preponderates. The distinction will, therefore, be made between "*activation*" of a catalyst by a substance relatively inert catalytically, or by a small quantity of a relatively active substance, and "*co-activation*" of a number of catalysts each by the rest. Thus in homogeneous catalysis, neutral salt action is a clear case of simple activation, since the salt by itself is without noticeable effect. In the synthesis of ammonia, the iron-molybdenum catalyst furnishes an interesting example of co-activation. Iron and molybdenum are both catalysts for the reaction. A mixture of equal parts of the two, however, is a much superior catalyst to either one alone.

Information on the subject of promoter action is widely scattered through the literature and is in general meagre, being largely limited, in the field of heterogeneous catalysis, to simple statements in patent specifications that certain substances are able to activate some particular catalyst. While it is known that in the industries the field has been developed to a considerable extent, almost no useful information on the subject has found its way into the literature. The purpose of this paper is to collect what information is available and to draw attention to promoter action as a promising field for investigation. Some experimental work on promoter action is at present being carried forward in this laboratory.

It is not intended that the present communication should deal intensively with the causes of promoter action. Rather is the aim to collect examples of such action already to be found in the existing literature. At the same time, it is to be understood that several cases of promoter action have been exhaustively investigated. Especially is this true in the case of neutral salt action in ester hydrolysis and in similar reactions of this type.

In order the better to systematize the material available, the literature had been analyzed with respect to different reactions and differing types of reactions. Thus, the examples of promoter action in the case of a particular reaction have been collected together and are summarized in the succeeding sections. Owing to their more general technical importance, cases of promoter action in heterogeneous catalysis are first discussed.

Promoter Action in Catalytic Hydrogenation Processes

A number of cases of promoter action are known in connection with catalytic hydrogenation processes. The standard catalysts for hydrogenation are the platinum group metals, especially Pd and Pt, which work at room temperatures in some cases, and Ni, Co, Cu and Fe, the activity of these metals decreasing roughly in the order named.

Ipatiew appears to have been among the first to detect promoter action in a heterogeneous system and this quite by accident. He found[1] that in the presence of CuO and in a *copper* tube, amylene was only one-third converted into isopentane by hydrogen at 200 atm. and 300° C in 28 hours; whereas with CuO in an *iron* tube under the same conditions complete conversion was effected in 12 hours. He has repeated this experiment with the same results and has found the same relation to hold in the reactions:

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[1] Ber. deutsch. chem. Ges., 43, 3387 (1910).

tetrahydrobenzene ⟶ hexahydrobenzene
tetrahydrotoluene ⟶ hexahydrotoluene

as well as for the hydrogenation of pinene and carvene.

Badische patents[1] state that for general hydrogenation, such as the hydrogenation of fats, of phenol to cyclohexanol, nitro-benzene to aniline, and oxides of carbon to hydrocarbons, Fe, Ni, Co or Cu may be used as catalysts and may be improved by addition of one or more of the following—often in quantities of less than 1 percent: oxides or oxygen-containing salts of the alkaline earth or rare earth metals or Be, Mn, Mg, U, V, Nb, Ta, Cr, Ti, or B or difficultly soluble phosphates, tungstates or selenates of the alkaline earths (or Li) or compounds of F, Te and Sb, or elementary Te or Sb. An example states that 40 parts $NiCO_3$ and 1 part of ammonium tellurite, ignited and reduced, will hydrogenate cotton-seed oil at 100°. It would be interesting to know what the velocity of hydrogenation was at this temperature since the working temperature of Ni alone is normally nearer 200°.

Another Badische patent[2] for the catalytic reduction of nitro-aromatic compounds to the corresponding amino compounds states that the copper used as catalyst may be considerably improved by addition of Zn, Ag, MgO, Al_2O_3 or sodium silicate. Satisfactory catalysts are: Cu-Zn; pumice impregnated with Cu, Ag and Mg nitrates, ignited and reduced; or 130 g pumice, 24 g $CuCO_3$, 3 g $ZnCO_3$ and 20 g commercial water-glass, ignited and reduced. It may be pointed out that for this reaction, too active a catalyst is undesirable since further hydrogenation of the ring may take place or the compound be completely broken up. Thus, Sabatier and Senderens[3] found that Ni, which is a more active hydrogenation catalyst than Cu, tended to split off NH_3 or even to form CH_4 at 300°. Hence the use of Cu.

Dewar and Liebman state[4] that for the catalytic hydrogena-

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[1] Brit. patent 2306, 1/28/14, C. A., 10, 287; German patent 282,782, 12/12/13, Ibid., 9, 2461.

[2] Brit. patent 5,692, 4/15/15, Ibid., 10, 2510.

[3] Comptes rendus, 133, 321 (1901).

[4] U. S. patents 1,268,692, C. A. 12, 1841; 1,275,405, Ibid., 12, 2139.

tion of fats, Ni, Co and Cu can be activated if two or three of them are mixed together or with finely divided Pt, Pd, Ag or Ag_2O. Another advantage claimed is that the oxides of the metals may be reduced in the fat at ordinary hydrogenation temperatures (180–200°), whereas Ni oxide alone requires a temperature in the neighborhood of 250° for reduction—a temperature which results in some decomposition of the fat. A solution of Cu and Ni nitrates corresponding to 10 percent Cu and 90 percent Ni after evaporation and ignition, yields an oxide which can be reduced at 190° C and the product will hydrogenate cotton-seed oil rapidly at the same temperature.

That a mixture of two catalysts is not in all cases superior to either one alone is indicated by some interesting experiments by Paal and Windisch[1] on catalytic hydrogenation, using as catalysts either platinum or palladium deposited on various other metals. Of the metals used as supports, Ni, Co, Fe and Cu are by themselves hydrogenation catalysts working at temperatures in the neighborhood of 200°, Ni being the most active and Cu and Fe the least, whereas Pt and Pd will work at room temperature. It was found that deposition on Ni and Co had no appreciable effect on the activity of the Pt or Pd while deposition on Fe or Cu rendered the Pt or Pd almost completely inactive even at somewhat increased temperatures and pressures. Thus, those catalysts whose activity is most widely different from the Pt and Pd appear actually to act as poisons. Experiments at considerably higher temperatures to determine whether there was any improvement in the activity of the Fe or Cu catalysts were not made but would be of great interest. Of the other metals employed as supports, all but magnesium completely inhibited the action of the Pt and Pd. On the other hand, the activity with Mg was very high. The activity of magnesium by itself is unknown, but by analogy with effects here produced by Ni and Co would appear to be rather great and is worthy of investigation.

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[1] Ber. deutsch. chem. Ges., 44, 1013 (1911); 46, 4010 (1913).

The results for deposition on Pd are given below. Cottonseed oil was the substance hydrogenated. The catalyst was placed in a shaking vessel connected with a burette containing hydrogen. 2-5 g of oil and 2 g of catalyst were placed in the vessel, connection to the gas burette made and the diminution in volume of hydrogen read off. The experiments were carried out at room temperature and pressure, the results being for the first hour of the run. The efficiency of Pd by itself is not given but is said to be approximately that obtained with Ni, Co and Mg.

Pd Deposited on	Cu	Fe	Ni	Co	Mg[1]		Zn	Al	Ag	Sn	Pd
Weight, Pd—mg	60	60	30	60	60	60	60	60	60	60	60
Weight, metal—g	2	2	2	2	2	1	2	2	2	3	3
H_2 absorbed—cc	2	3	58.4	70.4	104	20	4	0.6	0	0	1

The palladium and platinum were deposited from HCl solutions of their respective chlorides. In certain cases, the inhibition noted may be due to this method of preparation. Thus, in the case of silver, a thin film of AgCl might form a protective coating over the catalyst. However, apart from this, there is evidently a specific effect of support metal on catalyst which is a function of the catalytic activity of the support. A further investigation of this case should yield valuable results in connection with promoter action.

The above investigation was suggested by Ipatiew's observations on promoter action in hydrogenation of an ethylenic linkage (q. v.).

Dehydrogenation of Methyl Alcohol

Hochstetter has found[2] that higher yields of formaldehyde may be obtained from methyl alcohol, in the presence of oxygen, if a catalyst consisting of a mixture of Ag and Cu or one of the Pt group metals is used in place of any one of these metals separately. Two reactions may occur when

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[1] Mg powder was used for the first experiment and ribbon for the second.

[2] U. S. patents 1,100,076, C. A., 8, 2770; 1,110,289, Ibid., 8, 3618.

CH_3OH and air are led over the catalyst. HCHO may be formed by oxidation:

$$CH_3OH + O \rightleftharpoons HCHO + H_2O$$

or by dehydrogenation:

$$CH_3OH \longrightarrow HCHO + H_2.$$

The latter reaction may proceed further to give

$$HCHO \longrightarrow CO + H_2.$$

Pt or Cu deposited on asbestos are energetic catalysts for the complete dehydrogenation of CH_3OH to give CO and H_2 acting at 95° and 300–400°, respectively,[1] although at lower temperatures (200–300°) the reaction proceeds to give more HCHO in presence of Cu, according to Sabatier.[2] Kuznetzov[3] was able to obtain maximum yields of 50 percent and 70 percent with Cu and Ag, respectively, and found that the amount of further decomposition to CO and H_2 depended on the temperature, as Sabatier states. It appears, therefore, that the function of the mixed catalyst is either to accelerate the oxidation reaction (or primary dehydrogenation) or to depress the complete dehydrogenation reaction. Further information as to the course of this conversion and the effect of mixed catalysts on the relative velocities of these reactions would be of interest. Hochstetter emphasizes the fact that "* * such an association of metals as will allow the vapors to contact with each of the metals as individuals" is to be used. He believes that the increased yields (he claims 100 percent conversion) in the presence of two metals are to be explained by the fact that one metal catalyses more particularly the oxidation reaction and the other the dehydrogenation reaction. By causing the two reactions to proceed simultaneously, a more complete conversion is secured. He cites especially as suitable catalysts, a copper tube containing metallic silver; and silver associated with a Pt group metal, particularly rhodium.

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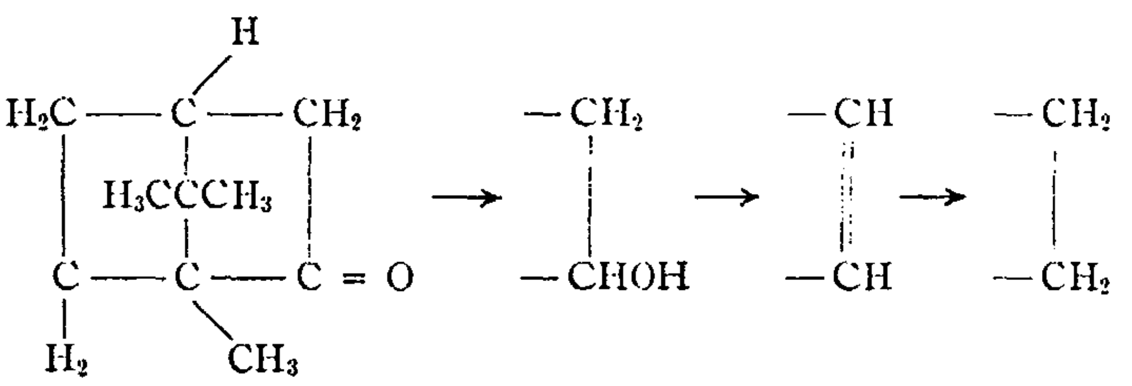
[1] Orlov: Jour. Russ. Phys. Chem. Soc., 39, 855, 1023; C. A., 2, 263, 1692.

[2] La Catalyse en Chimie organique, 161 (1913).

[3] Jour. Russ. Phys. Chem. Soc., 45, 557; C. A., 7, 3126.

An interesting case of promoter action, in which a hydrogenation and a dehydration catalyst appear each to activate the other when the two are used together to carry out a reaction which would ordinarily involve a number of successive steps, has been noted by Ipatiew.[1] The reactions taking place are, hydrogenation of a carbonyl group, dehydration to give an ethylenic linkage and, finally, hydrogenation to give the saturated hydrocarbon.

He found that camphor was hydrogenated in presence of NiO at 320–350° to borneol. This in turn could be dehydrated at 350–360° in presence of Al_2O_3 to camphene, which could then be easily hydrogenated at 240° to give camphane. By using a mixture of NiO and Al_2O_3 in presence of hydrogen, camphor could be converted directly into isocamphane at 200° or less. The steps involved are:



Camphor Borneol Camphene Camphane

Similarly, fenchone[2] may be hydrogenated to give fenchenol in presence of NiO at 240°, but the dehydration of the latter and subsequent hydrogenation of the fenchene are very difficult to effect directly at all. Yet, in presence of a mixture of Al_2O_3 and NiO, fenchone can be directly converted to fenchane at 215° C.

Promoter Action in Ammonia Synthesis

The Badische Company has patented a great number of catalysts for use in ammonia synthesis. One patent covers[3]

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[1] Ber. deutsch. chem. Ges., **45**, 3205 (1912).

[2] Jour. Russ. Phys. Chem. Soc., **44**, 1695; C. A., **7**, 1170.

[3] Brit. patent 19,249, 8/16/10, Ibid., **6**, 1346.

the use of Fe, Ni or Co with Mg, Al, Zr, V, Ta, Cr, Mn, Mo, W, U, Th, Nb, the alkali, alkaline earth or rare earth metals or their compounds. Another[1] covers the use of mixtures of metals or their compounds from different groups or subgroups of the periodic table.

According to Maxted,[2] Fe activated by KOH is probably used in the Badische plants.

The use of the nitrides of the alkali metals with other metals such as Ni has been patented by the General Chemical Company.[3] According to the patent claims, these are particularly active catalysts working at 500–550° C and 30–100 atmospheres as against 200 atmospheres used in the German plants. In an example, a mixture of Co (59 parts) and Na (69 parts) is treated with NH_3 at 300° C and the resulting nitride used as a catalyst for ammonia synthesis at 520–540° and 80–90 atmospheres.

An interesting suggestion has been made as to the function of the mixed catalyst in ammonia synthesis. In the case of the iron-molybdenum catalyst, which is used to a considerable extent, iron is known to be a good absorbing agent for H_2 and molybdenum for N_2. It is possible that the mixture of the two owes its superiority to the bringing together of the two in increased concentrations by means of the mixed catalyst. Indeed, the Badische Company has patented the use of a catalyst which shall consist of one substance capable of absorbing H_2 and another capable of absorbing N_2.[4] Palladium-molybdenum is cited as an example. While there is no direct evidence to support this assumption, the fact that ammonia can be prepared by alternately passing H_2 and N_2 over a catalyst consisting of Mo alone or a mixture containing Mo, in which the absorption of N_2 by Mo would seem to be one step, lends support to the hypothesis.[5]

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[1] Brit. patent 26,167, 12/14/11, C. A., 7, 1958.

[2] Jour. Soc. Chem. Ind., 36, 777 (1917).

[3] U. S. patents 1,151,537, 1,159,365, 1,143,366, *e. g.*, C. A., 9, 2295.

[4] Brit. patent 21,151, 9/25/11, Ibid., 7, 1083.

[5] German patent 265,294, 5/3/12, Ibid., 8, 408.

Promoter Action in Ammonia Oxidation

In the catalytic oxidation of ammonia, Maxted[1] has published curves indicating the relative efficiencies of iron alone and admixed with other metals as promoters. The percentage compositions are not stated nor are any data available to show

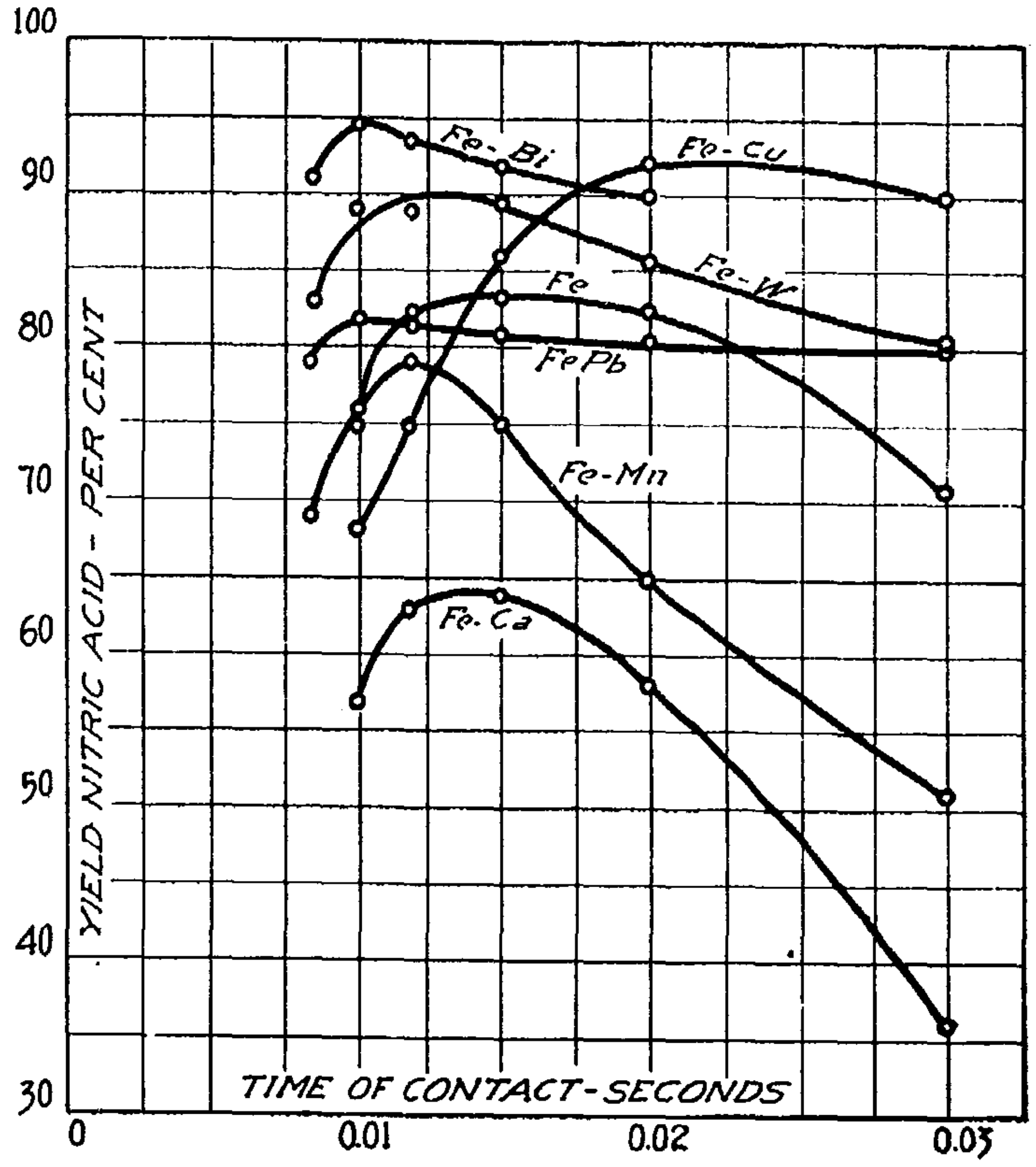

Fig. 1

the efficiencies of the promoters by themselves. It seems probable, however, that the mixtures are those of maximum activity in each case and that the promoters, with the exception of Cu, are not particularly active by themselves since their

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[1] Jour. Soc. Chem. Ind., 36, 777 (1917).

use has not been patented. An examination of the accompanying curves (Fig. 1) indicates that Bi, W and Cu (also Th and Ce) render the iron considerably more active while Ca and Mn have the opposite effect. Addition of Pb gives a very flat curve, that is, the yield of nitric acid, though low in any case, is not appreciably affected by the rate of passage of the gases over the catalyst. The Fe-Sb mixture was found to give high initial results (as would be expected from the close relationship of Sb to Bi) but to approximate to the value for iron alone after a short time, probably because of the slow oxidation of the Sb and volatilization of the oxide. KOH had little effect on the activity of the iron.

Maxted and Ridsdale[1] claim that tubes of Fe, Ni, Co, Cu or Pt alone or coated with the corresponding metals, by treating with a solution of Cu, W, Ce, Th, Bi or Pb nitrate and reducing, are satisfactory catalysts. The above-mentioned metals may also be "coupled" with Cu or Ag. They have also patented[2] the use of a mixture of iron oxide, oxide of a metal electro-negative to Fe, which will be reduced but not fused under working conditions, such as Cu, and the oxide of an alkaline earth metal. A mixture of Fe, Cu and Ca nitrates is precipitated by NaOH or Na_2CO_3 and the precipitate molded, dried, calcined and used as a catalyst.

Some of the catalysts given in the Badische patents for oxidation of ammonia[3] are mixtures of substances from any two of the following groups:

oxides of metals of the iron group
oxides of the rare earth metals
Bi oxide.

One such was presumably in use at the plant at Oppau.

Examples: Fe and La or Yt oxides
Fe and Bi oxides.

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[1] Brit. patent 126,083, 12/4/16, C. A., 13, 2259.

[2] Brit. patent 10781, 7/26/15, Ibid., 13, 1625.

[3] Brit. patent 13,848, 6/18/14, Ibid., 9, 3338.

Other Badische patents[1] give metals of the iron group with Bi or its compounds. Thus, 45 parts Fe or Mn nitrate with 1 part Bi nitrate, precipitated with NH_3, dried and heated, will give a 90 percent yield of oxides of nitrogen at 700° C. Again it is stated that Bi or its compounds plus Ti, Si or MgO or that Pt group metals deposited on carriers and activated by Bi may be used. Te or its compounds may be substitued for Bi or its compounds. Other examples given are granular copper oxide impregnated with ammonium telluride and one or more of Ag, Au and the Pt group metals with tellurium or its compounds.[2] A later patent covers the use of lead or its compounds as promoters.[3]

In the United States, platinum gauze containing iridium is used as catalyst for this reaction. The function of the iridium is merely to increase the mechanical strength of the gauze, the activity of the platinum not being appreciably altered by its presence in small quantities.[4]

Contact Sulphuric Acid Process

Experiments have been conducted to discover cheap substitutes for platinum catalysts in the contact sulphuric acid process. Burnt iron pyrites appears to be the only one that has been used on a large scale. According to Rideal and Taylor,[5] oxides of Cu, V, U, Cr, Ni or Co incorporated with oxides of Al, Be, Zr or Zn have been suggested.

It is of interest that arsenic oxide, which acts as a poison to Pt catalyst, is itself a fair catalyst for the reaction, working at a somewhat higher temperature. In other words, a mixture of these two catalysts, working separately at somewhat different temperatures, is by no means better than the platinum alone. Whether or not it is superior to the arsenic oxide alone,

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[1] German patents 283,824, 4/15/14, C. A., 9, 2577; 287,009, 5/24/14, Ibid., 10, 1583.

[2] Brit. patents 7,651, 5/21/15, Ibid., 10, 2971; 13,297, 5/21/15, Ibid., 11, 528.

[3] Brit. patent 13,298, 5/21/15.

[4] Parsons: Jour. Ind. Chem. Eng., 11, 549 (1919); see, however, Perley: Ibid., 12, 11 (1920).

[5] "Catalysis in Theory and Practice," p. 87 (1919).

is not stated. The problem of the behavior of mixed solid catalysts will be seen to be complicated by the difficulty of estimating the surface of each exposed and by the fact that they may work alone at quite different temperatures. A case similar to that described above will be found under "Catalytic Hydrogenation."

Preferential Combustion of Carbon Monoxide in Presence of Hydrogen

Harger and Terry[1] have found that carbon monoxide present in hydrogen may be preferentially oxidized in the presence of certain catalysts, the hydrogen being practically untouched provided the temperature is not too high. The process consists in leading H_2 containing small quantities of CO and a little more than enough oxygen to combine with the CO over the catalyst at suitable temperatures and rates of flow. In the examples given, the catalysts are the mixed oxides of

Fe, Cr and Ce, or Th, or both
Fe, Cr, Al and Ce
Fe, Bi and Ce.

The following experimental results are contained in the patent specifications. A catalyst is prepared by dissolving in water:

194 parts ferric nitrate
5 parts ammonium bichromate
1 part thorium nitrate.

The solution is evaporated and the residue calcined at a low temperature. Hydrogen containing 1.5 percent CO with air was passed over this catalyst at different rates of flow and the CO_2 in the effluent gases determined. 10 cc of catalyst were used.

Temp. °C	Rate Lit/Hour	Percent CO_2
260	10.5	1.5
255	15.0	1.5
240	12.0	1.5
215	9.0	1.5
190	9.0	1.0

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[1] Brit. patent 127,609, 4/28/17.

The CO was completely removed in all but the last experiment at the lowest temperature.

The mixed oxides named above have been found to be the most satisfactory. The working temperature of iron oxide alone is about 300° C.

Rideal and Taylor[1] have applied the above process to the determination of small quantities of CO in hydrogen. They find that whereas iron oxide alone is catalytically active at 300°, addition of chromium oxide lowers the working temperature to about 250°, while a mixture of 97 parts iron oxide, 2.5 parts chromium oxide and 0.5 parts cerium oxide gives a catalyst working at 180°.

The Water Gas Reaction

Promoter action has been studied in connection with the water gas reaction carried out catalytically at low temperatures for the removal of carbon monoxide from hydrogen. The reaction involved is:

$$CO + H_2O \rightleftharpoons CO_2 + H_2.$$

The following table will give an idea of the effect of adding various promoters to the iron oxide catalyst. The results are for a water gas containing 25 percent CO and 75 percent H_2, steam having been introduced to make the steam-H_2 ratio 2 : 1. The term space velocity is used to express the ratio of cc gas per hour to cc apparent volume of catalyst and may be taken, together with the quantity of carbon monoxide converted, as a measure of the activity of the catalyst.

The following catalysts were employed after ignition:

(1) Spathic iron ore ignited at 600° C.
(2) 85-Fe nitrate and 15-Cr nitrate
(3) 40-Fe nitrate, 5-Cr nitrate and 5-Ni nitrate
(4) 194-Fe nitrate, 5-$(NH_4)_2Cr_2O_7$ and 1-Thorium nitrate.

All tests were made at 440-450° C.

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[1] The Analyst, **44**, 89 (1919).

Catalyst	(1)	(2)	(3)	(4)
Gas flow—lit/hour	3.1	21.5	8	16
Apparent volume, catalyst—cc	5	3	2	3
Space velocity	620	7000	4000	5300
Percent CO_2 in effluent	20.2	24.5	25.2	25.0

With iron oxide alone, the oxidation was incomplete at the relatively small space velocity of 620. Addition of approximately 3 percent of chromic oxide and 0.5 percent thorium oxide resulted in complete conversion at a space velocity of 5300—over eight times as great.

In the results given above, the comparatively great effect produced by so small quantities of promoters becomes somewhat more explicable if one takes into account the fact that the catalysts were prepared by evaporation of a solution of the soluble salts of the metals and subsequent ignition. In the evaporation, the promoters, being present in small quantities, will only begin to deposit toward the end of the evaporation while the iron oxide begins to come down fairly early as a flocculent precipitate. This forms a pasty mass on the surface of which it is to be expected that the promoter salts will be slowly deposited. The mass is stirred during the evaporation. The promoter will therefore presumably be largely concentrated on the surface of the iron oxide finally obtained, where the gas reaction is subsequently to take place. An experimental test of the validity of this view-point would not be without interest.

The Badische Company have made comprehensive claims in the case of this reaction also. Thus, one patent[1] states that suitable catalysts are mixtures of Fe, Ni or Co oxides with Cr, Th, Ce, U, Be or Sb oxides; Fe, Ni and Cr oxides; Fe, Cr and Th oxides; Zn, Pb, Cu, V, Mn or Ti oxides with a promoter; and oxides of the following pairs of metals: Zn-Cr, Pb-W, Cu-Zr, Mn-Cr, Ti-Sb, V-Cr and Ce-Cr.

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[1] Brit. patent 27,963, 12/4/13, C. A., 10, 97.

The Incandescent Mantle

Auer von Welsbach has found that additions of small quantities of ceria to the thoria used as refractory in incandescent mantles considerably increased the light emissivity, the latter reaching a maximum for the mixture, 99.1 percent thoria, 0.9 percent ceria.

If one may consider that the thoria acts in part as a catalyst for the oxidation of the gas, then it would not appear improbable that the ceria played the rôle of a promoter. It has usually been assumed that the thoria acts simply as a radiator and that the ceria is possibly an oxygen carrier. From the point of view of catalysis, we are dealing here with a case of surface combustion. The mantle is a catalyst for the oxidation of illuminating gas. In the light of this, the increased emissivity of a mantle containing ceria is due in part at least to more rapid combustion, which results in the mantle attaining a higher temperature. In general, ceria appears to be especially useful as a promoter in oxidation reactions. A direct determination of the catalytic activity in this reaction, of thoria, alone and containing small quantities of ceria, would be of interest. Discovery of a maximum in catalytic activity corresponding to the maximum in light production would go a long way toward explaining what is at present a very puzzling phenomenon.

As already mentioned, 0.5 percent of ceria has a marked accelerative influence on the catalytic preferential combustion of CO in presence of H_2 by the iron-chromium oxide catalyst. It is not known whether or not there is in this case a maximum activity corresponding to a small amount of ceria. A study of this point would be of interest.

Hydrolysis—The Twitchell Reagent

The Twitchell reagent for the saponification of fats furnishes a very interesting example of what may properly be considered as intra-molecular promoter action.

It has been known for a long time that sulphuric acid is a catalyst for the saponification of fats. If the fat is mixed with 2–3 percent H_2SO_4, heated for a short time at 150° and then boiled with water, hydrolysis takes place. The preliminary heating is essential and is supposed to lead to the formation of stearo-sulphonic acid, which then acts as a catalyst for the reaction.

Twitchell has found that by introducing a benzene or naphthalene ring into this compound, thus forming benzene- (or naphthalene-) stearo sulphonic acid, a much superior catalyst is obtained. This substance is much more stable than stearo-sulphonic acid, not being hydrolyzed even by boiling water, when the latter is very largely hydrolyzed. It is more soluble in both fat and water and is highly ionized, which property an efficient catalyst for hydrolysis must possess. About 0.5 to 1.0 percent of this catalyst is sufficient.

The benzene or naphthalene ring may be regarded as a sort of promoter which has been added to the stearo-sulphonic acid molecule.

Siccatives

The drying of oils, such as linseed oil, when exposed to air is an oxidation process, and it is generally agreed that the action is auto-catalytic, that is, a catalyst appears to be formed in the oil during the reaction. This is shown by the fact that the velocity "constant" increases markedly in the initial stages of the reaction. The auto-catalyst is probably a peroxide of the oil.

It has been found that addition of various substances, known as "siccatives," such as salts and especially organic salts soluble in the oil, accelerates the oxidation considerably. Mn, Pb, Zn, Co, V and W are suitable metals employed in the form of salts such as the borates and especially soaps such as lead oleate, manganese rosinate and cobalt linoleate. The inorganic salts, being insoluble in the oil, are much less effective and in some cases the solid particles appear to inhibit the reaction by assisting in the decomposition of the auto-catalytic peroxides.

It is a matter of uncertainty whether the siccative itself acts as a catalyst or is in reality a promoter which accelerates the reaction by hastening the formation of the auto-catalyst or by giving it greater stability.

Ingle and Mackey[1] have come to the following conclusions with regard to the action of different siccatives:

1. When present as a soap soluble in the oil, those metals which exist in more than one state of oxidation act as driers, provided the salts of the lower oxides are the more stable.
2. Metals which form a number of oxides are the more active.

It was found, however, that sodium and silver, which are univalent, were more active than this fact would lead one to expect.

Promoter Action in Homogeneous Catalysis

Several well defined cases of promoter action in homogeneous liquid systems have been investigated. Few problems in catalysis have been more thoroughly studied than that of ester hydrolysis by hydrogen-ion catalysts and certainly no case of promoter action has received so much attention as has the accelerative action of neutral salts of strong acids on the catalytic effect of the corresponding acid. It is beyond the scope of this paper to describe in detail the work that has been done or to summarize the literature. (For such a summary one may consult Lewis: System of Physical Chemistry, Vol. I, p.423 et seq. (1918).)

The reaction

$$RCOOR_1 + H_2O \rightleftarrows RCOOH + R_1OH$$

is known to be catalyzed by hydrogen-ion, If, in addition to a strong acid, a neutral salt of that acid is added to the reaction mixture, it is found that the velocity of the reaction is increased rather than diminished as would be expected from the fact that according to the law of mass action, the dissociation of the acid (and therefore the hydrogen-ion concentration) is repressed by addition of the ion possessed in common by both acid and salt. As the neutral salt by itself has no appreciable effect on the hydrolysis, this is clearly a case of

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[1] Jour. Soc. Chem. Ind., 35, 454 (1916); 36, 317 (1917).

simple activation—which is, however, not as simple as it sounds if one may judge by the amount that has been published on the subject.

A number of cases of co-activation in homogeneous liquid systems have been observed.

Bredig and Brown[1] have found that in the catalytic oxidation of aniline by sulphuric acid according to the equation

$$(C_6H_5NH_2)_2SO_4 + 28H_2SO_4 \longrightarrow (NH_4)_2SO_4 + 28SO_2 + 12CO_2 + 3H_2O,$$

$CuSO_4$ and Hg_2SO_4 are together more active than their separate catalytic activities would lead one to expect.

The progress of the reaction was followed by means of the volume of gas evolved, the above equation being quantitative for very dilute aniline solutions. In Fig. 2 are given curves representing total volume of gas evolved against time. Curves I and II are for Hg_2SO_4 and $CuSO_4$, respectively, alone. Curve III gives the value calculated for the two used together on the assumption that they act independently,

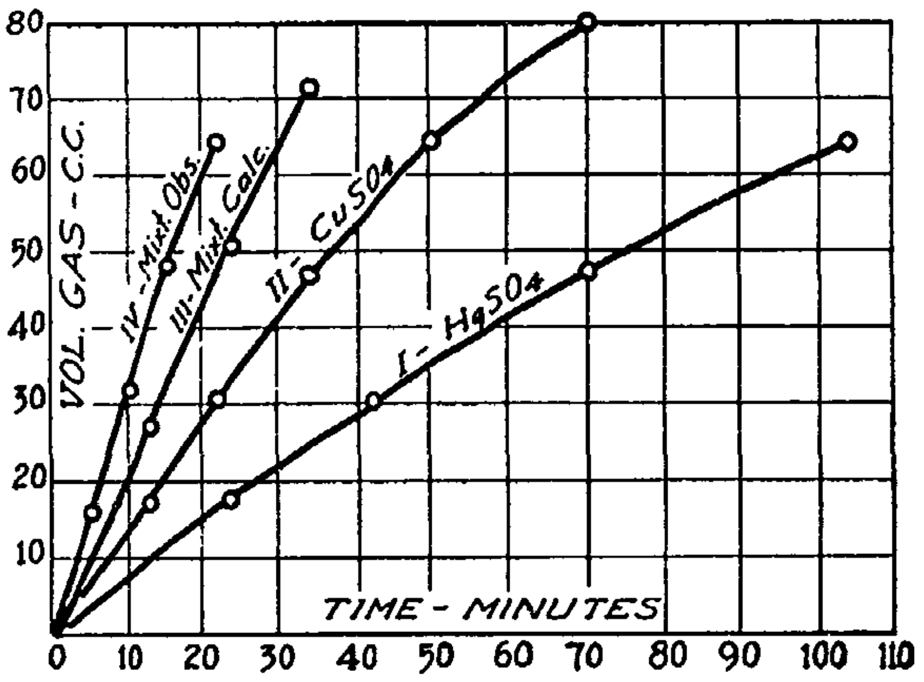

Fig. 2

Oxidation of aniline sulphate by conc. H_2SO_4 in presence of various catalysts. Temp. 275° C $(C_6H_5NH_2)_2SO_4$ = 0.0556 g; $CuSO_4$ = 0.3746 g; Hg_2SO_4 = 0.14 g; H_2SO_4 = 44.0 cc

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[1] Zeit. phys. Chem., 46, 502 (1903).

that is, that their effects would be simply additive and Curve IV gives the observed results for the mixed catalyst. It is clear that the observed velocity for the mixed catalyst is greater than that calculated; that is, the two catalysts have activated one another. Bredig and Brown consider that a reciprocal oxidation and reduction of Cu and Hg may be the cause of these unusual results. As no further results for other pairs of salts are given, it is not possible to say whether either one of these two is particularly susceptible to activation or what relation holds between the acceleration noted and the proportion of salts present.

Price[1] has very thoroughly studied the effects of catalysts on the reaction

$$K_2S_2O_8 + 2KI \rightleftharpoons 2K_2SO_4 + I_2.$$

He has found that the effects of $CuSO_4$ and $FeSO_4$ together are more than additive. Below are given the accelerations observed and those calculated on the assumption that the effects were additive.

N/80 $K_2S_2O_8$ *N*/40 KI

Conc. Catalysts—Each Molar	Acceleration	
	Observed	Calculated
1/16000	525	190
1/32000	238	99
1/64000	122	51
1/128000	64	27

It will be noted that the observed accelerations are considerably greater than the calculated.

$FeSO_4$ alone is rather active; $CuSO_4$ is only slightly so. $MnSO_4$ and $ZnSO_4$, which are also only slightly active, each gave results with $FeSO_4$ which were less than additive. With $CuSO_4$ they gave additive results.

Similar results were obtained by Brode[2] in the reaction

$$H_2O_2 + 2HI \rightleftharpoons 2H_2O + I_2.$$

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[1] Zeit. phys. Chem., 27, 499 (1893).

[2] Ibid., 37, 257 (1903).

$FeSO_4$ was found to be a good catalyst for the reaction and $CuSO_4$ a rather poor one. A mixture of the two was found to be extremely active as Traube[1] had previously reported. The latter suggested its use in testing for H_2O_2 in the presence of acids with starch-KI.

This probably represents the first observation of promoter action.

Enzyme Action

Cases of promoter action are to be found in the field of enzyme action. A number of these, taken from Bayliss: "The Nature of Enzyme Action" (1914), will be given.

Effront has found that amylase, which is present in malt, and converts starch into maltose, was rendered considerably more active by the addition of asparagine (p. 103).

Mendel and Blood have found that papain was activated by HCN and H_2S. No others of a number of substances tried had a similar effect. This is puzzling since the only distinctive property which these two possess in common, beside a low hydrogen-ion concentration, is their reducing action, which has no apparent connection with the hydrolysis of proteins.

The action of laccase, an oxidizing enzyme present in the pancreatic juice, is accelerated by the presence of manganese salts and, in general, manganese and iron have a decided influence on the action of various oxidases. Since one or other of these substances is always present in the ash of these enzymes, Bayliss suggests that the enzyme may simply be a means of rendering these metals extremely active and that addition of the salts to the enzyme merely increases the concentration of the former present in the active state. Indeed, Dony-Henault has been able to prepare artificial laccase by precipitation with alcohol of a solution of gum arabic, manganese formate and acid sodium carbonate, which is about as active as true laccase.

Enzymes have been found to be especially susceptible

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[1] Ber. deutsch. chem. Ges., 17, 1062 (1884).

to electrolytes as would be expected because of their colloidal nature (p. 102). Thus, Cole has found that ptyalin was much more active in the digestion of starch in the presence of acids in low concentrations and of neutral salts. Somewhat similar results were obtained with invertase. Again, trypsin is activated by low hydroxide-ion concentrations while practically inert in neutral or acid solution (p. 87).

It is possible that the auto-accelerative property of invertase noted by Victor Henri (p. 88) is due to the formation of acids during the reaction. As mentioned above, acids activate invertase and it does not appear improbable that this may be the explanation. The fact that Kullgren has observed the formation of acids in the inversion of cane sugar at 100° is significant. Such an example of auto-catalysis, if authentic, is to be distinguished from simple auto-catalysis, in which a reactant or product has a direct catalytic effect on the reaction. Here the specific effect of the product is on the catalyst. Bayliss recognizes this, but is inclined to include both under the term "auto-catalysis," From the point of view of promoter action such a term as "auto-activation" or "auto-promotion" would be more appropriate.

Co-Enzymes

Certain enzymes furnish us with a special limiting case of promoter action which has no analogue in other fields of catalysis. It is sometimes observed that an enzyme is completely inactive in the absence of certain substances called "co-enzymes" or is made up of two or more components, each by itself inactive. Thus, Harden and Young (p. 124) have found that if zymase be dialyzed under pressure, the colloid left on the gelatin is inert, but becomes active again on addition of a portion of the filtrate, which is also inactive by itself. It was further found that the filtrate contained two substances, both of which were required to activate the non-dialyzed portion. One of these was soluble inorganic phosphate, which is known to accelerate the action of the original yeast juice. The nature of the other substance is not known, but its existence is proven by the fact that phosphates alone are not able to bring about the activation.

Magnus has obtained similar results with extract of liver, which contain lypase. Loevenhart has shown that bile salts possess all the properties of the co-enzyme in this case and can probably be so designated.

Many other examples of this phenomenon might be cited in which the co-enzyme is an inorganic salt. Thus Bierri, Giaja and V. Henri have found that dialyzed pancreatic juice, which is inactive, can be rendered active by addition of chloride or bromide-ion.

. . . .

As to the explanation of the phenomena here grouped together, it can only be pointed out that since catalysis itself is as yet unformulated one cannot at present expect to elucidate promoter action. If the intermediate compound theory of catalysis were the correct one it might be assumed that the promoter was in reality a catalyst for the formation or decomposition of the intermediate compound, thus hastening reaction. If the explanation of catalysis is to be found in the surface condensation or adsorption theory, that is, if catalysis depends upon certain surface characteristics of the catalyst, the catalytic influence of a mixture of substances would not be expected to be consistently additive, for this is not the case with the properties of mixtures in general.

It seems likely that a study of promoter action may lead to at least a partial solution of the problem of catalysis. By its means it is possible to alter the properties of a catalyst as gradually as desired while keeping its general nature qualitatively the same. Some uncertainty must attach to deductions arrived at by comparison of measurements on totally distinct substances used as catalysts. Necessary differences in manner of preparation alone will result in this. On the other hand, a series of catalysts containing varying quantities of promoter can be made up and used under conditions which will at least vary in a regular manner even though they may not be precisely the same in each case.

Summary

In this paper, promoter action in catalysis has been defined and a distinction made between two types which have been termed "activation" (of a catalyst by a substance relatively inert catalytically) and "co-activation" (of two or more catalytically active substances each by the others). This is followed by a number of examples from heterogeneous and homogeneous catalysis and from enzyme action.

Princeton, N. J.
January, 1920

A COMPARATIVE METHOD FOR DETERMINING VAPOR DENSITIES. II

BY PHILIP BLACKMAN

Expansion of the Mercury

It is interesting to note that $(V_1 + V_2) > (v_1 + v_2)$. When the apparatus is heated, the mercury must expand, and as the expansion of mercury is about seven times that of glass, the mercury can expand mainly only at the expense of the volumes of the gases in the bulbs; consequently the sum of the gas-volumes at $t_2°$ is less than the sum of the air-volumes at $t_1°$. The coefficient of cubical expansion of mercury is 0.00018; if its volume at $t_1°$ be M, then its volume at $t_2°$ is $M(1 + 0.00018[t_2 - t_1])$, and the increase $= M(t_2 - t_3)\,0.00018$; and so—not neglecting the comparatively insignificant expansion of the glass—

$$v_1 + v_2 + M(t_2 - t_1)0.00018 - (v_1 + v_2)(t_2 - t_3)0.000026 = V_1 + V_2.$$

This consideration, however, does not in any way affect or enter into either the practice or the theory of the method.

Expansion of the Glass-Bulbs

One may, with justice, assume that allowance should be made for the expansion of the bulbs; but, as is shown here, it may be entirely left out of account in practice.

Let the room-temperature when v_1 and v_2 are measured be $t_3°$ (it will not differ considerably from $t_1°$).

The coefficient of linear expansion of glass is 0.0000086; therefore the coefficient of cubical expansion is 0.0000086 × 3 = 0.000026 nearly.

At $t_2°$, v_1 was $v_1\,(+ [t_2 - t_3]\,0.000026)$ and v_2 was $v_2(1 + [t_2 - t_3]\,0.000026)$. Substituting these corrected values for v_1 and v_2, respectively, in the formula, we have

$$\left\{ \frac{(p-m)\left(V-\frac{w_1}{s_1}\right)}{V-\frac{w_1}{s_1}} \pm m_1 \right\} \left\{ \frac{1}{273+t_1} \right\}$$

$$\left\{ \frac{V_1-\frac{w_1}{s_1}}{v_1(1+[t_2-t_3]0.000026)} - \frac{V_2-\frac{w_2}{s_2}}{v_2(1+[t_2-t_3]0.000026)} \right\}$$

$$\pm \frac{m_2}{273+t_2} + \frac{31068\,w_1}{d_1v_1} = \frac{31068\,w_2}{d_2v_2}$$

or

$$\left\{ \frac{1}{1+(t_2-t_3)0.000026} \right\} \left\{ \frac{(p-m)\left(V-\frac{w_1}{s_1}\right)}{V_1-\frac{w_1}{s_1}} \pm m_1 \right\}$$

$$\left\{ \frac{1}{273+t_1} \right\} \left\{ \frac{V_1-\frac{w_1}{s_1}}{v_1} - \frac{V_2-\frac{w_2}{s_2}}{v_2} \right\}$$

$$\pm \frac{m_2}{273+t_2} + \frac{31068\,w_1}{d_1v_1} = \frac{31068\,w_2}{d_2v_2}.$$

On making the actual calculations, the term

$$\frac{1}{1+(t_2-t_3)0.000026}$$

reduces the value of

$$\left\{ \frac{(p-m)\left(V-\frac{w_1}{s_1}\right)}{V_1-\frac{w_1}{s_1}} \pm m_1 \right\} \left\{ \frac{1}{273+t_1} \right\} \left\{ \frac{V_1-\frac{w_1}{s_1}}{v_1} - \frac{V_2-\frac{w_2}{s_2}}{v_2} \right\}$$

by at most 0.01, thus producing a change of ±0.01 in the value of $31068\,w_1/d_1v_1$, equivalent to less than ±0.1%, which is insufficient to produce any alteration in the first decimal figure of d_2.

In an experiment with diethyl ether, $(C_2H_5)_2O$ — d_1 = 37.0, s_1 = 0.73— and ethyl alcohol, $C_2H_5.OH$ — d_2 = 23.0, s_2 = 0.79 — p = 753 mm, $t_1°$ = 16, t_2 = 185°, t_3 = 15°, m = 3 mm, m_1 = 0, m_2 = —15 mm, V = 3.25 cc, V_1 = 3.55 cc, V_2 = 3.75 cc, v_1 = 3.00 cc, v_2 = 4.05 cc, w_1 = 0.0605 gram, w_2 = 0.0524 gram, (A cooled), (M = 8.2) then assuming d_1 = 37.0, d_2 unkown, d_2 calculated = 22.986 and 22.983.

If in the equation

$$\left\{\frac{(p-m)\left(V-\frac{w_1}{s_1}\right)}{V_1-\frac{w_1}{s_1}} \pm m_1\right\}\left\{\frac{1}{273+t_1}\right\}\left\{\frac{V_1-w_1/s_1}{v_1}-\frac{V_2-w_2/s_2}{v_2}\right\}$$

$$\pm \frac{m_2}{273+t_2}+\frac{31068\,w_1}{d_1v_1}=\frac{31068\,w_2}{d_2v_2},$$

(I) w_2 is put equal to O, the equation becomes

$$\left\{\frac{(p-m)\left(V-\frac{w_1}{s_1}\right)}{V_1-\frac{w_1}{s_1}} \pm m_1\right\}\left\{\frac{1}{273+t_1}\right\}$$

$$\left\{\frac{V_2}{v_2}-\frac{V-\frac{w_1}{s_1}}{v_1}\right\}-\frac{m_2}{273+t_2}=\frac{31068\,w_1}{d_1v_1}.$$

(NOTE. $+\frac{m_2}{273+t_2}$ in the original equation, because as is seen under I further on, the mercury in B stands on a higher level than in A); and (II) w_2 is put equal to O, the equation becomes

$$\left\{\frac{(p-m)V}{V_1} \pm m_1\right\}\left\{\frac{1}{273+t_1}\right\}$$

$$\left\{\frac{V_1}{v_1}-\frac{V_2-\frac{w_2}{s_2}}{v_2}\right\}-\frac{m_2}{273+t_2}=\frac{31068\,w_2}{d_2v_2}.$$

(NOTE. $-\frac{m_2}{273+t_2}$ in the original equation, because as is seen under II further on, the mercury in B stands on a lower level than in A).

These two equations show that the apparatus may be used in two ways for determining the vapor density of a substance *directly* (that is, without having to employ a second substance for comparison) thus greatly simplifying the manipulation and reducing the chances of error.

The following are brief but clear descriptions of the simplified alternative methods.

I and II

In both cases the apparatus consists of two bulbs (4 to 6 inches long), made of disused graduated tubing (*e. g.*, burette) joined together by a narrow U-tube (see Note 1 at the end). The bulbs are open at the free ends which are drawn off narrow. They are filled at least half full with pure dry mercury. The substance to be experimented on is introduced into a thin glass tube (see Note 2)—which has been previously weighed—and weighed, the difference giving the weight w_1 or w_2 (see I or II, respectively) of the enclosed substance (see Note 3).

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The weighing tube is placed in one bulb A (Fig. 1), which is sealed, and when it has cooled to room-temperature $t_1°$ the position of the mercury is noted, so that the volume V of the contained air can be afterwards determined. The difference in height m between the mercury levels is measured (see Note 4). The external atmospheric pressure p is observed, and the specific gravity s_1 of the substance is determined (Fig. 2).

The other bulb, B, is sealed, and when it has cooled to room-temperature, the positions of the mercury in A and B are noted in order to determine later the respective volumes V_1 and V_2 of the air enclosed. The difference in height m_1 between the mercury levels is measured (Fig. 3).

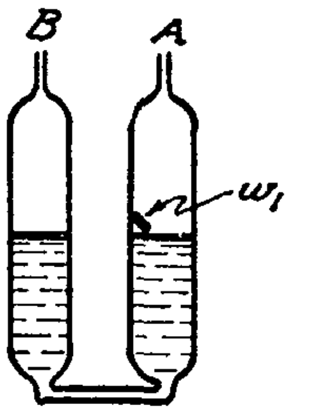

FIG. 1

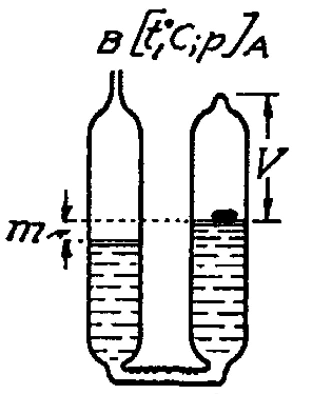

FIG. 2

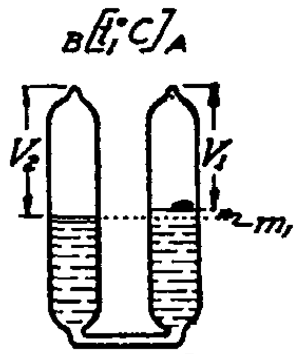

FIG. 3

The apparatus is placed upright in a deep beaker containing a suitable heating medium, *e. g.*, glycerin or paraffinwax, and heated to t_2° to cause complete vaporization of the substance. The positions of the mercury in A and B are noted in order to measure later the respective volumes v_1 and v_2 of the enclosed gases and also to determine the difference in height m_2 between the mercury levels (Fig. 4).

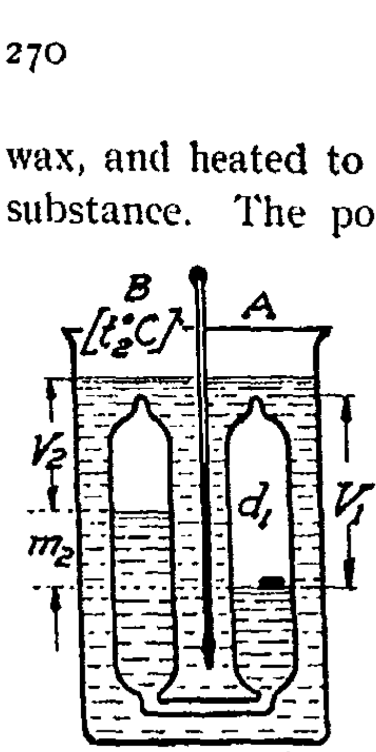

FIG. 4

The apparatus is removed, the room-temperature t_3° is noted; m_2 is measured; the bulbs are cut off, the mercury is removed, and mercury is poured into the bulbs from a burette to determine V, V_1, V_2, v_1, and v_2 (see Note 5). All measurements throughout are carried out with the apparatus in a vertical position. The vapor density d_1 is then calculated from the formula

$$\left\{\frac{(p-m)\left(V-\frac{w_1}{s_1}\right)}{V_1-\frac{w_1}{s_1}} \pm m_1\right\}\left\{\frac{1}{273+t_1}\right\}\left\{\frac{V_2}{v_2}-\frac{V_1-\frac{w_1}{s_1}}{v_1}\right\}-\frac{m_2}{273+t_2}$$

$$= \frac{31068\,w_1(1+[t_2-t_3]0.000026)}{d_1v_1} \qquad \ldots\ldots\ldots\ldots(1)$$

or from the almost equally accurate but simpler formula

$$\left\{\frac{(p-m)V}{V_1} \pm m_1\right\}\left\{\frac{1}{273+t_1}\right\}\left\{\frac{V_2}{v_2}-\frac{V_1}{v_1}\right\}-\frac{m_2}{273+t_2}$$

$$= \frac{31068\,w_1(1+[t_2-t_3]0.000026)}{d_1v_1} \qquad \ldots\ldots\ldots\ldots(2)$$

or (when no great degree of accuracy is required) from the formula

$$\left\{\frac{(p-m)V}{(273+t_1)V_1}\right\}\left\{\frac{V_2}{v_2}-\frac{V_1}{v_1}\right\} = \frac{31068w_1(1+[t_2-t_3]0.000026)}{d_1v_1} \quad ..(3)$$

(for $\{1 + [t_2 - t_3]0.000026\}$ see Note 6).

See Table I.

TABLE I

	p mm	t_1°	t_2°	t_3°	m mm	m_1 mm	m_2 mm	V cc	V_1 cc	V_2 cc	v_1 cc	v_2 cc	w_1 gram	s_1	d_1			
															(1)	(2)	(3)	Theory
Toluene	750	14	197	15	3	—2	46	4.25	4.55	4.70	6.50	2.50	0.0265	0.87	46.0	46.2	45.4	46.0
Pyridine	753	13	188	15	1	—4	47	3.95	4.15	4.10	6.00	2.00	0.0250	1.00	39.5	39.6	38.2	39.5
Methyl alcohol	756	15	120	16	3	4	45	4.15	4.35	4.00	6.10	2.05	0.0093	0.78	15.9	15.4	15.4	16.0
Ethyl alcohol	763	16	157	16	4	—3	51	3.60	3.80	5.85	7.45	2.00	0.0314	0.80	22.4	22.6	21.9	23.0
Methyl cyanide	765	18	127	19	2	2	57	4.05	4.35	5.00	7.05	2.10	0.0171	0.79	18.1	18.2	17.5	20.5
Ethylene chloride	764	17	171	18	4	2	23	3.05	3.15	4.20	5.20	1.95	0.0322	1.26	49.5	49.6	49.2	49.4
Ether (diethyl)	767	18	164	19	7	—15	47	3.15	3.45	5.45	6.10	2.50	0.0270	0.72	37.2	37.3	35.9	37.0
Carbon tetrachloride	766	14	188	16	6	3	62	5.65	5.95	5.95	8.25	3.35	0.0516	1.61	76.9	77.1	73.6	76.9
Acetone	766	19	173	19	8	1	39	4.80	4.95	5.00	7.05	2.65	0.0190	0.79	29.0	29.0	28.2	29.0
Chloroform	751	17	150	19	5	—1	43	4.55	4.85	4.65	6.50	2.70	0.0284	1.50	58.0	58.0	57.9	59.7
Acetaldehyde	752	14	155	16	2	3	43	4.00	4.20	4.35	6.00	2.45	0.0123	0.80	24.7	24.7	23.9	22.0
Amyl nitrite	754	16	181	18	3	—5	41	4.55	4.75	4.70	6.55	2.65	0.0301	0.87	57.0	57.1	54.9	58.5
Benzene	761	19	160	19	5	—3	40	4.30	4.40	4.60	6.20	2.55	0.0207	0.88	39.0	39.1	37.6	39.0
Amyl acetate	759	13	196	16	4	0	38	3.85	4.20	4.40	6.15	2.20	0.0368	0.88	60.0	60.1	58.7	65.0
Ethyl acetate	757	20	167	20	1	1	30	3.30	3.45	6.05	7.00	2.35	0.0544	0.90	47.0	47.1	46.5	44.0
Amyl alcohol	755	15	194	16	3	0	69	4.75	4.05	5.55	7.30	2.10	0.0649	0.81	44.1	45.0	43.4	44.0

II

One bulb, A, is sealed, allowed to cool to room-temperature t_1° and the position of the mercury in it is noted in order to determine later the volume V of the enclosed air. The difference in height m between the mercury levels is measured (Fig. 5).

The weighing tube is introduced into the other bulb, B, which is sealed and left to cool to room-temperature. The positions of the mercury in both bulbs A and B are noted so that the volumes V_1 and V_2, respectively, of the enclosed air can be determined later. The difference in height m_1 between the mercury levels is measured. The atmospheric pressure P is observed, and the specifid gravity s_2 of the substance determined (Fig. 6).

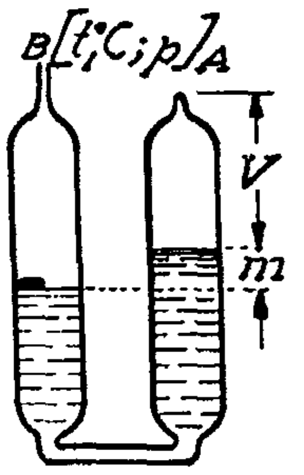

FIG. 5

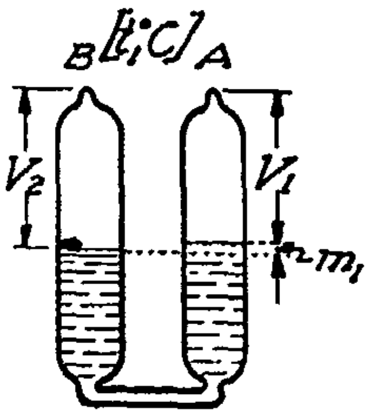

FIG. 6

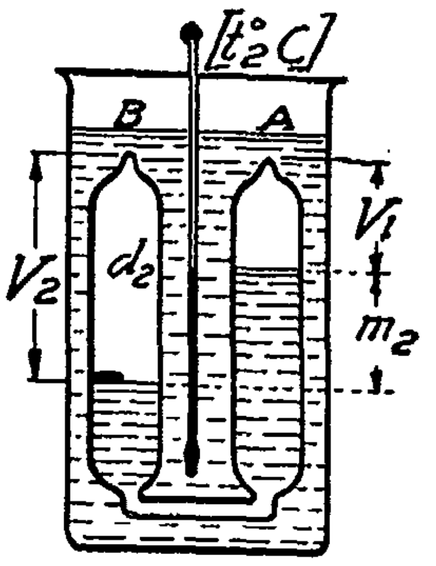

FIG. 7

As described under I, the apparatus is heated to cause complete vaporization of the substance, and the quantities t_3, V, V_1, V_2, v_1, v_2 and m_2 are determined (Fig. 7). The vapor density, d_2, is then calculated from the formula

$$\left\{\frac{(p - m)V}{V_1} \pm m_1\right\}\left\{\frac{1}{273 + t_1}\right\}\left\{\frac{V_1}{v_1} - \frac{V_2 - \frac{w_2}{s_2}}{v_2}\right\} - \frac{m_2}{273 + t_2}$$
$$= \frac{31068\, w_2(1 + [t_2 - t_3]0.000026)}{d_2 v_2} \qquad \ldots\ldots\ldots\ldots(1)$$

or from the almost inappreciably less accurate formula

$$\left\{\frac{(p - m)\mathrm{V}}{\mathrm{V}_1} \pm m_1\right\}\left\{\frac{1}{273 + t_1}\right\}\left\{\frac{\mathrm{V}_1}{v_1} - \frac{\mathrm{V}_2}{v_2}\right\} - \frac{m_2}{273 + t_2}$$
$$= \frac{31068w_2(1 + [t_2 - t_3]0.000026}{d_2v_2} \ldots\ldots\ldots\ldots (2)$$

or (when great accuracy is not required) from the formula

$$\left\{\frac{(p - m)\mathrm{V}}{(273 + t_1)\mathrm{V}_1}\right\}\left\{\frac{\mathrm{V}_1}{v_1} - \frac{\mathrm{V}_2}{v_2}\right\} = \frac{31068w_2(1 + [t_2 - t_3]0.000026)}{d_2v_2} \ldots (3)$$

See Table II.

The modified method and apparatus as described under I and II are analogous to the far simpler—and better in every respect— method and apparatus of the author's, described in the Zeitschrift für Physikalische Chemie, 65, 549-552 (1909), Journal of Physical Chemistry, **12**, 671-677 (1908), and Chemical News, 100, 174 (1909). (See also Journal of Physical Chemistry, 15, 871 (1911), and Chemical News, 113, 241 (1916).)

Note 1 (upon the bulb).—The bulbs are joined by a narrow U-tube, instead of the whole being made of one wide tube bent into U-shape, to avoid using a greater quantity of mercury, the expansion of which must necessarily reduce even if only to a small extent the limited vaporizing capacity of the bulbs.

Note 2 (upon the weighing tube).— It is generally unnecessary to seal up the weighing tube. When experimenting with any volatile substance the weighing tube was made extremely thin, and dumb-bell shaped (Fig. 8; *a*, sealed, *b*, sealed; *d*, substance enclosed), the neck *c* being of hair-thinness and breaking immediately on agitating the mercury.

Fig. 8

On several occasions a thin-walled tube, sealed, was enclosed with a short piece of glass rod to break it on agitation, in these cases V, V_1, V_2, v_1 and v_2 being corrected for the volume of this piece of glass rod, but this procedure is not at all desirable, because it reduces considerably the available vaporizing volume of the bulb.

The simplest and most effective weighing tube is the following: The substance is weighed out in a short, narrow, thin-walled glass tube closed at one end, the open end being

TABLE II

	p mm	t_1°	t_2°	t_3°	m mm	m_1 mm	m_2 mm	V cc	V_1 cc	V_2 cc	v_1 cc	v_2 cc	w_2 gram	s_2	d_2			
															(1)	(2)	(3)	Theory
Ethylene chloride	757	13	134	16	4	—4	53	5.65	5.85	5.20	3.00	7.85	0.0390	1.27	49.4	49.3	47.3	49.4
Amyl nitrite	764	14	181	16	3	—3	33	5.05	5.15	4.95	2.70	7.05	0.0423	0.87	57.0	56.9	55.5	58.5
Acetaldehyde	762	16	120	17	5	5	46	5.25	5.50	5.05	3.05	7.20	0.0154	0.80	25.0	24.9	24.2	22.0
Methyl cyanide	760	15	174	16	2	0	54	5.05	5.20	5.30	2.20	8.00	0.0195	0.79	18.1	18.1	18.6	20.5
Amyl alcohol	756	18	188	19	3	5	55	4.65	4.95	4.75	2.25	7.15	0.0368	0.80	44.0	44.1	43.0	44.0
Toluene	747	17	190	17	7	2	48	6.75	6.90	3.45	3.00	7.05	0.0478	0.87	46.0	46.0	46.7	46.0
Benzene	750	17	157	19	4	—5	49	5.50	5.80	5.05	3.20	7.40	0.0244	0.89	38.9	38.8	37.3	39.0
Carbon tetrachloride	758	18	163	18	8	2	51	4.80	5.00	5.05	2.50	7.20	0.0555	1.61	76.8	77.1	77.4	76.9
Acetone	763	20	149	20	5	—4	40	4.25	4.55	4.55	2.55	6.25	0.0143	0.79	29.0	28.9	27.9	29.0
Pyridine	768	16	191	16	4	0	47	3.90	4.00	5.05	2.00	6.85	0.0274	1.00	39.4	39.7	38.4	39.5
Ethyl ether	754	17	151	18	6	3	53	6.45	6.85	6.05	4.05	8.65	0.0236	0.72	37.0	37.1	35.8	37.0
Chloroform	755	16	155	17	5	25	43	5.85	6.00	4.25	3.00	7.00	0.0464	1.50	58.0	58.1	57.3	59.7
Ethyl alcohol	757	16	150	18	3	—2	48	4.95	5.25	5.75	3.30	7.45	0.0102	0.80	22.6	22.5	21.2	23.0
Methyl alcohol	759	15	180	17	6	—17	50	7.00	7.20	4.85	3.80	8.10	0.0124	0.78	15.9	15.7	14.0	16.0
Ethyl acetate	758	17	188	18	2*	0	59	5.50	5.85	5.50	3.15	8.00	0.0332	0.91	47.2	47.3	45.1	44.0
Amyl acetate	760	19	193	20	0	—1	55	3.90	4.00	6.25	2.00	8.00	0.0459	0.87	60.0	60.3	57.9	65.0

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* See Note 4.

inserted in another similar, but slightly wider tube, the outer covering being included in the weighings and the tubes handled with a pair of clips and not with the bare fingers; this method proves quite effective in preventing loss of substance by evaporation. The liquid to be experimented on is introduced into the tube by the aid of simple glass re-fill made by drawing out fine one end of a piece of glass tubing.

If the substance be a non-volatile solid, it is simply weighed out in a very thin-walled glass tube.

In all cases the weighing tube is best made from thin test-tube glass, as it is then extremely thin-walled and of negligible volume.

Note 3 (upon w_1 *and* w_2*).*—As the available vaporizing volumes of the bulbs are small it is advisable to use only very small weights (w_1, w_2) of substances, firstly, to facilitate rapid evaporation and, secondly, to avoid the gases in one bulb being of such a great volume as to force the mercury completely out of that bulb into the other (though this evidently must be impossible if the bulbs are originally more than half full of mercury).

Note 4 (upon m*).*—After one bulb has been sealed and left to cool to room-temperature, more mercury may be added to the other bulb until the mercury is on the same level in both bulbs, so that $m = 0$, after which the V-position is observed; but in actual practice there is as little trouble in measuring m and in making the necessary allowance in the calculation as in manipulating the mercury to make $m = 0$.

Note 5 (upon measuring V, V_1, V_2, v_1, v_2*).*—The volume of mercury poured in to reach the volume—(V, V_1, V_2, v_1, v_2) positions do not represent the *true* volumes occupied by the air or gases as the case might be, the true volume being more than this. The correction is easily made.

Suppose (Fig. 9) the mercury reaches a position which may be called the V-mark; then the true volume V is equal to the volume between this mark and the upper end, A, of the tube *plus* the volume, Z, of the triangular-shaped annular space between this mark and the mercury. Now, on inverting the tube (Fig. 10) so that A is downward, the mercury is poured in to reach this V-mark; but the true total volume of the original air (or gas) was clearly as far as the upper curve corresponding to the mercury surface in Fig. 10, that is, it is short by an amount equal to 2Z. Thus a volume equal to 2Z must be added in each case.

This quantity 2Z may be thus determined: The tube, or a piece of the original tube, open at both ends, has one end evenly closed with a flat stopper, and mercury, of volume A, is poured in from a burette up to any convenient height *c* (Fig. 11); the volume B of the mercury between the stopper *a* and the point of contact *b′* of the mercury meniscus and the glass is read off by aid of the graduations on the tube; the tube is next viewed from one side so that the position *b′* is in front, (Fig. 12), and more mercury of volume *c* is added until the point of contact of the mercury meniscus and glass is now on a level with *c*. The volume between *b′* and $c = A - B =$ the volume between *c* and *d*; but the total volume between *bc* and $d = C = (A - B) + 2$, whence $2Z = 2c - 2A + 2B =$ amount to be added.

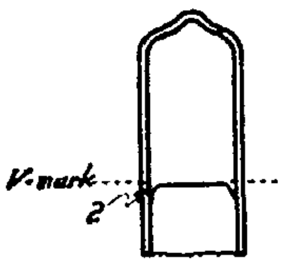

Fig. 9

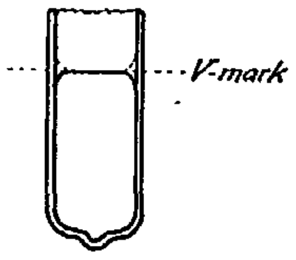

Fig. 10

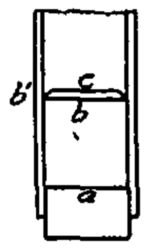

Fig. 11

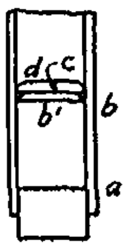

Fig. 12

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HYDROUS OXIDES. I

BY HARRY B. WEISER

Hydrous Ferric Oxide

In a recent communication on adsorption by hydrous ferric oxide,[1] prepared by the method of Péan de St. Gilles, attention was called to some interesting and important properties of the precipitated oxide that will now be considered in detail.

HISTORICAL

Preparation of Colloidal Ferric Oxide

The Péan de St. Gilles Colloid.—Péan de St. Gilles[2] prepared colloidal ferric oxide by continued boiling of a solution of ferric acetate. The red-brown color which is characteristic of the acetate became brick-red as the boiling continued and the peculiar taste of ferric salts gave place to that of acetic acid. The colloid was distinctly turbid in reflected light, but was perfectly clear in transmitted. Potassium sulphocyanate did not change the color, whereas the solution of the ordinary acetate was appreciably reddened. Potassium ferrocyanide as well as all the other potassium salts, produced a brown ochreous precipitate which assumed a green shade after long standing.

"A trace of sulphuric acid or of an alkaline salt precipitates all the iron in the form of a red-brown deposit that is insoluble in the cold in all acids even the more concentrated. By boiling it is dissolved by hydrochloric acid, but is not attacked by nitric.

"When the liquid is poured into hydrochloric acid there is formed a finely divided, granular, brick-red precipitate which readily settles to the bottom of the vessel. This precipitate, which in appearance in no way resembles the ordinary ferric hydroxide, may be washed without change with the same acid, however concentrated; and even may be treated

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[1] Weiser and Middleton: Jour. Phys. Chem., 24, 30 (1920).

[2] Comptes rendus, 40, 568, 1243 (1855).

with water. But if the salt water, together with most of the acid enclosed by the precipitate, is removed by one or two decantations with distilled water, the solid disappears at once with the formation of a brick-red, opalescent liquid, similar in every respect to that originally obtained. An indefinite number of alternate precipitations and dissolutions can be carried out if hydrochloric or nitric acid is employed; but if any other acid is used with the exception of acetic, the precipitate once formed will no longer redissolve in water."

Scheurer-Kestner[1] obtained a similar modification of the hydrous oxide by heating a solution of ferric nitrate for three days at 100°. The addition of a few drops of hydrochloric acid precipitated the oxide, which was dried on a porous plate and later was peptized with water, forming a tasteless brick-red liquid. Krecke[2] prepared it by heating a $^1/_2$ percent solution of ferric chloride for a suitable length of time at 100° to 130°. Giolitti[3] has extended the experiments of Péan de St. Gilles on the colloid prepared by boiling the acetate. He confirmed the interesting observation that the physical character of the precipitated colloid was different with different precipitating agents. He found that the addition of a small quantity of sulphurous, sulphuric, selenious, iodic, periodic, boric or phosphoric acid produced a gelatinous precipitate that was not redissolved by water: while the addition of a small amount of hydrochloric, hydrobromic, hydriodic, nitric, perchloric or perbromic acid caused slight precipitation of a finely divided brick-red powder, which could not be removed by ordinary filtration. The addition of a larger amount of the latter group of acids caused complete precipitation and the powder was readily peptized by water as Péan de St. Gilles observed.[4]

The Graham Colloid.—Graham[5] prepared a colloid that

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[1] Ann. Chim. Phys., (3) 57, 23 (1850).

[2] Jour. prakt. Chem., (2) 3, 286 (1871). Cf. Debray: Comptes rendus. 68, 913 (1869).

[3] Gazz. chim. ital., 35, II, 181 (1905).

[4] Cf. Weiser and Middleton: Loc. cit.

[5] Jour. Chem. Soc., 15, 250 (1862).

differs in certain respects from the Péan de St. Gilles colloid by the dialysis of a ferric acetate solution in the cold; or more usually, by peptizing gelatinous ferric oxide in ferric chloride solution and then dialyzing out the excess ferric chloride. This colloid is colored deep reddish brown and is comparatively clear. "The red solution is coagulated in the cold by traces of sulphuric acid, alkalis, alkaline carbonates, sulphates and neutral salts in general; but not by hydrochloric, nitric and acetic acids nor by alcohol or sugar. The coagulum is a deep red-colored jelly resembling the clot of blood, but more transparent." The precipitate can not be peptized by washing by either hot or cold water; but it is readily dissolved in dilute acids. On the other hand, the Péan de St. Gilles precipitate is relatively insoluble in acids and under certain conditions can be peptized by water. Graham considered his colloid to be ordinary hydrated "peroxide" of iron and the Péan de St. Gilles colloid to be "metaperoxide" of iron.

Krecke[1] obtained the Graham hydrous peroxide by hydrolysis of ferric chloride at concentrations ranging from $^1/_{16}$ to 1 percent at temperatures from 20° for the more dilute solutions to 83° for the more concentrated. Solutions of higher concentration up to 32 percent gave the same product at higher temperatures, but ferric chloride was re-formed when the temperature was lowered. Biltz[2] obtained the Graham colloid by dialysis of a dilute solution of ferric nitrate. Grimaux[3] prepared a similar product by pouring an alcoholic solution of ferric ethylate into water. Neidle[4] oxidized ferrous chloride with hydrogen peroxide and dialyzed.

The Composition of Colloidal Ferric Oxide

The Question of Hydrates.—The colloid prepared by boiling the acetate gives much more intense light cones[5] since it is more granular and less hydrous than the Graham colloid.

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[1] Loc. cit.

[2] Ber. deutsch. chem. Ges., **35**, 4431 (1902).

[3] Comptes rendus, **98**, 105, 1434 (1884).

[4] Jour. Am. Chem. Soc., **39**, 2334 (1917).

[5] Zsigmondy-Spear: "Chemistry of Colloids," 163 (1917).

This is due to the dehydration and agglomeration of the particles of the former at the higher temperature. The same thing may be accomplished by long standing of the latter at a lower temperature. Thus Giolitti[1] found that the Péan de St. Gilles colloid was fairly uniform, whereas the Graham colloid changed gradually from the more hydrous to the less hydrous form on standing. Zsigmondy found that certain commercial colloids prepared by the Graham method have properties that lie intermediate between the newly formed Graham colloid and the Péan de St. Gilles colloid. The effect of temperature and time of standing on the degree of hydration of hydrous ferric oxide, both precipitated and colloidal, has been the subject of numerous investigations, chiefly for the purpose of establishing the existence or non-existence of definite hydrates. Thus, Péan de St. Gilles[2] writes: "Having observed the transformation produced by a temperature of 100° on the acetic acid solution of ferric hydrate, I determined what would happen at the same temperature on the same hydrate in the free state.

"I prepared the hydrate by decomposing ferric chloride in the cold with ammonia (brown chocolate hydrate) and also with bicarbonate of soda (yellow ochreous hydrocarbonate). When assured that the precipitate was entirely free from alkali by washing a great number of times with cold water, I suspended it in water and heated it. After boiling some time, manifest action was noted by a change in the color of the precipitate and especially, by the property it had acquired of no longer dissolving completely in concentrated nitric or acetic acid. On continuing to heat the hydrate on the water bath I noted that little by little it took on the brick-red color, characteristic of the modified acetate. In this condition not only acetic but also dilute nitric and hydrochloric acids caused the precipitate to disappear instantly producing a liquid, cloudy by reflected light but clear by transmitted; and colored

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[1] Loc. cit.

[2] Comptes rendus, 40, 1244 (1855).

brick-red. In a word, it was similar in all respects to the substance produced directly from the acetate."

Péan de St. Gilles[1] considers that the brick-red colloid has the composition $Fe_2O_3.H_2O$. Schiff[2] claims to have gotten the same thing by keeping precipitated hydrous ferric oxide for many years at ordinary temperature. Wittstein[3] says that the hydrate $Fe_2O_3.3H_2O$ is obtained by precipitating a ferric salt with ammonia and drying for a short time at 100°. Brescius' experiments[4] indicate that there are no definite hydrates of ferric oxide; but Ramsay[5] believes he prepared the hydrate $Fe_2O_3.H_2O$ by drying the precipitated oxide to constant weight at 100°. Tommasi[6] recognizes two series of oxides, yellow and red, the properties of which depend on the method of preparation. The members of the red series are obtained by precipitating a ferric salt with alkalis. These hydrates dissolve in dilute acids and are dehydrated even by boiling water. The members of the yellow series are obtained by oxidation of ferrous hydrate or carbonate. According to Tommasi the members of the two series are identical in composition, but differ in color and stability. The yellow hydrates are denser; are but sparingly soluble in concentrated acids; and require a higher temperature to dehydrate them. Moreover, they retain a molecule of water even on long boiling with water.[7] Carnelley and Walker[8] conclude from their investigations that no definite stable hydrates are formed, inasmuch as the precipitated hydrous oxide loses water gradually and continuously from 15° to 500° where Fe_2O_3 is formed.

Van Bemmelen[9] has made an extended study of both the yellow and red hydrous oxides under various conditions and

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[1] Ann. Chim. Phys., (3) 46, 47 (1856).

[2] Chem. Centralblatt, (2) 5, 1768 (1860).

[3] Ibid., (1) 24, 367 (1853).

[4] Jour. prakt. Chem., (2) 3, 272 (1871).

[5] Jour. Chem. Soc., 32, 395 (1877).

[6] Bull. Soc. chim. Paris, (2) 38, 152 (1833).

[7] Cf. Muck: Zeit. für Chemie, 41 (1868).

[8] Jour. Chem. Soc., 53, 89 (1888).

[9] Rec. trav. chim. Pays-Bas., 7, 106 (1888); Zeit. anorg. Chem., 20, 185 (1899).

has shown with considerable certainty that there is but one definite crystalline hydrate of ferric oxide and that this can be prepared only under special conditions—the decomposition of sodium ferrite by water at ordinary temperature.[1] In the hydrous oxides as ordinarily prepared, the ratio of oxide to water depends entirely on the method of treatment. Thus a certain reddish brown colloid exposed to air for a year contained 4 to 4.1 moles of water.[2] In dry air this fell to 1.6 moles, in 4 months. By heating to 100° in dry air, the composition fell to 0.96 mole, but the final composition depends on the state of aggregation. A particular sample kept for 6 months contained 1 mole of water at 15°, which went to 0.45 mole in only 5 hours at 100°. Between 100° and 300° the dehydration was slow and regular to about 0.25 mole, but if heated sufficiently long at any intermediate temperature the result was the same. After heating at temperatures between 100° and 300° the oxide regained only a part of its water when placed in an atmosphere saturated with moisture. The yellow colloid showed similar variations. It contained 2.43 moles of water when dry but when kept for a month in a saturated atmosphere it contained 7.4 moles. When heated from 15° to 270° in a stream of dry air, the water fell from 1.7 moles to 0.24 mole. Above 200° the composition was the same as the reddish brown colloid, but between 50° and 300° it retained its water more strongly. From these results, and a large number of others, van Bemmelen concluded that a hydrate with a definite composition was obtained only by chance. "The determinations of the water content of the substances prepared in different ways by different investigators (Davies, Lifort, Péan de St. Gilles, Wittstein, Schaffner, Muck, Tommasi, etc.) are of no value other than representing the transient and accidental state of the colloid."

Mineralogists distinguish at least six hydrates of ferric oxide: Haematite, Fe_2O_3; Turgite, $Fe_2O_3.{}^1/_2H_2O$; Göthite, $Fe_2O_3.H_2O$; Limonite, $Fe_2O_3.{}^2/_3H_2O$; Xanthosiderite, Fe_2O_3.-

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[1] Van Bemmelen and Klobbie: Jour. prakt. Chem., 46, 497 (1892).

[2] Cf. Spring: Rec. trav. chim. Belg., 17, 222 (1898).

$2H_2O$; and Limnite, $Fe_2O_3.H_2O$. Of these, haematite is sometimes found in nature as a well crystallized substance; but of the hydrates, göthite only occurs in a definite crystalline form. Ruff[1] has heated freshly-prepared, red ferric oxide under 5000 atmospheres and claims to have gotten definite hydrates. Between 30° and 42.5° he claims to get limonite; between 42.5° and 62.5° göthite, and above this hydrohaematite. A yellow non-crystalline hydrate, $Fe_2O_3.{}^2/_3H_2O$, prepared by the oxidation of moist hydrous ferrous oxide, was unchanged between 40° and 70° under high pressures. From this he concludes that the yellow hydrate is a compound of constant composition.

In the light of all the investigations it seems probable that not more than one definite crystalline hydrate of ferric oxide exists. The different formulas mean merely that a number of hydrous oxides of variable water content have been analyzed under such conditions that their percentage composition happened to approach that of a definite hydrate. It is very unlikely that any of the colloidal solutions of ferric oxide contain definite hydrates. Bancroft[2] concludes that any number of hydrous ferric oxides can be prepared differing among themselves in the degree of hydration and the size of the particles. This is borne out by Zsigmondy's observation that the small hydrous particles of the Graham colloid go over gradually to the larger, less hydrous particles of the Péan de St. Gilles colloid.

The Question of Basic Salts.—The colloid prepared by Graham's method is comparatively free from electrolytes, but it always contains traces of chlorides that can not be removed completely, however long the dialysis may be continued.[3] On this account a number of investigators consider the various dialyzed colloids as chlorides of condensed ferric hydroxide like, $Fe_2(OH)_6.{}^1/_{150}Fe_2Cl_6$, or as oxychlorides of

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[1] Ber. deutsch. chem. Ges., **34**, 3417 (1901).

[2] Jour. Phys. Chem., **19**, 232 (1915).

[3] Linder and Picton: Jour. Chem. Soc., **87**, 1920 (1905); Ruer: Zeit. anorg. Chem., **43**, 85 (1905); Desch: Liebig's Ann., **323**, 28 (1902).

variable composition. This idea was advanced by Wyrouboff[1] and his pupils and was later taken up by Jordis,[2] Duclaux,[3] Linder and Picton,[4] Nicolardot,[5] Malfitano,[6] Michel,[7] and others.[8] Thus, Nicolardot finds that the colloid in which the ratio of iron to chlorine in equivalents is 6, gives no tests for ferric and chloride ions by adding potassium ferrocyanide or sulphocyanate and silver nitrate, respectively.[9] He concludes that at this point in the dialysis the colloid contains a definite compound, a ferric oxychloride. He states further that after continuing the dialysis for several months, no more hydrochloric acid can be removed; and then the ratio of iron to chlorine in equivalents is 125. He considers this to be another definite compound and believes that all ratios between these two result from mixtures of the two compounds. Neidle[10] points out that Nicolardot's conclusions do not represent the facts and concludes from his own investigations that clear hydrous ferric oxide sols. containing ferric ion may contain a definite oxychloride which is a colloid having the ratio, 21 equivalents of iron to 1 of chlorine. He postulates the existence of other theoretical oxychlorides and attributes the increasing stability of the colloids with increasing hydrochloric acid content, to the reversal of hydrolysis and the formation of stable oxychlorides. On the other hand, Giolitti[11] concludes that there is no evidence for the existence of oxychlorides of definite composition in the colloidal ferric oxides;

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[1] Bull. Soc. chim. Paris, 21, 137 (1899).

[2] Zeit. anorg. Chem., 35, 16 (1903); Zeit. Elektrochemie, 10, 509 (1904).

[3] Comptes rendus, 138, 144, 809 (1904); 140, 1468, 1544 (1905); 143, 296, 344 (1906); Jour. chim. phys., 5, 29 (1907).

[4] Loc. cit.

[5] Ann. Chim. Phys., (8) 6, 344 (1905).

[6] Malfitano and Michel: Comptes rendus, 145, 185, 1275 (1907); Malfitano: Zeit. phys. Chem., 68, 232 (1909).

[7] Comptes rendus, 147, 1052, 1288 (1908).

[8] Neidle: Jour. Am. Chem. Soc., 39, 2334 (1917); Dumanski: Zeit. Kolloidchemie, 8, 232 (1911).

[9] Cf. Ruer: Loc. cit. and Desch: Ibid.

[10] Loc. cit.

[11] Gazz. chim. ital., 36, 1157 (1906); cf. Van Bemmelen: Zeit. anorg. Chem., 36, 380 (1903).

and Fischer[1] points out that if there are any basic ferric chlorides, they can be stable only at low temperatures. From a study of the system: ferric oxide, hydrochloric acid and water, Cameron and Robinson[2] find that no definite basic chlorides are formed at 25°.

It seems to the author that the existence of colloidal oxychlorides of definite composition is doubtful; and moreover, that it is of questionable use to postulate the formation of a series of complex oxychlorides to account for the properties of the different hydrous oxides; particularly, when the independent existence of no single one has been established with any degree of certainty. The properties can be explained from the point of view of specific adsorption. Any number of hydrous ferric oxides are possible, differing among themselves in the degree of hydration and the size of the particles, both of which factors affect the amount of adsorption. The colloid prepared by the Graham method is formed in the presence of ferric chloride, ferric ions and hydrogen ions. Accordingly we might expect the colloid to adsorb some ferric chloride and it will always adsorb ferric, hydrogen, and chloride ions in amounts depending on the nature of the colloid, the specific adsorbability and the concentration. Now it is well known that a substance always shows a strong tendency to adsorb its own ions and hydrogen ion is usually very strongly adsorbed; on the other hand, chloride ion is not strongly adsorbed, as a rule, and this preferential adsorption results in a stable positive colloid. It is likely that most of the chloride ion present in the Graham colloid is not adsorbed by the hydrous oxide but its concentration is a measure of the adsorbed ferric and hydrogen ions which give the colloid its stability. Adsorbed chloride ion will not give a test with silver nitrate. Moreover, Ruer[3] has shown that the presence of small amounts of unadsorbed chloride in the presence of colloidal iron oxide can not be detected by precipitation with silver nitrate, since

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[1] Zeit. anorg. Chem., **66**, 38 (1910).

[2] Jour. Phys. Chem., **11**, 690 (1907).

[3] Zeit. anorg. Chem., **43**, 85 (1905).

the protecting action of the hydrous oxide does not allow the particles of the silver chloride to become large enough to cause turbidity. Since there is an equilibrium between the amount of a substance adsorbed and the amount in solution, prolonged dialysis will result in the loss of part of the adsorbed cations (together with an equivalent amount of anions) and this will decrease the stability of the colloid. It is unnecessary to postulate the existence of oxychlorides of varying composition to account for the observation that only a part of the chlorine present appears to exist as ion.[1]

The Color of Hydrous Ferric Oxide

That hydrous ferric oxide exists in a variety of colors varying from yellow to violet-red is evident from the colors of the minerals. Thus, haematite is black when crystalline and red when powdered; turgite is a deep brown; limonite varies from a light brown to yellow; and limnite is a full yellow.[2] By referring to the formulas usually assigned to these minerals, it might seem that the yellow color is a question of hydration of the oxide. This can not be the case as pointed out by Robinson and McCaughey:[3] "By heating limonite or any hydrate of ferric oxide, it loses water, changes color and becomes in fact red haematite. There is, however, no satisfactory measurement of a temperature of inversion of limonite to haematite, and it is doubtful if such an inversion point exists. At ordinary pressures limonite does not lose water appreciably at any temperatures which may be realized under field conditions."

As has been stated, the preparation of both yellow and red ferric oxides was accomplished a long time ago by Muck, whose work was extended by Tommasi. The latter clearly implied that the color was not a question of degree of hydration, since he assigned the same formula to hydrous oxides of different color. Antony and Giglio[4] and Goodwin,[5] at about

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[1] See Dumanski: Loc. cit.

[2] Dammer's, "Handbuch der anorganische Chemie," 3, 304 (1893).

[3] Bureau of Soils, Bull. 79, 18 (1911).

[4] Gazz. chim. ital., 25, 1 (1895).

[5] Zeit. phys. Chem., 21, 1 (1896).

the same time and independently, made the interesting observation that the conductivity of a dilute solution of ferric chloride increases on standing and that this is accompanied by color changes. "I observed also that the solution which was as good as colorless at the start became quickly yellow-red and then brown-red." Nicolardot[1] recognized four modifications of hydrous ferric oxide: white, dark brown, yellow and red. He obtained the white hydrous oxide by pouring a concentrated solution of a ferric salt into cold liquid ammonia. He believed that the different colored forms were derived from the colorless oxide by molecular condensation. Moreover, he suggested that the red oxide was an open chain compound while the yellow was of cyclic nature. Malfitano[2] ascribed the different colors of the colloidal oxide to different complex compounds of the general type of the cobalt amines. Although the existence of a series of complex salts of widely varying composition is improbable, the experimental work recorded in Malfitano's paper is of particular importance, since it brings out the relationship between the size of particles and the color of hydrous ferric oxides. Accordingly, I will quote from it in some detail:

"Freshly prepared ferric chloride solutions are clear and run through the collodion membrane completely. After a while, and the quicker the weaker the solution and the higher the temperature, the solution undergoes a marked change. The hydrolysis of the solution produces color changes and the solution appears heterogeneous. Three cases can be distinguished:

"(a) Dilute solutions (*e. g.*, 1 percent) at low temperatures (25° to 50°) and the more concentrated solutions slowly heated to 100° assume an ochre-yellow color, become opalescent and opaque; and if the concentration is sufficiently high, a precipitate forms which settles to the bottom of the clearing solution. In this solution the ultramicroscope reveals particles which appear on an almost entirely dark back-

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[1] Comptes rendus, 140, 310 (1905).

[2] Zeit. phys. Chem., 68, 232 (1910).

ground. The ultrafilter retains all the colloid as the filtrate is entirely clear and is not clouded by the addition of potassium chloride and sulphate. If one completes the filtration while exerting a slight pressure on the inside of the filter, the colloid agglomerates on the bottom of the little sack and forms a very thin solid residue.

"(b) Ferric chloride solutions of like concentrations when they are suddenly heated to 100° assume a red-brown color becoming heterogeneous; but less so than in the previous case. However a precipitate never forms. Small particles of very different sizes are seen with the ultramicroscope. In contrast to the former case, the background on which the particles appear is clear, since most of the particles are too small to be observed optically; but they serve to light up the background of the field. By ultrafiltration this solution gives a filtrate, which at the outset is entirely homogeneous, possesses a light yellow color and is not clouded by the addition of electrolytes; soon, however, there passes through the filter a redder solution, which appears homogeneous in the nephelo-scope but becomes quite cloudy on the addition of hydrochloric acid, potassium chloride or potassium sulphate. There is, therefore, an extremely finely divided colloid which runs through the membrane. It should be noted that the colloid can exist in complete solution, homogeneous to light.

"If the ochre-yellow liquid in case (a) were filtered through the membrane, the latter is intensely colored after the filtration. It is impregnated with the iron compound and its electrical nature has changed. Before this filtration it became negative during electric osmose; after filtration it became positive. After the membrane was changed in this way, it allowed the red solution through unchanged. The micellae of small dimensions appear to settle firmly in the pores of the membrane or else they fix themselves on these pores only at the outset. After the membrane is impregnated they can run through, but the membrane always retains a part of the colloid as a thick slimy solution or as a doughy precipitate. In order to get a large amount of colloidal material, one must take a slightly permeable collodion membrane.

"(c) If the ferric chloride solution is heated to a high temperature (134°) or is kept for a long time at 100°, the liquid which was red-brown at the outset goes over into a brick-red. The heterogeneity becomes pronounced, and there form differently colored plates and finally even a precipitate. In such a solution one can detect the presence of particles of large dimensions without the ultramicroscope. By ultrafiltration is obtained a red-brown filtrate and within the sack there remains a pulverulent precipitate.

"As we see therefore the colloid is composed of particles of different size, depending on the nature and method of the hydrolysis. * * * * "

"If we dissolve the residue after filtration in pure water we find the dimensions of the micellae easily change.

"(a) The residue of ochre-yellow colloid can be suspended again quite readily and one can repeat this process frequently. It loses in this way a part of its chlorine and at the same time loses the property of dividing itself uniformly in the solution.

"(b) The residue from the filtration of the red-brown colloid which partly runs through the membrane, forms a quite stable colloid with water. If this is filtered again, the iron compound goes through the membrane; and if the solution is put on a new membrane, the latter is not colored at all. Therefore it is proven beyond doubt that impregnation of the membrane is a question of the dimensions of the micellae. By repeated washing, the colloid continues to lose more and more of its chlorine forming cloudy solutions which are stable, nevertheless. The residue, after a long series of filtrations, becomes more doughy and firm. By optical study it appears that the micellae decrease in number and increase in dimensions.

"(c) If the residue, after filtration of the solution which has become brick-red by long heating, is taken up with water, there is obtained a very heterogeneous and unstable solution.

Even after the first washing one can observe particles visible under the microscope and can detect them even with the unaided eye. They remain in solution but a short time and then settle to the bottom with different velocities.

"The dimensions of the particles are different, therefore; but not only this, the dimensions can easily change. In the main, as the colloid loses chlorine, the nuclei appear to group into ever-increasing masses. These masses can either remain in the solution or more or less readily settle out. One can also realize the reverse process:

"(a) If we add a ferric chloride solution to the ochre-yellow colloid which consists of large micellae, it goes into stable solution again. However, this solution is always very cloudy, no matter how much ferric chloride has been added. If this colloid is suspended in hydrochloric acid solution again, it takes up chlorine without appreciably changing its state of division. If a sufficient amount of hydrochloric acid is added, it precipitates the colloid. Afterwards this precipitate is attacked slowly by the acid and dissolves again as ferric chloride. The solutions of all other electrolytes with the exception of hydrobromic and nitric acids are unable to diminish the size of the particles; in general, they cause an increasing of the size and precipitation of the colloid.

"(b) If one adds ferric chloride to the residue after filtration of the red-brown colloid, it undoubtedly forms smaller micellae, for the colloid henceforth appears in the filtrate. If this colloid is now heated with ferric chloride, the color goes over into ochre-yellow and the entire colloid precipitates out. The red colloid can, therefore, be changed into the ochre-yellow colloid which one obtains also by slow heating or by gentle heating for a long time. If there is added to the residue after filtration of the red colloid, a hydrochloric acid solution which is more concentrated than that which has been removed by filtration, it must form small micellae, as the new solution appears a little cloudy and there is less acid in the solution than was added. The colloid adsorbed chlorine and with the same pressure of filtration, the volume of the residue is greater than before the addition of acid. If a larger amount of hydrochloric acid is added, the phenomenon changes. There is found in the filtrate not only the colloid but hydrochloric acid as well; and the residue becomes less voluminous and more doughy. If the amount of acid is further increased, the solution of the colloid is not only cloudy but deposits a sediment. If, soon thereafter, the solution is diluted, the precipitate vanishes and the colloidal solution is relatively stable. However, the precipitate changes slowly in the presence of a large amount of hydrochloric acid; it becomes insoluble and brick-red, exactly like the precipitate which was obtained by continued strong heating of ferric chloride solutions. Finally, the precipitate is attacked by the acid and changed to ferric chloride. The same phenomena can be observed in the presence of nitric acid. The other electrolytes never decrease the dimensions of the micellae; those with univalent anions increase the size of the micellae if they are present in large amount; those with polyvalent anions cause this even in slight concentration, thus precipitating the colloid.

"(*c*) If the brick-red colloid is treated like the two others, the same results obtain; however, the change appears more rapidly than with the ochre-yellow colloid and not stepwise as with the red-brown colloid.

"We see therefore that the size and with this also, the other properties of the colloidal solution alter as a function of the composition of the intermicellar liquid. In a few cases the change in the size is reversible; in a few others it is permanent."

Malfitano's investigations show clearly that a close relation exists between the color and size of the particles of hydrous ferric oxides. As before stated, he considers that the different colored colloids are different compounds of complex nature. This opinion is not shared by Fischer,[1] who believes that the parent substance or "K_0 substance" is a simple well-defined chemical compound: "By a physical-chemical method I have succeeded in showing the probable existence and formulas

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[1] Zeit. anorg. Chem., 66, 37 (1910).

of basic chlorides like $Fe_2Cl_5(OH)$. However, these substances appear to be stable only at low temperatures, say 0°; at 80°, their period of existence is but a few seconds at the most. Then they are decomposed by hydrolysis. For this reason their presence is entirely out of the question among the following mentioned substances prepared by long-continued hydrolysis at high temperatures. Besides, the chlorine content is much too small to suffice for a chemical compound of the normal type. Therefore, the only compounds that can be considered as K_o substances are oxides or hydrated oxides."

Fischer has made some interesting observations on the relationships among the different colored hydrous oxides, natural and artificial: "As van Bemmelen has shown, the gel alters only very slowly at low temperatures, therefore a method must be found for appreciably increasing the ageing process. To do this a method is known which consists of heating in the presence of acids or bases. By this process, the iron hydroxides must dissolve as a compound to a certain, even if small, degree; and must again separate out in a form poorer and poorer in energy and therefore older, in the same way as small crystals grow together into larger ones by prolonged action of the solvent. In this way a form of a definite "age" is obtained, the sooner the greater the solution is hydrolyzed, that is, the diluter and warmer it is.

"The first product of the hydrolysis of a ferric chloride solutions is the red-brown colloid of van Bemmelen. It results whenever one should expect the appearance of $Fe(OH)_3$, that is, by hydrolysis and by the precipitation of iron salts by alkalis. Its composition as a function of the vapor pressure of water is given by van Bemmelen.

"By the action of hydrochloric acid on this there is formed the yellow colloid which, to my knowledge, was first observed by Goodwin. It betrays its presence even in slight amount by a green opalescence; if more is formed the solution becomes very cloudy, opaque and opalescent in reflected light, while it is transparent with a deep red-brown color in transmitted light.

"The time which the yellow colloid needs for its formation can be determined easily by the opalescence; and so one can test the above-mentioned rule that heat and dilution favor the reaction; and it was found to hold true. The vessel must be cleaned by boiling with concentrated hydrochloric acid since an inoculation hastens the clouding. The velocity of the change is influenced also by the amount of hydrochloric acid present. For example, in a solution in which $^1/_5$ of the chlorine is neutralized, no yellow colloid appears in three hours, while the same solution without the addition of a base becomes cloudy in a short time. Likewise the solution in boiling water becomes cloudy in proportion to the amount of base added. If the suspension is carried down with barium sulphate and the partly washed precipitate is analyzed, there will be found a stoichiometrically incomplete amount of chlorine. The yellow colloid differs from the red-brown in its extreme insolubility in acids. Its loss-of-water curve is quite different. It loses more water at the beginning but later less than the brown substance (van Bemmelen). In dry air the water content is 1.7 moles at 15°; 1.68 at 100°; and 1.34 at 150°. The velocity of loss of water is therefore quite small. At 200° there enters in a sudden change: in something like 16 hours it loses its water to 0.38 mole; but then its color goes over to black.

"A final condition is by no means reached with the appearance of this yellow colloid. If the $N/10$ solution is heated a few days at 100° there results a precipitate which shows the red of powdered haematite. To obtain the same substance from a concentrated solution, it must be heated for a few hours at 200° in a bomb tube. The substance that settles on the walls under these conditions appears glistening black like haematite."

Fischer tabulated the results of a number of experiments in which solutions of different concentrations were heated to different temperatures in bomb tubes. His conclusions follow:

"First is shown that the higher the temperature, and the lower the concentration, the greater is the proportion of chlorine in the solution therefore, the further has the hydrolysis proceeded. The oxides obtained fall into two series: (1) into the yellow substances with a water content that amounts to at least 10 percent; however, this rises to as much as 50 percent in the more concentrated solution by the shortest heating (hence the youngest gel); (2) into the red or black substances with a water content under 5 percent. In these, also, the substances have the least water content which are obtained from the most dilute and the longest heated solutions, in spite of the fact that they are much more finely divided. In a particular series the color goes stepwise from red to black with increasing coarseness of grain. The substances obtained from solutions up to approximately tenth normal are black. With increasing dilution there is mixed with them always more and more red until finally at $^1/_{100}$ normal they are a clear, bright red. In the same way, haematite crystals which glisten violet-black give a red streak on a streak plate.

"The regularity is satisfactory throughout, when one thinks how involved is the process taking place by which is formed from red-brown ferric hydroxide, first the yellow colloid and from the latter the black-red colloid; that the velocity of the reaction hinges on so many uncontrollable secondary conditions; and finally that the heating method in the bomb tube is extremely primitive, assuming as it does constant temperature and exact measurement of the time of heating."

From similar observations on the naturally occurring oxides, Fischer concludes that limonite is identical with the yellow colloid and that haematite is identical with the red colloid. A consideration of the loss-of-water curves of the different hydrous oxides under varying conditions, leads Fischer to the conclusion that the parent substance of the brown colloid is $Fe_2O_3.1.5H_2O$; of the yellow colloid, $Fe_2O_3.H_2O$; and of the red colloid, Fe_2O_3.

Neither Fischer nor Malfitano suggested a possible connection between the color of colloidal ferric oxides and the size of the particles, although both showed conclusively that the color of the hydrous oxide went fron brown through yellow to red with increasing coarseness of grain. On the other hand, Wöhler and Condrea[1] conclude, without question, that the different colors of anhydrous ferric oxide are a question of the size of the particles. "These shades are obtained by high heating of ferric oxide with sodium chloride. The color is determined by the temperature, the time of heating and the amount of salt used (2 to 6 percent). According to the directions given in the technical handbooks, 2 percent of salt and 1 hour's heating gives the yellow color; 4 percent of salt and 3 to 4 hours' heating the brown; and 6 percent of salt and 6 to 7 hours' heating the violet. At the same time the rapidity of cooling, and the admission or exclusion of air will have an influence on the color and chemical stability. The statements fail to give the temperature of the reaction and there is nothing conclusive in the directions concerning the cause of the color and the role of the salt in the process. The suggested explanation that a uniform temperature will result from the evaporation of the small amount of salt added, is of course incorrect. Another explanation that the salt serves as a means of removing sulphuric acid thus neutralizing the acid that remains on the caput mortuum, is untenable since by using pure iron oxide the above-mentioned scale of colors is passed through at 800° in the presence of salt, but not without it."

Wöhler and Condrea first showed that the product, after the heating, was pure iron oxide that was almost anhydrous. After discussing the possible causes of the color changes, they conclude that the size of the particles is the all-important thing: "One should expect the following relationships to obtain if the changes in the color are produced by the agglomeration of smaller particles: (a) The mixture must be heated at least to the melting point of the added salt in order to produce the agglomerating effect on the iron oxide powder. (b) The same amounts of different salts at their melting point will act in the same manner on the iron oxide, providing the salt is stable at this temperature and does not react with the

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[1] Zeit. angew. Chem., 11, 481 (1908).

iron oxide. (c) In order to produce a definite color a definite minimum amount of salt and, at the same time, a definite temperature above the melting point, is necessary; within limits a deficiency of salt can be compensated by raising the temperature. Hence the color produced is a function of the amount of salt added and the temperature. (d) By producing a medium of lower viscosity, the water content of the salt and of the oxide will have an influence, even though a lesser one, on the change of the size of the particles and therefore on the color. (e) By the reverse process of fine division, the violet substance may be changed into the reddish yellow color of the original oxide."

By numerous experiments Wöhler and Condrea established each of the above points. Since most of the experiments involved heating to relatively high temperatures, the colors and color changes refer to the anhydrous oxide. However, they consider that certain color changes are influenced by water of composition: "The violet product which results from heating hydrous iron oxide to 250° can be changed back easily into the reddish yellow color by grinding in a mortar. If the powder so obtained is moistened with water and again heated to 250°, it undergoes no further change in color. It follows, therefore, that the original water was a different water chemically combined which escapes at 250° and thereby produces a medium of lesser viscosity and brings about the growth of the particles. Between 250° and 550°, where a further deepening in color takes place, the rest of the water will be freed which is generally evolved from the colloidal hydrous oxides at a surprisingly high temperature.

"A brown coloration of the yellow-red iron oxide can be obtained at ordinary temperatures by rubbing iron oxide with a hydrated salt. For example, if iron oxide is ground with hydrated calcium chloride, the color changes to dark brown. This color is not altered by washing out the calcium chloride. The salt-free product so obtained can readily be changed back into the original yellow-red by rubbing finely in a mortar.

"The cause of the color at ordinary temperatures is the crystal water of the salt just as the color at 250° and 550° is brought about by the water of constitution of the hydrated oxide. In both cases, however, the changing in the size of grain is the reason for the change in color; since the change to the original color is readily obtained by fine grinding."

Inasmuch as the change in color is a question of change in the size of grain, it would seem unnecessary to postulate that water of chemical constitution rather than adsorbed water plays the role to which they ascribe it. Their final experiments are interesting and conclusive: "In a similar manner the violet color obtained by heating to 800° can be changed into a much lighter color, but not into the yellow-red original substance. It was to be expected that the technical product obtained by heating left the edge mill with a color but slightly lighter. However, the lightest color obtained in the agate mortar can be further subdivided by alternate elutriation and grinding. In this way was finally obtained not only the yellow-red color of the original material, but over and beyond this, a color that was more yellow than red and consisted of a still more finely divided reddish yellow iron oxide."

Bancroft[1] has suggested that the yellow color of hydrous limonites may be due to the adsorption of an iron salt. But in a later communication from his laboratory, Keane[2] arrived at the conclusion that the yellow color of the so-called Mars pigments is due to finely divided ferric oxide, which is kept from agglomerating by the presence of hydrous aluminum oxide; and, further, that the yellow color which iron imparts to bricks is due to sufficiently finely divided anhydrous ferric oxide. When the particles are larger, the color is red. This is quite in line with the conclusions reached by Wöhler and Condrea.

EXPERIMENTAL

The experiments to be described in the following pages are concerned with the factors which affect (a) the physical character and (b) the color of hydrous ferric oxide. In so

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[1] Jour. Phys. Chem., 19, 232 (1915).

[2] Ibid., 20, 734 (1916).

far as practicable these will be considered under separate headings.

The Physical Character of Hydrous Ferric Oxide

Attention has been called to the interesting observation that the physical character of precipitated hydrous ferric oxide prepared by the method of Péan de St. Gilles varies with the nature of the precipitating electrolyte: Thus, such acids as hydrochloric and nitric precipitate the colloid as a granular mass; whereas such acids as sulphuric and phosphoric, as well as certain salts, precipitate it in a gelatinous form. In discussing this phenomenon Bancroft[1] says:

"This precipitation of ferric oxide as a sandy mass by hydrochloric acid and as a gelatinous one by sulphuric acid is an important matter about which we appear to know very little theoretically. The formation of the gelatinous precipitates can not be a matter involving the hydrogen ion because we get the effect with sodium sulphate and do not get it with hydrochloric acid. Since it occurs with a number of different acids and salts, the effect can not be due to a specific anion. The one common characteristic is that the anions precipitate in low concentration and are, therefore, adsorbed strongly but this does not enable us to distinguish between the possible hypotheses of the effect being due to the solvent action of the adsorbed salt. It has been shown by von Weimarn that cellulose can be converted into a gelatinous mass by treating with concentrated salt solutions, preferably under pressure. In the particular case of ferric oxide, the salt concentrations are low, which makes it a little more probable that we may be dealing with the effect of the anion rather than of the salt; but, on the other hand, it is open to anybody to postulate a high salt concentration in or at the surface of the ferric oxide."

In order to acquaint ourselves with the exact nature of the differences in the physical character of the precipitates with different electrolytes, a series of precipitations were

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[1] Loc. cit.

carried out on a Péan de St. Gilles colloid. The colloid was prepared as follows: Twenty-five grams of ferric chloride were precipitated with a solution of sodium carbonate and the precipitate thoroughly washed by decantation. This was accomplished by placing the solution and precipitate into two 250 cc. bottles and centrifuging for ten minutes at 1500 r. p. m. The supernatant liquid was poured off and replaced with water, after which the precipitate was stirred up well and the centrifuging repeated. This was done until the removal of the electrolyte was so complete that the oxide started to go into colloidal solution in the wash water. To the precipitate suspended in 200 cc of water were next added 10 cc of glacial acetic acid which is less than the amount necessary to dissolve the oxide completely as ferric acetate. After standing for a few minutes a clear, dark red solution was obtained indicating that the excess oxide had been peptized by the acetate formed. This solution was diluted to 2500 cc and boiled until it became cloudy and of a brick-red color. From 30 to 40 hours were required.

In earlier experiments[1] the solution of the hydrous oxide was accomplished by adding acetic acid in the presence of relatively little water. Under these conditions a considerable amount of oxide remained undissolved unless an excess of acid was employed. There resulted a highly concentrated solution of ferric acetate containing excess acetic acid. The method above given ensures fairly rapid and complete solution with no excess of acetic acid.

Precipitation of the Colloid.—For the sake of uniformity of procedure the precipitations were carried out in the apparatus described in a previous communication.[1] This consists essentially of a glass tube 4 cm in diameter and 20 cm in length, closed with rubber stoppers. Concentric with the larger tube and held in place by the bottom stopper, is a smaller tube 2.5 cm in diameter and 7 cm in length. Twenty cubic centimeters of the colloid were placed in the inner compartment and a definite amount of normal or half-normal

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[1] Weiser and Middleton: Loc. cit.

electrolyte was placed in the outer compartment and diluted to 30 cc. Thus the precipitation took place always in a volume of 50 cc. After precipitation, the liquid was poured into a 50 cc eudiometer tube and at intervals observations were made of the volume and physical character of the precipitates. The volume occupied by the precipitate furnishes a good indication of its character since the most gelatinous precipitates are the most voluminous, and vice versa. Such precipitations were carried out with hydrochloric, nitric, sulphuric and phosphoric acids and with potassium sulphate and potassium chloride. These will be considered in detail.

(a) *Hydrochloric Acid.*—The precipitations with hydrochloric acid were carried out as above described. A portion of the observations are summarized in Table I. Under the heading "Volume of precipitate" is recorded the number of cubic centimeters which the precipitate occupies at the different time intervals. A blank space indicates that no precipitation has taken place. A star (*) after a number indicates that precipitation is incomplete; and the absence of a star shows that all or nearly all is precipitated.

TABLE I
Hydrochloric Acid as Precipitant

N acid cc	Volume of precipitate				Character of precipitate
	1 hr.	2 hr.	3 hr.	5 hr.	
8	—	0.2*	0.3*	0.4*	Granular, orange-red
9	0.6	0.5	0.5	0.5	Granular, orange-red
10	0.6	0.5	0.5	0.5	Granular, orange-red
11	—	—	—	0.3*	Granular, orange-red
12	—	—	—	—	No precipitate for 12 hours
13	—	—	0.3*	0.5*	Granular, orange-red
14	—	0.8*	0.8	0.7	Granular, orange-red
15	1.0	0.9	0.8	0.7	Less granular, brown brick-red

The colloid to which 15 cc of acid were added settled out in 15 minutes, but in all other cases settling was not observed until the solution had stood more than a half hour. The solutions were cloudy from the start, a condition that was less marked with the higher concentrations of acid. Even under the most favorable circumstances the agglomeration was relatively slow and the supernatant liquid continued more or less cloudy for hours. After the addition of acid, the suspensions became orange-red in color and came down as an orange-red powder. After precipitation was complete a portion of the supernatant liquid was tested for iron. A decided test was obtained, showing that the acid had an appreciable solvent action on the hydrous oxide.

From the table it will be noted that almost complete precipitation was obtained with 9 cc of acid in an hour; whereas with 12 cc of acid there was no precipitate in 5 hours. As a matter of fact, precipitation was only partial in this case after standing 24 hours. It is evident that we are dealing here with a so-called "abnormal series" similar to that observed by Freundlich[1] with other colloids. This will be taken up later in the paper.

(b) *Nitric Acid.*—Precipitations were carried out with nitric acid in the same manner as with hydrochloric. The observations are given in Table II.

TABLE II

Nitric Acid as Precipitant

N acid cc	Volume of precipitate				Character of precipitate
	1 hr.	2 hr.	3 hr.	5 hr.	
8	—	—	—	—	Precipitates after long standing, granular, orange-red
9	—	—	0.4*	0.5*	Granular, orange-red
10	1.7	1.5	1.3	0.9	Somewhat gelatinous, brownish brick-red
11	1.8	1.6	1.3	0.9	Somewhat gelatinous, brownish brick-red
12	2.0	1.6	1.3	0.9	Somewhat gelatinous, brownish brick-red
13	2.0	1.6	1.3	0.9	Somewhat gelatinous, brownish brick-red
15	2.1	1.7	1.4	0.9	Somewhat gelatinous, brownish brick-red

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[1] Zeit. phys. Chem., 73, 385 (1910); Kapillarchemie, 459 (1909); Freundlich and Schucht: Zeit. phys. Chem., 85, 641 (1913); cf. Bechhold: Ibid., 48, 385 (1904).

As with hydrochloric acid, immediate precipitation did not take place, but agglomeration was observed much sooner at the higher concentration than with hydrochloric. Precipitation was incomplete after 5 hours with 9 cc of acid; and several days were required with 8 cc. These precipitates came out slowly and were of the same character as the hydrochloric acid precipitate. With higher concentrations agglomeration was more rapid and the precipitate was somewhat gelatinous; much more so than with hydrochloric acid. Moreover, there was no region of non-precipitation above the first precipitation value, such as was observed with the halogen acid.

(c) *Sulphuric Acid.*—With sulphuric acid agglomeration took place at once and in every case the precipitate was distinctly gelatinous and brick-red in color.

TABLE III

Sulphuric Acid as Precipitant

N acid cc	Volume of precipitate				Character of precipitate
	$^1/_2$ hr.	1 hr.	2 hr.	3 hr.	
0.5	7.0	4.6	3.2	2.6	Gelatinous, brick-red
5.0	7.0	3.5	2.2	1.6	Gelatinous, brick-red
15.0	7.0	2.0	1.8	1.4	Gelatinous, brick-red

Although the precipitate was gelatinous in every case, it was less voluminous the more concentrated the acid used. After the precipitate settled, a portion of the supernatant liquid was removed and tested for iron with potassium ferrocyanide: The solution containing 0.5 cc of acid gave no test; that containing 5 cc showed a trace; and that containing 15 cc somewhat more.

(d) *Phosphoric Acid.*—The solution used in this experiment was normal $H_2(HPO_4)$.

TABLE IV

Phosphoric Acid as Precipitant

N acid cc	Volume of precipitate				Character of precipitate
	½ hr.	1 hr.	2 hr.	3 hr.	
0.5	6.8	5.2	4.4	4.2	Gelatinous, brick-red
5.0	6.0	4.0	3.3	3.1	Gelatinous, brick-red
15.0	5.2	3.3	2.4	2.1	Gelatinous, brick-red

Here, again, it will be noted that the precipitate is quite voluminous; and it is more so the smaller the concentration of acid used. The supernatant liquid gave no test for iron in the solution containing the most dilute acid; but in the most concentrated solution a slight test was obtained.

(e) *Potassium Sulphate.*—A half-normal solution of potassium sulphate was used. The observations are given in Table V.

TABLE V

Potassium Sulphate as Precipitant

N/2 salt cc	Volume of precipitate				Character of precipitate
	½ hr.	1 hr.	2 hr.	3 hr.	
0.5	6.5	5.0	4.5	3.5	Gelatinous, brick-red
5.0	6.0	4.2	3.6	3.5	Gelatinous, brick-red
15.0	5.0	4.3	3.7	3.5	Gelatinous, brick-red

The precipitate with potassium sulphate was somewhat more voluminous than with the corresponding acid; and as the electrolyte showed no solvent action, the volume was practically the same in the presence of varying concentrations of electrolyte.

(f) *Potassium Chloride.*—It was found that the stability of the colloid was such that the precipitation value under the conditions chosen was somewhat less than 5 cc of half-normal potassium chloride. Accordingly, 5 cc of salt solution was the smallest amount used. The results are given in Table VI.

TABLE VI

Potassium Chloride as Precipitant

$N/2$ salt cc	Volume of precipitate				Character of precipitate
	1/2 hr.	1 hr.	2 hr.	3 hr.	
5	5.8	4.5	3.9	3.8	Gelatinous, brick-red
10	5.4	4.1	3.8	3.7	Gelatinous, brick-red
15	5.4	4.1	3.8	3.6	Gelatinous, brick-red

From the above table it will be noted that the precipitate was of the same general character and occupied approximately the same volume as that obtained with potassium sulphate; but it is very different from the hydrochloric acid precipitate.

Discussion of Results.—A survey of the results obtained shows the marked difference in the character of the ferric oxide precipitate with different precipitating agents. Under the conditions outlined above, hydrochloric acid gives a distinctly granular precipitate while that obtained with sulphuric acid is gelatinous, as Giolitti observed. It is evident, however, that the formation of a gelatinous precipitate is independent of the valence of the precipitating ion since both potassium chloride and potassium sulphate give the same thing. The outstanding facts disclosed by the experiments are: that the most voluminous precipitate is obtained when there is immediate agglomeration throughout the entire solution; and when the precipitating agent has no solvent action on the particles. As a matter of fact, this is exactly what one might expect:

A gelatinous precipitate consists of a network of particles which has carried down with it a greater or lesser amount of water. It is well known that the slow formation of a precipitate from a supersaturated solution is conducive to the formation of large particles; whereas if the conditions are such that there is a rapid formation of finely divided particles, a gelatinous precipitate may be obtained. This has been observed by von Weimarn[1] in the case of precipitated barium sulphate, which ordinarily comes down in a distinctly granular form but which may, under certain conditions, form a gelatinous precipitate or even a jelly. In a colloidal solution we have very finely divided particles which are essential to the formation of a gelatinous precipitate. Moreover, in the case of the colloidal oxides the particles are hydrated to a greater or lesser extent, depending on the method of preparation. Other things being the same, we should expect to get the most gelatinous precipitate from a colloidal solution containing the most finely divided and the most highly hydrous particles. A low temperature is conducive to the formation of small and highly hydrous colloidal particles, while a high temperature will favor the formation of larger and less hydrous colloidal particles.[2] Therefore, the newly prepared Graham colloid will be more hydrous than that prepared by boiling the acetate. Accordingly, when the latter colloid agglomerates gradually, the particles that are not very highly hydrous, may form into more or less granular masses that will entangle relatively little water. On the other hand, if the colloid agglomerates rapidly throughout the entire solution, the hydrous particles will form a network that will enclose and adsorb a relatively large amount of water and hence will be relatively voluminous. This accounts for the fact that a gelatinous precipitate is always obtained when the precipitating anion is polyvalent. Under such conditions a relatively low concentration causes rapid agglomeration throughout the entire solution with the consequent formation of a gelatinous mass.

Although substances containing anions having a high precipitating power will cause rapid agglomeration and hence gelatinous precipitates, this property is obviously not confined to electrolytes with strongly adsorbed anions. Thus potassium chloride produces a very voluminous precipitate and yet choride ion is not strongly adsorbed as a rule. On the other hand, hydrochloric acid causes the precipitate to come

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[1] "Zur Lehre von den Zuständen der Materie," 10 (1914).

[2] Cf. Bancroft: Loc. cit.

down granular. The difference in the character of the precipitate with these two electrolytes having the same anion results from the difference in the solvent action and the rate of agglomeration. Potassium chloride possesses no solvent action and the stabilizing influence of potassium ion is relatively slight; hence, rapid agglomeration takes place at the precipitation value. With hydrochloric acid conditions are quite different: On account of the stabilizing influence of hydrogen ion, the precipitation value of hydrochloric acid is greater than of its potassium salt. Now it is usually stated that hydrochloric acid has no solvent action on the Péan de St. Gilles colloid since the latter is precipitated even by highly concentrated solutions of the acid. As a matter of fact, however, hydrochloric acid has a marked solvent action on the hydrous oxide, a property which is likewise possessed, but to a lesser degree, by both nitric and sulphuric acids. It is quite obvious that the solvent action will be greater while the oxide is in the colloidal state than after agglomeration into larger particles has taken place. Accordingly, the slower the colloid is agglomerated by a given acid the greater will be the amount dissolved. Although the Péan de St. Gilles colloid is fairly uniform compared to an old Graham colloid, there is unquestionably considerable variation in the size of the individual particles such as Zsigmondy and others have observed with colloids generally.[1] Now it is the smallest particles that are the most readily attacked; hence the solvent action will, to a greater or lesser extent, prevent the formation of a continuous network of particles, thus cutting down the amount of water that can be enclosed and carried down; and so decreasing the volume of the precipitate.

As before stated, hydrogen ion has a marked stabilizing action on the colloidal oxide. The solvent action of the acid replaces hydrogen ions with ferric ions and the latter are slightly more strongly adsorbed than the former. Even above the precipitation value, the combined stabilizing effect of the two cations will cause a gradual rather than an im-

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[1] Cf., however, Tolman: Jour. Am. Chem. Soc., 35, 307 (1913).

mediate agglomeration and the resulting precipitate will be granular rather than gelatinous in character.

From what has been said, it follows that if a sufficiently high concentration of hydrochloric or nitric acid is added to the colloid to cause quite rapid agglomeration before the solvent action of the acid has had time to manifest itself appreciably, we should get a precipitate that is distinctly more gelatinous than is obtained in the region of the precipitation value. Furthermore, it follows that a less gelatinous precipitate should be obtained with a relatively highly concentrated solution of sulphuric acid than with the quite dilute solutions in the region of the precipitation concentration. As pointed out, this tendency was shown in the precipitation experiments with sulphuric acid, above described. Finally, if the stabilizing influence of the cation tends to cut down the rate of agglomeration, then salts with polyvalent cations and univalent anions will produce a granular precipitate under certain conditions. Fortunately, all of these conclusions are readily verified experimentally.

Effect of the Concentration of Acid.—To determine the effect of the concentration of acid on the physical character of the precipitated oxide, 10 cc of 10-normal acid were diluted to 30 cc and placed in the outer compartment of the mixer; and 20 cc of colloid in the inner compartment. After mixing, the solution was transferred to a 50 cc eudiometer tube and observations made of the volume of the precipitate as previously explained. Precipitations were made with hydrochloric, nitric and sulphuric acids of the above concentration; and for the sake of comparison, a precipitation with 0.5 cc of normal sulphuric. The results are given in Table VII.

The precipitation was immediate in every case and was distinctly gelatinous in character. Indeed the precipitate with nitric acid was quite as gelatinous as with the concentrated sulphuric acid and that with hydrochloric was little less so. Moreover the precipitate with the concentrated sulphuric was not nearly so voluminous as with the dilute. The experi-

Table VII
Effect of the Concentration of Acid

Acid	Amount added	Volume of precipitate					Character of precipitate
		1/2 hr.	1 hr.	2 hr.	3 hr.	4 hr.	
Nitric	10 cc of 10 N	3.5	2.3	1.6	1.3	1.2	Quite gelatinous
Hydrochloric	10 cc of 10 N	3.3	1.6	1.2	0.9	0.9	Gelatinous
Sulphuric	10 cc of 10 N	3.6	2.4	1.6	1.3	1.2	Quite gelatinous
Sulphuric	0.5 cc of N	6.5	4.5	3.0	2.5	2.4	Very gelatinous

ments show conclusively that if the precipitation is sufficiently rapid, a gelatinous precipitate can be obtained with both nitric and hydrochloric acid; and, furthermore, that the precipitate with very dilute sulphuric acid is much more gelatinous than with the more concentrated acid which has an appreciable solvent action.

The Effect of the Nature of Salts.—Precipitations were carried out with thorium nitrate and with the chlorides of aluminum, iron, chromium, zirconium and potassium. The method was as follows: To 5 cc of colloid in a test-tube was added, drop by drop, a solution of the salt in question until there was noticeable clouding. To a second 5 cc portion was added a relatively large excess of electrolyte. The rate of precipitation and the physical character of the precipitate were noted in each case. The results are given in Table VIII.

Table VIII
Effect of the Nature of the Salt

Salt	Physical character of the precipitate on the addition of electrolyte	
	Not in excess	In excess
Potassium chloride	Gelatinous	Gelatinous
Aluminum chloride	Granular	Gelatinous
Chromic chloride	Granular	Granular
Ferric chloride	Granular	Gelatinous
Zirconium chloride	Granular	Granular
Thorium chloride	Granular	Gelatinous

From Table VIII it will be noted that the addition of enough electrolyte to cause clouding produced a granular precipitate with every salt with a polyvalent cation, while potassium chloride gave a gelatinous precipitate under these conditions. As was expected, the granular precipitate came out slowly, owing to the stabilizing influence of the cation and of the hydrous oxide formed by hydrolysis of the electrolytes. The addition of excess electrolyte caused almost immediate formation of a gelatinous precipitate in most cases; but with chromic chloride and zirconium chloride, the precipitate came out gradually and was granular under all circumstances. Again, the results show conclusively that the formation of a gelatinous precipitate of the hydrous oxide is a question of rate of agglomeration; and that it is possible to get either a granular or gelatinous precipitate with certain salts, by suitable variation in the conditions of precipitation.

The Two Precipitation Values with Hydrochloric Acid.—Attention was called in a previous paper[1] to Freundlich's observation that strychnine nitrate has two precipitation values for colloidal arsenious sulphide—one low and another relatively high. He considers that the lower value corresponds to negative arsenious sulphide while the higher value is for a positive colloid formed by the difficultly soluble strychnine base surrounding the particles. Freundlich and Schucht[2] observed a similar thing in determining the precipitation value for mercuric sulphide, of salts of heavy metals, like silver nitrate: "The explanation is the same as was previously recognized. In the lower precipitation zone we have the coagulation of negative mercuric sulphide. In the upper zone of non-precipitation the particles of mercuric sulphide are surrounded by silver oxide or the like, so that we have a positive colloid which is precipitated by nitrate ion in the upper zone of coagulation."

The explanation is a probable one in the cases above cited; but with hydrous ferric oxide, it seemed very unlikely that there

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[1] Weiser and Middleton: Jour. Phys. Chem., 24, 30 (1920).

[2] Zeit. phys. Chem., 85, 641 (1913).

could be a change of sign from positive to negative in a strongly acid solution. To make certain of this, however, the direction of migration of the colloid in the second zone of non-precipitation was determined. The colloid was prepared by adding 12 cc of normal hydrochloric acid diluted to 30 cc, to 20 cc of the original colloid. The direction of migration was determined in a modification of the Nernst apparatus recommended by Taylor.[1] It was found that the particles were positively charged.

It will be recalled that the concentration of acid in the immediate region of the first precipitation value caused a marked clouding at once; and that the solution remained distinctly clearer for a long time in the second zone of non-precipitation. A possible explanation seemed to be that the solvent action of the acid of a certain concentration resulted in the introduction of ferric ions which might be more strongly adsorbed and hence exert a greater stabilizing effect than hydrogen ions alone. This hypothesis proved not to be correct since the precipitation value of ferric chloride is not very much higher than that of hydrochloric acid. The following experiment illustrates that the presence of ferric ions has but little more effect than an equivalent amount of hydrogen ions: Thirteen cubic centimeters of normal hydrochloric acid were diluted to 29 cc and 1 cc of normal ferric chloride was added. This solution was mixed with 20 cc of colloid in the usual way and observation made of the time of precipitation. It was found that the agglomeration took place quite as rapidly as with 14 cc of acid instead of more slowly than with 13 cc, which would have been the case if the stabilizing influence of ferric ion was appreciably greater then that of an equivalent amount of hydrogen ion.

A second zone of non-precipitation can be accounted for best from a consideration of possible differences in the adsorption isotherms of hydrogen ion and chloride ion. It is well known that in relatively dilute solutions of hydrochloric acid the adsorption of hydrogen ion by ferric oxide is apprecia-

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[1] "Chemistry of Colloids," 78 (1915).

bly greater than that of chloride ion. Accordingly, the adsorption isotherm of the latter will lie under that of the former until such a concentration is reached that the adsorption of the two is equal; at which concentration, precipitation of the colloid takes place. Now it is quite conceivable that the two isotherms may coincide for a short distance within certain limits of concentration, then separate, and finally come together again at a higher concentration. This may be shown best by a diagram. In Fig. I, *A* and *B* may be considered

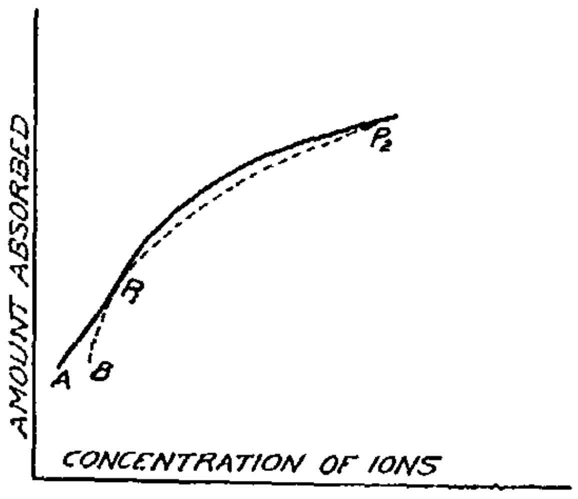

Fig. I

to represent a portion of the adsorption isotherm of hydrogen and chloride ion, respectively. At a certain concentration they coincide at the point P_1 which corresponds to the lower precipitation value. At a slightly higher concentration of acid, hydrogen ion is again more strongly adsorbed than chloride ion and the colloid is once more stable, although very much less so than the original colloid since the curves are quite close together relatively. At a still higher concentration of acid they come together again at the point P_2 which corresponds to the second precipitation value. At all concentrations above P_2 precipitation takes place. This explanation accounts for the two precipitation values, one above the other; and for the zone of non-precipitation between where the colloid is much less stable than the original colloid. It also accounts for the additional fact that the colloid does not change sign in the upper zone of non-precipitation.

Washing of Precipitated Hydrous Ferric Oxide.—Péan de St. Gilles called attention to the fact that the oxide precipitated with nitric acid or hydrochloric acid was carried back into colloidal solution by washing out the precipitating agent with water. This was not possible when the precipitation was effected with sulphuric acid. Since, in general, the precipitate obtained with hydrochloric acid is granular and with sulphuric acid is gelatinous, Bancroft[1] concludes that the determining factor is not the specific adsorbability of the ions but the physical character of the precipitate: "It seems to me more probable that the insolubility [of the sulphuric acid precipitate] in water is due to the precipitate being gelatinous and therefore coalescing into a continuous mass which is not peptized readily by water." While the physical character of the the deposit unquestionably has an effect, it is not the important factor as Bancroft supposed. Although it is true that the gelatinous precipitate with sulphuric acid is not peptized by washing, the very gelatinous precipitate obtained with potassium chloride is quite as readily peptized as the granular one gotten with hydrochloric acid. The following experiment illustrates this: Two 25 cc portions of colloid were taken and each diluted to 40 cc. To one were added 10 cc of $N/2$ potassium sulphate and to the other 10 cc of $N/2$ potassium chloride. The precipitates were thrown down by centrifuging for ten minutes at 1500 r. p. m.; after which the supernatant liquid was poured off and the inside of the container carefully rinsed with distilled water so as not to disturb the precipitate. Fifty cubic centimeters of water were added to each and after stirring up thoroughly, the centrifuging was repeated. It was found that practically all of the precipitate obtained with potassium chloride was carried back into a colloidal solution from which the particles were not separated by centrifuging. On the other hand, the precipitate obtained with potassium sulphate was not peptized by eight repetitions of the above process; and no further attempt was made. The experiment is conclusive evidence that the adsorbability

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[1] Loc. cit.

of the ion and not the physical character of the precipitate determines the degree of reversibility of precipitation of hydrous ferric oxide.

The Color of Hydrous Ferric Oxide

From the investigation to which reference has been made in the first part of this paper, it is evident that colloidal ferric oxide exists in three more or less separate and distinct colors: reddish brown, yellow and red. As might be expected, there are numerous intermediate shades. The variation in color of the hydrous oxide from brown, through yellow to red, was shown by Malfitano[1] and by Fischer[1] to be associated with an increase in the size of the particles; but they did not consider the possible connection between the two. Malfitano believes that the different colored substances obtained by hydrolysis of ferric chloride are complex compounds of different composition. Fischer does not share this view, but regards the brown colloid as hydrous $Fe_2O_3.1.5H_2O$; the yellow as hydrous $Fe_2O_3.H_2O$; and the red as hydrous Fe_2O_3. Ruff[1] believes that hydrous $Fe_2O_3.1.5H_2O$ is yellow rather than brown. As stated before, van Bemmelen was unable to prepare any definite hydrates under ordinary conditions, and it is doubtful if any exist. Moreover, Wöhler and Condrea[1] have shown that anhydrous oxides can be prepared that vary in color from yellow to red by simply varying the size of the particles. This has been confirmed by Keane[2] and by Scheetz,[3] who prepared a yellow anhydrous oxide by heating ferrous oxide in the presence of alumina, which prevents agglomeration to the red oxide.

Van Bemmelen[4] has called attention to the fact that the loss of water on heating the yellow hydrous oxide from 15° to 100° was slight; while if it is kept for some time at 200°, there is an appreciable loss of water and the color changes from yellow to red. This behavior led Fischer to the conclu-

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[1] Loc. cit.

[2] Jour. Phys. Chem., 20, 734 (1916).

[3] Ibid., 21, 570 (1917).

[4] Zeit. anorg. Chem., 29, 185 (1899).

sion that the yellow oxide is a hydrous hydrated oxide instead of a hydrous oxide. Wöhler and Condrea have likewise observed a change in color when a certain oxide lost water which they, too, considered was water of constitution rather than adsorbed water. They pointed out, however, that the loss in water favored the growth of particles by decreasing the viscosity of the medium; and that this growth in particles changed the color since the original color of the hydrous oxide was obtained by fine grinding of the dehydrated one. A number of experiments have been carried out which indicate that the different colors of hydrous ferric oxide are due to variation in the size of the particles.

Effect of the Velocity of Hydrolysis of Ferric Chloride.—Malfitano showed that the slow heating to 100° of a ferric chloride solution of suitable concentration resulted in the formation of an ochre-yellow colloid; while sudden heating produced a red-brown colloid that was apparently heterogeneous, but less so than the yellow. Krecke[1] poured a ferric chloride solution into boiling water and obtained a perfectly clear dark red-brown colloid. The difference in appearance of these three colloids is most likely due in part to a difference in the size of particles produced by difference in the rate of hydrolysis. To determine the extent of this influence, a series of experiments was carried out as follows: Fifty cubic centimeters of water were placed in an Erlenmeyer flask and brought to a certain temperature. To the water were then added 10 cc of an approximately 20 percent solution of $FeCl_3.6H_2O$; and the temperature, after mixing, was noted. The flask was then set on an electric hot-plate of constant temperature which brought the solution to the boiling point, where it was kept boiling vigorously for 5 minutes. Since the hydrolysis is most rapid at higher temperatures and is practically complete at 100°, the rate of hydrolysis depends on the temperature of the water to which the ferric chloride is added and the time necessary to bring it to the boiling point. The results of a series of experiments at various temperatures are given

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[1] Loc. cit.

in Table IX. In the first column is given the initial temperature of the solution; in the second and third, the color of the solution after two hours and the stability after standing for a day.

TABLE IX

The Hydrolysis of Ferric Chloride

Temperature (degrees)	Observations	
	Color	Stability (after 24 hrs.)
10	Ochre-yellow	Considerable precipitated
25	Ochre-yellow (brownish)	Considerable precipitated
40	Brownish yellow	Partly precipitated
60	Yellow-brown	Little precipitated
73	Brown	Trace settled out (cloudy)
84	Reddish brown	No precipitate (cloudy by reflected light)
100	Dark red-brown	Clear in both transmitted and reflected light

The above table shows very clearly the effect of the rate of hydrolysis on the size of the particles and hence on the color of the colloid. When the salt solution is added to boiling water the hydrolysis is most rapid and the particles are relatively small and red-brown in color. When added to water at 0° and heated gradually to boiling, the particles form slowly and hence are larger and yellower in color. Between these extremes lie all variations in size of particles and color of the colloid formed.

Effect of Hydrochloric Acid on the Size of Particles Formed during Hydrolysis of Ferric Chloride.—As observed by Goodwin and by Fischer, the brown colloid is apparently transformed into the yellow by the action of hydrochloric acid. This is what one might expect since it is well known that the solvent action of the medium, as well as the rate of formation, determines the size of particles separating from solution. In order to show the extent of this effect, the hydrolysis was carried out by introducing 10 cc of 20 percent ferric chloride solution into water containing a definite small amount of hydrochloric acid at 93°. The resultant solution, the temperature of which was 84°, was placed on the electric hot-plate and heated to boiling, where it was kept for 5 minutes. From the preceding table it will be noted that a stable reddish brown colloid is formed in this way when the salt solution is added to pure water. Under otherwise constant conditions, a difference in the size of the particles, and hence in the color, was noted by adding the salt solution to acid as dilute as $^5/_{100}$ normal. The results with varying concentrations of acid are given in Table X. In the first column is given the amount of normal hydrochloric acid added to 50 cc of water from a 2 cc Mohr's pipette.

TABLE X
Effect of Hydrochloric Acid

N HCl cc	Temperature (degrees)	Observations	
		Color	Stability (after 24 hrs.)
0.0	84	Reddish brown	No precipitate
0.1	84	Light reddish brown	No precipitate
0.3	84	Brown	No precipitate
0.5	84	Brownish yellow	Some precipitate
0.7	84	Ochre-yellow	Most precipitated
0.9	84	Ochre-yellow	Most precipitated

The above results show clearly the influence of the solvent action of hydrochloric acid on the size of the particles and hence on the color. Similar results were obtained with nitric acid. The two factors, rate of hydrolysis and solvent action of the electrolyte, go hand in hand in the formation of hydrous ferric oxide by the hydrolysis of a ferric salt. Which will be the determining factor depends entirely on the conditions under which the hydrolysis is brought about. It is evident that the rapid hydrolysis on slowly pouring a salt solution into water at the boiling point results in the formation of very small particles in spite of the solvent action of the water and of the acid which is a product of the hydrolysis. On the other hand, if the ferric chloride solution is added slowly to water that has been acidified slightly, the solvent action should result in the formation of larger particles, even at the boiling point. This is exactly what happens: To 50 cc of water acidified by the addition of 2 cc. of normal hydrochloric acid, were added slowly 10 cc of 20 percent $FeCl_3.6H_2O$ and the boiling continued for 5 minutes. An ochre-yellow colloid was obtained similar in every way to that prepared by slow heating of the aqueous solution of ferric chloride from room temperature to the boiling point.

The Action of Ferric Chloride.—Malfitano has pointed out that the residue after filtration of the yellow colloid is readily peptized by ferric chloride; but that the solution remains quite cloudy, no matter how much ferric chloride is added. This experiment has been confirmed.

Malfitano observed also that the particles obtained by filtration of the brown colloid are peptized by ferric chloride, forming a clear solution, the particles of which are not removed by the ultrafilter. He states that if this solution is now heated the color goes to ochre-yellow and the colloid precipitates out. From this he concludes that the brown colloid can be changed to the ochre-yellow by the action of ferric chloride. It seems to me that this experiment is open to the objection that heating the ferric chloride solution alone produces an ochre-yellow colloid; so that an ochre-yellow precipitate does not necessarily indicate that the brown colloid has been transformed to yellow by this process. Some experiments have been carried out which indicate that no such transformation takes place:

1. A solution of ferric chloride was precipitated with a slight excess of sodium carbonate and the precipitate thoroughly washed, making use of the centrifuge. The freshly prepared oxide was added to $N/2$ ferric chloride in small amounts at a time until it had taken up all the oxide that it could. In this way a very concentrated brown colloid was obtained. When this solution was heated, no clouding was observed.

2. In the first experiment, the concentration of ferric

chloride was low since most of the ferric ions were adsorbed by the hydrous oxide which was carried into solution thereby. A varying excess of ferric chloride solution was next added to several small portions of the colloid which was then heated. Precipitates were obtained which varied in color from brown to brownish yellow, depending entirely on the excess of ferric chloride and the rate of heating.

The results of the above experiments are quite in line with the observations made by Neidle.[1] The latter found that colloidal ferric oxide, prepared by dissolving the freshly precipitated oxide in excess ferric chloride, could not be dialyzed hot at the start, since the yellow ochreous variety of the oxide was formed. By dialyzing in the cold until the excess of ferric chloride was removed, the colloidal solution could be heated to boiling and the dialysis continued in the hot without the appearance of the yellow colloid.

Attention has been called to Bancroft's hypothesis that the yellow color of certain hydrous oxides may be due to adsorbed ferric salt. If this is the case, one might expect to get a yellow precipitate if the brown or red colloid were thrown down in a highly gelatinous form in the presence of excess ferric salt. In a previous experiment it was shown that the Péan de St. Gilles colloid was precipitated in a gelatinous form by excess ferric chloride. The precipitate so obtained was distinctly red in color even in the presence of a very large excess of electrolyte. Similar results were obtained by precipitating in the presence of excess ferric chloride, the dark red-brown colloid prepared by adding ferric chloride to boiling water. To a 5 cc portion of this colloid was added an excess of ferric chloride and enough potassium sulphate solution to cause agglomeration. A gelatinous red-brown precipitate resulted. Ferric sulphate solution likewise produced a red-brown precipitate. On account of the gelatinous character of the precipitate obtained in each of these experiments, there is certain to be considerable adsorption of ferric salt. The experiments indicate, therefore, that adsorption of ferric

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[1] Jour. Am. Chem. Soc., 39, 71 (1917).

salt by hydrous ferric oxide does not necessarily result in a yellow modification.

The Stepwise Transformation from the Brown to the Red Colloid.—As previously noted, the interesting observation has been made that the first product of the hydrolysis of ferric chloride is the brown colloid which goes over into the larger yellow particles at ordinary temperatures if the solution is sufficiently dilute; and, finally, that the yellow particles are transformed into the still larger brick-red, by continued heating. A number of experiments have been carried out which show the conditions under which this stepwise transformation takes place:

1. A 1 percent solution of ferric chloride was heated slowly; and it was noted that the solution became not only opalescent but that particles sufficiently large to be seen were obtained near the boiling point. On raising the temperature to boiling and then allowing the solution to cool, a yellowish brown colloid was obtained from which no precipitate deposited on standing for several hours. By boiling this solution vigorously for a few days, the oxide went over entirely into the brick-red particles which settled out on standing. From this experiment it is clear that if the conditions are chosen properly, one can bring about the stepwise change from the brown through the yellow to the brick-red.

2. A 4 percent solution of ferric chloride was heated slowly from 25° to 100°; a yellow ochreous colloid was obtained that was heated at 100° for several days with but slight change in color resulting. If this solution were heated to a higher temperature in a bomb tube, a precipitate having the red color of powdered haematite would result (Fischer).

3. 10 cc of a 20 percent solution of $FeCl_3.6H_2O$ were added to 50 cc of boiling water and the solution boiled for several hours. Under these conditions was obtained the brick-red precipitate identical with that resulting from the dilute solution used in Experiment 1.

4. 50 cc of solutions of ferric chloride were prepared of the following concentrations: *N*/50; *N*/100; and *N*/500.

When first prepared the $N/50$ solution was very light and the other two were almost colorless. On standing the $N/50$ solution became orange-yellow in color; the $N/100$ yellow; and the $N/500$ canary-yellow. The solvent action of the water was probably an important factor here, since the concentration of the acid was so low. These solutions were heated to boiling: the $N/50$ became scarlet-red; the $N/100$ orange-red; and the $N/500$ reddish orange. As the boiling was continued the transformation to the brick-red colloid took place gradually. A precipitate settled out of the most concentrated solution after boiling for a day; while the $N/100$ solution required more than twice as long to produce the same result. The $N/500$ acquired a bright red color, but boiling was discontinued before the particles were agglomerated sufficiently large to settle. Here, again, the direct transformation from the yellow to the red colloid was observed.

From the above experiments it is demonstrated that the yellow colloid formed under certain conditions can be transformed into the red colloid by prolonged boiling of the solution; and when formed under other conditions it is not transformed by the boiling process at atmospheric pressure. It will be recalled that Fischer showed that the degree of hydration of the colloids decreases in the order: brown, yellow, red. As previously pointed out, Keane and Scheetz have demonstrated that the yellow color of bricks is due to finely divided anhydrous ferric oxide which is kept from agglomerating by alumina and probably by certain other substances as well. This requires a rather high percentage of alumina. In the so-called Mars pigments which are yellow, the ferric oxide is in the hydrous state; and in this condition it agglomerates less readily to the red oxide and less alumina is required to prevent the transformation. From this it is clear that the failure of the yellow colloid to lose water when formed under certain conditions, accounts for the difficulty with which it is transformed into the red colloid at 100° and the relative ease with which the transformation takes place at higher temperatures.

The Stability of the Yellow Hydrous Oxide.—It has been shown that blue hydrous copper oxide is stabilized to such a degree by the adsorption of certain salts, that a suspension of it may be heated to the boiling point without dehydration taking place.[1] This immediately suggests that the stability of the yellow hydrous ferric oxide may be due to adsorption of some salt. The hypothesis seems all the more probable in view of the fact that the stability of the oxide is much greater under certain conditions of formation than under others, as shown by the results of the experiments in the preceding section. Referring once more to Bancroft's hypothesis, that the yellow color of the hydrous oxide is due to the presence of adsorbed ferric salt, we find that this suggestion was based on Fischer's observation that the brown colloid went over into the red in the presence of hydrochloric acid; on Malfitano's experiment that the brown colloid is transformed into the yellow by boiling with ferric chloride; and on Phillips' method of preparing the yellow oxide by oxidation of ferrous carbonate. The results obtained by Fischer and by Malfitano have been accounted for in another way. Moreover, the hydrous oxide has been precipitated in a gelatinous form in the presence of a large excess of ferric chloride,—a condition that would favor marked adsorption of ferric salt; and yet the oxide was distinctly red. Accordingly, it is probable that the color of the yellow colloid is not due to adsorbed iron salt. Bancroft's hypothesis was the outgrowth of the observation that the yellow colloid was formed under such conditions that the absorption of an iron salt was a possibility. The converse appears not to be the case, namely, that the adsorption of an iron salt always results in the formation of a yellow hydrous oxide. Although the adsorption of an iron salt probably does not impart a yellow color to a hydrous ferric oxide, it is altogether possible that the yellow hydrous oxide which is not converted to the red by heating at 100°, is stabilized by absorbed iron salt. This hypothesis is in line with the results of experiments above described. The

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[1] Blucher and Farnau: Jour. Phys. Chem., 18, 629 (1914).

following may be mentioned: (1) The yellow hydrous oxide resulting from the hydrolysis of a dilute solution of ferric chloride, is formed under conditions that are unfavorable to the adsorption of ferric salt, and this colloid is transformed readily into the red by continued boiling. (2) The yellow hydrous oxide produced by the slow heating of more concentrated solutions of ferric chloride is formed under conditions favorable to the adsorption of ferric salt; and this hydrous oxide is distinctly stable at 100°. (3) The hydrolysis of ferric chloride is very rapid at 100°. Accordingly the hydrous oxide formed by the addition of ferric chloride to boiling water will not be stabilized by adsorption of ferric salt and so will be converted to the brick-red oxide by boiling. (4) Finally, the yellow hydrous oxide formed by hydrolysis of ferric chloride poured into dilute hydrochloric acid solution at elevated temperatures, is stable as we should suppose. These results all support the hypothesis that the yellow hydrous oxide is stabilized by adsorption of ferric salt.

The Color of the Péan de St. Gilles Colloid.—The Péan de St. Gilles oxide is always described as brick-red in color; but early in the investigations on this oxide, I noted that the shade of different preparations varied from a brown-red to a dark brick-red, even though the same general method was employed in the preparation. At first I was inclined to attribute the variation in color to difference in the time of boiling; but some later observations disclosed that this was not the case:

1. A solution of ferric acetate was prepared by adding 10 cc of glacial acetic acid in 200 cc of water to the freshly prepared and thoroughly washed oxide obtained from 25 g. of $FeCl_3.6H_2O$. This solution had stood for three weeks when a portion of it was made up to approximately *N*/20 and boiled for 30 hours. Much to my surprise, the colloid was not even a shade of red, but was distinctly yellow colored and gave a yellow precipitate with salts instead of brick-red. The following experiment was then carried out: From the concentrated acetate solution were prepared 750 cc of an *N*/20

solution which was boiled for 40 hours. Samples of 10 cc each were withdrawn at intervals and the color of the colloid observed. These samples were then diluted to 20 cc; precipitated by the addition of 5 cc of $N/2$ potassium sulphate; and the color of the precipitate noted. The results are given in Table XI.

TABLE XI

Boiling of $N/20$ Ferric Acetate

Time (hours)	Color of colloid	Color of precipitate
0	Light red	Brown
1/6	Light red	Brown
1/2	Orange-red	Light brown
1	Reddish orange	Light brown
3	Light reddish orange	Brownish orange
5	Orange	Reddish orange
10	Orange	Reddish orange
15	Orange	Orange
20	Orange	Orange
30	Orange-yellow	Yellow
40	Orange-yellow	Yellow

From the above experiments it is quite evident that the hydrolysis of the acetate resulted in the formation of the yellow hydrous oxide which was sufficiently stable that it was not converted into the red oxide by boiling.

2. A solution of ferric acetate was prepared by suspending in 150 cc of water, the ferric oxide obtained from 25 grams of $FeCl_3.6H_2O$; adding 10 cc of glacial acetic acid; and diluting to 250 cc. This solution was allowed to stand for 10 days, after which 20 cc were taken and diluted to 100 cc, making a solution which was approximately 2.2 N. By diluting the latter, were prepared 50 cc portions of other solutions of various concentrations as given in Table XII. A new solution of ferric acetate was next prepared of the same concentration as the old; and as soon as possible, this new solution was diluted in the same manner as the old. The two series of solutions in 150 cc beakers were placed on an electric hotplate and boiled vigorously for 15 hours, replacing the water

as it evaporated. A difference in the color of the two series of colloids was soon noted, which became quite pronounced as the boiling continued: the colloids from the old ferric acetate were yellow; and from the new were red.

After the boiling, a 2 cc portion of the most concentrated solution of each series was diluted to 45 cc and 5 cc of $N/2$ potassium sulphate added to precipitate the colloid. In the same manner, 4 cc, 8 cc, 16 cc and 32 cc portions of the other solutions of each series were diluted to 45 cc and precipitated. In this way the same amount of precipitate was obtained and the color was observed. The result with the two series are recorded in Table XII and Table XIII.

TABLE XII
Hydrolysis of Old Solution of Ferric Acetate

Solution boiled		Color of colloid	Color of precipitate
Ferric acetate 2.2 N	Water		
50.0	0.0	Reddish orange	Yellow
25.0	25.0	Orange	Yellow
12.5	37.5	Light orange	Yellow
6.25	43.75	Yellow	Yellow
3.13	46.87	Canary	Yellow

TABLE XIII
Hydrolysis of New Solution of Ferric Acetate

Solution boiled		Color of colloid	Color of precipitate
Ferric acetate 2.2 N	Water		
50.0	0.0	Very dark red	Dark brick-red
25.0	25.0	Dark red	Dark brick-red
12.5	37.5	Red	Dark brick-red
6.25	43.75	Light red	Dark brick-red
3.13	46.87	Orange-red	Dark brick-red

It is evident from the above experiments that the formation of the red colloid in one instance and the yellow in another, is not a question of the dilution or the duration of boiling, but of the length of time that the acetate solution is allowed to stand before it is diluted and boiled. This is what one might expect from the previous observations on the stability of yellow hydrous ferric oxide:

Reinitzer[1] showed that a ferric acetate solution can be evaporated to crystallization only in the presence of excess acetic acid. The solution of the normal acetate is fairly stable at low temperatures; but Herz[2] finds that at 44° it decomposes quite rapidly with the precipitation of $Fe(OH)_2C_2H_3O_2$. Rosenheim and Muller[3] prepared a ferric acetate to which they assign the formula $Fe_2(C_2H_3O_2)_5OH$, by the action of glacial acetic acid on ferric oxide. A solution of this salt containing 9.772 grams per liter hydrolyzes completely in 216 hours at 20° with the formation of colloidal hydrous ferric oxide.

The concentrated solutions of ferric acetate prepared by us contained no excess acetic acid and so hydrolysis took place slowly at ordinary temperatures. This was proven by the fact that a few drops of potassium sulphate solution caused no precipitation of the newly formed acetate for almost an hour; whereas a copious precipitate resulted at once in the old. The very slow hydrolysis in the presence of excess ferric salt furnished ideal conditions for the formation of the yellow hydrous particles stabilized by adsorbed ferric salt. Therefore, an old solution of ferric acetate does not go over to the brick-red colloid on boiling. The newly formed solution diluted and heated at once hydrolyzes very rapidly under conditions much less favorable for the formation of the stable yellow colloid and consequently the brick-red colloid is always obtained under such circumstances.

Investigation of the properties of negative hydrous ferric oxide[4] are being made and will be reported on in a subsequent communication.

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[1] Monatshefte f. Chemie, **3**, 256 (1883).

[2] Zeit. anorg. Chem., **20**, 16 (1899).

[3] Rosenheim and Muller: Zeit. anorg. Chem., **39**, 175 (1904).

[4] Fisher: Biochem. Zeit., **27**, 223 (1910); Grimaux: Comptes rendus, **98**, 1485 (1884); Powis: Jour. Chem. Soc., **107**, 818 (1915).

The results of this investigation may be summarized briefly as follows:

1. A survey of the investigations on the composition of colloidal ferric oxide has been made. The existence of no definite basic ferric salt has been established with certainty and but one definite crystalline hydrate has been prepared. The latter is formed only under special conditions: the decomposition of sodium ferrite by water at ordinary temperature. Accordingly it is probable that the different ferric iron colloids are not composed of basic salts of varying composition or of hydrous hydrated oxides; but instead are hydrous ferric oxide.

2. A study has been made of the physical character of colloidal and precipitated hydrous ferric oxide.

3. The difference in properties of colloidal hydrous ferric oxides prepared by different methods and of different ages, is due to a difference in the degree of hydration and in the size of the colloidal particles.

4. It is unnecessary to postulate the existence of basic chlorides or complex salts of varying composition in order to account for the observation that only part of the chlorine present in the dialyzed Graham colloid appears to exist as ion.

5. Certain electrolytes precipitate the Péan de St. Gilles colloid in a gelatinous form while others precipitate it in a granular form. The nature of the precipitate depends on the conditions of precipitation; the same electrolyte may produce either a granular or gelatinous mass under suitable circumstances.

6. The most gelatinous precipitate is obtained when there is very rapid agglomeration of the hydrous particles throughout the entire solution and when the electrolyte possesses no solvent action; the most granular precipitate results when the agglomeration progresses slowly and when the electrolyte possesses a solvent action.

7. Acids and salts with polyvalent anions precipitate the Péan de St. Gilles colloid rapidly in extremely low concentration and so produce a gelatinous precipitate. Similar re-

sults are obtained at somewhat higher concentrations with salts both of whose ions are univalent.

8. Acids with univalent anions and salts with univalent anions and polyvalent cations, precipitate the Péan de St. Gilles colloid only at relatively high concentrations. The stabilizing influence of the cation causes relatively slow agglomeration of a granular mass in the region of the precipitation value. Sufficiently high concentration of such electrolytes may cause rapid agglomeration with the consequent formation of a gelatinous precipitate.

9. The smallest particles in a colloidal solution are most readily attacked by an electrolyte that has an appreciable solvent action. The agglomeration of a colloid by such an electrolyte will tend to make the precipitate more granular by destroying or preventing the formation of the continuous network of particles necessary for producing a gelatinous mass.

10. Hydrochloric acid possesses two precipitating values for the Péan de St. Gilles colloid: one above the other with a zone of non-precipitation between where the colloid is stable but less so than the original colloid. An explanation of this phenomenon has been offered.

11. The degree of reversibility of the precipitation of hydrous ferric oxide is determined for the most part by the specific adsorbability of the precipitating ion, although the physical character of the precipitate doubtless has some effect.

12. An investigation has been made of the factors that affect the color of colloidal ferric oxide. It is not probable that the different colors are due to complex salts or to hydrous hydrated oxides; but to variation in the size of the particles of hydrous ferric oxide.

13. Three different colors of colloidal hydrous ferric oxide are generally recognized: reddish brown, yellow and red. Under suitable conditions, it is possible to make the stepwise transformation from brown through yellow to red by increasing the size of the particles.

14. The rapid hydrolysis of ferric chloride on adding the

salt solution to boiling water, produces very small particles that are reddish brown in color; the slow hydrolysis of a dilute solution at ordinary temperatures or of a more concentrated solution heated slowly to the boiling point, produces larger particles that are yellow. Continued boiling of the brown or the yellow colloid formed under certain conditions causes agglomeration to still larger particles that are red. All variations in shade can be realized from the very small brown to the large dark red particles.

15. The hydrolysis of a ferric chloride solution poured into hot water, produces small brown particles; but if poured into hot, dilute hydrochloric or nitric acid, the solvent action of the acid results in the formation of larger particles that are yellow. All variations in shade from reddish brown to yellow can be realized by suitable variation in acid concentration and hence in the size of the particles.

16. Anhydrous ferric oxide varies in color from yellow to red with increasing coarseness of grain. The yellow anhydrous oxide agglomerates much more readily to the red oxide on heating, than does the yellow hydrous oxide.

17. The yellow colloidal hydrous oxide formed under conditions that favor the adsorption of ferric salt, is not readily dehydrated at 100°, and so does not readily agglomerate to the red oxide until a higher temperature is reached. The stability of this oxide under certain conditions is probably due to adsorbed ferric salt.

18. A yellow colloid has been prepared by the Péan de St. Gilles method by allowing the acetate solution prepared in a given way, to stand for a few days before diluting and boiling. The slow hydrolysis of the acetate favors the formation of yellow hydrous oxide stabilized by adsorbed ferric salt. When such a solution is boiled, a stable yellow colloid is formed instead of the usual brick-red.

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NEW BOOKS

Creative Chemistry. *By E. E. Slosson. 20 × 14 cm; pp. x + 311. New York: The Century Co., 1919.*—In the introduction Stieglitz says that the chemists saved Germany from an early disastrous defeat, both in the field of military operations and in the matter of economic supplies. Without the tremendous expansion of her plants for the production of nitrates and ammonia from the air by the processes of Haber, Ostwald, and others, the war would have ended in 1915 or early in 1916 from exhaustion of Germany's supplies of nitrate explosives, if not indeed from exhaustion of her food supplies as a consequence of the lack of nitrate and ammonia fertilizers for her fields. It is the object of the author to bring before the public the importance of chemistry, to tell some of the great results of modern chemical activity, and to call attention to some of the large problems which must continue to engage the attention of our chemists. It is not easy to do this without presupposing a technical knowledge which the general public does not have.

Mr. Slosson calls his separate chapters: three periods of progress; nitrogen; feeding the soil; coal-tar colors; synthetic perfumes and flavors; cellulose; synthetic plastics; the race for rubber; the rival sugars; what comes from corn; solidified sunshine; fighting with fumes; products of the electric furnace; metals, old and new. He considers that there are three stages distinguishable in the conquest of nature; the appropriative period in which the savage discovers things; the adaptive period in which the barbarian improves on them; and the creative period in which civilized man invents things.

The chapter on nitrogen begins with the words: "In the eyes of the chemist the Great War was essentially a series of explosive reactions resulting in the liberation of nitrogen. Nothing like it has been seen in any previous wars. The first battles were fought with cellulose, mostly in the form of clubs. The next were fought with silica, mostly in the form of flint arrow-heads and spear-points. Then came the metals, bronze to begin with and later iron. The nitrogenous era in warfare began when Friar Roger Bacon or Friar Schwartz—whichever it was—ground together in his mortar, saltpeter, charcoal and sulphur." The invention of smokeless powder in 1887 marked the beginning of the nitrocellulose period. In all powders, smokeless or not, nitrogen is the essential element.

Nitrogen is essential both in war and in agriculture. "The Great War not only starved people; it starved the land. Enough nitrogen was thrown away in some indecisive battle on the Aisne to save India from a famine. The population of Europe as a whole has not been lessened by the war; but the soil has been robbed of its power to support the population. A plant requires certain chemical elements for its growth and all of these must be within reach of its rootlets for it will accept no substitutes. A wheat stalk in France before the war had placed at its feet nitrates from Chile, phosphates from Florida and potash from Germany. All these were shut off by the firing line and the shortage of shipping."

In the chapter on coal-tar colors we read that "the tar, which for a hundred years was thrown away and nearly half of which is ye. thrown away in the United States, turns out to be one of the most useful things in the world. It is one of the strategic points in war and commerce. It wounds and heals. It supplies munitions and medicines. It is like the magic purse of Fortunatus from which anything wished for could be drawn. The chemist puts his hand into the black mass and draws out all the colors of the rainbow. This evil-smelling substance beats the rose in the production of perfume and surpasses the honeycomb in sweetness." Among the important synthetic perfumes made from coal tar are geraniol, citral, violet, musk, orange blossoms, heliotrope, and jasmine, while most of the vanillin and oil of wintergreen on the market are synthetic products and a great deal of camphor is made from turpentine.

Under cellulose we have paper, cotton, collodion, artificial silk and artificial leather. When camphor is added to a nitrated cotton we get celluloid of which the author says, p. 132: "It is hard but light, tough but elastic; easily made and tolerably cheap. Heated to the boiling point of water it becomes soft and flexible. It can be turned, carved, ground, polished, bent, pressed, stamped, molded or blown. To make a block of any desired size simply pile up the sheets and put them in a hot press. To get sheets of any desired thickness, simply shave them off the block. To make a tube of any desired size, shape or thickness, squirt out the mixture through a ring-shaped hole or roll the sheets around a hot bar, cut the tube into sections and you have rings to be shaped and stamped into box bodies and napkin rings. Print words or pictures on a celluloid sheet, put a thin transparent sheet over it and weld them together, then you have something like the horn book of our ancestors, but better."

"The problem of synthetic rubber has been solved scientifically but not industrially. It can be made but can not be made to pay. The difficulty is to find a cheap enough material to start with. We can make rubber out of potatoes —but potatoes have other uses. It would require more land and more valuable land to raise the potatoes than to raise the rubber. We can get isoprene by the distillation of turpentine—but why not bleed a rubber tree as well as a pine tree? Turpentine is neither cheap nor abundant enough. Any kind of wood, sawdust for instance, can be utilized by converting the cellulose over into sugar and fermenting this to alcohol; but the process is not likely to prove profitable."

In the first paragraph of the chapter on beet and cane sugar, p. 164, we read that "among the marvels that the Greeks heard from the Far East two of the strangest were that in India there were plants that bore wool without sheep and reeds that bore honey without bees. These incredible tales turned out to be true and in the course of time Europe began to get a little calico from Calicut and a kind of edible gravel that the Arabs who brought it called 'sukkar.' But of course only kings and queens could afford to dress in calico and have sugar prescribed for them when they were sick." In the chapter on corn we learn some more facts. "The discovery of America dowered mankind with a world of new flora. The early explorers in their haste to gather up gold paid little attention to the more valuable products of field and forest, but in the course of centuries their usefulness has become universally recognized. The potato and tomato, which Europe at first considered as unfit for food or even as poisonous, have now become indispensable among all classes. New World drugs like quinine and cocaine have been adopted into every pharmacopeia. Cocoa is proving arival of tea and coffee, and even the banana has made its appearance in European markets. Tobacco and chicle occupy the nostrils and jaws of a large part of the human race. Maize and rubber are becoming the common property of mankind, but still may be called American. The United States alone raises four-fifths of the corn and uses three-fourths of the caoutchouc of the world."

These extracts will show that there is a great deal of value and interest in the book. One is continually coming across unsuspected information as, for instance, that the red rubber sponge and eraser tips for pencils may be made from a gum extracted from the corn germ. There are relatively few mistakes, though one doubts the estimate of 14-20 cents per gallon for alcohol made from sawdust, p. 191, and Baekeland was born in Luxemburg instead of in Belgium. Owing to the desire to be interesting the author has forced the humorous note too much. In spite of occasional defects the book is an extremely valuable one and the chemists of the country are indebted to Mr. Slosson for the time, energy and brains which he has put into this volume. *Wilder D. Bancroft*

Chemistry from the Industrial Standpoint. *By P. C. L. Thorne. 19 × 13 cm; pp. xvi + 244. London: Hodder and Stoughton, 1919. Price: 4/6.*— In the introduction Mr. Briscoe says: "I am continually astonished to find the real control of large industries in the hands of men who have not the haziest idea as to the basic principles upon which their industry depends. All this, of course, is not the fault but the misfortune of the business man, who is practically always in the position of having to learn in the hard school of experience, at an undue cost, many things essential to success which should have been inculcated in his youth. In other words, the radical defect is in our system of education—and despite the efforts of the last few decades, the present system of education is still defective in the same general manner, if not quite to the same extent, as that which produced this deplorable result. The fault lies partly at the door of the teacher himself; he has too often taught his subject on the basis that it is of interest for its own sake. This may do well for the hundredth pupil, who has a natural or acquired liking for that particular subject, but it leaves the ninety-nine stone-cold. Their interest can only be awakened when they are brought to realize that the subject has an intimate relation to their daily life and that its study will help them to *live* in one or other sense of the word.

"A praiseworthy prejudiceagainst purely utilitarian education causes many teachers to handle their subjects in an atmosphere of entire detachment from their practical applications. Chemistry in particular has suffered in this way and the book Mr. Thorne has now written is the first of its kind. It is a departure from standard practice which is, I believe, of the first importance."

The subject is presented under five headings: solids, liquids, and gases; chemical change; elements and compounds; the rate of chemical change; use of electricity in chemical changes. Under the first head the author discusses, among other things, the extraction of sulphur by smelting, the extraction of salt by solution and crystallization; filters, hydro-extractors, etc.; fractional distillation; removal of dust and fog from gases, and sublimation. Under chemical change the author takes up the slaking of lime; the preparation of ammonium sulphate and of zinc oxide, the burning of fuels, the Goldschmidt method of preparing metals; general methods of smelting ores; the replacement of metals in solution; the production of water gas; the chlorination of benzene, and the manufacture of nitric acid and of sodium carbonate.

Under the rate of chemical change we find the contact sulphuric acid process, the Deacon process, and the hydrogenation of oils. In the last section, on the use of electricity in chemical changes, there are such interesting subdivisions as: carbon bisulphide, calcium carbide, fixation of atmospheric nitrogen; refining of copper, electroplating, caustic soda and chlorine.

The book is really a very interesting one. It should be in the chemical libraries and should be read by the chemical students. Just where it fits in with the regular class-room work is hard to say. It covers too much ground for the man specializing in chemistry and it is scarcely popular enough for the lay reader. It can be recommended as collateral reading for the student beginning chemistry and it might well be recommended to people who wish to read a book which will give them some idea of chemistry and its applications. *Wilder D. Bancroft*

Solubilities of Inorganic and Organic Compounds. *By Atherton Seidell. Second revised edition, 24 × 16 cm; pp. xxii + 843. New York: D. Van Nostrand Company, 1919. Price: $7.50.*—The second edition is an imposing volume and the author has recognized fully the importance of the phase with reference to which the solution is saturated. Even with the present size of the volume it is impossible to include everything which might be considered as solubilities. The author has therefore made no attempt to gather either figures or references for the following:

(*a*) Melting-point data for mixtures of metals (alloys).

(*b*) Melting-point data for mixtures of minerals, except a few of relatively simple composition.

(*c*) Freezing-points of very dilute solutions made for the determination of molecular weights of electrolytic dissociation.

(*d*) Data for the solubility of gases in molten metals.

(*e*) The so-called solubility of metals in various solvents, due to a chemical reaction which occurs.

(*f*) Data for solid solutions.

(*g*) Data for compounds of unknown or variable composition.

On the other hand, many data have been included for ternary mixtures which form two liquid layers. One interesting case is that of morphine in ether and water. Although morphine is less soluble in ether than in water, it is nearly sixty percent more soluble in water saturated with ether than in pure water.

The new edition is very much more valuable than the first one and is a book of which the author may well be proud. *Wilder D. Bancroft*

SPONTANEOUS EVAPORATION

BY HARRY B. WEISER AND EVERETT E. PORTER

More than sixty years ago Babington carried out some interesting experiments on the spontaneous evaporation of salt solutions. An abstract[1] of this work was called to our attention by Professor Bancroft. "The object of this communication," says Babington, "is to make known certain powers of attraction and repulsion, hitherto, so far as I know, unnoticed, which are possessed by soluble substances in relation to their solvent, and which, in the case of water (the solvent here considered) are measured by the amount of loss, on spontaneous evaporation, in the weight of solution of different salts and other substances, as compared with the loss of weight of water.

"The force which holds together the particles of the vaporizable liquid is gradually overcome, if that liquid be exposed to air, by another force which separates, expands and diffuses those particles in the form of vapor; and this separation takes place, even at common temperature, so rapidly, provided the surface be sufficiently extensive, that an easy opportunity is offered of determining the loss of weight by a common balance."

The method of experimentation followed by Babington consisted in exposing to the atmosphere for a definite period, solutions of different salts and also pure water under like conditions of quantity and area, temperature, atmospheric moisture and atmospheric pressure. As evaporating pans were employed, vessels of tinned copper 5 inches square and 3/4 inch high. The solutions were weighed before and after exposure on a balance that was sensitive to a grain even with a weight of 4 pounds on each pan. From a study of the rate of evaporation of a number of salt solutions he arrived at the following conclusions: "(1) That in any aqueous solution of salts and other soluble substances evaporation is retarded,

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[1] Proc. Roy. Soc., 10, 132 (1859).

as compared with the evaporation of water. (2) That in solution of salts which retard evaporation that retardation is in proportion to the quantity of the salt held in solution. (3) That different salts and other substances soluble in water have different degrees of power in retarding its evaporation. (4) That the power of retarding evaporation does not depend on the specific gravity of a solution. (5) That in aqueous solutions of salts, the power of retardation does not depend on the base, whether we compare solutions containing like weights of the salt, or solutions of like specific gravities. (6) That in aqueous solutions of salts, the power of retarding evaporation does appear to depend upon the salt radical or acid, although the retardation is not altogether independent of the influence of the base. (7) That salts with two equivalents of an acid have a greater power of retarding evaporation than salts with one equivalent. There are, however, exceptions. (8) That there are some salts which, being dissolved in water, do not retard evaporation, and some salts which, so far from retarding, actually accelerate evaporation."

An investigation of the data submitted in support of the first seven conclusions, disclosed that for the most part his results were readily interpreted in the light of the modern theory of solutions. However, the accuracy of the eighth conclusion seemed questionable, namely, that certain salt solutions evaporate more rapidly than water. In support of it the following data were given: "The eighth proposition which seems extraordinary and even paradoxical is proved by an experiment in which *saturated* solutions of 1, ferrocyanate of potassa, 2, bitartrate of potassa, 3, sulphate of copper, 4, chlorate of potassa, and 5, distilled water, were compared. In 9 hours and 20 minutes, their losses by evaporation were, respectively, 34 grs., 38 grs., 29 grs., and 29 grs., where we perceive that in the chlorate of potassa solution there has occurred no retardation at all, while in the following experiment, in which 120 grains of each of the salts examined were dissolved in 1200 grains of water, namely, 1, solution of sulphate of copper; 2, solution of ferrocyanate of potassa, 3, solution of carbonate of soda; and 4, distilled water; the number of grains lost by evaporation after 15½ hours' exposure were: 1, 120 grains; 2, 113 grains; 3, 106 grains; 4, 103 grains. It is thus perceived that in all the three solutions a more rapid evaporation had taken place than in distilled water alone."

Since Babington's experiments apparently were carried out with considerable care we were not at first inclined to question their accuracy. Granting that the atmospheric conditions under which the evaporation took place were constant, the most obvious explanation of the higher rate of evaporation of certain salt solutions than of pure water seemed to be that the temperature of the solutions became higher than the solvent during the evaporation. In order to bring about the observed results, this temperature difference would have to be great enough to overcome the lowering of the vapor pressure of water by the dissolved solute. A difference in temperature between the solutions and the water might result from the heat of precipitation (in the case of saturated solutions) and the change in concentration, dissociation and hydration occasioned by evaporation of the solvent. Calculation of the maximum heat energy available from the above sources under the conditions of Babington's experiments disclosed that the effect on the temperature of the solutions was so slight relatively and was spread over such a long period of time that it was entirely negligible compared to the errors in weighing. A series of experiments were, therefore, carried out to determine the accuracy of Babington's observations.

Experimental

At the outset we were convinced that there was nothing to be gained by working with a large volume of solution and weighing with approximate accuracy. Accordingly 2-inch crystallizing dishes were used as containers for 10 cc portions of the several solutions which were weighed on a sensitive balance. To prevent evaporation of the solutions during the weighing periods, the edge of each container was carefully ground and fitted with a ground glass plate. Before carrying out the earlier experiments the inside of the dishes was given a thin coat of paraffine to guard against "creeping" of the solutions; this was later discontinued since it was found that, in general, the rate of evaporation was more uniform from dishes that were not paraffined. The first evaporations were carried out on a stationary platform in the center of a room ten feet square. The dishes were set the same distance apart on the circumference of a circle of 10-inch radius. It was hoped to secure uniform exposure in this way; but the results were not entirely satisfactory and a rotating platform was later employed as subsequently described.

The first experiments were carried out with salt solutions containing 10 grams of salt per 100 cubic centimeters which was the concentration used by Babington. Ten cubic centimeters of each were placed in dishes which were arranged on a stationary platform as above described. The loss on evaporation was determined in a series of experiments, the results of which are given in Table I.

TABLE I
Evaporation from a Stationary Platform

	Loss on evaporation in grams				
	I 20 hrs.	II 24 hrs.	III 16 hrs.	IV 18 hrs.	V 12 hrs.
Water	1.569	1.269	0.446	0.658	0.973
Water	1.586	1.278	0.419	0.653	0.963
Water	1.609	1.311	0.414	0.684	0.043
Copper sulphate	1.540	1.235	0.411	0.620	—
Potassium ferrocyanide	1.539	1.216	0.391	0.597	—
Potassium bicarbonate	1.495	1.202	0.380	0.624	—
Potassium nitrate	1.441	—	—	0.563	—
Potassium tartrate	1.441	1.132	—	0.555	—
Potassium carbonate	—	1.057	—	0.488	—
Potassium sulphate	1.390	1.135	—	0.568	—
Sodium carbonate	1.327	1.022	—	0.509	—
Potassium chloride	1.318	0.974	0.3235	0.481	—
Sodium chloride	1.309	0.897	0.2415	0.432	—

From the above table it will be seen that, contrary to Babington's observations, all solutions evaporated more slowly than water. However, the results are not entirely satisfactory as different samples of the pure solvent showed considerable variation in the rate of evaporation. Moreover, if the 10 percent salt solutions are arranged in the order of evaporation rate, this order is not always the same. Such a variation can be due only to experimental errors. The most likely source of error seemed to be the failure to get uniform conditions of exposure. To obviate this it was decided to carry out the evaporations on a rotating disk that was 16 inches in diameter. This disk was turned once every half minute by means of an electric motor geared down by the mechanism of an old Edison phonograph. The conditions of exposure were evidently much more uniform, as shown by the uniformity of the results given in Table II. In this experiment 6 samples of pure water were arranged the same distance apart on the edge of the circular platform which was rotated during the entire period of exposure. The loss in weight in $2^1/_2$ hours, 5 hours, 10 hours and 20 hours was determined.

Table II

Evaporation of Water from Rotating Platform

Sample	Loss in weight in			
	$2^1/_2$ hours	5 hours	10 hours	20 hours
1	0.234	0.509	1.039	1.716
2	0.238	0.519	1.053	1.743
3	0.237	0.514	1.042	1.721
4	0.235	0.510	1.044	1.724
5	0.236	0.513	1.041	1.725
6	0.232	0.506	1.032	1.711

As the above table shows the rate of evaporation was almost the same from each container. Accordingly, the rotating platform was used throughout all the subsequent experiments.

For the purpose of determining whether there was any advantage in using paraffined dishes, the rate of evaporation of water and of 10 percent copper sulphate was determined, using both paraffined dishes and dishes thoroughly cleaned with hot chromic acid. The results are given in Table III. The time of exposure was 15 hours.

TABLE III
The Effect of the Nature of the Container

Sample	Loss in weight from	
	Cleaned dishes	Paraffined dishes
Water	0.993	0.925
Water	0.994	0.925
Water	0.999	0.937
10% Copper sulphate	0.962	0.903
10% Copper sulphate	0.950	0.922
10% Copper sulphate	0.962	0.898

The above results show two things; first, that 10 percent copper sulphate evaporates more slowly than water instead of faster, as Babington found; and second, that a clean dish makes a better container than a paraffined one. The use of the latter is most likely to give erroneous results with saturated solutions which tend to creep up the sides and deposit crystals if the dish is not thoroughly clean. This effect is shown in a striking way in the experiments recorded in Table IV.

TABLE IV

No.	Sample	Loss on evaporation Gms.
I	Water	0.917
	Saturated potassium sulphate	0.955
II	Water	2.029
	Saturated potassium sulphate	2.342
III	Water	1.805
	Saturated potassium chlorate	2.005

The above experiments might be considered to indicate that certain saturated solutions evaporate more rapidly than water. In every case, however, the solutions crept badly, depositing crystals on the sides of the dish. This increased the surface from which the evaporation took place and so the results are not comparable. It is altogether probable that Babington's failure to take this into account resulted in the erroneous conclusion that certain saturated solutions evaporate as fast as, or faster, than the pure solvent.

From the above considerations it follows that if the saturated solutions do not creep during the process of evaporation, their rate of evaporation would be much smaller than the pure solvent. This is well illustrated in the experiments recorded in Table V. In this experiment particular care was taken to clean the containers and there was no creeping, so that all crystals deposited on the bottom of the dish instead of on the sides. Under these conditions the solutions evaporated much slower than water as the results show. It is interesting to note that the solutions used were the same as Babington found to evaporate more rapidly than water.

TABLE V

Sample	Loss on evaporation Gms.
Water	0.735
Saturated potassium chlorate	0.669
Saturated copper sulphate	0.654
Saturated potassium ferrocyanide	0.617

A fairly accurate comparison of the relative lowering of the vapor pressure of water by different salts is obtained by comparing the loss on evaporation of solutions of suitable concentration. In the following experiment half-molar solutions of several salts were employed. The results are given in Table VI. In the first column the salts are arranged in the order in which they decrease the rate of evaporation; in the second is recorded the loss in weight after 14 hours exposure; in the third, the approximate degree of ionization, α, determined from conductivity; and in the fourth, the approximate value of i (the ratio of the number of particles after dissociation to the number of particles before dissociation) calculated from the expression $i = 1 + (f - 1)\alpha$, where f is the number of parts into which a molecule dissociates.

TABLE VI

Evaporation of Half-Normal Solutions of Salts

Sample	Loss on evaporation Gms.	α	i
Water	0.735	—	—
$M/2$ Copper sulphate	0.696	23.8	1.24
$M/2$ Sodium chloride	0.679	74.3	1.74
$M/2$ Potassium chloride	0.675	79.9	1.80
$M/2$ Sodium carbonate	0.665	40.0	1.80
$M/2$ Potassium carbonate	0.633	60.0	2.20
$M/2$ Potassium sulphate	0.655	62.0	2.24
$M/2$ Potassium ferrocyanide	0.633	43.0	2.72

As the above results show the loss by evaporation of equimolecular solutions is least with salts that give the greatest number of ions, which is exactly what one might expect. The conformity of the results to the theory suggests the possibility of using the rate of evaporation as a means of determining the molecular weight of certain dissolved solutes. The applicability of the method is limited, however, on account of the necessity of working always with fairly concentrated solutions and the experimental difficulties involved in securing and maintaining suitable conditions of exposure. That the rate of evaporation does give a good indication of the condition of a dissolved solute is emphasized by the following experiment:

Ostwald[1] has shown that when CrO_3 is dissolved in water there is formed dichromic acid, $H_2Cr_2O_7$, instead of chromic acid, H_2CrO_4, as might be expected from analogy with the action of SO_3 and water. To verify this, two solutions of CrO_3 in water were prepared: the first contained 1 mole of CrO_3 per liter; and the second one-half mole of CrO_3 per liter. The rate of evaporation of these two solutions was compared with the rate of evaporation of $M/2$ sulphuric acid. The time of exposure was 14 hours. The results are given in Table VII.

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[1] Zeit. phys. Chem., 2, 78 (1888).

TABLE VII

Sample	Loss on evaporation Gms.		
	1	2	Mean
Water	1.149	—	1.149
M/2 Sulphuric acid	1.071	1.070	1.071
M Chromic anhydride	1.062	1.057	1.060
M/2 Chromic anhydride	1.094	1.113	1.104

From the above results it is evident that molar CrO_3 which corresponds to *M*/2 $H_2Cr_2O_7$ evaporates at almost the same rate as *M*/2 H_2SO_4; while half-molar CrO_3, which would correspond to *M*/2 H_2CrO_4, evaporates considerably faster than *M*/2 H_2SO_4, showing that it is not *M*/2 H_2CrO_4 but *M*/4 $H_2Cr_2O_7$. This confirms Ostwald's conclusion that CrO_3 reacts with water to form chiefly dichromic acid rather than chromic acid. The fact that *M*/2 sulphuric acid evaporates somewhat faster than the same concentration of dichromic acid is due to the fact that the degree of ionization of the latter is greater than the former in *M*/2 solutions.[1]

From the above series of experiments it is proven that Babington's conclusion is erroneous, namely, that certain salt solutions evaporate more rapidly than water under constant conditions of exposure at ordinary temperature and pressure. As has been shown, the chief source of error in Babington's work probably is the failure to maintain constant conditions of exposure. The factor which is the most difficult to maintain constant is the extent of surface exposed, particularly if the containers are not uniformly clean. This source of error is magnified with saturated solutions which will creep badly if the sides of the container are not thoroughly clean. By carrying out the evaporations with clean glass containers on a rotating platform results can be duplicated consistently to within 1 percent. All the results obtained under these conditions are readily explained in terms of the modern theory of solutions.

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[1] Walden: Zeit. phys. Chem., 2, 71 (1888).

CHARCOAL BEFORE THE WAR. III

BY WILDER D. BANCROFT

While there has been a good deal of interesting work done on the oxidation of charcoal by oxidizing agents at moderate temperatures, its significance is obscure because nobody knows exactly what the material was which was oxidized. At 150° pure and freshly ignited lampblack gives off much carbon dioxide when in contact with aqueous sodium chlorate and a little osmium tetroxide.[1] When heated in an open vessel a very considerable reduction of the chlorate to chloride took place in twenty hours, whereas there was less than one percent as much reduction when the osmium tetroxide was omitted. This experiment is more interesting as showing the catalytic action of osmium tetroxide on chlorate oxidations than as illustrating the properties of charcoal. Since the solution contained mellitic acid, it seems certain that hydrocarbons were being oxidized. Cane sugar charcoal behaved similarly while retort carbon was oxidized very much more slowly.

Hofmann, Schumpelt and Ritter[2] report that calcium hypochlorite in dilute aqueous solution oxidizes certain charcoals very rapidly, carbon dioxide being evolved. The gas may contain up to 9 percent CO, which they believe is due to the intermediate formation of high-molecular, dark brownish red to black colored, fluorescing carbonyl compounds which decompose to carbon dioxide and carbon monoxide on further oxidation. If black amorphous charcoal in presence of alkali is exposed for a long time to the action of the air at 120°-150°, it is converted into dark brown to red colloids, which change next to formates and oxalates, and finally to oxalates. The different charcoals behave so much alike, except as to initial reaction velocity, that there is no reason to assume any essential difference of chemical constitution.

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[1] Hofmann, Ehrhart and Schneider: Ber. deutsch. chem. Ges., **46**, 1665 (1913).

[2] Ber. deutsch. chem. Ges., **46**, 2854 (1913).

When charcoals are oxidized by a solution of 25 g $NaClO_3$ and 0.05 g OsO_4 in 100 g water, the rate of attack decreases in the following order: lampblack, purified bone-black, ignited sugar charcoal, soot, linden charcoal, acetylene black. If these charcoals receive a preliminary treatment with caustic soda at 120° or with a hypochlorite solution, these differences in the rate of attack disappear very largely and this is especially true if the charcoals are washed afterwards with hydrochloric acid and ammonia to remove the mellogen-like substances produced during the etching by caustic soda. Addition of small amounts of acetic acid, primary sodium phosphate, ruthenium chloride, or manganese sulphate increases the catalytic action of osmium tetroxide so remarkably that acetylene black can be oxidized readily without any previous etching, the manganese sulphate being the least effective of the four.

If cane sugar is charred with sulphuric acid, heated to 500° to drive off the acid, extracted with ammonia, and dried at 250°, an activated potassium chlorate mixture in a heat-insulated flask will attack the resulting charcoal so rapidly as to cause foaming. About 70 percent of the theoretical amount of carbon dioxide is obtained and also a mellogen-like, reddish brown product equal in weight to about 35 percent of the charcoal taken. If the solution is boiled, considerable amounts of formic acid are distilled over.

When beechwood charcoal is heated with 25 percent $NaClO_3$ and 0.05% OsO_4, the gas consists of 99 percent CO_2 and 0.6 percent CO. When ignited sugar charcoal is heated with the same solution plus 1 percent primary sodium phosphate, the composition of the gas was 93 percent CO_2, 6 percent CO and 0.5 percent O_2. It is unfortunate that the nature of the charcoal and the composition of the solution should have been changed simultaneously, because we have no way of telling the relative importance of the two factors. In the experiment with the beechwood charcoal, the gas accounts for practically all the carbon consumed and consequently little or no mellogen or mellitic acid can have been formed.

With the ignited sugar charcoal, the authors state that 5 g mellogen and 2 g mellitic acid were formed. Mellogen can be obtained best by starting with freshly ignited lampblack and boiling it with the activated chlorate solution (30 g $KClO_3$ to 10 g charcoal) using a reverse cooler, until the charcoal, after being washed, dissolves almost completely in dilute aqueous ammonia. In this operation small amounts of formic acid are formed. If the ammoniacal solution is evaporated to dryness and extracted with hydrochloric acid, a brilliant black residue is obtained which dissolves in ammonia forming a deep blackish brown solution, which is, of course, really a suspension and not a true solution. The material is taken up very slowly by pure water forming a yellowish brown suspension which is precipitated by acids. Alcohol and ether have scarcely any dispersing action. This substance is very like the mellogen of Bartoli and Papasogli.[1] When dried at 100°, the composition is approximately $C_{10}H_2O_3$. The substance can be oxidized easily to mellitic acid by acidified, activated chlorate solution or by hypochlorites.

The Griesheim Elektron Co. makes a calcium hypochlorite containing 75 percent effective chlorine which will give stable concentrated solutions running fifty-three grams of oxygen per liter. The preliminary rate of attack by these solutions is quite different from that by the chlorate solutions. The rate of oxidation decreases in the order: beechwood charcoal, lampblack, acetylene black, soot, linden charcoal, cane sugar charcoal, and charcoal obtained by the interaction of carbon dioxide and magnesium. If one washes these charcoals with hydrochloric acid and with ammonia after the preliminary attack by calcium hypochlorite, and then dries at 140°, all these charcoals are attacked at practically the same rate by hypochlorite. Treatment with concentrated caustic soda at 150° in presence of air has much the same effect. A previously treated acetylene black or linden charcoal reacts at once with hypochlorite solutions containing 40 g oxygen per liter, the solution heating up, and foaming violently.

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[1] Gazz. chim. ital., **11**, 468 (1881); **12**, 113 (1882); **13**, 37 (1883).

With the purest charcoal obtained by reducing carbon dioxide with magnesium, boiling takes place in a few minutes. It follows, therefore, that the differences in the preliminary rates of oxidation of the different charcoals are due to differences in surface conditions. Hofmann considers that the preliminary treatment or etching makes the oxidizing agent more readily adsorbed; but he does not go into any details. With all the etched charcoals the oxidation products are quite similar, very little carbon monoxide being given off and a great deal of carbon dioxide. When the residual charcoal is washed with dilute hydrochloric acid and then with ammonia, large amounts are obtained of the brownish black colloid which was also obtained with the activated chlorate solutions.

When an excess of any charcoal was heated with hypochlorite solution containing 25 g oxygen per liter, the gases had the following compositions:

	CO_2	CO	O_2
1. Beechwood charcoal	89.8	9.3	0.3
2. Lampblack	93.4	6.0	0.4
3. Acetylene black	94.5	4.0	1.5

When beechwood charcoal was heated with bleaching powder, the composition of the gas was 92.8 percent CO_2, 5.8 percent CO, 0.2 percent O_2. With the beechwood charcoal and the hypochlorite solution, the amount of CO_2 is only about one-half the theoretical, the balance being used up in forming mellogen and mellitic acid. If the charcoal is not present in excess, some of the mellogen is oxidized to carbon dioxide and mellitic acid. It is interesting to note that there is practically no catalytic decomposition of hypochlorite to chloride and oxygen. Hofmann apparently considers that mellitic acid is formed from pure carbon and he does not refer to the work which contradicts that view.

Acheson graphite is not changed perceptibly after standing for several days in contact with hypochlorite solution. Diamond powder was attacked perceptibly in the course of fourteen days' treatment with the ten-fold amount of hypochlorite solution containing 43 g. oxygen per liter. The residue consisted of diamond powder, chlorate and carbonate but no hypochlorite. When the diamond powder was washed with hydrochloric acid and then treated with aqueous ammonia, a heavy, white, milky suspension was obtained which ran through a dense double filter and was coagulated by acids to an almost white, amorphous precipitate. The yield was about one percent of the diamond powder and the composition was apparently 86.74 percent carbon and 10.33 percent water. If the undissolved diamond powder was evaporated with aqua regia and again treated with hypochlorite solution, a fresh amount of milky solution could be obtained in the same way as before.

Haber and Bruner[1] found that wood charcoal dissolves in fused caustic at 500°, forming carbonate and hydrogen, while LeBlanc[2] showed that pure carbon, made by reducing carbon dioxide with sodium, reacts with caustic potash at 650°, setting free three hydrogen atoms per carbon atom, carbonate being formed and potassium volatilizing. At lower temperatures, Millon[3] showed that wood charcoal, prepared at 320°, reacts with caustic alkali in presence of air to form a humus-like substance which goes into apparent solution in water. Hofmann, Schumpelt and Ritter[4] have made experiments at 150–180° because they were anxious to see what were the first products and how far the different charcoals behaved alike.

The first experiments were made with intensely ignited sugar charcoal having a composition of 96.5 percent carbon and 0.6 percent hydrogen. When 15 g charcoal, 20 g purest NaOH, and 40 cc water were heated 40 hours at 160° in presence of CO_2-free air, the resulting aqueous solution was beautifully brown-red with a green fluorescence and, therefore, contained

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[1] Zeit. Elektrochemie, 10, 697 (1904).

[2] Ber. deutsch. chem. Ges., 45, 2309 (1912).

[3] Jahresber. Chemie, 1860, 68.

[4] Ber. deutsch. chem. Ges., 46, 2854 (1913).

Bartoli and Papasogli's compound, $C_{11}H_6O_7$. There were also small amounts of mellitic acid, and oxalic acid corresponding to 1.7 g calcium oxalate. Further treatment of the residual charcoal gave the same products in approximately the same amounts. It is, therefore, not a surface film which reacts. If the air acts longer, the amount of oxalic acid does not increase much but the amount of carbonate does. If water is added continuously to prevent drying, the reaction proceeds more rapidly but the amount of oxalate does not change much. It seems certain, therefore, that oxalate is a preliminary step in the formation of carbonate. Addition of an oxygen carrier, such as one gram ammonium vanadate, increases the rate of formation of carbonate but decreases the recoverable oxalate to about 2 mg and causes the disappearance of the red colloid. If the caustic soda is not made from metallic sodium, it usually contains some vanadate which accounts for Millon and Berthelot not finding oxalate. Above 220° the carbonate is formed so rapidly that the preliminary oxidation stages cannot be isolated. At 120°-130° considerable amounts of oxalate and of reddish brown oxides are formed and the conversion to carbonate proceeds very slowly. A little formate is obtained at 120°-150°. In a nitrogen atmosphere, formate and a little carbonate are the only products. The yield of formate is apparently due to oxygen present in the charcoal and Hofmann believes that in the complete absence of oxygen, charcoal and caustic potash would not react at 180°.

Lampblack behaved like sugar charcoal even after being purified by heating in a current of chlorine and then in a current of hydrogen. Acetylene black is oxidized somewhat more slowly and gives less of the brownish red colloid. There is nothing in all this to show to what extent the decomposition products are those of pure carbon or of hydrocarbons. It is worth noting that since we can get formic, oxalic, and carbonic acids from carbon monoxide or dioxide, there is no apparent theoretical reason why pure carbon should not be oxidized to mellitic acid. The argument against it is merely that the yield of mellitic acid drops off practically to zero as the charcoal is purified more and more; but it is still possible that changing the conditions of oxidation would enable us to get mellitic acid from a charcoal which yields none under the ordinary treatment. All we can say at present is that the evidence is against the view that mellitic acid is an oxidation product of pure carbon. The electrolytic oxidation of carbon[1] does not introduce any new feature because there is the same uncertainty as to what is oxidized.

While we do not know definitely, whether the colloidal materials obtained by oxidation of the charcoals are or are not oxidation products of pure carbon, there is always the possibility that these substances may play a more or less important part in adsorption under certain circumstances, and, therefore, it is desirable to see what we know in regard to colloidal carbon. Sabbatani[2] has described the preparation of colloidal carbon and the matter has been taken up in more detail by Thorne.[3]

"Finely powdered sucrose was added gradually as in Sabbatani's preparation to concentrated sulphuric acid, the proportions being 1 gram of sucrose to 10 cc of acid..... When all the sucrose was added, the liquid was allowed to remain for twenty-four hours, and was then poured into four times its volume of cold distilled water. The whole was then filtered to remove the larger particles which were always present to a greater or less degree.

"The filtrates obtained in this way varied in color from yellow to dark reddish brown, which seemed to depend largely on the accidental formation of lumps in the process of preparation. On dialysis through parchment paper, much of the acid diffused out first, but afterwards the outer liquid became yellow owing to the diffusion of other substances. In order to remove the last traces of sulphuric acid very prolonged dialysis

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[1] Millot: Bull. Soc. chim. Paris, (2) 37, 337 (1882); Comptes rendus, 101, 432 (1885).

[2] Zeit. Kolloidchemie, 14, 29 (1914).

[3] Jour. Chem. Soc., 109 I, 202 (1916).

was necessary. On examination in an electric field, the particles moved towards the anode, that is, were negatively charged. In the ultra-microscope not many particles were visible; and gold chloride was reduced by the dialyzed filtrate, in some cases in the cold, but sometimes only on heating. On the addition of small quantities of electrolytes (for example, when 0.5 cc of *N*/20 barium nitrate was added to 10 cc of the liquid) a cloudiness appeared, which finally settled to the bottom of the vessel as a brown powder. Even if a considerable quantity of electrolyte was added, no further precipitation occurred, and the substance, which colored the solution brown, remained, presumably in ordinary solution, as it diffused (although slowly) through parchment paper......

"Experiments were made with dehydrating agents other than sulphuric acid. Fuming sulphuric acid and a hot solution of zinc chloride gave results similar to those obtained with sulphuric acid, except that the carbon produced was more compact and less suspended. With phosphoric oxide no action occurred if the mixture of it with the sugar was kept dry, but on addition of a drop either of sulphuric acid or of water a vigorous action took place with the formation of a spongy mass. On adding water and filtering, a liquid was obtained with similar properties to those obtained by the action of sulphuric acid.

"Thus it is clear that although some carbon in the suspensoid state is produced by the dehydration of sucrose, etc., with excess of concentrated sulphuric acid, its properties are obscured by more complex products of decomposition, the presence of which is obvious from the odor of burnt sugar arising from the solution during the dehydration process or when evaporated to dryness on the water bath. They do not appear to exert a protective action on the carbon.

"When an electric current (0.4–4.0 amperes at 200 volts) is passed through dilute sodium hydroxide solution using carbon electrodes, one of the electrodes being immersed in the solution and the other just touching the surface, the liquid becomes dark owing to the disintegration of the electrodes.

On filtration, most of the particles pass through the filter and, if the sol is then diluted, remain suspended for many months; otherwise a slow deposition of some of the dispersed matter ensues, presumably removing excess of alkali. On varying the positions and signs of the electrodes, it was found that most dispersion occurred when the positive pole just touched the surface of the liquid, thus giving a high current density at its surface; on immersing it further, electrolysis was more vigorous, but little dispersion occurred. With the negative pole touching the surface, an arc was set up between carbon and liquid and the electrode was burnt away, some large particles being formed from its violent disintegration. Only large particles could be obtained by striking an arc between the carbons under the surface. It was also found that almost all the sol originated from the positive pole, for when the other electrode was surrounded by a soaked thimble of parchment paper only the outer liquid became dark. Under ordinary conditions, however, if the current was reversed after it had been flowing for some time, a cloud of dark particles arose from the negative pole immersed in the liquid; this appears to be due to the removal from that pole of particles which were formed from the positive pole and were carried through the liquid and deposited by cataphoretic action.

"Most of the sols were obtained from electrodes of ordinary arc carbons, but similar results were obtained with electrodes of crude gas carbon and of Acheson graphite. A solution of sodium hydroxide containing 2–3 grams per liter is best for the formation of the sol; a more dilute solution does not permit a sufficiently heavy current to pass, while a greater concentration precipitates the sol, and the positive electrode is not so finely broken up. The formation of a sol is noticeable, however, at as low a concentration as 0.4 gram per liter, that is, $N/100$; and although a more concentrated solution is more efficient for the actual preparation, the sol is more stable if diluted soon after formation.

"The sols thus obtained when subjected to dialysis in a bag or thimble of parchment paper are completely precipitated if the alkali is entirely removed in this manner; the dialysis can be stopped when just enough alkali is left to render the sol stable. (In this the sol is similar in behavior to a ferric hydroxide sol, which is precipitated if all the acid is dialyzed away from it.) The deposit formed in the dialyzer can be suspended in part by addition of water containing a little alkali.

"The sol showed a very distinct Tyndall cone, and in layers more than a few mm in thickness was black; in very thin layers it was of a brown tint. Under the microscope no particles were seen, but with the ultra-microscope a large number were visible in vigorous Brownian movement. Thus the particles were of a size similar to that of the particles in metallic sols. When exposed to the action of an electric field in the ordinary Y-tube apparatus, the particles in the sols prepared invariably moved towards the anode, that is, they were negatively charged, as are most hydrosols of elements, whether metals or non-metals. If the sol was acidified, no change in the sign of the charge took place.

"The sols were particularly sensitive to electrolytes, so much so that if tap-water was used in preparing them, precipitation of the particles occurred as fast as they were formed. An experiment with a sol containing about 0.3 gram of carbon per liter (by the loss in weight of the electrodes) and $N/40$ barium chloride gave the following results. Ten cc of the sol were used in all cases.

$N/40$-Barium chloride cc	Result
0.10 0.15	No precipitate apparent at once; very slight precipitate after a week
0.20 0.25	No precipitate apparent at once; mostly precipitated after a week
0.30 0.40	Some aggregates after one hour; completely precipitated in a week
0.50 0.70	Some aggregates at once; partly settled in one hour
0.80 1.00	Flocculation at once; mostly settled in one hour
3.00	Flocculation at once; mostly settled in twenty minutes

"Thus, taking 0.3 cc as the minimum concentration to effect precipitation of the sol employed, it will be seen that this concentration is one of 0.078 gram of barium chloride (that is, 0.36 millimol.) per liter of sol. This concentration is of the same order as that required to precipitate other suspensoids of similar dispersity and concentration (both of which in the case of sols used in this work were only approximately known). For example, an arsenic trisulphide sol containing 7.54 millimols. per liter required a concentration of 0.691 millimol. per liter of barium chloride to precipitate it.[1] The coagulum from the sol was black, and was only partly dispersed again on prolonged washing with distilled water.

"It was thus seen that the sols formed in this way were typical suspensoids; and it now remained to see whether the particles were pure carbon or a product of oxidation.. With this end in view, the sol was made on a considerable scale, and after filtration and keeping was precipitated by barium chloride and the solid collected in order to determine its composition by combustion. The precipitate was washed with distilled water and then with dilute hydrochloric acid to remove the barium carbonate which had gradually accumulated in the mass. On doing this, a yellow liquid passed through the filter; it was apparently not colloidal, as it gave no Tyndall cone and diffused easily through parchment paper. On distilling a portion of the filtrate, the colored substance remained in the non-volatile portion, and on evaporation on the water bath a small quantity of brown residue remained; if sulphuric acid was present during the evaporation, an odor of burnt sugar was noticeable, but there was not sufficient of the substance to permit of its identification.

"The precipitate was washed with dilute hydrochloric acid until the filtrate gave no precipitate with dilute sulphuric acid; on finally washing with distilled water, some of the colloid passed through the filter paper, so it was washed with very dilute hydrochloric acid until the filtrate ceased to be

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[1] Freundlich: Zeit. phys. Chem., 44, 144 (1903).

yellow. It was then dried in the air for a week, ground, and kept for a similar period in a vacuum desiccator.

"On burning it in oxygen in the ordinary apparatus for organic combustion, the following results were obtained:

	I	II	Mean values
Carbon	65.73	67.50	66.61
Hydrogen	2.07	1.93	1.99
Residue	15.85	14.66	15.25
	83.65	84.09	83.85
	16.35	15.91	16.15
Difference	100.00	100.00	100.00

The 'residue' remains unburnt even when heated to bright redness in pure oxygen, and on examination it was found to consist mostly of silica with a trace of iron. Thus it is probably derived from impurities in the arc carbons used to make the sol. The difference is presumably oxygen.

"When the results are calculated on the basis of percentage of combustible material they agree fairly well with those obtained by Söhngen,[1] who obtained C = 81.2, H = 0.85 and O = 18 percent, while the mean results in this work are C = 78.59, H = 2.35, O = 19.05 percent. It is clear that very considerable oxidation occurs during the disintegration of the electrodes, as organic compounds occur in the washings, and possibly in the above product. The results of analysis of the latter may point to the existence of a carbohydrate, or more likely to water firmly retained by the carbon; the latter seems probable in view of the washing of the precipitate until free from colored soluble matter, but in any case organic matter is present in the sol and seems necessary for a stable dispersion.

"The carbon formed by the reduction of carbon dioxide with magnesium was prepared, and the crude product treated with dilute hydrochloric acid to remove magnesium oxide and carbonate. On powdering it and adding it to water, no perma-

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[1] Chem. Weekblad, 11, 593 (1914).

nent suspension was noted after some months, neither did the addition of alkali to the water cause a colloidal solution to be formed. Silicon, when prepared in this way, readily forms a suspension.[1]

"When acetylene reacts with chlorine, a fine soot is produced. It was found to be impossible to produce it in water by simultaneously bubbling the two gases through the liquid. If produced by spontaneous combustion of the gases, it was difficult to moisten it and no suspension ensued.

"Carbon, prepared by the dehydration of sucrose by sulphuric acid, was treated with excess of the acid in order to dehydrate, if possible, the intermediate compounds formed. The mass was then washed with water until free from acid, but it did not form a suspension either in water or alkali; a brownish yellow solution was observed after some time in the alkali used, while in the aqueous liquid a fungus began to grow showing that organic compounds were still present. Similarly, if the carbon was heated to a red heat either in air or in chlorine, the residue gave no sol with water or alkali......

"On examination of pieces of an Acheson graphite electrode, it was found that although they were more difficult to disintegrate when used in place of arc carbons in the electrolytic method, a similar sol was obtained. A finely powdered portion could not be dispersed in water or alkali, but floated on the surface. However, on the addition of a few crystals of tannic acid to either solution, the powder was immediately dispersed to give a violet sol which had almost the same properties as those obtained by the electrolytic method. The precise action of the tannic acid has not yet been determined, but it may have a surface-tension effect, thus permitting the particles to be made wet, or it may exert a protective influence on the carbon particles.

"Animal charcoal was extracted with concentrated hydrochloric acid to remove inorganic salts, and then well washed with water and dried. The powder thus obtained did not form a suspension in water, alkali, or tannic acid. When some

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[1] Astfalk and Gutbier: Zeit. Kolloidchemie, 15, 23 (1914).

of it was treated with about twenty times its weight of concentrated sulphuric acid, a brown liquid was obtained. On dilution with water to ten times the volume, almost the whole was precipitated in brownish black flocks, which when filtered and washed were suspended, but only for a short time, both in alkali and in tannic acid. Patterson[1] has obtained the sulphuric acid solution, and regards it as evidence that organic matter is still left in animal charcoal, and to this he attributes the superior adsorptive power of such charcoal over other varieties of carbon. Comparing these results with the others obtained in this work, they seem to confirm the supposition of the existence of organic matter in the charcoal."

Herzog[2] shows that animal charcoal adsorbs sugars from aqueous solution and that a reversible equilibrium is reached which can be expressed by the equation $x/m = kC^n$, where x is the amount of sugar adsorbed by m grams of charcoal, and C is the concentration of the unadsorbed sugar, while k and n are constants. Starting with 100 cc of solutions and 5 grams of animal charcoal, the following values were obtained for k and n with different sugars:

Sugar	k	n
Dextrose	0.766	0.474
Laevulose	0.338	0.539
Galactose	1.016	0.694
Sucrose	0.106?	0.127
Maltose	1.142	0.133
Lactose	1.138	0.135

Rona and Michaelis[3] point out that the adsorption of sugar by charcoal may be entirely inhibited by the presence of a sufficient quantity of another substance, such as acetone or acetic acid, which is adsorbed more powerfully than the sugar. The practical value of this observation lies in the fact that a dilute solution of sugar to which 10 percent of acetic

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[1] Jour. Soc. Chem. Ind., **22**, 609 (1903).

[2] Zeit. physiol. Chem., **60**, 79 (1909).

[3] Biochem. Zeit., **16**, 489 (1896).

acid or acetone has been added, may be decolorized by shaking with 5 percent of charcoal without any loss of sugar. This applies both to dextrose and to sucrose, and the charcoal has no inverting action on the latter sugar. The presence of albumin does not influence the adsorption of sugar or acetone by charcoal.

On the other hand, Clark[1] found that a bad decolorization with animal charcoal is always obtained when fruit sugar and salts are present in considerable quantity showing that these substances interfere with the adsorption of the coloring matter. This is in line with some of the earlier observations by Anthon.[2]

"A molasses containing 109 parts of non-sugars to 100 parts of sugar was filtered through bone-black and then washed with water. A large part of the non-sugars was removed. A red infusion of Pernanbuco wood was passed through bone-black until the charcoal took up no more color. The bone-black was washed with water until the water came off colorless. On treatment with clear sugar solution a red color was obtained. After the charcoal was washed until the sugar solution came off colorless a nearly saturated soda solution took out large amounts of color. When this latter removed no more color a solution of potassium carbonate took out some and after this caustic potash removed color. Anthon questions the necessity of using bone-black at all. Its adsorption of organic substances is very slight in presence of free alkalies and its adsorption of lime is limited to a few percent of the weight of the charcoal. On the other hand there is a distinct loss of sugar."

Bauer[3] found that both hydrochloric acid and acetic acid decrease the adsorption of sugar by charcoal without interfering with the removal of the color.

Glassner and Suida[4] made experiments with a large num-

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[1] Jour. Soc. Chem. Ind., **32**, 262 (1913).

[2] Chem. Centralblatt, (2) **13**, 1003 (1868).

[3] Jour. Soc. Chem. Ind., **7**, 636 (1888).

[4] Liebig's Ann., **357**, 95 (1907).

ber of organic dyes and found that "the vegetable charcoals (wood, sugar) do not take up appreciable amounts of dyes. Charcoals having a high ash content (sodium and sponge charcoal) behave similarly. Soot has a distinct adsorbing power for basic dyes but takes only the slightest amounts of acid dyes out of solution with the exception of the following dyes which have a peculiar physical condition in aqueous solution: fast red A, fast red A acid, alizarin yellow GGW, alizarin yellow RW. These results with soot are in harmony with those previously found by Lehmann. Glue and wool charcoals also have very slight adsorbing powers for all dyes. A very different behavior was observed with the charcoals obtained from Merck: bone-black, blood charcoal and animal charcoal. If one compares the composition of the different charcoals with the adsorbing power for dyes, it appears that the vegetable charcoals, which decolorize badly, contain no nitrogen or only traces, while the animal charcoals are relatively rich in nitrogen. This cannot be the sole cause of the difference because certain animal charcoals, such as glue charcoal, have a relatively low ash content and high nitrogen content; but are bad decolorizers, while soot which contains relatively little nitrogen or ash can take up appreciable amounts, at any rate of the basic dyes. Also, the best decolorizing animal charcoal has the lowest nitrogen and hydrogen content and the highest ash content of the good animal charcoals. It is, therefore, probable that the nature of the ash is important and the way in which the nitrogen is bound.

"The addition of sodium chloride and tri-calcium phosphate has relatively little beneficial effect with blood charcoal but more with soot which does not adsorb well.

"When basic dyes (chlorides) are taken up by blood charcoal the chloride remains in the solution, which, however, does not become acid. The amount of the color bases which can be extracted by alcohol or ether is very much less than clings to the amount of chloride in the decolorizing solutions. It seems certain, therefore, that a large part of the color bases is held by the charcoal very firmly. It is easier to wash the dye out of soot than out of blood charcoal. Experiments show that there has been no appreciable oxidation of the dyes.

"It seems probable that the high decolorizing power of some of the animal charcoal is due to the presence of polymeric cyanimide derivatives, such as melam, melamine, etc. As a matter of fact, it appears that the best animal charcoal which was tested came from a Prussian Blue manufacture, and, therefore undoubtedly contained cyanogen in some form. Platinized asbestos has practically no decolorizing action on any of the dye solutions studied.

"Heating charcoal with potassium carbonate increases the adsorption power for crystal violet and crystal ponceau. This is apparently due chiefly to the formation of cyanide compounds because the increase in adsorbing power is much less when the charcoal is heated with potassium carbonate in an atmosphere of CO_2."

Knecht[1] also harks back to the effect of nitrogen, showing that decreasing the percentage of nitrogen in an animal charcoal decreases its adsorption of acid dyes like crystal scarlet. The decrease in the percentage of nitrogen has practically no effect on the adsorption of a basic dye like methylene blue. If, on the other hand, purified animal charcoal be heated with aluminum powder or zinc dust and then treated successively with hydrochloric and hydrofluoric acids to remove impurities, the adsorbing power for methylene blue is decreased very much while that for crystal scarlet is decreased to a much lesser extent (probably owing to unavoidable loss of nitrogen). This seems to be pretty strong evidence that the impurities in the charcoal are very important. Knecht agrees with Patterson and with Glassner and Suida that the decolorizing action of animal charcoal is due to the presence of organic compounds which are stable at a red heat. He believes that absolutely pure, amorphous carbon probably has no decolorizing action either for acid or basic dyes. Knecht also claims that the adsorption by animal charcoal of iodine dissolved in

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[1] Jour. Soc. Chem. Ind., **26**, 949 (1907); **28**, 700 (1909).

a potassium iodide solution depends on the amount of fixed nitrogen in the charcoal.

Rosenthaler and Türk[1] have studied the adsorption of various pharmaceutical substances from their solutions when treated under standard conditions with different kinds of charcoal. These charcoals may be divided, according to their adsorbent powers, into strongly adsorbent: bone, flesh, and "vegetable blood" charcoals, in the above order; and weakly adsorbent or non-adsorbent: blood, lime-wood, and sponge charcoals. For the same kind of charcoal, the adsorption of any substance varies with the solvent which is employed. The adsorption is by far the strongest in aqueous solutions, it is less with ethyl alcohol, methyl alcohol, ethyl acetate, acetone, and least of all with chloroform solutions. The speed of adsorption depends on the same factors as influence the amount of adsorption, being the greatest in the case of bone charcoal and aqueous solutions. The quantity of substance adsorbed by a given quantity of charcoal is relatively less for concentrated solutions than for dilute solutions. All the circumstances which favor adsorption act in a similar degree in resisting the re-extraction of the adsorbed substance. The decolorizing power of the charcoal is dependent on its adsorbing power. As regards the use of charcoal for decolorizing purposes, they state that the charcoal must be carefully purified before use and the quantity of charcoal employed should be as small as possible. It is not necessary to heat the liquid with the charcoal; several hours' contact at the ordinary temperature will suffice. The decolorization should not, for preference, be effected on an aqueous solution, because the loss of substance by adsorption is at a maximum in that solvent the solution should be as concentrated as possible. Easily oxidizable substances should not be decolorized by animal charcoal, because this charcoal has a powerful oxidizing action; the oxidation of alkaloids is retarded by treating them in the form of salts. Blood charcoal has the strongest oxidizing action, lime-wood charcoal has hardly any. Bone and

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[1] Arch. Pharm., 244, 517; Jour. Soc. Chem. Ind., 25, 1172 (1906).

flesh charcoals can be employed in the determination of caffeine without loss of alkaloid, but in the determination of sugars, etc., in wine and other liquids, charcoal should not be used unless it has proved that no loss by adsorption takes place under the conditions of the experiment. The close interdependence of the decolorizing and adsorbing properties of charcoals suggests that the decolorization is due to adsorption of the coloring matters. The fact that successful results can be obtained in practice depends first on the circumstance that the amount of coloring matter is generally only a fraction of the total substance in solution, and secondly, on a selective adsorption, according to which the quantity adsorbed is generally proportional to the molecular weight, most coloring matters being substances of high molecular weight."

Since adsorption is selective, we may have three extreme cases with a salt in aqueous solution. The charcoal may have strong selective adsorption for the salt itself, or for one of the hydrolysis products, the free base or the free acid. All three cases are known. Liebermann[1] showed that with barium formate, sodium and lead acetates, calcium glycollate, zinc lactate, ammonium oxalate and potassium sodium tartrate solutions, bone-black removed the basic constituents to a greater extent than the acid ones, thus leaving the solution acid. Calcium and barium benzoates are adsorbed without change, as is also the case with sodium chloride, nitrate and sulphate. From a solution of aniline benzoate, charcoal takes out more benzoic acid than aniline while with aniline acetate, more aniline is removed than acetic acid.[2]

The decomposition of salts as a result of selective adsorption was studied many years ago by Weppen.[3] He found that bone-black would easily remove all traces of the metal from ammoniacal solutions of copper, zinc, silver, and lead, that lead oxide is taken out of an alkaline lead plumbite solution, and that the acids are removed from potassium antimoniate and

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[1] Sitzungsber. Akad. Wiss. Wien, **75**, II, 331 (1878).

[2] Freundlich and Masius: "Van Bemmelen Gedenkboek," 100 (1910).

[3] Liebig's Ann., **55**, 241 (1845); **59**, 354 (1846).

sodium tungstate solutions. Mercuric iodide was adsorbed quantitatively from a solution in ammonium iodide and arsenic sulphide from a solution in ammonium sulphide. In presence of ammonia, some barium hydroxide is taken out of a barium chloride solution. From ferrous sulphate and mercuric chloride solutions basic sulphates are adsorbed. Chevallier[1] found that charcoal takes lead oxide out of lead nitrate or acetate dissolved in water, alcohol or acetic acid. More is taken from a hot than a cold solution.

Charcoal takes out ferric chloride without decomposition from solutions in pure acetone and in ethyl acetate;[2] but takes out chiefly the iron from solutions in water or 95 percent alcohol. Exposure to sunlight increases the hydrolysis.

In addition to causing hydrolysis and dissociation, charcoal may also reduce salts. Heintz[3] reports on a case of this sort: "I believed that bone-black, when washed carefully and then ignited would not precipitate platinum chloride. To my surprise, I found recently that platinum is actually precipitated from its solution by charcoal. If one takes bone-black which has been boiled thoroughly with hydrochloric acid and with water and then ignited, and lets it stand in contact with a platinum chloride solution, one notices after awhile that the color of the solution is distinctly lighter. If the solution is boiled for a few minutes with the charcoal the color becomes very much less; but the liquid takes on a reddish shade. If sufficient charcoal is present and if the boiling is kept up the solution becomes entirely colorless, containing hydrochloric acid but no platinum. It is not surprising that platinum chloride is precipitated by bone-black. It has long been known that organic dyes, many colorless organic substances, and certain colored and colorless organic substances are precipitated by charcoal. It is perhaps new, however, that bone-black decomposes a boiling platinum chloride solution chemically. It seems improbable that the reduction is due to char-

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[1] Comptes rendus, **19**, 1279 (1845).

[2] Oeschsner de Coninck: Comptes rendus, **130**, 1627; **131**, 275 (1900).

[3] Liebig's Ann., **187**, 227 (1877).

coal itself. Since charcoal, no matter how highly heated, always contains hydrogen it is probable that hydrogen causes the reduction since it is known that platinum chloride is easily reduced by hydrogen with formation of hydrochloric acid.

"On the other hand the reduction of platinum chloride by a simultaneous action of carbon and water is not impossible; but in this case carbon dioxide or carbon monoxide must be formed in addition to platinum and hydrochloric acid. An experiment showed, however, that neither of these gases was formed. In this experiment platinum chloride was not used; I took ferric chloride since I had found that its aqueous solution is reduced at the boiling point to ferrous chloride by freshly ignited bone-black. If one takes a solution of pure ferric chloride which gives no trace of Prussian Blue with potassium ferricyanide and boils it with purified and freshly ignited bone-black, the filtered solution gives a tremendous precipitate of Prussian Blue. One can see that reduction has taken place, because the intense yellow color of the solution decreases very much when boiled with bone-black. If an air current free from carbon dioxide is passed through the boiling liquid and then through a mixture of calcium chloride and ammonia, no clouding takes place in the latter solution. The same result is obtained if the air current is passed previously over glowing copper oxide. During the reduction of ferric chloride to ferrous chloride by charcoal there is, therefore, formed neither carbon dioxide, carbon monoxide nor any other gas containing carbon. The charcoal used was free from heavy metals and even iron was present only in extraordinarily small amount.

"The marked reducing action of bone-black is, therefore, to be ascribed to hydrogen which is always present even in charcoal which has been raised to a white heat. The ferric chloride may give rise to a complicated carbon compound just as we know that potassium permanganate converts charcoal into mellitic acid. In this case the reaction should take place both in alkaline and in acid solution. As a matter of fact if one filters the ferric chloride solution which has been boiled with charcoal, precipitates the iron with ammonia, washes, and evaporates both the filtrate and the solution, both residues contain traces of carbonaceous matter. While the formation of a small amount of organic substances certainly occurs when ferric chloride solution acts on ignited bone-black, the amount of this substance is so very small that one must seek another cause for the considerable amount of ferrous chloride formed. It is practically certain, therefore, that the greater part of the reduction is due to the hydrogen in the charcoal."

Avery[1] came to quite a different conclusion.

"Charcoal is used largely for the precipitation of gold from its solutions in the extraction of this metal from its ores by the 'chlorine' or the 'cyanide' process. In the former case, the solution of gold chloride, is heated, and filtered through tubs filled with wood charcoal. The precipitation is rapid and complete. The charcoal with which the solution first comes into contact soon becomes covered with a beautiful, tough yellow deposit of metallic gold; as the solution becomes more dilute no deposit is visible on the charcoal; but the ash left on incineration is colored pink by the finely-divided metal. In the cyanide process, the filtration through charcoal takes place in the cold. The solutions are much more dilute with respect to their gold content, a longer column of charcoal is used, and no metallic deposit appears. After the charcoal has been in use for some time, the precipitation of gold takes place less actively, but it can be renewed by heating the charcoal to redness in absence of air and replacing in the filters. It has also been noticed that if a current of electricity is passed for a short time through a filter, so arranged that the charcoal is the cathode the gold is afterwards precipitated for some time by the charcoal so treated, even more readily than by freshly-burnt material. The reaction that takes place during this reduction does not appear to have been satisfactorily investigated, although it has been noticed and various suggestions made regarding it. The reducing action of lampblack, animal charcoal, bone-black, and coke, on various metallic salts has

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[1] Jour. Soc. Chem. Ind., 27, 255 (1908).

been described by several investigators, who have attributed the action to impurities in the carbon, to occluded hydrogen, or to the mechanical attraction of carbon for the dissolved salts. In most cases no quantitative work has been attempted. Weppen[1] found that the greater part of the acid was present in the free state after the reduction of the salt, and that it was very difficult to recover the last portions of the acid. König,[2] working with purified charcoal, found that carbon dioxide was formed. He assumed the reaction to be in accordance with an equation which, expressed in modern form, would be, $4AuCl_3 + 6H_2O + 3C = 4Au + 12HCl + 3CO_2$; but in his experiment he found only $^1/_{20}$ of this theoretical amount of carbon dioxide. He concluded that this fraction only of the reduction of gold chloride was due to the charcoal, the rest being due probably to physically adsorbed gases.

"Attempts were made to prepare charcoal free from all occluded reducing gases, so that the part played by the charcoal alone might be determined. Sugar was first heated to a high temperature in absence of oxygen, but it was found that the light porous mass so obtained was less suitable for manipulation than wood charcoal, and, moreover, that even after prolonged heating it still contained appreciable quantities of hydrocarbons. Ordinary wood charcoal was used, crushed to small size, treated with acids to dissolve out mineral matter, heated in chlorine to decompose hydrocarbons, and then in nitrogen to get rid of the chlorine. It was found that even after prolonged heating in nitrogen, traces of chlorine were still present. Finally a very pure form of charcoal was obtained from cocoanut shell. This was strongly heated in closed clay crucibles for some hours, then boiled with nitric acid for 5 or 6 hours, and washed thoroughly till the washings were nearly free from acid—the washing taking several days. It was then dried in the air, crushed and sieved, collecting the particles between 1 and 3 mm diameter. These were dried first in a desiccator over strong sulphuric acid, then over phosphorus pentoxide,

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[1] Liebig's Ann., 55, 241 (1845).

[2] Chem. News, 45, 215.

and finally heated to redness in a closed platinum crucible and cooled in a desiccator over phosphorus pentoxide. The crucible was heated in a muffle in an oxidizing atmosphere to avoid the possibility of adsorption of hydrogen or other reducing gases from the furnace. This charcoal was examined, first by heating it for one or two hours in a current of pure nitrogen and finding its loss of weight. It was then heated in a current of oxygen and the amount of water formed, determined. From this the amount of hydrogen still present in the charcoal was calculated. The weight lost when heated in nitrogen was found to be due to water and carbon dioxide. The gas current was carried through another combustion furnace containing copper oxide, but no hydrogen, hydrocarbons, or carbon monoxide were found present.

"The results of the analysis of the charcoal were as follows:

	Heated in nitrogen Loss Percent	Combustion in oxygen	
		Water formed, calculated as hydrogen Percent	Ash Percent
No. 1	5.0[1]	0.16	0.26
No. 2	0.1	0.25	0.23
No. 3	0.5	0.15	0.20

"The results show that the amount of adsorbed gases in this charcoal is very small—the loss in nitrogen and amount of hydrogen found on combustion (0.25 percent at most), being due to a large extent probably, to moisture still present. In the subsequent work the charcoal is regarded as pure, the small amount of reducing agent other than carbon, possibly present being ignored." This charcoal was heated in nitrogen to remove other occluded gases and was then added to the gold chloride solution. By taking special precautions to remove

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[1] No. 1 was dried over phosphoric anhydride but not ignited in platinum crucibles. Nos. 2 and 3 were dried, ignited and cooled over phosphoric anhydride before analysis.

all the carbon dioxide formed, it was found that the reaction apparently proceeded according to the equation $4AuCl_3 + 6H_2O + 3C = 4Au + 12HCl + 3CO_2$."

In view of the fact that carbon monoxide will reduce gold chloride solutions, and in view of the fact that carbon is known to react with oxygen slowly, there is no reason why charcoal should not reduce gold salts. On the other hand, unless special precautions are taken, the reduction in any particular case may well be due to impurities in the charcoal.

Lazowski[1] states that ignited wood charcoal reduces not too concentrated solutions of the salts of tin, copper, mercury, silver, platinum, palladium and gold, provided they contain no free acid. One of the interesting things about this is that with copper the metallic coating varies from blue to red which presumably means that he had colloidal copper.

Cornell University

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[1] Chem. Gazette, 1848, 43.

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ANODE CORROSION OF LEAD IN SODIUM HYDROXIDE SOLUTIONS

BY O. W. BROWN, C. O. HENKE AND L. T. SMITH

Lead, used as anode in a sodium hydroxide solution, is dissolved and precipitated on the cathode as a sponge, in a very finely divided condition.

Glaser[1] has obtained sponge lead by the electrolysis of feebly acid or neutral solutions of lead nitrate and acetate. However, with a more strongly acid solution of the nitrate or acetate, he obtained brilliant crystalline deposits of metallic lead. The formation of the sponge lead was attributed to the basic salts, which are almost insoluble, and which impede the uniform crystallization of the metal at the cathode.

Elbs and Rixon[2] have also made a study of the electrolysis of lead salts. In their experiments on phosphorous acid with lead electrodes, they observed that, with small current densities, the anode goes into solution and at the same time remains bright, and a crystalline deposit of lead forms at the cathode. If the current density is increased, the polarization potential increases from a few tenths to about 1.9 volts, and at the same time the anode becomes covered with a dark gray layer, while the deposit of lead on the cathode becomes spongy. They state that lead is dissolved in the electrolyte forming plumbic salts and on electrolysis sponge lead is formed at the cathode. If plumbic salts had not been present the deposit would have been crystalline.

Tommasi[3] produced sponge lead by the electrolysis of a solution of the double acetates of lead and sodium, using lead anodes and a rotating disk cathode.

Elbs and Forssell[4] have investigated the behavior of lead as an anode in sodium hydroxide solutions. They state that

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[1] Glaser: Zeit. Elektrochemie, 7, 365 (1900).

[2] Elbs and Rixon: Ibid., 9, 267 (1903).

[3] Tommasi: Electrochem. Ind., 1, 498 (1902).

[4] Elbs and Forssell: Zeit. Elektrochemie, 8, 760 (1902).

at first the lead anode remains bright and does not gas. Then there appear dark gray spots which spread out over the whole anode, later brown spots appear and soon the anode is covered with a brown coating. At the same time the anode begins to gas and yellow particles fall off the anode, which soon ceases, and then only gas is given off. These phenomena do not change with increasing concentration of the sodium hydroxide or with increasing current density, except that the single phases cannot be distinguished.

They also state that the electrolytic corrosion of the anode is not essentially influenced by the concentration. With increasing temperature the formation of lead peroxide only begins later. High current density and a quiet electrolyte are said to favor the formation of lead peroxide.

In our experiments we found that the temperature, concentration of the sodium hydroxide solution and the current density affected very greatly the corrosion of the anode.

The lead which we used as anode was purified twice by electrolysis in a Betts bath. The purified lead was then melted and cast into anodes. A new anode was used for each electrolysis so as to have the condition of the anode the same at the beginning of each experiment. The anodes in the experiments given in the first three tables had a surface of 56 square centimeters, while the anodes used in all the other experiments had a surface of 64 square centimeters, counting both sides. The anode was hung on a glass rod in the middle of the cell, which was a beaker 9 cm in diameter by 12 cm high. The cathode consisted of two thin strips of lead, of the same size as the anode, placed against the sides of the beaker, one on each side of the anode. Enough electrolyte was used to cover the anode, which required about 550 cc. The cells were kept in water baths and within 2° of the indicated temperature. The current was measured by a copper coulometer the current strength being indicated by an ammeter.

The quantity of lead corroded was determined by the loss in weight of the anode. Theoretically one ampere hour should dissolve 3.8642 grams of lead.

TABLE I

Effect of concentration of sodium hydroxide solution on anode corrosion at 20° C.

Current strength—1.5 to 1.6 amperes.

Electrode tension—3 to 3.1 volts after electrolysis had been started for some time.

Concentration Grams NaOH[1] per liter	Current per sq. dcm in amperes	Ampere hours passed	Lead corroded in grams	Corrosion in percent of theory
38	2.68	12.256	0.9102	1.93
			0.8337	1.76
43	2.86	2.587	0.0550	0.55
			0.0930	0.93
152	2.68	12.256	2.5430	4.95
			2.1448	4.46
174	2.86	2.587	0.0926	0.93
			0.2356	2.36
304	2.68	12.256	0.6073	1.28
			0.6873	1.45
348	2.86	2.587	0.0814	0.81
			0.0487	0.49

The two figures given for each concentration in each of the last two columns are results from two runs that were carried out under the same conditions. It will be noted that these do not check. Thus in the two runs with a concentration of 174 grams per liter the one result is 2.16 percent, over 2 1/2 times the other result which is 1.03 percent. Apparently they should be the same but the explanation is apparent upon watching the behavior of the lead anode. When the current is first started there is no gas given off and the lead dissolves quantitatively. Suddenly a gray spot will appear which will rapidly spread over the anode. Then dark brown spots of PbO_2 appear which likewise spread over the surface of the anode. At the same time gas is liberated and the corrosion of the anode is very materially reduced.

The results in Table I show that at this temperature and current density the corrosion of the lead anode is poor at best,

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[1] The sodium hydroxide used contained a trace of chlorine.

the greatest amount of corrosion taking place in a sodium hydroxide solution containing 152 grams per liter.

TABLE II

Effect of concentration of sodium hydroxide solution on anode corrosion at 60° C.

Current strength—1.4 amperes.

Electrode tension—about 1 volt at start.

Concentration Grams NaOH per liter	Current per sq. dcm in amperes	Ampere hours passed	Lead corroded in grams	Corrosion in percent of theory
35	2.50	3.628	0.6271	4.47
			0.9975	7.12
71	2.50	3.628	7.7483	55.28
			6.0721	43.32
110	2.50	3.824	14.5169	98.27
			13.9598	94.50
152	2.50	3.628	13.7798	98.32
			13.7854	98.36
192	2.50	3.824	8.8748	60.08
			8.4815	57.41
220	2.50	3.824	9.2573	62.67
			8.9166	60.36
304	2.50	3.628	5.2875	37.73

The increase in temperature very materially increased the corrosion at the anode. Also the effect of concentration is quite marked, the corrosion varying from 98.3 percent where we have 152 grams of sodium hydroxide per liter to 37.7 percent where the concentration is 304 grams per liter and 6.4 percent where the concentration is 35 grams per liter. This is directly at variance with the statement of Elbs and Forssell that the corrosion of the anode is not essentially influenced by the concentration of the sodium hydroxide solution.

It will be noted that when the corrosion is near 100 percent, the duplicate runs check very well, while when the corrosion is low as in the run where the concentration is 304 grams per liter the duplicate runs do not check within 10 percent.

The results in Tables I, II and III are plotted in Plate I.

The curves show the effect of concentration on the anode corrosion at the temperatures indicated. In each case we have

TABLE III

Effect of concentration of sodium hydroxide solution on anode corrosion at 75° C.

Current strength—1.4 to 1.5 amperes.

Concentration Grams NaOH per liter	Current per sq. dcm in amperes	Ampere hours passed	Electrode tension in volts		Lead corroded in grams	Corrosion in percent of theory
			Start	End		
38	2.68	7.584	1.2	3.2	3.3971	11.6
					2.7538	9.4
110	2.50	3.603	1.0	0.2	13.9149	99.95
			1.0	0.3	13.8476	99.46
137	2.50	3.603	1.0	0.2	13.8825	99.71
			1.0	0.3	13.8304	99.34
152	2.50	3.603	1.0	0.2	13.9085	99.9
	2.68	7.584	1.0	0.3	29.5476	100.8
169	2.50	3.603	1.0	0.2	13.9064	99.88
					13.8940	99.80
304	2.68	7.584	—	—	13.3050	45.40
					16.4268	56.06

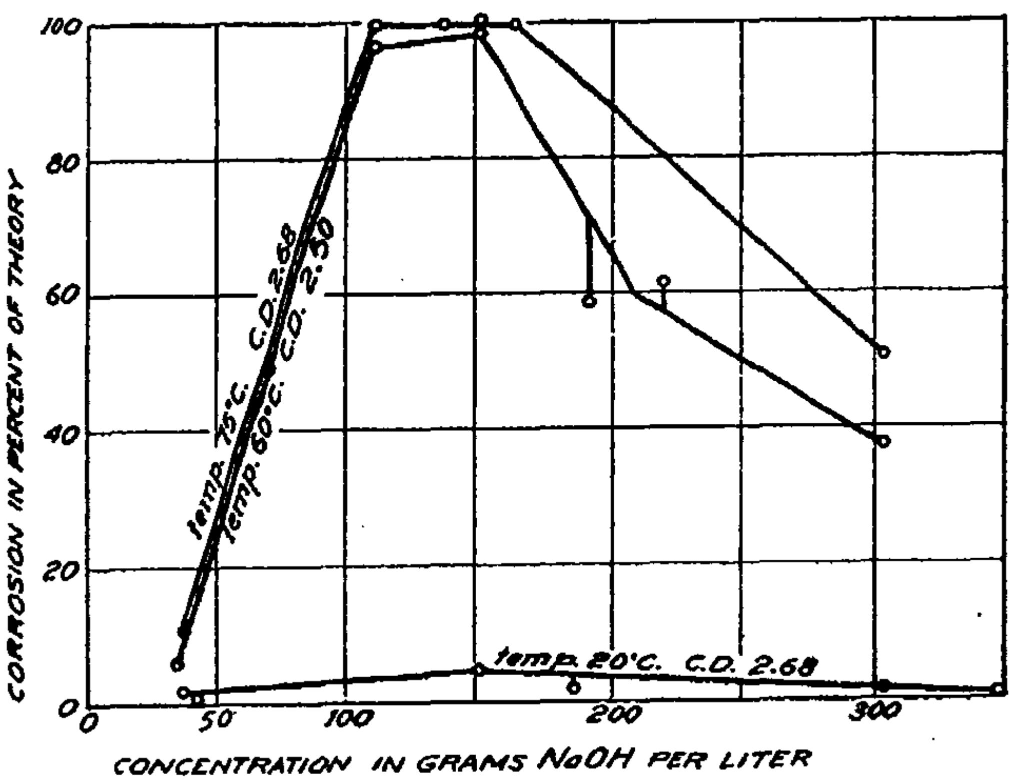

Fig. 1

but little corrosion at low and high concentrations. But at intermediate concentrations, that is from about 110 to 170 grams sodium hydroxide per liter, we have theoretical corrosion of the anode at 75° C, and nearly theoretical corrosion at 60° C. At 20° C the corrosion is very low at all concentrations, though even here it is highest at a concentration of 152 grams per liter.

In the foregoing experiments the current density, although not always the same, was usually 2.5 amperes per sq. dcm though in some cases it was 2.68 and 2.86 amperes per sq. dcm. For the following experiments the concentrations 38, 152 and 304 grams sodium hydroxide per liter were chosen and the current density was varied at each temperature and concentration. Also a few runs were made at 85° C. The results are given in Table IV.

It will be noted that with a concentration of 38 grams per liter and a current density of 0.16 ampere per sq. dcm. the corrosion was 102.5 percent. This indicated that the lead was soluble in this strength of caustic soda. To prove this an anode of the same size as those used in Table IV was placed in a solution of sodium hydroxide containing 38 grams per liter. After standing, without current passing, at 20° C for an hour and a half, which was the length of time that the electrolysis was carried out, the anode had lost 0.0114 gram, which was equivalent to 1.92 percent in the case mentioned.

When the anode corroded quantitatively it remained bright, but when it became covered with a coating of oxide it did not corrode quantitatively. However, in Table IV, with a concentration of 304, at 29° and a current density of 1, it was noticed that the anode was bright although the corrosion was only 4.8 percent of theory. The same was true with the same concentration and a current density of 4 at 60° and 75° when the anode corrosion was only 6.3 and 26.7 percent of theory. This does not seem to agree with the statement of Elbs and Forssell that as long as the anode remains bright it corrodes quantitatively.

The results in Table IV are plotted in Plates II and III,

Table IV

Effect of current density on anode corrosion at the various temperatures and concentrations of the sodium hydroxide solutions.

Concentration Gm NaOH per liter	Temperature °C	Current per sq. dcm in amperes	Ampere hours passed	Electrode tension in volts		Lead corroded in grams	Corrosion in percent of theory
				Start	End		
38	20	0.16	0.1533	1.2	0.84	0.6071	102.5
38	60	0.16	0.1533	0.9	0.14	0.6047	102.1
38	75	0.16	0.1533	0.9	0.14	0.6067	102.4
152	20	0.16	0.1533	1.0	0.94	0.5951	100.4
304	20	0.16	0.1533	1.0	1.0	0.4358	73.6
304	60	0.16	0.1533	0.8	0.2	0.5928	100.1
304	75	0.16	0.1533	0.8	0.24	0.5968	100.7
38	20	1.0	0.867	1.6	—	0.4391	13.1
38	60	1.0	0.8714	1.2	0.6	3.3193	98.8
38	75	1.0	0.8714	1.3	0.2	3.3964	100.8
152	20	1.0	0.8714	1.2	3.0	0.5415	16.1
152	60	1.0	0.8714	1.1	0.4	3.3719	100.2
152	75	1.0	0.8714	1.3	0.2	3.3758	100.2
304	20	1.0	0.867	1.4	—	0.1601	4.8
304	60	1.0	0.867	1.1	0.5	3.2517	97.1
304	75	1.0	0.867	1.2	0.24	3.3259	99.3
152	60	4.0	3.3698	1.5	—	0.8507	6.6
152	75	4.0	3.9003	1.3	—	7.0840	47.0
152	85	4.0	3.9003	1.4	—	14.9453	99.2
304	60	4.0	3.3698	1.4	—	0.8227	6.3
304	75	4.0	3.3698	1.3	—	3.4707	26.7
304	85	4.0	3.9003	1.4	—	6.4122	42.6
152	75	6.6	6.3619	1.35	3.3	2.3888	9.7
152	85	6.6	6.3619	1.4	3.3	9.1647	37.3

the data for the curves at the current densities of 2.68 and 2.5 being obtained from the first three tables.

In Plate II the corrosion is plotted against temperature. The concentration is in grams sodium hydroxide per liter and the current density in amperes per square decimeter. The curves show the rapid increase in current efficiency with increase in temperature. This is especially marked where the concentration is 152 and the current density 4.

In Plate III the current density is plotted against corrosion. With a suitable current density the anode corrosion is

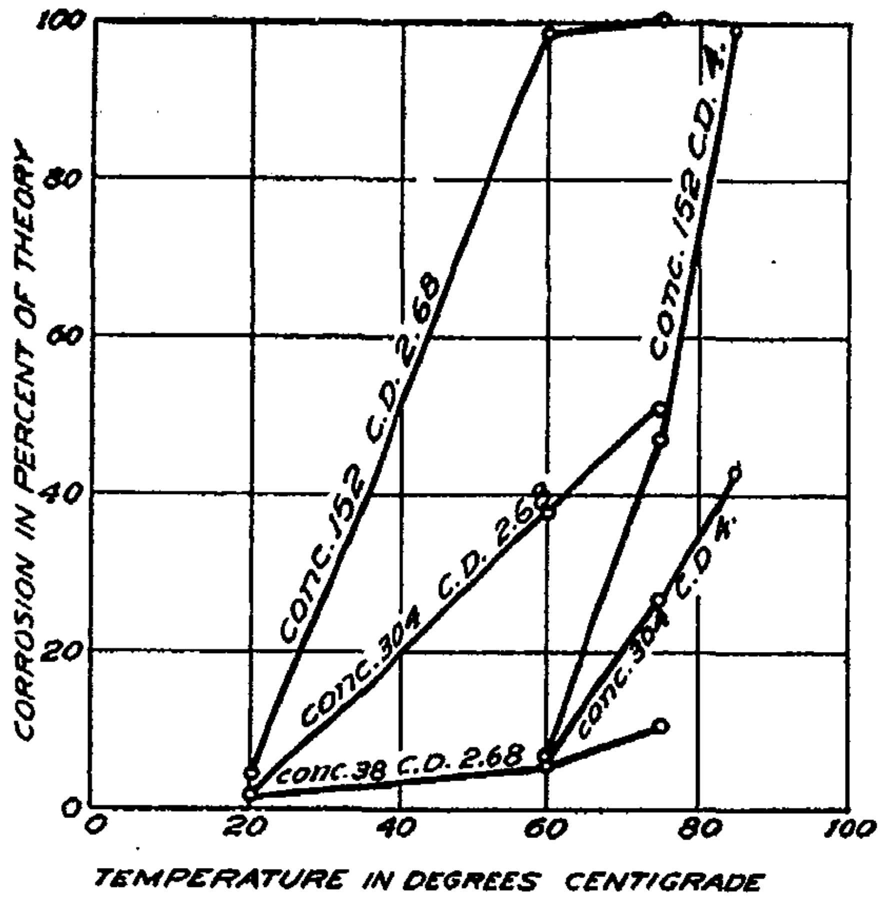
CORROSION IN PERCENT OF THEORY
100
80
60
40
20
0
0
20
40
60
80
100
TEMPERATURE IN DEGREES CENTIGRADE
conc. 152 C.D. 2.68
conc. 304 C.D. 2.68
conc. 38 C.D. 2.68
conc. 152 C.D. 4.
conc. 304 C.D. 4.

Fig. 2

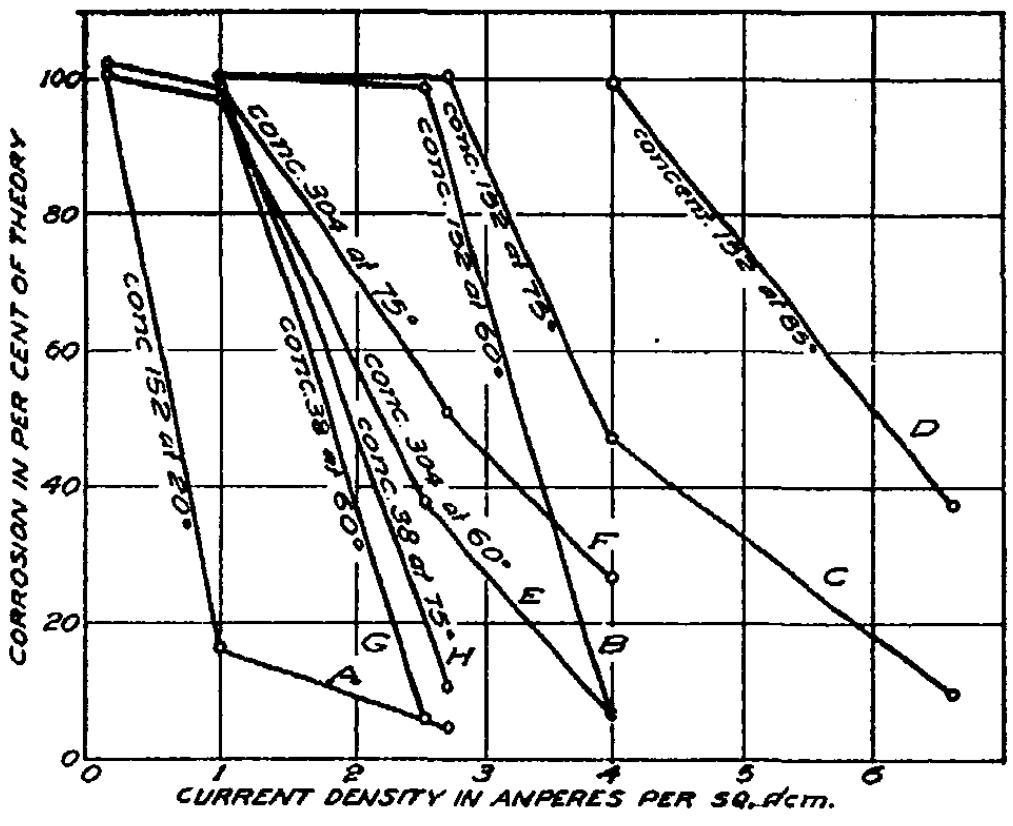
CORROSION IN PER CENT OF THEORY
100
80
60
40
20
0
0
1
2
3
4
5
6
CURRENT DENSITY IN ANPERES PER SQ. dcm.
conc 152 at 20°
conc. 304 at 75°
conc. 152 at 60°
conc. 152 at 75°
concen. 152 at 85°
conc. 38 at 60°
conc. 38 at 75°
conc. 304 at 60°
A
B
C
D
E
F
G
H

Fig. 3

theoretical in nearly every concentration at any temperature. This table shows how high a current density can be used under any of the given conditions of concentration and temperature with an anode efficiency of 100 percent. Thus in Curves A, B, C and D, it is seen that with each increase in temperature a rapidly increasing increase in current density is possible without the anode corrosion dropping. The same is also shown by Curves E and F for a concentration of 304 grams per liter and by Curves G and H for 38 grams per liter.

The plate also shows the effect of concentration. Thus at 75° the Curves H, F and C show that a higher current density is permissible at 152 grams sodium hydroxide per liter than at either of the other two concentrations.

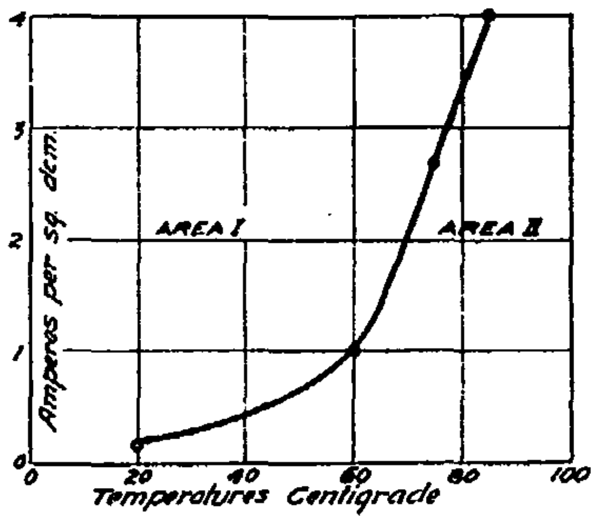

Fig. 4

In Plate IV the current density is plotted against the temperature. The concentration is 152 grams per liter.

The points on this curve represent the highest current density that was used at the indicated temperatures with 100 percent anode corrosion. Thus at 75°, 100 percent corrosion was secured with a current density of 2.68, while, when this was increased to 4 the corrosion decreased to 47 percent. Hence the current density 2.68 is the one used in the curve. Interpreting the graph we see that at any point in Area I less than 100 percent corrosion is secured, while at all points in Area II the corrosion is 100 percent of theory.

In Table I the electrode tension was about 3 volts after the electrolysis had been started for some time, while in Table II the electrode tension was only about one volt at the beginning of the electrolysis. In Table III the electrode tension was measured at both the start and end of the electrolysis At the start it was about one volt while at the end it was only 0.2 to 0.3 volt except where the concentration is 38 grams per liter and here it is 3.2 volts at the end. On examining the figures in the corrosion column of Table III it is seen that where we have 100 percent corrosion the bath tension is low, 0.2 and 0.3 volt, while at 38 grams per liter where we have low corrosion the voltage is high at the end, being 3.2 volts. A similar condition is found on examining Table IV.

In order to examine this further a study of the discharge potentials was made. To get the discharge potentials of each electrode a normal calomel electrode was used as auxiliary, the electromotive force of which was taken as —0.56 volt. The discharge potentials were measured by means of a specially designed make and break switch, which interrupted the current and then instantly made contact with the normal electrode circuit, in which the pressure to be measured was balanced against a pressure of known value, a galvanometer being used as the zero instrument.

The results are given in Table V. No measurements were taken until after the current had passed 70 minutes, because on first starting the current hydrogen is liberated at the cathode and hence the voltage is higher than at a later time when the lead is being deposited. Each time after increasing the current the readings were made as rapidly as possible which was about one minute after increasing the current. In the last column headed voltmeter is the reading of the voltmeter immediately after breaking the circuit.

The results in Table V are plotted in Plate V. The readings at the end of each period being the ones used.

All three curves make a very sudden bend at 2.81 to 3.75 amperes per sq. dcm. This is the point at which the anode quits corroding quantitatively. The change in the anode discharge potential at this point is very marked, from +0.285 to —1.317, a change of 1.602 volts. The total polarization increases from —0.146 to —2.464, an increase of 2.318 volts.

Curve C of Plate III shows that up to 2.68 amperes per square decimeter the corrosion is 100 per cent, but when this is increased to 4 amperes the corrosion drops to less than 50

TABLE V

Discharge potentials and total polarization at different current densities.

Temperature—75 ° C.

Electrolyte—550 cc of a solution containing 152 grams of sodium hydroxide per liter.

Minutes after start at which measurement was made	Current per sq. dcm in amperes	Electrode tension in volts	Discharge potentials in volts		Total polarization	Voltmeter
			Anode	Cathode		
70	1.56	0.5	+0.292	+0.471	—0.179	0.1
85	1.56	0.42	+0.292	+0.392	—0.100	0.09
86	2.10	0.6	+0.285	+0.457	—0.165	0.12
100	2.10	0.58	+0.292	+0.400	—0.107	0.1
101	2.81	0.68	+0.285	+0.442	—0.150	0.12
115	2.81	0.75	+0.285	+0.428	—0.146	0.12
116[1]	3.75	0.95	+0.277	+1.002	—0.788	0.14
145[2]	3.75	3.6	—1.317	+1.104	—2.464	1.3
146	4.22	4.0	—1.317	+1.167	—2.484	2.0

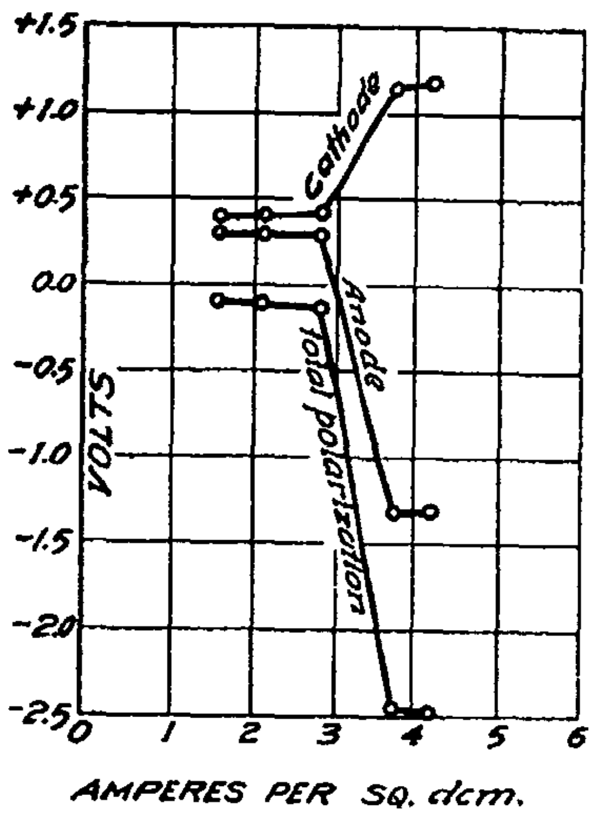

Fig. 5

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[1] Oxides of lead started to appear at the anode.

[2] Anode was gassing vigorously.

percent. Comparing this with Plate V it will be seen that when the anode is corroding properly the discharge potential is low, about 0.2 volt, but, when it stops corroding quantitatively its discharge potential immediately rises to about —1.317 volts.

The voltmeter reading immediately after breaking the circuit is in each case a little lower than the total polarization due to the fact that it cannot be read quick enough. Yet the change in voltmeter reading is over one volt, being from 0.12 to 1.3, a change of 1.18 volt. Hence the corrosion of the anode can be carefully watched by merely noting the voltmeter reading immediately after interrupting the current.

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ON THE DISTRIBUTION OF OZONE IN THE DIRECT CURRENT CORONA

BY ERIC K. RIDEAL AND JAKOB KUNZ

The mechanism by which ozone is formed from oxygen in the various diverse methods of preparation such as chemical, photochemical, thermochemical, or by collision with the aid of α-particles or electrons and finally by the silent electric discharge,[1] the most general method, is by no means clearly understood. It is generally assumed that the reaction proceeds in stages as follows:

$$O_2 \rightleftarrows O + O \qquad (1)$$
$$O_2 + O \rightleftarrows O_3$$

a somewhat more plausible hypothesis than the assumption of a termolecular reaction of the type

$$3O_2 \rightleftarrows 2O_3 \qquad (2)$$

It might be suggested, however, that the mechanism of ozone formation proceeds through a series of dimolecular reactions of the type

$$O_2 + O_2 \rightleftarrows O_4 \qquad (3)$$
$$O_4 + O_2 \rightleftarrows 2O_3$$

All these hypotheses assume that ozone is not produced through the intermediary of gas ions or electrons, except insofar as the ions or electrons serve to activate the oxygen molecule. The hypothesis that ozone can be produced without gas ionization was indicated by Lenard[2] and supported by Ludlam.[3] In all reactions, however, in which ozone is produced the presence of gas ions can be detected, and the possibilities of ozone formation by the interaction of gas ions are much more varied than in the preparation of H_3 owing to the relative complexity of the oxygen molecule. The experiments of Sir J. J. Thom-

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[1] For a résumé of the literature on the formation of ozone see F. O. Anderegg: Jour. Am. Chem. Soc., **39**, 2581 (1917) and forthcoming book "Ozone" by one of the authors.

[2] Ann. Phys., (4) **1**, 480 (1900).

[3] Phil. Mag., **23**, 757 (1912).

son[1] and F. Horton[2] have indicated the existence of electric allotropes of oxygen of the form $\ddot{O}$, $\dot{O}$, O', O'', as well as positively charged polymers of electric molecular weights $\Big(\frac{aM}{ne}$, as a is an integer, M the atomic weight, and ne the electron charge), 8, 16, 32, 48, 96. We can thus also assume the formation of ozone through ionic reactions of the types

$$O_2 \longrightarrow \dot{O} + O'$$

$$\dot{O}_2 + O' = O_3$$

$$O_2' + \dot{O} = O_3$$

These, however, presuppose not only an activation of the molecule but a subsequent ionization in addition, entailing a greater expenditure of energy.

Chemically, there is little evidence for the existence of atomic oxygen, not only on account of the great reactivity which this element would possess but also from a study of the decomposition of ozone. The decomposition of ozone, if a monomolecular reaction, would proceed through a series of reactions as in (1) while if bimolecular according to (2) or (3). In the free state the decomposition of ozone is bimolecular[3] except in the presence of solid catalysts[4] where a monomolecular reaction ensues owing to the possibility of removal of the third oxygen atom without its

$$O_3 + 2Ag = O_2 + Ag_2O$$

temporary existence in the free state.

$$O_3 + Ag_2O = 2Ag + 2O_2$$

The heat of formation of ozone which is endothermic is approximately 34,000 calories per g mol.[5] An approximation to the heat of formation of ozone may also be made on the

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[1] Phil. Mag., **13**, 501 (1907), et seq.

[2] Ibid., **22**, 214 1914).

[3] Chapman and Jones: Jour. Chem. Soc., **93**, 1638 (1908); **97**, 2463 (1910); Weigert, Zeit. phys. Chem., **80**, 78 (1912).

[4] J. Strutt: Proc. Roy. Soc., **87**, 302 (1913).

[5] Jahn: Zeit. anorg. Chem., **60**, 357 (1908); **68**, 250 (1910).

radiation theory of chemical action.[1] With Perrin[2] we may make no assumption as to the mode of mechanism but write the equation of reaction

$$3O_2 = 2O_3$$

and assume that the wave length of the ozonizing light is 165 $\mu\mu$ (the mean of Warburg's[3] and Regener's values[4] who noted that the absorption band extended from 120 $\mu\mu$ to 180 $\mu\mu$) and that of the deozonizing light 260 $\mu\mu$. (The mean of the deozonizing absorption band limits 230 to 290 $\mu\mu$.) From the relationship

$$Q = Nh\nu_{O_2} - Nh\nu_{O_3} = Nh\,(1.8 \times 10^{15} - 1.15 \times 10^{15})$$

where N is the Loschmidt number = 6.062×10^{23} and h Planck's constant 6.585×10^{-27}, we obtain the value Q = 62,830 cals or 31,415 cals per g mol. of ozone. (Perrin's 31,000 with approximate values of N and h.)

This method of calculation, however, although leading to a satisfactory numerical result, is open to serious objection from the standpoint of the quantum hypothesis, for it will be noted that Perrin has arbitrarily assumed the values of N*hr* derived from an assumed maximum line in a broad band to correspond to one g. mol. of reactant, oxygen, and one g mol. of product, ozone, arriving at the heat of formation of two g mols of ozone. It is tacitly assumed that the ozonizing light falls on a molecular complex of 3 molecules of oxygen acting as one, and the deozonizing light quantum is emitted from a complex consisting of two molecules of ozone. Now we have seen that in homogeneous decomposition the mechanism is bimolecular and, therefore, this latter assumption, viz., that ozone only decomposes when two molecules come in contact with one another and that photochemical decomposition accelerates the reaction only by increasing the number of effec-

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[1] Haber: Ber. deutsch. phys. Ges., **13**, 1117 (1911); W. McC. Lewis: Jour. Chem. Soc., **111**, 1086 (1917); Perrin: Ann. de Physique, **11**, 5 (1919).

[2] Loc. cit.

[3] Deutsch. phys. Ges. Verh., **17**, 10 (1915 .

[4] Ann. Phys., (4) **20**, 1033 (1906).

tive contacts (virtually a photochemical decomposition of $(O_3)_2$) might be accepted although it is more reasonable to suppose that one quantum of energy is derived from each molecule. The formation of ozone, however, through ter-molecular contacts which enduce the complex with properties so as to make it act as an individuum and capable of being activated by a single large quantum seems highly improbable.

W. McC. Lewis[1] adopts the hypothesis that ozone may be formed by the activation of each of the oxygen molecules to an equal degree, calculating from Chapman and Jones' figures[1] on the thermal decomposition of ozone, the value of Nhr_{O_3} = 10,690 cals, is obtained. Adopting the expression $3O_2 = 2O_3$ to explain the mechanism of ozone formation and the heat of formation as 69,000 cals per 2 g. mol. we obtain with Lewis a value for the critical energy increment for each oxygen molecule per g. mol. Nhr_{O_2} = 30,127 cal corresponding to $\lambda = 904\ \mu\mu$. Thus it should be possible to produce ozone from oxygen by illumination with light near the visible red end of the spectrum. It is, however, unknown whether photochemical ozone formation does take place at this point, and as will be readily observed, this photochemical synthesis involves the simultaneous coincidence of, not only three oxygen molecules, but of three activated oxygen molecules which would result in an extremely small reaction velocity.

It, therefore, appears likely that ozone can be photochemically prepared by at least two distinct methods, by illumination with light of wave length $\lambda = 1000\ \mu\mu$ and by illumination with light of wave length 120 — 180 $\mu\mu$, the former being represented by the usual reaction $3O_2 = 2O_3$, while for the latter we must adopt some other hypothesis than the simultaneous coincidence of three activated oxygen molecules.

The energy of activation of oxygen to its highest point may be calculated in a variety of ways, thus the ionizing potential of oxygen is found at 9.2 volts. From the relationship

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[1] Loc. cit.

$hr = Ve$ and $Q_2 = Nhr$, we obtain the value $Q_{O_2} = 210{,}680$ calories. Nernst[1] from e. m. f. measurements showed that the equilibrium concentrations of ozone and the active form of oxygen if it existed would be in the ratio of $10^{20} : 1$. Or, the heat of formation on the assumption that atomic oxygen and ozone were the reactants would be approximately in the ratios $\frac{20}{3} : 1$. Since $Q_{O_3} = 34{,}000$ calories per g. mol., $Q_{O_2} = 226{,}900$ calories per g. mol. Again, we have already noted that the ozonizing band lies within the spectral region 120 — 180 $\mu\mu$, and it is reasonable to make the assumption that activation can take place by irradiation with a band or more probably a series of lines and not only with a single line, owing to the fact that some molecules in the gas are already partly activated with infra-red quanta (see ante). These partly activated molecules, of course, require less energy, or light of longer wave length, than those not activated at all or which have received no critical energy increment from thermal radiation. Adopting 120 $\mu\mu$ as the wave length necessary to activate a non-active oxygen molecule we obtain the value

$$Nhr_{O_2} = 233{,}300 \text{ cals.}$$

The mean value obtained from these three determinations is $Nhr_{O_2} = 223{,}620$ calories per g. mol. or 111,810 calories per g. atom of oxygen Nhr_O (since one quantum splits up a molecule forming two atoms). It is uncertain in what form the active oxygen exists but since the value of Q exceeds by far the dissociation value of hydrogen $H_2 = H + H — 100{,}000$ cals per g. mol. and the computed value for nitrogen $Q = 160{,}000$ to $190{,}000$ cals per g. mol. it would appear likely that this value for the activation of oxygen includes not only the dissociation into atoms $O_2 = O + O$, but also the secondary ionization of those atoms $O = \dot{O} + \ominus$; the liberated electron then attaching itself to a neutral oxygen molecule, $\ominus + O_2 = O'_2$, and a subsequent reaction produces ozone $O'_2 +$

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[1] Zeit. Elektrochemie, 9, 891 (1903).

$\dot{O} = O_3$, a hypothesis supported by the value derived from the ionizing potential of oxygen.

For the activation of the oxygen molecule but a small quantum of energy is required. McC. Lewis has calculated a value of $Nhr_{O_2} = 30{,}127$ calories from Chapman and Jones' figures[1] for such an activation, while Ladenberg and Lehman[2] have noticed lines in the red and infra red position of the oxygen ozone spectrum. A distinct line is said to exist at $\lambda = 1040\ \mu\mu$, corresponding to a value of $Nhr_{O_2} = 28{,}000$ cals, or a mean value of $Nhr_{O_2} = 29{,}060$ calories per g mol.

For the photochemical decomposition of ozone taking the value in the region 230–290 $\mu\mu$ adopted by Perrin, viz., 260 $\mu\mu$ the critical energy increment for ozone is $Nhr_{O_3} = 109{,}000$ cal per g mol. Thus, the heat of formation of ozone is given by the relationship

$$\begin{aligned} Q &= Nhr_{O} + Nhr_{O_2} - Nhr_{O_3} \\ &= 111{,}810 + 29{,}060 - 109{,}000 = 31{,}870 \text{ cal. per g. mol.} \end{aligned}$$

By the silent discharge in oxygen 180 g per kw hr. is the best yield obtained; according to the above calculation where 140,870 calories are required per g mol., the theoretical yield should be 295 g per kw hr., or a technical efficiency of 61 percent obtains in practice. It may be noted if r_O corresponding to a value of $\lambda = 120\ \mu\mu$ represents the frequency necessary to split up a molecule into its atoms and also remove an electron from the atom the corresponding photochemical decomposition band $\lambda = 230\text{–}290\ \mu\mu$ should contain the light of the correct frequency not only to decompose ozone but to ionize it as well. It is hoped to investigate this point experimentally at a later date, but it appeared necessary first to determine the distribution of ozone in the corona discharge taking place in oxygen, and further, to note whether the light usually apparent in the corona tube was accompanied by any ultraviolet light as would be expected on the assumption that the formation of ozone is accompanied by the emission of light within the wave lengths 230–290 $\mu\mu$.

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[1] Loc. cit.

[2] Ber. deutsch. chem. Ges., 4, 175 (1906).

Experimental.—The corona tube consisted of a thin brass tube 25.4 cms long and 2.54 cms internal radius, along the axis of which was stretched a bright platinum wire 0.41 mm in diameter. The ends of the tube were sealed with thin pieces of quartz glass and gas inflow and eflow tubes were provided at each end. The corona was excited by means of a series of direct current coupled dynamos driven at a constant speed by means of a voltage regulator. The average voltage as determined by a calibrated Kelvin electrometer was 16,500 volts and no difficulty was obtained in maintaining this value when the wire was the seat of positive discharge and the tube earthed and negative (positive corona). With a negative corona on the other hand, fluctuations in voltage (±250 volts) were frequent.

A slow stream of dry oxygen was passed through the tube at a steady rate of 10 liters per hour, and the distribution of ozone in the oxygen between the wire and the tube was determined by two independent methods.

(*a*) *Chemically.*—A fine glass capillary was inserted at right angles to the axis and in the middle of the tube. Through the capillary, the tip of which could be adjusted to various positions in the annular space between the wire and the tube wall, a sample of the gas could be withdrawn and analyzed by aspiration through a solution of 2 *N* potassium iodide. The rate of aspiration was 1 liter per hour. All glass connections were employed and the analysis was performed by titration, after acidification, with sodium thiosulphate solution (10 cc = 1 mg ozone) which was standardized before and after each set of determinations.

(*b*) *Photochemical Analysis.*—In order to confirm the chemical analysis, and provide against distortion of the field in the corona tube by the insertion of any dielectric a photo analytic method was devised. For this purpose the method of Krüger and Möller[1] and of Fabry and Buisson[2] was modified so as to determine directly the distribution of ozone in the corona at

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[1] Phys. Zeit., 13, 779 (1912).

[2] Comptes rendus, 156, 789 (1913).

different distances from the wire. A diagram of the general arrangement is given in Fig. 1.

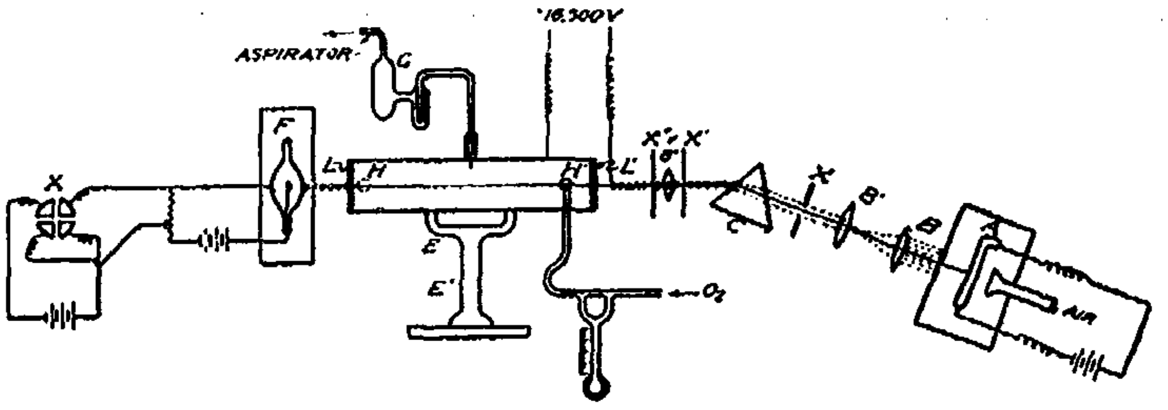

Fig. 1

A parallel beam of ultraviolet light (ca 2 mm wide and broad and within the spectral region $\lambda = 250$ to 350 $\mu\mu$, obtained, through the slits XX'X", from a quartz mercury vapor lamp A by the quartz optical system of lenses BB'B" and prism C, was passed through the quartz plates I'I, of the corona tube E provided with the gas inlet and outlet tubes H'H, and gas sampling arrangement G. The distance of the glass capillary of the sampling tube and of the ultraviolet light beam from the platinum wire in the corona tube could be adjusted by means of the screw thread E'.

Much trouble was caused by the alteration in intensity of the ultraviolet light from the lamp with the time, this was finally minimized but not entirely removed by keeping the lamp cool and at a uniform temperature by means of an air blast. The intensity of the emergent beam was measured by means of a photoelectric cell F. This photoelectric cell constructed of clear quartz and containing potassium was made extremely sensitive by submitting the alkali metal to the action of a spark discharge in hydrogen before replacement of this gas by helium. The applied voltage to the potassium cell was 163 volts and the alteration in current measured in the usual way by means of a sensitive electrometer shunted across a high resistance in the main circuit.

Owing to the fact that the corona was excited by means of a high d. c. voltage of 16,500 volts, elaborate precautions has to be taken to ensure against electrical leakage to the photoelectric cell circuit. This leakage was finally reduced so that the deflection of the galvanometer produced by the corona was less than 1 mm.

The concentration of ozone in the corona tube was calculated on the basis of de Beer's law $I_{emergent} = I_{entrant}\, e^{-kcd}$ where $I_{emergent}$ and $I_{entrant}$ are the intensities of the emergent and entrant beams, the deflection of the electrometer being assumed strictly proportional to the intensity of the light falling on the photoelectric cell; d = the thickness of the gas column 25.4 cm,. c the concentration of ozone in percent by volume, and k the specific absorption coefficient or extinction coefficient of ozone. Owing to the fact that the dispersion obtained by the optical system was rather small and that a relatively wide beam of ultraviolet light was passed through the corona tube, no definite value could be assigned to K, such as those given by Meyer[1] or Krüger and Möller.[2] The mean K value was accordingly calculated from a comparison of the figures obtained in this way with the determinations by the chemical method and found (approximately) equal to 2.30.

The results obtained by the two methods are indicated in the following curves, where the ordinates represent percentage of ozone by volume in the oxygen and the abscissae the distance in millimeters from the wire or tube axis to the point where the determination was made (Fig. 2). As examples of the figures obtained may be cited the following:

Chemical Method.—Positive corona.

Distance from wire, 0 mm.

Strength of the thiosulphate, 10 cc. = 1.3728 mg. O_3.

Titre for 500 cc. (aspirated at one liter per hour), 17, 17.3, 17.2, 17.4 cc thiosulphate solution.

Mean percent by volume, 0.220.

Optical Method.—Negative Corona.

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[1] Ann. Phys., (4) 17, 849 (1903).

[2] Loc. cit.

Owing to the fact that the corona light affected the potassium photoelectric cell, it was found necessary to perform the operations in the following manner: After having obtained the zero of the instrument the ultraviolet light intensity was measured after passing through the tube containing oxygen.

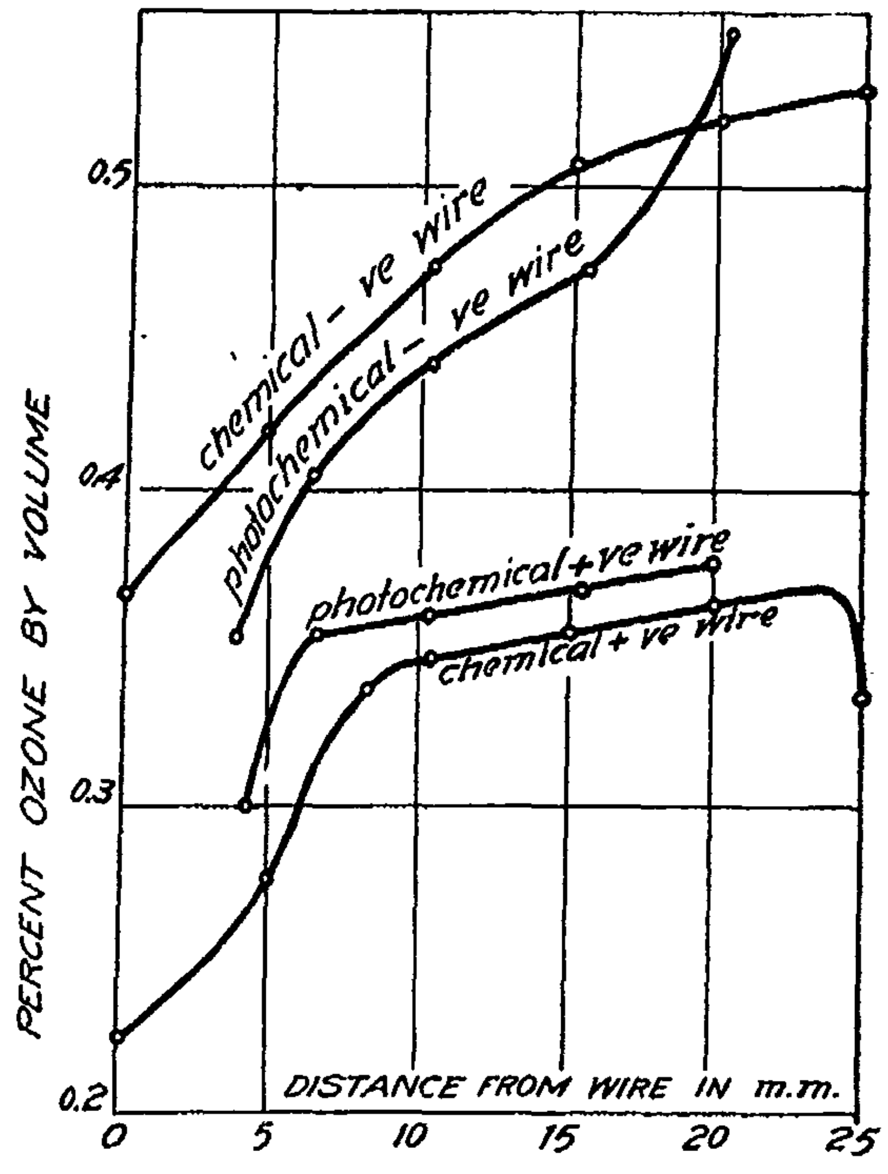

Fig. 2

The corona was then turned on and the new deflection obtained, somewhat greater than before owing to the effect of the additional light derived from the corona. The discharge was allowed to pass until a stationary deflection of the galvanometer was obtained, a period of from three to five minutes, being usually, amply sufficient, the reading thus obtained being noted, the corona discharge was then stopped and the new deflection immediately determined as instanced by the following figures:

Applied voltage, 16,500 volts.

Current, 0.68 milliampere.

Distance from wire, 15.5 mm. to center of beam.

Deflection of electrometer with ultraviolet light cut off = deflection 50 mm.

Deflection of electrometer with oxygen in tube, 190.2 mm. (mean of 3).

Deflection of electrometer with oxygen in tube when corona light appears 194 mm. (mean of three).

Mean deflection (1) without corona light, 140.2 mm.; (2) with corona light, 144 mm.

Deflection of electrometer when dynamic equilibrium has been established with corona light, 161.5 mm. (mean of three); after corona is cut off, 156 mm. (mean of three); mean deflection with corona light, 111.5 mm.; without corona light, 106.5 mm.

Inserting these values in the equation

$$\log_e \frac{I}{I_0} = -kcd$$

where $d = 25.4$ cm. and $K = 2.30$, we obtain values for $c = 0.462$ percent, 0.469 percent, average 0.465 percent.

It will be noticed that the distribution of ozone in the corona varies very notably with the sign of the discharge, the negative corona producing higher concentrations than the positive, this in agreement with Warburg's results.[1] According to the data obtained by Anderegg[2] although in a closed corona tube the total quantity of ozone formed is practically identical for a positive or negative corona yet it will be observed that the rate of formation of ozone as deduced from the slope of the *c*, *t* curves obtained by him is considerably greater for a negative corona, and one would, therefore, infer that in a corona tube through which oxygen was passing continuously

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[1] Loc. cit.

[2] Jour. Am. Chem. Soc., 39, 2591 (1917).

the yield from a negative corona would exceed that from a positive, which is actually found to be the case.

The average yield of ozone obtained was as follows: Negative corona, 0.045 g per coulomb; positive corona, 0.024 g per coulomb. While Warburg obtained with a negative corona 0.043 g per coulomb, and with a positive 0.017 g per coulomb.

It has usually been assumed (see 1) that ozone formation occurs in the corona, or in the luminous part of the discharge; in the case of the positive corona it will be noted that there is a rapid rise in ozone concentration until a distance of 7 mm from the wire is reached after which the ozone concentrated remains approximately constant. This rapid rise can be accounted for on the assumption either that the ozone is photochemically destroyed in the neighborhood of the corona, or that the ozone molecules lose electrons and as a consequence the positive ozone gas ions are repelled from the wire and thus give rise to the phenomenon of corona pressure. In this case it is evident that the ozone molecules must lose electrons more easily than oxygen or that the ionizing potential of ozone must be appreciably lower than oxygen (see ante).

In the case of the negative corona, a somewhat different type of curve is obtained and it would appear that in this case the ozone is again made at the positive electrode, as in the case of the positive corona, and diffuses from the positive electrode, the tube, to the wire where a slight decomposition obtains. It does not seem possible to account for the steady rise of the ozone concentration away from the wire on the assumption that ozone is formed in the luminous part of the negative corona.

The corona discharge is accompanied not only by the emission of visible light but of ultraviolet light in addition. Comparative figures for the fraction of ultraviolet light (between $\lambda = .200\ \mu\mu$ and $\lambda = 400\ \mu\mu$) emitted from the positive and negative corona were obtained by measuring the intensity of radiation falling on the photoelectric cell through the quartz plate (lower limit $\lambda = 200$) and noting the fall in radiation intensity by the insertion of a thin glass plate (lower limit of transmission $\lambda = 400\ \mu\mu$). The following figures were obtained:

	Corona		
	Positive	Negative	
Zero deflection	76.0	68	74
Deflection with corona discharge	91.5	82.5	90
Deflection after insertion of thin glass plate	81	74.5	82
$I_0 = K\ 15.5$	$I_0 = K\ 14.5$	$I_0 = K\ 16$	
$I = K\ 5.0$	$I = K\ 6.5$	$I = K\ 8$	
$\frac{I}{I_0} = 32\%$	$\frac{I}{I_0} = 46\%$	$= 50\%$	

Indicating that only 32 percent of the radiation received by the photoelectric cell in the case of the positive corona lies within the region 200–400 $\mu\mu$ and 68 percent in the ultraviolet portion of the spectrum, while with the negative corona the percentage of visible light emitted is nearly 50 percent. The actual ratio of ultraviolet light to visible in the corona is probably much higher than indicated by the figures owing to the partial absorption of the same when passing through the column of oxygen gas, since no light of wave length below 200 $\mu\mu$ is capable of passing through. The fact that the ratio of ultraviolet to visible light is less in the negative corona than that in the positive, although the ozone production is higher, substantiates the view that the ozone formation in the negative corona is not caused by radiation at the wire surface.

Summary

The various methods by which ozone can be prepared in the light of the radiation hypothesis are reviewed, and the conclusion is drawn that molecular species of one kind can be activated by radiation to different extents.

The distribution of ozone in the direct current corona has been measured by two independent methods; by chemical analysis and photometrically with the aid of potassium photoelectric cell of quartz. It is shown that the distribution of ozone in the positive direct current corona differ in a marked manner from that obtaining in the negative corona.

The ultraviolet light emission from the corona exceeds that of the visible and in the corona itself the ratio of ultraviolet to visible radiation is probably exceedingly high.

The writers are indebted to Professor A. P. Carman for the use of the dynamos in the corona laboratory.

University of Illinois
March 8, 1920

ESTIMATING IMPURITIES BY MEANS OF THE MELTING POINT CURVE

BY WALTER P. WHITE

Fourteen years ago Hüttner and Tammann[1] mentioned that it was possible, from the behavior of the temperature during crystallization, to draw a conclusion as to the amount of impurity. Other writers have since discussed the melting or freezing curve more at length, but little practical use has yet been made of Hüttner and Tammann's suggestion. The present paper considers under what conditions this method is most likely to be useful, and also discusses the technic.

Theoretical Basis

The underlying laws are familiar but may deserve to be summarized. Impurities may form solid solutions, or only eutectics, and the crystallization phenomena have significant differences in the two cases.

Where mix crystals only are formed, the temperatures and concentrations change as in Figs. 1 and 2. (More complicated freezing curves than these are known, but if the amount of impurity is small, so that the extreme right or left end only of the phase rule diagram is used, that end will rarely differ essentially from the end of 1 or 2.) As the liquid mixture cools for either figure its concentration and temperature follow the line UV. At temperature V mix crystals of composition W begin to form. The relation of V to W depends on the form of the double pointed figure CD, which is a characteristic of the combination of substances in question. Since the composition W is different from the original melt, the separation of crystals W changes the composition of the liquid, which moves toward composition X as solidification proceeds. At the same time, if complete equilibrium persists, the composition of the crystals, including those already deposited, changes along WY.

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[1] K. Hüttner and G. Tammann: "Ueber die Schmelzpunkte und Unwandlungspunkte einiger Salze," Z. anorg. Chem., 43, 218 (1905).

But this change in material already solid cannot be counted on to be complete, and may occur only to a slight extent. In such cases the liquid composition at the end of the crystallization will evidently contain less of the component A than the liquid at X in Fig. 1, and will be represented by a point to the right of X. (In Fig. 2 it will contain more of A and come to the left of X.) The form of the temperature curve during solidification is, therefore, likely to be affected by the rate of cooling. If meltings are used instead of crystallizations the curve may be affected by the rate and also by the way the preceding crystallization was conducted.

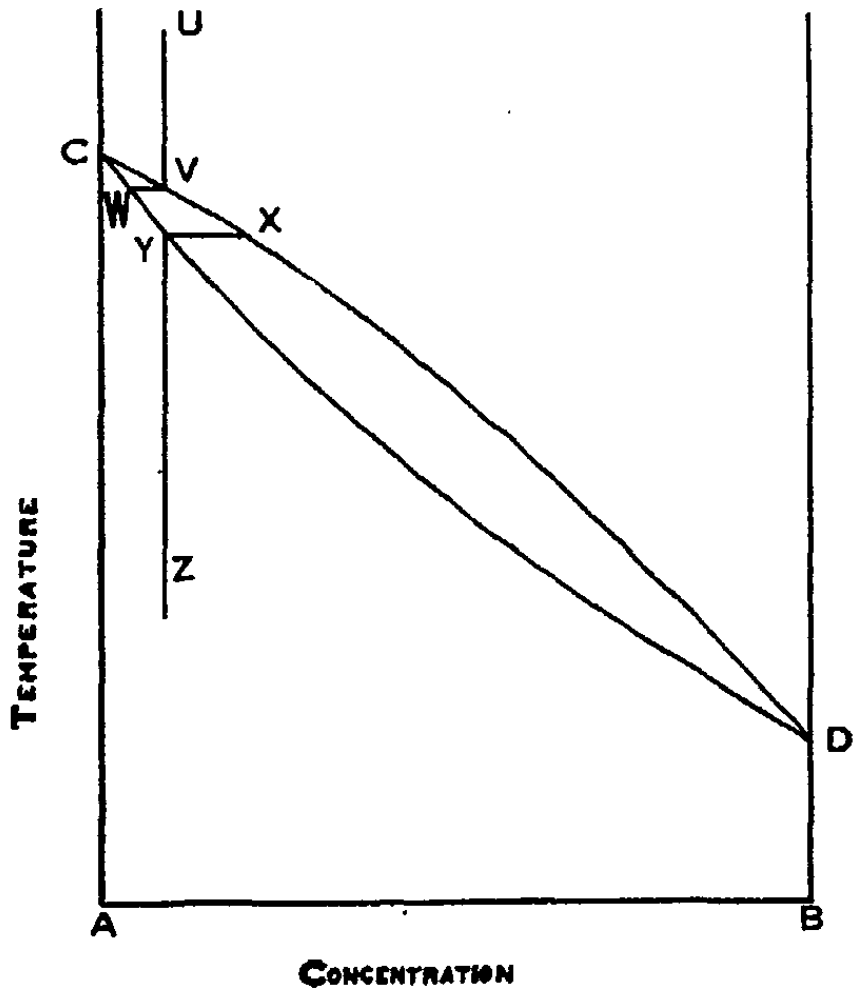


Fig. 1

With an impurity which forms a eutectic but no solid solutions, the phenomena are more certain, and a comparatively simple law for the progress of the melting can be stated. It is this simple case which has been mainly considered by those who have discussed the temperature-*time* melting curve and

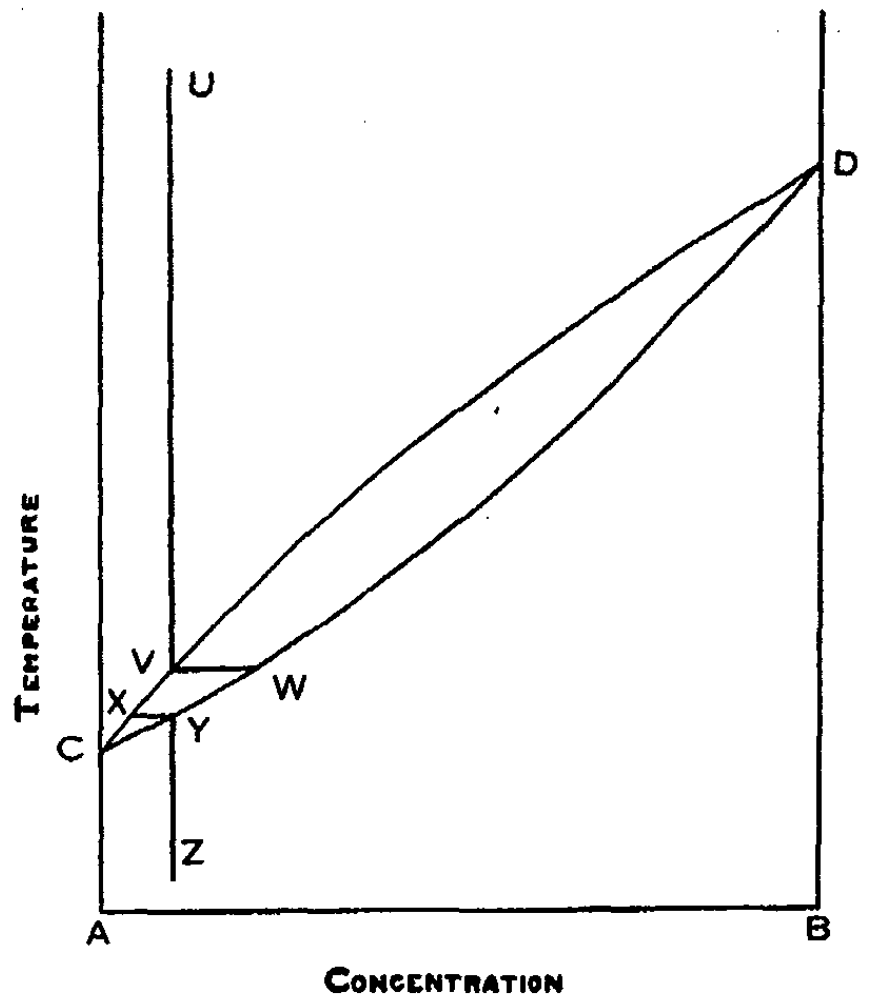
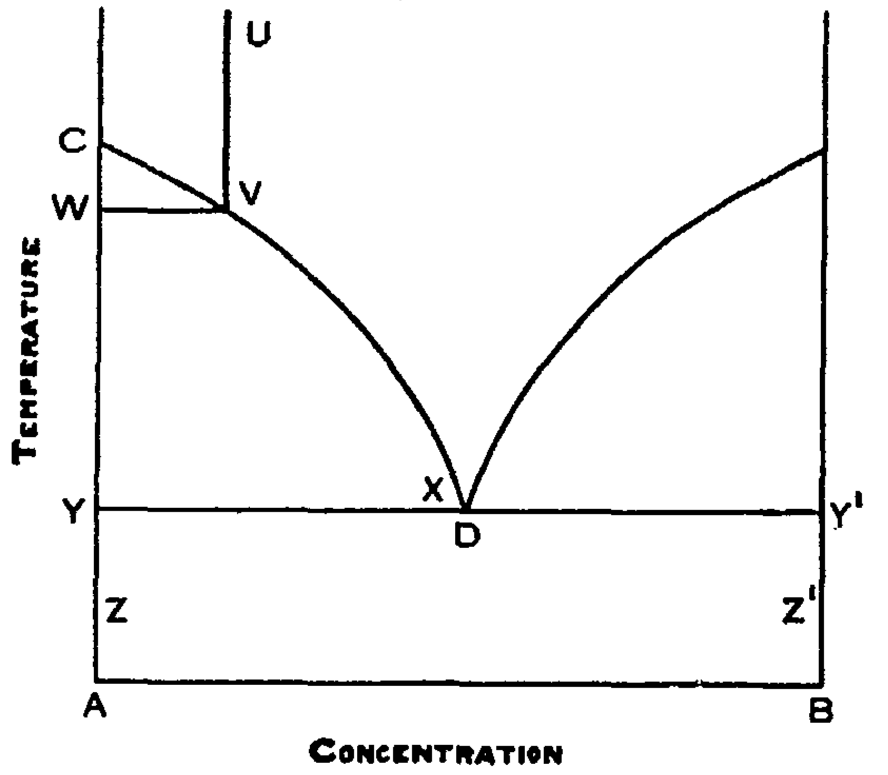

U
D
TEMPERATURE
V
X
W
C
Y
Z
A
B
CONCENTRATION

Fig. 2


U
C
W
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TEMPERATURE
X
Y
D
Y'
Z
Z'
A
B
CONCENTRATION

Fig. 3

its connection with impurity. The well-known equilibrium diagram is given in Fig. 3. The composition U cools as liquid along UV. V is the point at which crystallization begins. This is the crystallization of the pure majority component, and the product is, therefore, represented by W. The removal of W from the solution leaves a greater concentration of impurity, and, therefore, a crystallization temperature farther from the margin on the descending *liquidus* curve VXD. As the liquid composition moves down this curve the solid moves down WY, that is, pure solid keeps crystallizing out, at lower and lower temperatures. Finally the process comes to an end as both components, A and B, crystallize simultaneously from liquid of the eutectic composition and temperature, D.

The Temperature-Time Curve

If we are dealing with small amounts of impurity the important phenomena are confined to the uppermost part of the curve CVD. This part of the curve can, to a rather close approximation, be accounted for by saying that the melting point of the pure substance is lowered by the impurity in accordance with Raoult's Law, according to which the lowering

$$\Delta\theta = -\frac{R\theta^2 C}{L}$$

is proportional to concentration C, of the impurity, with L the latent heat of the solvent. This approximation makes the top of CVD a straight line. It has been used by all those who have discussed the freezing point determination curve. According to it the lowering of the melting point, being proportional to the concentration, is inversely proportional to the amount of solvent remaining melted. If heat is abstracted at a regular rate during cooling, and if T_0 minutes are needed to solidify the whole quantity, the amount left melted will be proportional to $T_0 - T$, the lowering, therefore, proportional to $\frac{1}{T_0 - T}$. This gives a curve like Fig. 4. This is a temperature-*time* curve, to be contrasted with the temperature-*concentration* curves in Figs. 1, 2 and 3. The curvature in

Fig. 4 is not a consequence of the curvature of CVD in Fig. 3, but was obtained by treating CVD as not curved at all.

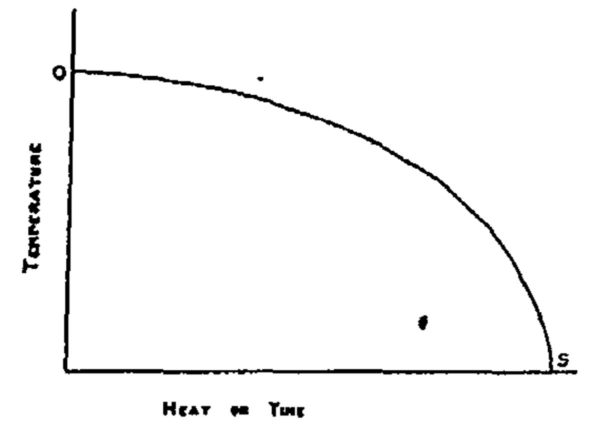

Fig. 4

Crystallization curve, assuming a linear liquidus curve

If $T = \frac{T_o}{2}$, that is, when half the substance has solidified, the temperature lowering is proportional to $\frac{2}{T_o}$ against $\frac{1}{T_o}$ for the initial point of the curve. That is, the fall of the curve from $T = 0$ to $T = \frac{T_o}{2}$ is equal to the melting point lowering of the substance. A shorter section of the curve can also be used. For instance, if $T = \frac{T_o}{4}$ the total lowering is proportional to $T_o - \frac{T_o}{4} = \frac{4}{3}\,\frac{1}{T_o}$, and the melting point lowering is evidently 3 times the temperature drop observed from $T = 0$ to $T = \frac{T_o}{4}$. On the other hand, by running till the solidification is nearly completed a drop is obtained which is several times the initial lowering. The results then are usually not proportionally very accurate, for a reason to be given later, but the detection of a lowering is much more sensitive than by measuring the melting temperature directly.

Advantages of the Curve Method

It is now possible to compare this method with the common one, where the melting temperature is observed and compared with the known value for the pure substance, or with a previous value for the same material at an earlier stage of purification.

Both methods give the lowering as a temperature difference, leaving the purity to be inferred from this. Both are rendered uncertain when the impurity forms a solid solution, except that the present method gives some indication when this is so, as will be considered further on.

With regard to substances whose melting point is well known, the curve method has the advantage of not requiring a knowledge of the exact calibration of the thermometer, since only temperature differences are measured. That is, it renders the experimenter perfectly well able to proceed without knowledge of the melting point. This is still more an advantage where there is doubt of the previous results. The curve method, with the same thermometer, also is more sensitive, as already shown. It also lends itself readily to the use of sensitive thermoelements which may increase the precision. It can, however, be used with a mercury thermometer, though it requires more material if this is a large one. The observing may be a more considerable affair; in such cases the curve method is not so likely to be taken up by those who are already satisfied with the other.

If the melting point determinations are desired to control the purification of a new substance, a considerable saving of time may be added to the advantages already enumerated. In checking purity by the melting of substances in a capillary tube it is customary to work until further purification produces no change. That is, after getting the substance pure another purification is necessary to see if the previous sample was pure. With the curve method such purity is recognized as soon as it is reached. Even more important, perhaps, is the following consideration. In making successive purifications it is possible that through decomposition, solution of the containing vessels, contamination from the air, or some such cause, an attempted purification may cause no further change in a substance already nearly pure. In such a case the method of successive melting points would indicate that complete purity had been reached. The curve method would at once show the true state of the substance.

In a recent paper,[1] Wilhelm and Finkelstein say: "Experiments made here and in other laboratories have demonstrated that the capillary-tube melting point method will not usually give so consistent nor so accurate results as the constant-temperature method."

Experimental Requirements

The experimental requirements, aside from sufficient precision and the absence of undue lag, are two. The thermometer must measure the temperature belonging to the melt as a whole, not to some aberrant part of it; and the heat must be abstracted at a known rate.

Temperature uniformity has often been promoted by stirring, but easier and more satisfactory ways are available in the present case. Smallness of diameter greatly diminishes temperature differences, and may also be made to shorten the time required. In extreme cases high uniformity can be obtained by very thin radial conducting plates of silver, gold, or aluminum, but this is a very special arrangement.

The rate of heat loss varies with the thermal head, i. e., the temperature difference causing flow of heat, here the difference between the surface of the tube containing the test substance and the inner surface of whatever incloses this. It is not difficult to measure the thermal head during the time taken for the freezing point measurements, but this is ordinarily unnecessary. The temperature of a fairly pure substance changes very little during most of the freezing, so if it is surrounded by a fairly constant bath or other large mass the thermal head remains nearly constant, and the heat loss can be taken as simply proportional to the time.

The gains, both in quickness and accuracy, which come from using a cylinder of small diameter urge the use of a small thermometer. Here the thermoelement has a great advantage. It is also easier to read, can be read from a distance, requires

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[1] Bur. Standards, Sci. Paper 340, 187 (1919).

no tapping, and gives no trouble about emergent stem. The technic of the thermoelement has been elsewhere described, and potentiometers especially adapted to it are on the market. The commoner slide-wire potentiometers, also, will do well enough for reading to 0.01° at 100°, by means of a thermoelement of 2 or more couples.

The foregoing is perhaps sufficient to convey an idea of the essential features of the curve method for freezing points and of its value. Those wishing to use it will probably like to go further into the various approximations involved, and into the possible sources of error. These will, therefore, now be discussed. A very wrong impression will be obtained, however, if it is not realized that the precautions and corrections to be discussed are unnecessary for ordinary work. In particular, graphic methods will seldom be needed, though they are used here in discussing various errors, and may be advantageous in work of special refinement.

The Approximation Used for the Liquidus Curve

As already mentioned, taking the melting point lowering as proportional to impurity-concentration is equivalent to assuming a straight "liquidus" curve, CVD in Fig. 3. If the true form of the liquidus is known, it can easily be used to get a result free from most of the approximation. We have merely (for instance) to take the observed fall of temperature, $\delta\theta$, for a doubling of concentration, and then by trial find where on a plotted liquidus curve that difference in temperature corresponds to a doubled concentration, that is, where $y_1 - y_2 = \delta\theta$ gives $x_2 = 2x_1$. Or else, by finding the temperature lowering corresponding to a doubling of concentration for various abscissas (i. e., concentrations on the drawn curve), and then plotting the lowerings against the concentrations, an auxiliary curve can be made which will at once give the concentration corresponding to any given temperature lowering due to double concentration. Again, if the liquidus is known as $\theta = f(x)$ we have

$$\theta_0 - \theta = f(x_0) - f(2x_0) \qquad (1)$$

as a substitute for the reckoning given with Fig. 4. $f(x) = ax + bx^2$ gives a much better approximation than a linear law, and will probably always be sufficient. If the function is as simple as that, (1) can readily be solved in any given case. Another ratio of concentrations than 2 can, of course, be taken. If $f(x) = ax + bx^2$ is taken as accurate the proportional error from using the linear law is readily shown to be $\frac{2b}{a}$ for doubled concentration, $\frac{20b}{a}$ for five-fold increase, etc. This is one of several reasons why the determination is likely to be more accurate (though less sensitive) where only the first part of the freezing curve is used. It seems hardly worth while, however, to spend time on the more accurate calculation till it is known that the experimental precision is worth it. This also applies to the further corrections given here.

Effect of Specific Heat

A second reason why the preceding results are only approximate is that the heat used in lowering temperature has been neglected. This produces complication in two ways. The first regards the determination of the duration of the solidification. In practice the temperature-time melting curve of Fig. 4 becomes steeper and steeper until its end is lost in the slope of the linear cooling curve of the completely crystallized solid. Not only is this end hard to find, but it should not be taken at all as the end of the solidification when the purpose of the work is that discussed here. For the object of the time coördinate is solely to measure the loss of heat, and the object of this is to find the proportion of material that has crystallized. Now if the substance crystallizes pure, and then cools as solid only, it will follow the heavy line OPZ in Fig. 5, first losing heat at constant temperature; and then cooling regularly, since specific heat and rate of heat loss are (by hypothesis) constant. In this case OP unquestionably represents the heat loss necessary for crystallization. But if as a result of impurity the temperature falls during crystallization, as along OS, the body will be in the same state as before when it reaches S, that is, it will be all solid, and will have been cooled to the temperature of S. But the heat lost in cooling the solid is still represented by the horizontal projection of PS, and therefore, OP, which represents the total less this heat PS, represents the heat loss due to the change from liquid to solid. An apparent objection is that on the curve OS some material cooled while liquid, when its specific heat was greater than that of the solid, and, therefore, not consistent with the slope PS. This, however, is offset by the fact that if the substance solidifies at a lower temperature its latent heat is less, and by an amount which (except for the very small effect due to the change in dilution of the impurity) must be equal to the difference in the specific heats multiplied by the temperature difference. Hence, with the trifling exception mentioned, the horizontal OP gives the heat abstraction needed to solidify all the material at the temperature of O, that is from a state of purity, regardless of the temperature at which it actually did solidify. And it is this total heat of solidification of the perfectly pure substance which will be most convenient in the subsequent operations.

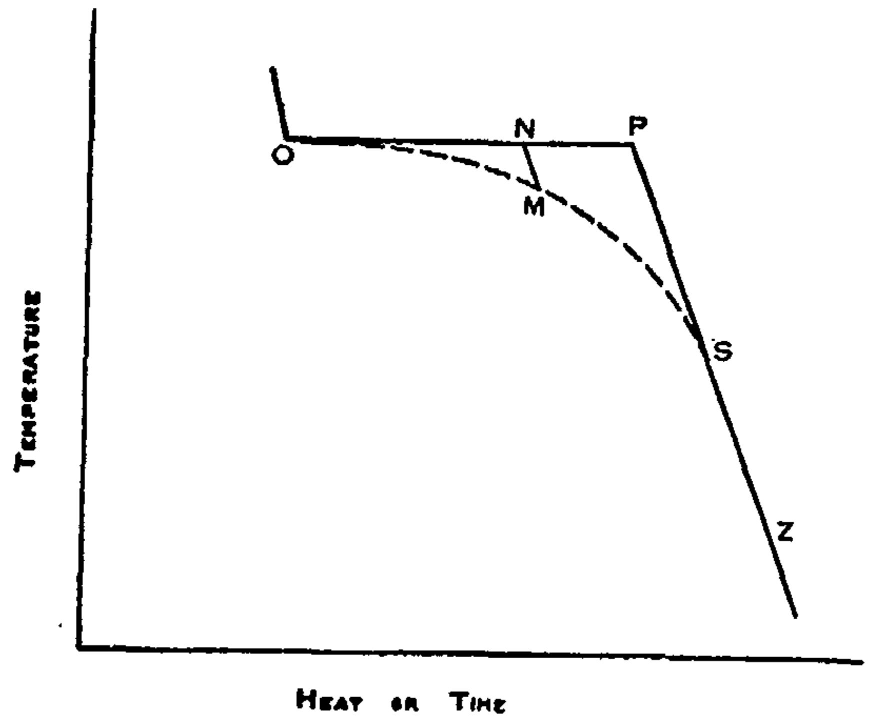

Fig. 5
Freezing point determination

The second complication connected with the specific heat comes in the determination of the amount of material crystallized at intermediate points on the curve, as at M in Fig. 5. Here the material not yet crystallized has been cooled with a higher specific heat, but it has not yet crystallized with a lower latent heat. For the greatest rigor it seems necessary to take separate account of the two portions of the charge. (1) The heat lost in cooling the solidified substance is found by drawing MN upward parallel to SP (Fig. 5). This method gives the latent heat given out, ON (the thing we wish to know) as of the pure substance, and thus directly comparable with the total heat of all the pure substance, which we got by finding the point P. The horizontal projection of MN, however, gives the heat loss required to cool all the material as solid to the temperature of M, and we have in fact cooled only a portion of it, proportional to $\frac{ON}{OP}$, as solid. Hence, a line MR only $\frac{ON}{OP}$ times as long as MN (Fig. 6) gives the true correction for the specific heat of the material already solidified. The fraction $\frac{NP}{OP}$ is still liquid, and should be corrected for by a line with slope AO, representing the liquid specific heat but of length $RN' = MN \frac{NP}{OP}$. These two lines, reaching OP in N′ (Fig. 6) give the true amount of material solidified at M as proportional to ON′. This discussion is given for completeness, rather than with the idea that so accurate a treatment of the specific heat will often be desirable in practise.

The use of considerable heat-conducting material in some cases has been recommended. Such material may add to the specific heat, and in any case an appreciable addition will be made by the container and thermometer. All such specific heats, however, cancel out completely with the method just given, as long as the slope of AO for the liquid specific heat is obtained by observation and not by calculation. For we may think of the inert material as distributed to the tested material, so that each infinitesimal mass element of the tested material has assigned to it a proportional share of the other. The effective specific heat of the tested material may then be regarded as the sum of its own specific heat and that of the inert material assigned to it. It is evident that these compound heats are the ones actually determined by the curves AO and PZ, and that when any element of substance solidifies and its specific heat changes from the liquid to the solid value, its compound specific heat does the same. These compound specific heats thus have all the properties of the specific heats that were used in getting the methods connected with Fig. 6.

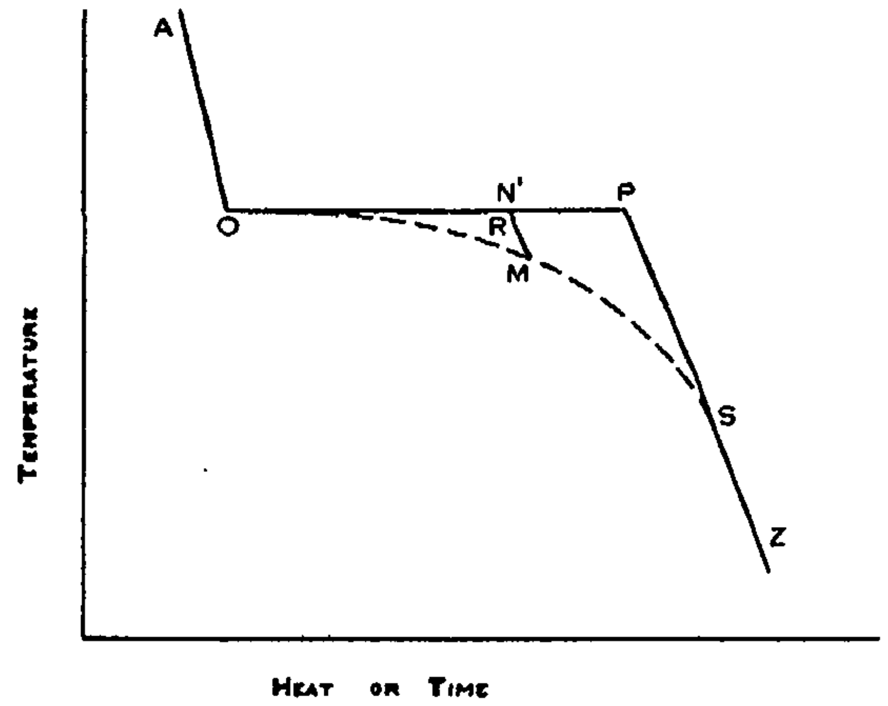

Fig. 6
Freezing point determination

This conclusion, it is important to note, supposes uniform temperature throughout the cooling material. It might hold very closely where radial conducting vanes are present. With material simply inclosed in a tube the tube will be a little below the temperature of the solidified material, which is next the outside, while the thermometer will be at the temperature of the still liquid center.

Uncertainty in the End of the Curve

A third approximation comes from the fact that, even with perfectly uniform heat abstraction, the line SZ does not as soon become straight as Fig. 5 would indicate. According to the assumption of Fig. 4 it never does so; practically it does not till the eutectic solidification is past. Hence, the true construction might start from a point below the somewhat indefinite S in Fig. 5, making OP longer. MN would also be steeper, but this evidently will not increase ON in the same proportion as OP. To project ZP upward, however, from a point below the eutectic is likely to bring in experimental errors greater than those from neglecting the curvature of the line below S, which is very small if the substance is nearly pure. These experimental errors next deserve consideration.

The Special Experimental Errors

Hitherto in this discussion it has been assumed that all of the solidifying charge is at the same temperature, and that the rate of heat loss is constant. Four processes, whose effects are inextricably mixed, interfere with the truth of this assumption.

I. *The Gradient through the Solid.*—The first solid to crystallize naturally forms on the outside of the mass and immediately begins to serve as the path through which passes the heat from the liquid though solidifying interior. A temperature gradient must thus exist in it, and its mean temperature will be below that of the portion still liquid. This cooling will have supplied some of the heat given out by the whole mass, and so the amount of material crystallized will not be as great as would be inferred from the time the solidification has continued. As the solid layer becomes thicker the gradient and the amount of material both are increased, so the correction increases approximately as the square of the time—really, somewhat more, since the inner solid layers, having a smaller section normal to the heat flow, have a steeper gradient. The container, also, being outside, will be at a temperature still lower than the solid part of the substance, as already noted.

II. *The Readjustment at the End of Freezing.*—As the last thin thread of liquid crystallizes at the center, a considerable source of heat is suddenly cut off. The solid material must cool, usually, from 50° to 70° in order to give out as much heat as was liberated in the crystallization. Hence after the end of solidification the gradient becomes much less steep in the interior of the charge. The change occurs as quickly as conduction can bring it about. If the thermometer is in the center it will experience a sharp drop, which does not give the true slope for the cooling solid. This sharp drop is usually advantageous, for its occurrence gives a sign that the solidification is practically done. In most cases this indication is sufficiently exact, as well as the easiest method of locating the point S.

III. *General Irregularity.*—There may also be some general irregularity, perhaps shown by a slight fluctuation of the reading, 0.1° or so. This may be due to irregular growth of crystals, or to some lack of symmetry. With reasonably good arrangements such effects are seen only toward the end of melting, before the sharp drop. Both these and the drop do little harm, since the temperature reading at that time does not need to be known very accurately.

IV. *Change in Rate of Heat Loss.*—If the rate of cooling is 2° a minute the solidification will occupy around 25 minutes. To produce this will usually require a thermal head from 10° to 30°. The change per minute in thermal head, and, therefore, in cooling rate, along AO or PZ in Fig. 6 will then be from 20 percent to 7 percent. Even during crystallization the change in rate of heat loss may be from 3 percent to 10 percent if the temperature falls 1° during the process. A quicker determination will usually be desired, and can be had unless it is necessary to allow considerable time for the substance to recover from undercooling. With a quicker rate the proportional change in rate per minute will evidently be the same as before, but the change per degree will be less. It will not be feasible, however, to get a constant rate in this way. Hence, the slope SZ of Fig. 5 cannot be obtained truly unless the thermal head is measured and its variation allowed for. This is not an elaborate undertaking, since only 3 to 6 measurements and simple calculations will be needed. The rate of heat loss, however, is not quite proportional to the thermal head, so for extreme rigor the relation between them must be found by observations on some body of known specific heat. In fact, the determination of heat loss is a calorimetric experiment, and while relatively a rather simple one it inevitably has some complications. Ordinarily, however, as has already been said, only the relative heat losses during freezing need be considered, and with a fairly constant inclosure they may be taken as simply proportional to time. P in Fig. 5 is then about the same as S, and the main uncertainty is in determining S, for which the slope SZ is not definite enough to offer much assistance. The precision should be 10 percent or better. But this gives much more information than a mere observation of the highest freezing point. Plotting is not at all necessary. Indeed, even the quasi-calorimetric determinations can perhaps as well be done without it, though this is somewhat a question of taste.

The Experimental Curve for Mix Crystals

The liquidus line CVD in Fig. 1 has much the same form as the liquidus line CVD in Fig. 3. If the substance is nearly pure in Fig. 1, V will be near C and the first crystals separating will be very nearly pure majority component. Hence for nearly pure substances the relation between the amount of material crystallized and the change of temperature will be much as in Fig. 3. This is doubtless the reason why the method of Fig. 3 has proved so generally applicable. Re-constitution of the original crystals will tend to increase the concentration of majority component, but this process is limited. We have seen that when half the substance is solid this solid forms a compact layer covering the inside of the container. It is certain that nothing further will happen to the composition of the material in this layer. Hence, on the whole, while the observed time-temperature curve for substances represented by Fig. 1 would differ somewhat from that of Fig. 3, it would at the very least require very careful experimental work to discriminate between the two.

If any impurity is present tending to raise the freezing point, as in Fig. 2, the resulting *time*-temperature curve runs as in Fig. 7. If a small amount of impurity causing a curve of this type accompanies some causing the other type (Fig. 4) and if we suppose that the effects of the two, being small, can be superposed, we may have something like a downward sloping straight line at first, with the steeper downward curve finally emerging. I have met with several such curves, but cannot say how common they are, nor have I proved that they were due to the cause here suggested. A theoretical investigation into the possibilities would prove interesting and might be valuable. The large amount of work already done on two-component systems appears to deal, mainly at least, with temperature-concentration, not temperature-time curves.

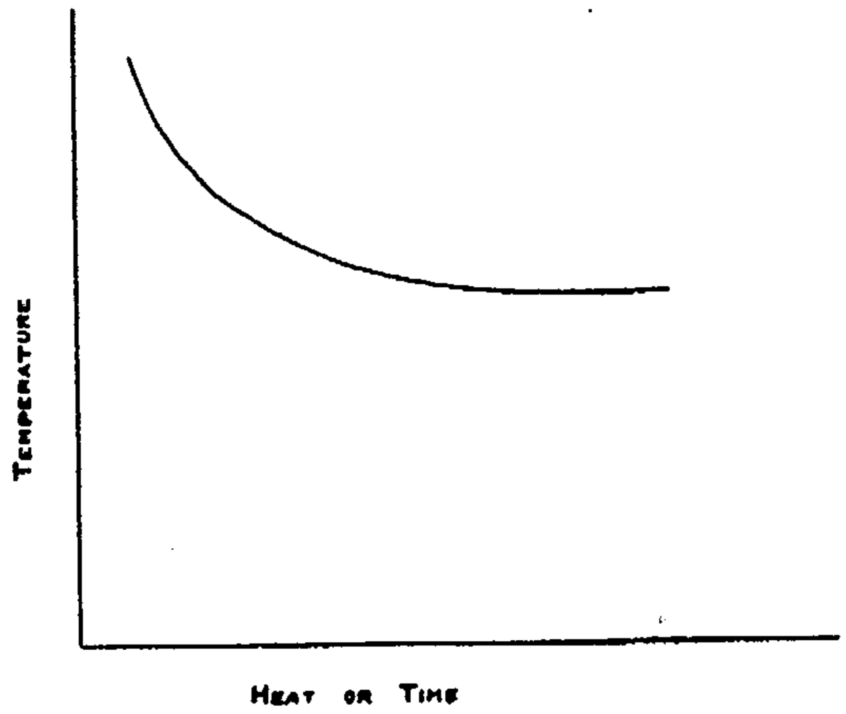

Fig. 7
Approximate crystallization curve with impurity forming a mix crystal of higher freezing point

Experimental Illustrations

In order to check some of the preceding statements, and also to test certain details of method, a freezing point curve was run with naphthalene. This was contained in a glass tube 6.8 mm inner diameter and 8 cm high, wrapped with tinfoil to check radiation and so permit a larger thermal head for the same rate of heat loss. It was used in a tube 3.5 cm wide, which could be transferred from the heating bath, at 100°, to the cooling bath, which happened to become constant at 47°. The width of the inclosing tube also diminished the cooling rate, that is, the ratio of heat loss to thermal head, though it made that rate more variable as a result of convection currents. The smaller tube was handled by being stuck in a cork to which a stiff iron wire was attached. A plug of cotton in the top of the inclosure was the only thing used to shut out the effect of room temperature. A copper cap dipping in the bath fluid would have been more efficient (perhaps in addition to the plug) and is to be recommended where any amount of work is being done.

The temperature was measured by a single couple of No. 36 constantan and No. 40 copper wire (0.13 mm and 0.08 mm), stretched axially in the tube, passing through the center of a cork in the bottom. Beyond the junction the constantan wire was bent around to the outside of the substance, where was another junction, held against the inside of the glass tube by a small roll of writing paper. The difference between the two junctions gave the maximum horizontal difference of temperature in the substance.

The record of a cooling is given in Table I. The readings were taken each minute. They are given in microvolts. One microvolt corresponds to slightly over 0.02°, so a tenth division is 0.002°. No attempt was made to record accurately to the last tenth, because the couple, an old one, proved to be not quite perfect, and showed continual slight fluctuations.

The undercooling is noticeable. The arrows mark the beginning, middle, and end of the solidification. The end is a little uncertain. The fact that in spite of the rapid drop from the 20th to the 22nd readings, the difference temperature does not decrease, shows two things: First, that the outside layer responds almost completely in less than a minute to change in the center; second, that crystallization was still going on

TABLE I

	Central temperature	Change	Center-outside
1	3783		
		163	—
2	3620		
		150	—
3	3470		
		133	—
4	3337		
		61	—
5 →	3276		
		—3	—
	79		
		—3	9
	82		
		0	12
	82		
		2	—
	80		
		1.5	16
10	78.5		
		2	20
	76.5		
		1.2	—
	75.3		
		2.3	32
→	73.0		
		3.0	39
	70.0		
		1.3	47
15	68.7		
		3.5	57.5
	65.2		
		4.7	67
	60.5		
		10.0	77
	50.5		
		11.0	88
	39.5		
		24.0	88
20	3215.5		
		40.0	98
21	3175.5		
		98.5	97
22 →	3077		
		143	53
23	2934		

in the center at about the same rate as before. The change in the difference temperature between readings 22 and 23 shows that the liquid material was now practically gone, and the drop of 143 microvolts was more than one-third due to the approximate establishment of the temperature distribution for a solid mass.

At half solidification the difference temperature was about 36 microvolts, or 0.75°. It is interesting to compare a calculation with this. With a tube of 3.4 mm radius an outer layer containing half the material is approximately 1 mm thick and 19 mm wide. The radial heat conductance of such an annulus per centimeter length is $\frac{1.9}{.1}$ K or that of 19 centimeter cubes of the same material. The conductivity of naphthalene was found by Lees to be 0.00095, the conductance, therefore, 19 × 0.00095, is 0.0181 per second, or 1.09 calories per minute. The volume latent heat of naphthalene is about 35, the volume per linear cm is 0.362; since it crystallized in 17 minutes the heat transmitted per minute is 35 × 0.362/17 = 0.75 cal. The calculated temperature gradient is, therefore, 0.75 ÷ 1.09, or within 9 percent of that observed.

Since the heat required to raise the solid 1° is about 1/70 of the latent heat, this annular layer, whose mean temperature is 0.4° lower than the liquid, has, in cooling below that, given out 0.6 percent of the heat already given out in the solidification. At the 20th reading, with 7/8 of the material solid and about 3 times as strongly cooled, the heat corresponding to this extra cooling is easily shown to be almost 1.5 percent of the whole given out if the gradient is taken as linear, and somewhat more in fact, perhaps near 2 percent. This is about the same as the heat given out by all the material in cooling from the initial temperature to that read by the thermometer at reading 20. That is, this systematic experimental complication is here as great as the specific heat correction of Figs. 5 and 6. A tube of less diameter can easily be used, and then this parasitic heat conduction effect will be diminished.

The lowering of the temperature is a little over 0.2° during the first half of the crystallization, which, in accordance with page 4, indicates that the highest melting point is 0.2° low. Since the material was combustion standard from the Bureau of Standards, for which any such lowering is wholly abnormal, the result called for further investigation. A calibration of the thermoelement by means of a standard mercury thermometer showed that the melting point was really low, apparently by 0.2°, though the calibration was made indefinite to about 0.1° by the emergent stem correction. Other freezing point tests were also made, with greater care as to contamination, and with a new and very good thermoelement. The silk was removed from the wires by caustic soda; the naphthalene touched nothing but these bare wires and glass tube from the supply, that had been cleaned with bichromate mixture and distilled water. The constantan wire ran through a glass capillary 0.5 mm in external diameter, and the copper wire was wound back on the outside of this. The results are given in Table II.

TABLE II

Number	Reading	Change	Reading	Change
			3675	
				201
1	3544		3474	
		164		152
2→	3380		3322←	
		98		30
3	3282		3292	
4	3293		3294.7	
		—		0.7
5	3293.5		94.0	
		0.8		0.7
	92.7		93.3	
		0.7		0.6
	92.0		92.7	
		0.7		0.9
	91.3		91.8	
		0.8		0.8
	90.5		91.0	
		0.8		0.8

Table II—(*Continued*)

10	89.7	1.0	90.2	1.0
	88.7	0.7	89.2	1.2
	88.0	1.1	88.0	0.8
→	86.9	1.3	87.2	1.0
	85.6	1.4	86.2	
15	84.2	1.9		
	82.3	1.5		
	80.8	0.8		
	80.0	2.7		
	77.3	0.3		
20	77.0	6.0		
	71.0	5.4		
	65.6	14.1		
	51.5	14.3		
	27.2	33.7		
25→	3194.5	87.5		
	3107.0			

This couple reads 5 microvolts higher than the other for the same temperature, so the melting point is now actually 5 microvolts, or over 0.1°, higher than the previous one. The fall during half solidification is still around 8 microvolts, however, or nearly 0.2°. Thanks to the excellence of the thermoelement it is now seen to be more nearly linear than accords with Fig. 4. From readings 17 to 25 the fall is progressively steeper than according to Fig. 4. This discrepancy between the first and last portions of the curve seems to offer an interesting problem for investigation. The slope of the first part is not normal in Bureau of Standards naphthalene, and probably indicates moisture absorbed from the air.

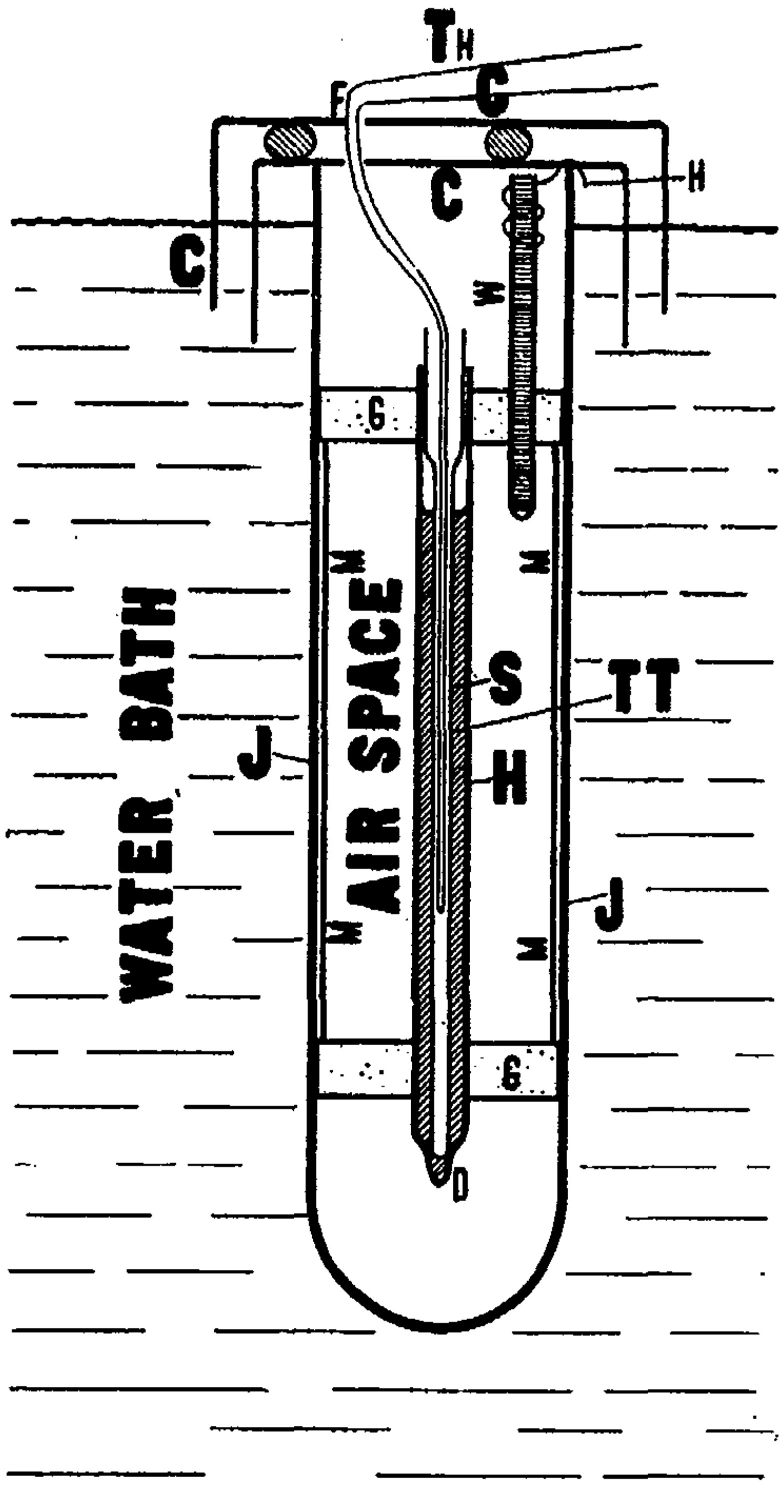

Fig. 8

Freezing point apparatus. 1/3 size. Th, thermoelement; CC copper caps or covers; F, openings in the same, which may be at the end of slots running up from the lower margin; J, jacket; M, sheet metal reflecting surface; H, container, drawn down at D to center the thermoelement tube TT; S, substance tested; G, cork guides; W, wooden or glass pin, and H, wire hook, for support

The two arrangements just described, with wires embedded in the substance, do not facilitate cleaning. Inclosure of both in the smallest possible capillary seems one of the best procedures, but great care must be taken to see that the depth of immersion is enough to prevent the temperature reading from being affected by conduction along the wires. A change in the depth of immersion furnishes a test. A good thermal connection between wires and capillary is by all means to be sought. Heavy oil, naphthalene, or any electric insulator may be used which does not change its state within the temperature range where the temperature is to be read.

Ordinarily, below the capillary the crystallization will go to the center, while above the junction it will stop at the surface of the capillary. It seems advisable to continue the capillary downward, perhaps to the bottom. This not only gives more symmetrical conditions, but it avoids altogether the crystallization at the center, which tends to be a disturbing influence.

Fig. 8 shows an arrangement recommended for freezing curve work. The greatest emphasis is to be placed on the necessity for saving the thermoelement wires from mechanical strains of all sorts.

Where a number of determinations are made on the same substance each one can be materially shortened if the total time of freezing is known and kept constant. There is then no need of running beyond the midway point. This necessitates having bath temperature and the position of the specimen tube the same each time, and keeping metal reflecting surfaces always clean.

Summary

Freezing points where the thermometer is immersed in the substance are more reliable and precise than those by the capillary tube method. If, in addition, the form of the freezing curve is observed, there is obtained an indication of the amount of impurity which is independent of all previous knowledge or uncertainty as to the melting point of the pure substance, and even of the absolute accuracy of the observer's thermometer. If the determinations are a control of a purification process there is also a saving of time and the avoidance of certain serious chances of error.

Smallness of dimensions diminishes local temperature differences, and is very often a superior substitute for stirring of the tested substance. It also economizes both time and material. A small thermocouple or thermel of several couples lends itself very well to use in small test samples.

The complications, usually almost negligible, arising from specific heat, uneven temperature, and other causes are considered, and suitable experimental arrangements are suggested.

Geophysical Laboratory
Carnegie Institution of Washington
Washington, D. C.

NEW BOOKS

The Organization of Industrial Scientific Research. *By C. E. Kenneth Mees. 22 × 14 cm.; pp. x + 175. New York: McGraw-Hill Book Co., 1920.*— The book is intended as a study of the best methods of organizing research work for industrial purposes and of the conditions under which such work should be conducted. The subject has been treated under the following heads: introduction; types of research laboratories; co-operative laboratories; the position of the research laboratory in an industrial organization; the internal organization of industrial laboratories; the staff of a research laboratory; the building and equipment of the laboratory; the direction of the work; the design of a research laboratory for a specific industry; bibliography.

Of special interest are the author's remarks on the position of the research laboratory, p. 58. "In order to understand the proper relation of the research laboratory to the organization the general nature of any organization must be considered briefly. As a general rule, the functions of an organization can be divided into two distinct classes, which, to borrow a military term, may be termed 'line' and 'staff' functions. Staff functions are concerned with planning, line functions with operation.

"In an army the line organization is paralleled throughout by staff organization. The Commanding Officer, who is the head of the line, has at his General Headquarters the Headquarters Staff, each Army Commander has his own Army Staff, each Divisional Commander a divisional staff, each brigade a brigade staff, and the staff functions of each battalion are carried out by officers to whom they are assigned. In operation, the line officers are supreme; it is their duty to be responsible for the execution of the work; in planning, the work is done by the staff, and once approved, the plan is put into operation by the line.

"Now, in industry there has not often been any clear separation of these two functions. The founders of industrial enterprises have usually taken staff functions on themselves, creating a line organization to carry them out. And even when businesses have grown beyond the point at which any one man can be responsible for all the planning necessary, a definite staff organization has very rarely been created; men have simply been employed with definite functions of a staff nature, but without any interlinking organization.

"The oldest definite staff function in industry is that of accounting. In its nature the accounting department is a purely staff department, touching the sales department in its bookkeeping accounting, and the production department in its cost accounting. It often creates a branching organization permeating the whole business, each works having its own accounting department and even each department having one or two clerks who attend to its accounts and who are responsible to the accounting department of the works.

"In an industry which is not primarily concerned with engineering, a chemical industry for instance, the engineering and maintenance department occupies a similar position. It is a staff department responsible for the supply of power, for the construction and maintenance of buildings, and for the production, supply and maintenance of the machinery with which the producing departments carry on their work. The efficiency department is another staff department, its function being essentially planning. In an engineering works the efficiency department should be a part of the engineering department as a whole, concerned with the design of product and the planning of operation. The employment and welfare department is another staff organization which may undertake also the educational work, which is now becoming so important in all industries.

"The production and distribution of technical knowledge, which is the function of a research laboratory in an industry, is a staff function, and the research work must therefore be organized along lines parallel to those of the accounting department. Like the accounting department, the research laboratory will often develop two sections, one dealing with manufacturing questions and having its closest relations with the production department, and the other concerned with the use of the products, taking the form of service to the customer and having its relations with the advertising and selling departments. It is not unusual for new products developed by the aid of the research laboratory to require a certain amount of assistance from the scientific staff for their introduction to the public.

"The position of the research laboratory in an industrial organization is perhaps best determined by the criterion that the research department should be responsible to the officer of the company who is in charge of the development of new products. If the introduction of new products is in the hands of the works organization, then the research department should be responsible to the works manager; if there is a definite development department, or, if new products are introduced through the agency of some definite executive, then it is to that executive that the research department should be responsible. The research laboratory, in fact, should be associated primarily with development."

The discussion of the direction of the work, p. 122, is also of interest. "Various methods for the direction of the work of a laboratory are in operation. In some cases each investigator is allowed to go his own way, discussing his work as he may wish with those around him, but not formally being required to take the matter up with any one. In university laboratories, and in many industrial research laboratories, all the scientific work is supposed to be directed by the professor in charge or by the director, but in an industrial laboratory of any size this is out of the question, since it is impossible for the director to understand sufficiently the wide field of science covered by his laboratory. If it is attempted, the system simply resolves itself into each senior man directing the work of his own division and possibly competing for men and apparatus with other workers in the laboratory insofar as he can influence the authorities to grant them to him.

"It is obviously better for the scientific work of a laboratory to be directed by a conference or series of conferences of all the men having knowledge applicable to the subject, and this will have the further advantage that, while it will relieve the director of the details of the direction of the scientific work, it will keep him constantly informed as to all the work going on in the laboratory.

"For the past six years the work at the research laboratory of the Eastman Kodak Company has been directed by such a conference system, and it has proved an unqualified success. To each day of the week there is assigned some groups of subjects. On Tuesday, for instance, all questions relating to chemical products may be discussed; on Wednesday, those which relate to the chemical properties of photographic materials; on Thursday, general photographic processes; on Friday, color photography, and so forth. Each group of subjects is discussed at a conference held at the beginning of the morning, and there is present at each conference every scientific worker of the laboratory, whatever his rank, who is directly engaged on the work under consideration, and also representatives from other departments of the laboratory in case their assistance and advice should be required.

"The number of those attending a conference should preferably be more than four and less than ten. The director presides at all conferences, and the agenda are drawn from the minutes of the last conference. These minutes are written each week by the director's secretary, who takes shorthand notes at each meeting.

"It will be realized that this conference system makes it certain that the work of everybody in the laboratory will be considered once a week, that the difficulties will be explained to, or discussed by, those best fitted to assist in removing them, and that, at the same time, there is a valuable check in the conference minutes against matters which have once been discussed being dropped and forgotten.

"Should any matters come up at a conference which seem to require the assistance of those who are not members of it, they are called in for consultation, and those conferences which are of interest to members of the staff outside the laboratory are attended by representatives of the departments interested, thus enabling the laboratory to co-ordinate its work more closely with the practical requirements of the company."

This is an excellent book by a thoroughly competent man.

Wilder D. Bancroft

The Condensed Chemical Dictionary. *Edited by F. M. Turner, Jr. 23 × 15 cm; pp. 525. New York: The Chemical Catalog Company, 1919. Price: $5.00.*—In the preface the editors say: "The increased importance of the chemical industries has brought into contact with these industries a large number of people not educated along chemical lines. Exporters and importers, brokers and jobbers, financial houses, lawyers, librarians, purchasing agents, insurance companies, and many other classes of firms and individuals have frequent need for detailed information regarding chemicals and chemical products. The large and increasing volume of such inquiries received by the Information Bureau of The Chemical Catalog Company, as well as by the public and technical libraries, has made obvious the demand existing for some one book that would supply the outstanding facts regarding the various chemicals and chemical materials ordinarily met with in commerce.

"A thorough search of chemical literature revealed no publication that would meet exactly the requirements of these people. Undoubtedly a collection of literature could be made that would give all the facts commonly needed; but few business men would be likely to go to the expense of accumulating such a library. The excellent facilities of the public technical libraries avail little, as business men have not the time to visit them, and, moreover, good technical libraries are not convenient to all trade and manufacturing centers. Finally, the books in which the information could be obtained would contain so much more commercially irrelevant material that men unaccustomed to the use of large scientific reference works would soon be in difficulties.

"One of the most frequent classes of inquiries concerned the uses of things. Importers and brokers would frequently find chemicals, oils, ores, etc., on their hands, the market for which was unfamiliar. In order to find whom to approach, it was necessary first to know the uses of the substances. In the Condensed Chemical Dictionary an attempt has been made to collect a mass of information on this subject scattered through hundreds of text-books, periodicals, government bulletins, etc., as well as to set down a great deal that is not known to be anywhere in print."

The statements under bromine are typical. Color and properties: very dark reddish-brown liquid; irritating fumes. Constants: specific gravity, 3.1883; melting point, 7.3° C.; boiling point, 58.7° C. Soluble in water, alcohol, ether, and potassium bromide. Derivation by direct electrolysis from waste brine of the salt industry. Method of purification: distillation. Grades: technical. Containers: carboys; earthenware bottles; glass bottles. Uses: organic synthesis, dyes; bromides; military poison gas. Fire hazard: none. Railroad shipping regulations: white label.

This book will be of great value to the chemist as well as to the layman. From the sales it is apparent that both classes of men appreciate the book.

Wilder D. Bancroft

Gas Chemists Handbook. *Edited by A. K. Kunsberger. 23 × 16 cm; pp. 354. New York City: The American Gas Institute. Price: $3.50.*—This volume contains the best methods of analysis so far as they can be determined by the committee on chemical tests of the American Gas Institute, though this does not mean that all the methods have been approved officially as final by the American Gas Institute. The subject is arranged under five heads: raw materials; products of gas manufacture; impurities in gas; tar products; miscellaneous. There are also seventeen pages of tables of conversion factors and of physical and chemical data. A handbook of this sort is very valuable and one must congratulate the American Gas Institute on getting out a revised version so promptly.

The reviewer was interested in the specification, p. 181, that the thermometer shall be made of resistance glass of a quality equivalent to suitable grades of Jena or Corning makes. The bottle thief and the pipe, p. 133, were new acquaintances. In the determination of unnitrifiable hydrocarbons, p. 190, one would have liked to know why the use of a too concentrated caustic soda solution causes the formation of an emulsion which is very awkward to manage.

Wilder D. Bancroft

THERMAL FILTERS

BY WILDER D. BANCROFT

If a flame be placed beneath an intense beam of light passing through a dust-laden atmosphere, there may be seen rising from the flame wreaths of darkness which resembles intensely black smoke but which are really air free from dust.[1] Under these conditions the dust is presumably burned; but the stream of darkness can be obtained without burning the dust particles. Tyndall placed a hot metal ball under the beam of light and permitted it to remain until its temperature had fallen below that of boiling water. It was then found that the dark current was still produced though it was not so marked. Tyndall believed that heating the air rarefied it without lightening the floating matter and that consequently a convection current of pure air was set up. This explanation was overthrown by the experiment of Lord Rayleigh[2] in which a cold glass rod was introduced into smoky air, whereupon a dark plane was formed extending downwards from the rod. As Lord Rayleigh says: "This result not merely shows that the dark plane is not due to evaporation, but also excludes any explanation depending upon any augmentation in the difference of densities of fluid and foreign matter." Lodge[3] concludes that "differences of temperature have nothing to do with the real nature of the phenomenon; we find that solid bodies have sharply defined dust-free coats or films of uniform thickness always surrounding them, and that these coats can be continually taken off then and as continually renewed by any current of air." The matter was studied in detail by Aitken,[4] who decided that the phenomenon was primarily a temperature one, the dust particles moving along the temperature gradient from the hot portion to the cold one. Of course, there are disturbing effects due to gravitation and

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[1] Tyndall: Proc. Roy. Inst., 6, 3 (1870).

[2] Proc. Roy. Soc., 34, 414 (1882); Nature, 28, 139 (1883).

[3] Nature, 31, 265 (1884).

[4] Trans. Roy. Soc. Edin., 32, 239 (1884).

there may be disturbing electrostatic effects; but the experiments can be arranged so that these effects are negligible.

Aitken draws some rather interesting conclusions from his work. "When we see a beam of sunlight shining into a darkened room through a small opening, and revealing, by illuminating, the suspended dust, making the beam look like a solid body, we have great difficulty in realizing that our atmosphere can be so full of dust as this experiment shows it to be, as it escapes our observation under ordinary conditions of lighting, and it gives us a feeling of discomfort to realize that we are breathing that dust-laden air. This uneasiness was by no means decreased when my experiments on cloudy condensation revealed the fact that, in addition to that mass of visible dust, there are enormous multitudes of particles so small that even the concentrated light of the sun does not reveal them. These minute particles are so numerous that hundreds of them are crowded into every cubic centimeter of air. On realizing these facts our feelings are those of wonder that our lungs can keep so clean as they do, while such vast quantities of impurities are constantly ebbing and flowing through them. At that time I was not aware that there is an influence ever at work, tending to protect the lungs by preventing, to a certain extent, the particles of dust coming into contact with their surfaces,—that nature had provided a subtle form of mechanism possessing some of the advantages of a filter without any of its disadvantages. The experiments here described show that a hot surface repels the dust particles in the air. The heat of our bodies will, therefore, exert a protective influence on the lungs, and tend to keep them free from dust.

"Our lungs, however, are not only hot, they are also wet. What influence will the constant evaporation which takes place at the surface of the tubes and passages have on the dust? To answer this question, I fitted the flat test surface in the dust-box, and through an opening in the top introduced a brush dipped in water, with which one-half of the surface was kept wet, the other half being dry, to compare the effects under the two conditions. When the surface was heated a few degrees, to even less than the temperature of our bodies, the result was most decided, the dust being driven more than twice as far from the plate in front of the wet part as it was from the dry. The evaporation, therefore, of the water from the surface of the bronchial tubes tends strongly to ward off the dust, and keep it from coming into contact with their surfaces. We must not, however, imagine that the heat, or the heat and the evaporation, are sufficient entirely to prevent the dust coming into contact with the surfaces of our bronchial tubes and passages, because dust really does come into contact with them, but it does not do so nearly to the extent to which we have been in the habit of supposing.

"The necessary conditions for this repulsive effect to be active are, that the air is acquiring heat and moisture. If the air has the same temperature as our bodies, and is saturated with vapor, this force no longer exists, and gravitation and other forces are free to act.

"Although the repulsions due to heat and evaporation are not powerful enough to form a perfect protection to the lung surface against the contamination of dust, yet it is very evident that their protective influence will have a most important effect on the condition of our lungs, and one towards which I wish to direct the attention of those who make this organ a special study. There seems to be but little doubt that we have here an explanation of some of the effects of different climates. For instance, what a difference there must be in the amount of dust deposited on the lungs from air breathed at, say, St. Moritz or Davos Platz, and at such places as Madeira or other similar health resorts? These remarks are altogether apart from the question of the amount of dust in the air at the different places, and refer only to the action of the lungs on the dust which may be present.[1] In the

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[1] The amount of dust breathed by invalids at the two places will not be greatly different, as most of their time is spent in the house, and the air in the rooms at the two places will be nearly equally dusty. The higher temperature inside will slightly reduce the thermal effect, but will not diminish the rate of evaporation.

Alpine resorts the air is cold and dry, and the tidal air, which flows backwards and forwards through the bronchial tubes, is in the very best condition for preventing the dust coming into contact with their surfaces, as the difference in temperature between the air and the body is great, and the air is also capable of causing a rapid evaporation. Whereas, at such places as Madeira, where the air is hot and moist, the repelling forces are both at a minimum. The effects of these different conditions on the lungs seem well worth study.

"In illustration of the protective influence of heat and moisture, many experiments may be made, but the following is perhaps the easiest. Take an ordinary paraffin lamp, raise the flame till a very dense cloud of smoke rises from it. Over the lamp place a very tall metal chimney, to produce a quick current of air and also to cool it. Have ready two porous cylindrical jars (porous jars are used because they keep up a supply of water for evaporation), one jar filled with water slightly heated, and the other with cold water. Cover both jars with wet white paper. Now introduce the hot one into the top of the chimney, and leave the black wreaths of smoke to stream over it for say half a minute, then take it out and put in its place the cold one, and leave it for the same length of time. The result will be, the hot one will be quite clean, not a speck of soot on it, while the cold one is covered with soot. It is not, however, so black as a cold, dry surface would be, as the slight evaporation from its surface tends to protect it.

"We must not, however, suppose that the lung surfaces are so well protected as the paper in this experiment. In the lungs the currents are quicker, they do not flow over such uniform surfaces, and further, they pass round curves, so that in the lungs dust tends to deposit where the currents flow quickly where they strike on the concave side of curved passages and on projecting edges. Further, all dust which penetrates beyond the tidal air and gets into the residual air will ultimately fall on the surfaces of the tubes and air-cells. This tendency of the dust in the residual air to settle is increased by the load of water deposited on it by the moist air. The amount to which our lungs are protected by heat and evaporation can scarcely be solved in a physical laboratory, and will be best determined by anatomical examinations of lungs which have lived under different conditions of temperature and moisture."

"Having observed that the dust particles tended to move away from hot bodies and to attach themselves to cold ones, I made some experiments on the subject to study the movements of dust particles when placed between hot and cold surfaces. Most interesting results were obtained by placing near the hot platinum wires, already referred to, a piece of glass or a plate of metal, and getting the dust deposited upon it. One arrangement of the experiment is to place the glass with its plane vertical and transversely over the wires, at such a height that its lower edge almost touches the wires, and fill the box with dust by blowing up some calcined magnesia or other fine powder. After all the currents had settled, and while the air is still full of dust, the electric current is turned on and the wire heated. A well-marked dark plane at once rises over the wire, and in its upward passage it is cut transversely by the glass plate. After the plate has been left for some time with the air current streaming over its surface, it is found to have a very beautiful impression of the dark plane imprinted upon it. The warm air, in streaming upwards over the surface of the glass, deposited its dust on it, and the fact of there being no dust in the dark plane is recorded by a well-defined line of clear glass, the deposit of dust on each side of the clean line being thickest just along the edge, and thinning away on each side. These impressions of the dark plane may be made permanent by causing the dust to be deposited on a plate newly coated with black varnish, and used while the varnish is still soft.

"It is not necessary to put anything on the surface of the glass to cause the dust to adhere, as it attaches itself to a clean surface of the glass with considerable firmness, but some adhesive substance on the plate enables the impression to stand rougher treatment. Impressions of the dark plane have also been made with charcoal dust deposited on opal glass. These black impressions are, of course, 'negatives' of the magnesia ones, the plane in the former case being white, surrounded by black dust. The charcoal dust was securely fixed by first coating the glass with a thin solution of gum, which was dried before the dust was deposited on it, and the dust fixed by breathing on the surface.

"If in place of putting a plate vertically over the wires, we place two plates vertically—one on each side of the wire—we then get the dust deposited on the plates, thickest opposite to the wires and thinner higher up. Arrangements were made for studying the action of surfaces placed on both sides of the wires. Fixing the plates parallel to each other and at a distance of 2 or 3 mm apart, with the platinum wire between, I carefully watched the motions of the particles carried up in the air current. As the particles approached the wires they gradually changed the direction of their motion, and instead of coming straight up they curved towards the sides, some of the particles striking and adhering to the side plates at a point below the wire. Some rose higher and stuck opposite to it, others went higher still, while others passed on to the top and escaped.

"I had for some time been trying to arrange an experiment in which I should be able to watch the movements of the individual particles of dust, so as to see them moving away from the hot surface. My intention was to examine the movements of the particles with a microscope of low power, or with a powerful magnifying glass. My great difficulty, however, was to get the movements due to the convection currents sufficiently slow to enable me to follow the moving particles when much magnified. After making the experiment last described, I saw it was possible to arrange for this much-desired observation. The use of the large particles of magnesia enabled me to dispense with the microscope, and use only a magnifying glass of moderate power; and by bringing the plates on each side of the wire close together, the velocity of the upward convection current could be greatly reduced by the friction of these surfaces, and by their cooling effect on the gases. The two side plates of glass were accordingly brought closer together, to a distance of about 1 millimeter.... The ascending current was now very slow, and no difficulty was experienced in following the movements of the individual particles, so I had at last the satisfaction of seeing the particles being repelled by the hot wire.

"When the wire, heated to a red heat in air filled with magnesia dust, was examined by means of a magnifying glass, the spectacle which presented itself was most curious and interesting. At a distance below the wires, the particles could be seen coming straight up between the glass plates, but as they approached the wires they seemed to get uneasy, and as if wishing to avoid the heat, some of them attached themselves quickly to the glass, others went further up, but soon curved towards the sides and adhered to them; while others boldly advanced straight up, almost to the wires, when their motion was suddenly arrested and they were driven downwards and sideways, and attached themselves to the glass. If the wires were hot enough, not a single particle got past them, and the glass plates had each a patch of magnesian powder adhering to its surface below the level of the wires....

"These experiments naturally suggested the possibility of constructing an air filter on thermic principles. They showed that the visible particles of dust could be thrown out of the air, as the particles tended to move from the hot parts, and to attach themselves to cold surfaces. But the question which naturally suggested itself was, Are the very small invisible particles also arrested? If the thermic filter turned out to be a success, it appeared to me it would also be the best way to get an answer to this question. In order to filter air on thermic principles, all that appeared necessary was to pass the air through a space or channel, the two sides of which were kept at different temperatures. In this way I hoped the dust would be driven from the hot side and attach itself to the cold one. Practically to carry out this idea, the simplest method that suggested itself was to pass the air through the space between two concentric tubes, the one tube being kept hot, and the other cold. In the preliminary instruments which have been made, the distance between the tubes forming the space through which the air passes, is in one instrument less than 1 mm, but in other instruments this space is nearly as much as 3 mm. The length of the passage in the different instruments is about 35 cm. One of these instruments has the outer tube jacketed by means of a larger pipe for the purpose of heating it with steam. The other instruments were heated simply by means of a gas flame.... The air, after passing through the space between the two tubes, was conveyed by means of a tube to a glass flask, in which there was a little water. The flask in turn was connected by means of another tube to an air-pump, in order to test the condition of the air after passing through the instrument. If cloudy condensation is produced when the pressure is reduced in the flask, we know that the air is not filtered; and, on the other hand, if the air remains perfectly clear on exhausting, we know that no dust, not even the visible particles, have passed into it.

"The apparatus was fitted up for trial, all the connections being made and tested. Using the instrument heated with flame, the first effect of the heat, as expected, was a great increase in the fogging. The temperature was raised as high as it safely could be, to cleanse the instrument thoroughly; after which, as we know, it will cease to give off nuclei at a lower temperature. When the tube was thoroughly cleansed by means of heat, and all the impurities swept out of it by a current of air, the temperature was lowered slightly, and the air allowed to pass slowly through the tube on its way to the test flask. After this, the fogging in the flask gradually diminished, and after passing through the rainy stage, it ceased entirely, proving that the filter was doing its work thoroughly, not a single particle—not even one of the very minute and invisible ones—escaping it. On equalizing the temperature, either making both tubes hot or both cold, the filtering action of course ceased.

"It does seem somewhat strange that air should be freed from all its dust in passing through a channel large enough for a fly to pass, if it has sufficient intelligence to keep always on the cold side. All who have experimented on this subject know that dust can get through any opening, however small. On testing this filter for the first time, I failed to get a satisfactory result. I however felt convinced that it ought to work, and the failure was attributed to some imperfection in the tubing or joints. Arrangements were, therefore, made for testing the tightness of the whole apparatus. The one end of the filter being connected, as described, to the glass flask in which the air was tested, I now connected a cotton-wool filter to the other end of the thermic filter, and proceeded to test if all was tight, by drawing in air from the cotton-wool filter through the apparatus, while it was cold. At first, I could not succeed in getting air free from dust; fogging always took place on reducing the pressure in the flask, showing that dusty air was leaking in somewhere and mixing with the filtered air. After much time spent in remaking all the joints, it was discovered that the air-pump valve was not quite tight; by allowing the leakage to bubble through the water in the flask, it was found to be very slight, only about 2 or 3 cc per minute. After this was put right, fogging still appeared, showing that there was still leakage. This time it was traced to the stop-cock between the filter and the test flask. This leakage was smaller than the other, yet it let in dust. After all leakages had been stopped, the cotton-wool filter was removed, and the thermic filter being heated, was now found to do its work satsfactorily, though more slowly than a cotton-wool filter. The ease with which dust passes through small openings is surprising; indeed, I have found that any opening which admits air, also allows these less than microscopic particles to pass, and yet the air in its passage through the wide channel of this filter had every particle of dust taken out of it by the thermal conditions to which it was subjected.

"If we cause the filter to purify air into which we have intentionally put a good deal of dust, such as dust of calcined magnesia, we find all the dust collected on the surface of the cold tube, near the end where the air entered, while the hot tube is quite clean. If we send the smoke of a cigar through the filter, nothing but perfectly transparent gases come out at the other end. The effect of coating the cold surface with glycerine has been tried, as it seemed possible that the dust deposited on the clean surface might be carried on by the air current. The dust, however, seems to be firmly held on a cold clean surface, and no decided improvement was got by the addition of the glycerine. No accurate experiments have been made to determine the best size of the filtering channel. The filters with very narrow passages and those with much wider ones all work well, but no quantitative experiments have been made as to their relative values."

"This tendency which the dust in our atmosphere has to move away from hot bodies, and attach itself to cold ones, will, I have no doubt, help to explain many phenomena which are not at present well understood. No doubt, many things will suggest themselves to different minds as receiving their explanation in this somewhat curious liking of dust for lodging in cold places. Among other things, it explains the reason why stove and hot-air heated rooms are always so much dirtier than those warmed by open fires. In a stove-heated room the air is warmer than the walls and than the objects in the room, the dust therefore tends to leave the air, and to deposit itself on every object colder than itself in the room; whereas, in a room warmed with an open fire, the heating being principally done by radiation, the walls and furniture are hotter than the air, they therefore tend to throw off the dust, and even when it does fall on them, it does not adhere with that firmness with which it does to a cold surface, and any breath of air removes it. Diffusion also, no doubt, plays some part in determining whether dust shall or shall not adhere to the walls and ceilings of rooms.

"Again, a knowledge of this tendency of dust to settle on cold surfaces is necessary to enable us fully to explain why so much soot adheres to the inside of chimneys. If the smoke were cold, so much soot would not settle in the chimneys, nor would it adhere so firmly.

"A simple experiment to illustrate this tendency of dust to leave warm and to settle on cold surfaces, is made in the following way: Take two narrow strips of glass mirror, any substance will do, but the mirror surface shows the result best. Arrange so as to hold these strips of glass face to face, and with their surfaces at a distance of a few millimeters, but before putting them into their places, heat them to a temperature of say 100° C. Have ready a tall glass vessel, large enough for the glass strips to enter freely. Now fill this vessel with some dust, by burning sodium or magnesium, or by shaking up some calcined magnesia or other powder. By the time the air in the vessel is settled and cooled, but before the dust settles, have ready the glass strips, one of them hot as directed, and placed in front of the other, face to face, with an air space between them. Now put the mirrors into the vessel among the dust. After a minute or so examine them. The following will be the result. The hot one will be quite clean, while the cold one will be white with dust. That the dust has no tendency to settle on the cold one, may be proved by putting at the same time in the vessel another cold strip some distance from the hot one, when it will be seen that this one is almost entirely free from dust, depending upon whether it was a little hotter or colder than the dusty air.

"When one looks at the enormous amount of dust deposited on the cold mirror in this experiment, we cannot help associating the result in some way with the condensation of vapors, and it takes some time before we can arrange our ideas and realize that the thick white deposit was truly thrown out of suspension and settled on the mirror in the solid state, and was not in the state of vapor before coming into contact with the cold glass.

"A somewhat curious experiment may be made with light calcined magnesia powder, which shows the action of this force in a marked way. The magnesia is heated to a good red heat in an iron vessel. If we now take a metal rod 5 or 10 mm diameter and heat it as hot as the powder, we may then dip it into the powder and stir it as much as we please, but on taking the rod out, it will be found quite clean. But if the rod is cold,[1] it comes out of the powder with a club-shaped mass of magnesia adhering to it, so thick that the magnesia-coated end is twice as thick as the rod itself. If the rod is kept in the hot powder for a short time, and then taken out, with its coating of powder adhering to it, whenever the powder gets outside the hot vessel, and exposed to the cold, it falls away, as the inside of the powder is now hotter than the outside.

"Most of us have noticed when heating powders, particularly if they are light, that while they are heating they take on a peculiar semi-fluid appearance if stirred, or if the vessel is tilted back and forwards. This I have always supposed was due to the escape of occluded gases from the powder, keeping it in a state of semi-suspension. Now, however, I think this peculiar effect is a result of the repulsion due to heating. My reason for supposing this is, that if after the powder is heated it is cooled quickly, and again heated before there is time for it to absorb gases, the same semi-fluid appearance is again produced while heating. Further, if the powder, instead of being heated in a closed vessel, is placed in a cup, so that the under side of the powder is kept hot, while the top is cooled by radiation, so long as these conditions are kept up the powder retains its fluid-like properties, moving about on the slightest tilting of the cup, and conducting itself in a way very suggestive of the spheroidal condition,[2] but without any generation of vapor to give rise to the irregular movements seen in liquids. It seems possible that something of the spheroidal condition may receive its explanation in this repulsion between hot and cold surfaces. This repulsion may be illustrated by placing a hot and a cold

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[1] See also Tammann: Drude's Ann., 18, 856 (1905).

[2] See also Stoney: Phil. Mag., [5] 4, 443 (1877).

surface together. A piece of cold glass, for instance, slides about in a remarkably easy way on a hot surface of glass.

"Many practical applications of this attraction and repulsion will no doubt be found. It might be easily applied to the condensation of those fumes from chemical works which at present are allowed to pollute the air. But perhaps the application of most general interest would be towards the prevention of smoke, or rather the prevention of the escape of smoke into the atmosphere. Whatever interest, however, it may have in this way, it is clear it can never meet with general adoption, save under compulsion, as it will effect no saving in fuel, such as would result from more perfect forms of combustion.

"I have, however, made some experiments in this direction, and find that by placing a tall metal chimney over a very smoky paraffin lamp, surrounding this chimney with another tube slightly larger, and causing the products of combustion to rise up the center tube, and descend through the annular space between the two tubes, the soot is all taken out, and nothing but a white vapor is seen escaping. On examining the tubes after they have been in use some time, the inside surface of the inner one is found to be slightly coated with soot, while its outer surface is perfectly clean and bright, not a speck of dust on it, and the inside of the outer tube, which is only a short distance from it, is thickly coated with soot. This arrangement, however, is too complicated, save for special purposes.

"It has been already stated that the reason why so much soot collects in chimneys is that the gases are hotter than the sides of the chimney. In cases where the gases are allowed to escape at a high temperature advantage might be taken of this tendency. If we simply cooled the smoke in the presence of plenty of depositing surface, much of its soot would be trapped out, and the escaping smoke made less dense. The amount that might be trapped in this way will depend on the extent to which the gases could be cooled.

"For works with large chimneys this plan evidently could not be adopted, and in their case the purification would require to be down at the bottom of the chimney. The evident objection to this is, that as the gases are cooled in the depositor, the draught in the chimney will be destroyed. This, however, can be avoided by the use of "regenerators." The impure air would be led to a cold regenerator, where it would be cooled and its impurities deposited; and when purified it would be led through another chamber, where it would be heated before being sent up the chimney. This arrangement would not require heat to be spent in working it, as the process would be reversed, and by simply reversing the direction of currents from time to time the heat stored up in cooling would be used for heating the purified gases before being sent up the chimney. This purifying process by heating and cooling would require to be done a number of times, and the air sent through a succession of regenerators before it could be made perfectly pure."

Aitken accounts for the dust particles moving from the hot zone to the cold one by assuming that "they are driven away, because the molecules moving from the hot surface have a greater kinetic energy than those moving towards it, and the particles are bombarded on the one side by a greater number of hot molecules than on the other. We have the same effect intensified when the hot surface is wet. When this is the case the vapor molecules diffusing outwards carry with them the dust particles to a much greater distance than the heat alone, as there is no inward current of vapor molecules to contend with the outward one, and tending to drive the dust particles inward; the result is, we get a dark plane at least twice as thick with heat and vapor as with heat alone. Of the two, the vapor seems to be the more powerful, as very little heat with moisture gives a thicker dark plane than double the heat would do. If we carefully fix the experimental test surface in a vertical position and simply wet it, the effect is to cool it by evaporation, and a downward current is produced; but at the same time, a clear space is formed showing that in this case the outward effect of the vapor is greater than the inward effect of the cold."

There is another way of accounting for the phenomenon which seems to me to have advantages. Around each particle of dust there is a film of adsorbed air. If the particle is heated on one side, this film will be diminished, but air will flow round the particle from the cooler to the warmer side tending to restore the equilibrium. This will cause a movement of the particle towards the cooler portions of the space. This means that the dust particle is sucked toward the cooler zone while Aitken considers that it is driven from the hotter one. Actually, both things are taking place simultaneously.

The fact that tobacco smoke could be stopped completely by passing it through a hot-cold tube was of distinct interest, but Aitken gave no data as to the necessary temperature gradient. In order to get some information on this point, some experiments were made by Messrs. Argo and Anderson in the Catalytic Laboratory of the Research Division of the Chemical Warfare Service. Experiments were made with concentric iron tubes, the outer one being cooled while the inner one was heated to about 85° by means of steam. The rates of flow in cc per minute were determined at which no tobacco smoke came thorugh a tube thirty inches long.

Temp. Diff.	cc/min.	Temp. Diff.	cc/min.
80°	550	35°	240
64°	450	20°	150
50°	360		

This is practically a linear relation. For zero temperature difference the permissible rate of flow of smoke drops to zero. With tubes 12 inches long and therefore having less surface, the permissible rates of flow become

Temp. Diff.	cc/min.	Temp. Diff.	cc/min.
80°	195	30°	105
65°	160	21°	70 (Estimated)
55°	150	15°	35 (Estimated)
45°	120		

The precipitation is not sufficiently rapid to make any arrangement of alternating hot and cold plates feasible for stopping smokes under war conditions. The theory of the process seems to be that the smoke particles are heated by the hot surface and then move to the cold one. This was confirmed by placing a heated wire in front of a paper filter and allowing the smoke to pass by the wire into the filter. Since it would be necessary to heat the smoke particles considerably above the temperature of the filter, experiments showed that the power consumption would be too great to make any such process successful under field conditions.

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NOTES ON THE COLORING AND THERMOLUMINESCENCE OF GLASS PRODUCED BY RADIUM RADIATION[1]

BY S. C. LIND

The coloring of glass and of transparent minerals by radiation has been a frequent subject of observation and investigation. Several different explanations of the phenomena have been proposed, none of which appears to be entirely satisfactory. The object of the present notes is not to attempt to decide between the different theories nor to propose a new one, but rather to assist in keeping the records straight by pointing out some of the errors of observation or generalization that are becoming rather commonly accepted, and by showing that the phenomena are perhaps more complicated than has been usually assumed.

A brief summary of the phenomena may be made as follows:

A. Coloring by radium radiation.

1. The coloring most commonly imparted to glass is a violet or bluish, which is darkened by increasing the layer of glass, or the intensity of radiation or its duration.

2. When fused silica, either of the opaque or transparent variety, is exposed to prolonged intense radiation, the same violet color is produced as in glass.

3. Some glass is colored brown. This is general for lead-glass and for hard glasses of the pyrex and Jena types. Soft glass also is occasionally colored brown; the color developing more slowly than in the case of the violet.

4. The initial shade always persists and deepens; that is, violet always begins in its own faint shade, and likewise the brown. One is never changed to the other by radiation alone. This observation has been previously made by Meyer and Pzribram.[2]

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[1] Published with the permission of the Director of the U. S. Bureau of Mines.

[2] Meyer and Pzribram: Sitzungsber. Akad. Wiss. Wien, 121 IIa, 1414 (1912).

5. Meyer and Pzribram report further that they have repeatedly observed the simultaneous development of *both the violet and brown colors on different parts of the same glass vessel*; for example, (violet) above and (brown) below the water line in a flask containing a radium salt solution, or (violet) above and (brown) below the salt contact line in vertical glass tubes partly filled with radium salt.[1] This interesting and important observation has never been made in this laboratory, although hundreds of tubes and glass vessels containing both solution and salts have come under observation for several years.

6. Apparently all three kinds of rays, alpha, beta and gamma, produce the same coloring. To the eye there is no difference in the color produced in the immediate glass container and an outer one receiving only Becquerel (beta and gamma) rays. A microscopic examination, such as made by Rutherford,[2] would doubtless reveal the limits of the zone penetrated by alpha rays.

B. Discharge of color.

1. By heat.

The discharge of the violet color does not begin to take place until the softening point of the glass is almost reached.

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[1] Meyer and Pzribram indicate that the difference in color in the same glass may be due to the difference of intensity of radiation in the different parts of the vessel. Above the solution, the greater concentration of emanation and the lower absorption of the gaseous medium for alpha rays both contribute to a more intense radiation. In the case of the solid salt, however, Meyer and Pzribram believed the radiation conditions to be reversed; that the violet color was now produced under conditions which they believed represented the less intense radiation. The writer is inclined to think that on account of the extreme non-penetrating character of alpha rays, the wall in contact with the gas phase would still receive the greater alpha radiation, on account of the spontaneous leak of some emanation from the solid salt into the gas phase, which would perhaps more than compensate for the close contact between the glass wall and the contiguous salt. At first thought, it would appear to be very simple to test this point directly by observing on what part of the tube containing salt the color is first produced, whether above or below the salt. But when the complications arising from the slow accumulation of emanation in the gas phase during the first month are taken into consideration, it does not appear to be so simple.

[2] Rutherford: "Radioactive Substances," 310 (1913).

If the heating takes place in a free flame, the sodium yellow begins to show at the temperature at which the violet color is discharged. The discharge of color from fused silica takes place at about the same temperature. Both glass and fused silica return to their original transparency and can again be colored by further exposure to radiation. Apparently the effect is repeatedly reversible without showing any fatigue.

2. By radiation.

The violet color of glass, which has been produced by radium rays, is very slowly discharged by sunlight. Several months exposure is necessary to produce a perceptible reduction. (Experiment of H. F. Yancey in this laboratory.) Brown-colored glass, according to Meyer and Pzribram,[1] is changed by sunlight or ultraviolet light to a bright yellow.

C. Change of color.

The interesting observation was made by Meyer and Pzribram that on heating brown-colored glass gently until its thermoluminescence is just discharged, the color is changed to the violet, which then persists nearly to the softening point of the glass, just as does the initially produced violet. This interesting observation has been fully confirmed by the writer.

The further observation has been made by the writer that if the violet-colored glass, which has been produced by heating the brown, is again subjected to Becquerel rays, the violet color gives way to the brown which goes on deepening in its original color. Apparently, the violet color produced on heating the brown is changed by Becquerel rays (and presumably also by alpha rays) back to the original brown. However, it is possible that it may be merely a case of masking of the violet by a more intense brown.

D. Thermoluminescence not accompanying change in color.

1. On heating a piece of violet-colored glass not above 200° C in the dark, it luminesces for a period which is longer

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[1] Loc. cit.

the lower the temperature, and finally ceases to luminesce. Its luminescence can only be restored by further radiation.

2. The violet color of glass which has been heated at 200° until all thermoluminescence ceases, is not at all diminished. In order to discharge the violet color, it is necessary, as has already been stated, to raise the temperature above 500° nearly to the softening point. No further luminescence takes place in the temperature interval 200–500° if thermoluminescence is first exhausted at 200°.

3. The more recently and intensely glass has been radiated, the lower the temperature at which thermoluminescence can be observed. Freshly radiated glass luminesced well below the boiling point of water, while glass which had not been radiated for two to three years had to be raised to the neighborhood of 200° before luminescence was observed.

E. Thermoluminescence accompanied by change of color.

1. As stated in paragraph C-1, Meyer and Pzribram[1] found that on heating glass colored brown by radiation to a temperature at which the thermoluminescence takes place, the brown color is changed to violet. Apparently the two effects are closely connected; that is, the change brown ⟶ violet and the thermoluminescence occur simultaneously and are probably connected.

F. The mechanical effects of radiation on glass and quartz.

Although a large number of glass and silica vessels have been exposed at various times for long periods to intense radiation, no mechanical effects have been observed in this laboratory, either on glass or silica, such as have been described by other writers. Rutherford[2] once found that a silica tube, which had been used as a container for radium salt, developed striations which finally resulted in mechanical disintegration of the tube. Hoenigschmid[3] also describes a similar effect on a silica tube in which radium salt had been

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[1] Loc. cit.

[2] Rutherford: "Radioactive Substances," 308 (1913).

[3] Hoenigschmid: Sitzungsber. Akad. Wiss. Wien, 120 IIa, 1624–5 (1911).

stored for several years. In stating that no such effects have been observed in this laboratory, this observation should be mainly restricted to glass tubes. No silica tubes have been employed for storing radium salt. A number of silica dishes have been used for crystallizing purposes, some of which became highly colored in the course of time; but naturally the radiation was not so intense as in the case where salt is actually stored in the tube.

Discussion

A careful consideration of the phenomena which have been described in the foregoing summary, all of which have been confirmed by the writer except the simultaneous production by radiation of two different colors in the same piece of glass, should convince one of the difficulties encountered in finding a theory that will explain them all. Any attempt to attribute difference in color to small quantities of impurities encounters an almost, if not wholly insurmountable difficulty, if it is admitted that the same piece of glass can take two different colors by merely changing the strength of radiation.

Bancroft[1] has suggested that colored glass is produced by the partial coagulation of coloring material in the colloidal state until a certain size of particle is produced capable of scattering some wave lengths and transmitting others. Attempts of the writer to verify this view by radiating a sample of decolorized gold ruby glass[2] to see if the ruby color would be restored, were complicated by the production of the usual violet color of ordinary glass.

Similar experiments by Doelter[3] resulted in producing the brown color. Doelter devoted a chapter in his work on "Das Radium und die Farben" to the coloring of glasses. He mentions four types of coloring: Amethyst, smoke-gray, brownish yellow and golden-yellow, between which are many stages of transition. Doelter also discusses decolorization by heat, not only in air, but in oxidizing and reducing atmo-

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[1] Bancroft: Jour. Phys. Chem., 22, 601, et seq. (1918).

[2] I am indebted to the Corning Glass Company for this sample of glass.

[3] C. Doelter: "Das Radium und die Farben," 1910.

spheres. Apparently, he made no observations in regard to thermoluminescence. The variety of kinds of glass examined by Doelter was so great, and the differences in their behavior so marked, that it is difficult to summarize his results; but it may be said in general that they were quite similar to those reported in the present notes. Doelter also pointed out that radium radiation and ultraviolet rays usually produce opposite effects.

The writer particularly desires to call attention to the erroneous impression that seems to be accepted in the literature that the thermoluminescence of glass and the discharge of color by heat are simultaneous phenomena, probably having a common cause. While this may be true, as has been pointed out, for the change brown ⟶ violet; in the case of violet-colored glass or silica, the two phenomena occur at temperatures differing at least by 300° C from each other. As has already been stated, the thermoluminescence can be wholly exhausted without diminishing the violet color in the least. So it appears that radiation produces at least two different reactions (or conditions) in glass, the reversal of which at two entirely different temperatures leads, the one to luminescence, the other to discharge of color.

If thermoluminescence is due to chemical action, the fact that it takes place at quite low temperatures (60°) with fair rapidity suggests that the same reaction may be proceeding at ordinary temperatures, but so slowly that no luminescence is visible. This view is supported by the observation in paragraph D-3 in regard to the diminished ability of old radiated glass to show thermoluminescence.

Meyer and Pzribram[1] found a rather pronounced photoelectric effect for radiated kunzite and fluorspar, and to a less degree for glass. This observation naturally leads to a physical theory of the coloring by a displacement of electrons. The theory has not been more fully developed.

Newberry and Lupton[2] have subjected a large variety

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[1] Loc. cit.

[2] Manchester Memoirs, 62, 10 (1918).

of substances, including glass and minerals, to Becquerel rays. They ascribe the effects to "the dissociation of minute traces of certain impurities," and state that:

"The products of the dissociation are removed to a very short distance from each other, and the size or density of these particles will determine the particular colors of light absorbed and transmitted. Disturbances of the molecular structure of the crystal by heat, daylight, etc., enable the dissociated particles to approach each other and recombine with consequent loss of color."

"The question as to whether a perfectly pure substance is capable of showing these colors is still open to doubt, although Goldstein's work seems to point to the conclusion that such is possible. With potassium chloride, Goldstein obtained a deep violet coloration in cathode rays, and the authors of this work (Newberry and Lupton) had no difficulty in repeating the experiment. With potassium bromide, Goldstein obtained a deep brown coloration, while the authors obtained a green color; also this sample required 20 minutes treatment before any appreciable color was obtained, while Goldstein's color was obtained in a few seconds. It seems still possible, therefore, that the colors may be due to traces of impurities which are always present in the purest obtainable samples. Goldstein estimates that certain impurities amounting to not more than 1 part in a million may produce quite perceptible color effects under the influence of cathode rays. He has also shown that the same impurity may give rise to different colors when present in different solids."

U. S. Bureau of Mines
Experiment Station
Golden, Colorado
April, 1920

ANOMALOUS OSMOSE OF SOME SOLUTIONS OF ELECTROLYTES WITH GOLD-BEATERS SKIN MEMBRANES

BY F. E. BARTELL AND O. E. MADISON

The phenomenon of osmosis appears to have been discovered in 1748 by Abbé Nollet.[1] He filled a vessel with alcohol, closed it with bladder, and submerged the whole in pure water. The volume of the alcohol was increased and the bladder distended, thus showing that the water had passed through the membrane more rapidly than the alcohol. Sömmering,[2] in 1814, made similar observations.

The first quantitative experiments on osmosis were carried out by Dutrochet[3] and Vierordt[4] between the years 1826 and 1848. They found that when a salt solution was separated from water by means of pig's bladder, the water diffused through the membrane more readily than the salt solution, thus producing a hydrostatic pressure. Dutrochet observed that there was always a current inward to the more concentrated solution side; this he called the endosmotic current. Simultaneously there was an outward current which he called the exosmotic current. In 1827 Dutrochet[5] brought forth an electrical theory to explain osmosis. He concluded that the two sides of the membrane developed different "degrees of electricity," but that the difference could not be detected with a galvanometer. The researches of Dutrochet and Vierordt established the fact that the difference between the rates of diffusion of pure water and of salt solutions depended not only on the concentration of the solution, but also on the nature of the salt solution and, as they later found, on the nature of the permeable septum used. Dutrochet also found that osmotic pressures were developed by porous inorganic membranes as well as by organic membranes.

About twenty-five years later, extensive investigations were carried out by Thomas Graham,[6] who used a variety of membranes, both organic and inorganic, with many different types of solutions. He obtained osmotic effects covering a wide range of magnitude. Certain anomalous effects he attributed mainly to the chemical disintegration of the membranes; in fact, he advanced the theory that an alteration of the membrane was an indispensable condition to the maintenance of the "osmotic force." He considered that one side of the membrane was always acid and the other side alkaline. The direction of the endosmotic current, he believed, was always from the acidic to the basic side. The effects he obtained with organic membranes were generally opposite to those he obtained with unglazed porcelain; however, he offered no explanation for this difference in behavior. Later, influenced by his own work on dialysis, and by the work of L'Hermite[7] on selective or preferential solubility of two liquids in a separating membrane, Graham came to the conclusion held by Liebig[8] that osmosis is due to the ability of the membrane to absorb the separated liquids. From this time on for nearly half a century the work on osmosis was directed mainly to the study of unidirectional currents. "Semi-permeable" membranes were used which were capable of producing maximum osmotic pressures. It had been pointed out by van't Hoff[9] that such pressures were expressible by the gas law formulations.

As work progressed and quantitative data increased, many of the investigators in this field appear to have almost entirely neglected to take into account the fact that anomalous osmotic effects of considerable magnitude are obtained when solutions of electrolytes are used with osmotic membranes. Abnormal effects were in nearly all cases attributed either to electrolytic dissociation, or to molecular association, or to hydration. The attention of these investigators has for the most part been directed to a study of the more perfect semipermeable membranes such as copper ferrocyanide with solutions of non-electrolytes such as sugar.

The tendency of electrolytes to produce osmotic pressures at variance with the values calculated from van't Hoff's generalization, even with the best of "semi-permeable" membranes, is easily detected when sufficiently refined measurements are made. This has been clearly shown by Lord Berkeley and E. G. J. Hartley[10] Morse and his collaborators,[11] and by other investigators who have observed the lack of conformity between the experimental and the calculated values of osmotic pressures of salt solutions. No generally accepted theory has been given to account for this osmotic behavior.

The anomalous effects of salt solutions with natural cells and tissues in the presence of an acid or alkali medium has been a perplexing problem and has been studied by Girard,[12] Lillie,[13] Osterhout,[14] Loeb[15] and others.

Girard studied the osmotic pressures of electrolytes with various animal membranes. He found that the osmotic pressures of electrolytes vary greatly with their nature, as well as with their concentration; in fact, he noted that in some cases the exosmotic current was greater than the endosmotic current, i. e., negative osmosis was obtained. In seeking an explanation, Girard announced his electrostatic theory. He considered osmosis of electrolytes to be due primarily to an electrical effect, and the process of osmosis to be dependent mainly upon two electrical factors: (1) the sign of the charged, movable, liquid layer adjacent to the walls of the capillaries in the membrane, and (2) the difference of potential existing between the two faces of the membrane. He regarded the membrane as being electrically charged. He considered the charge on the walls of the capillaries to be due to the effect of a small excess of hydrogen or hydroxide ions. The movable layer of liquid within the capillary was assumed to possess a charge opposite to that of the capillary wall. Girard found that the difference of potential between two solutions with a membrane interposed, may be greater or less than the potential between the two solutions when in direct contact, and further, that the orientation of the cell system may even be reversed by the interposition of the membrane. A reversal of this kind means that the sign of the interface potential has been changed.

It appears to be the rule that permeable membranes of almost any material whatever, interposed between a solution and water, or between two solutions, give differences of potential between the two faces of the membrane which are different from the contact potential of the two liquids. Examples of such potential differences exhibited by membranes are to be found in the work of Brünings,[16] Lillie,[17] Loeb,[18] Beutner,[19] Bartell and Hocker,[20] and others.

The precise nature of the membrane seems to be an important factor in determining the nature of the osmotic effect and the electrical condition of a cell system. The proportionality which has been shown to exist in osmotic cell systems between the osmosis measured in terms of hydrostatic pressure and the E. M. F. of the same cell system seems to conform fairly closely to Wiedemann's third law[21] for electrical osmose, which states that for a given diaphragm material, the difference in hydrostatic pressure maintained between the two sides of the porous diaphragm is proportional to the applied potential. Further analogies may be shown to exist between the phenomena of anomalous osmose and that of electrical osmose;[22] for example, in both cases a reversal of flow of liquid can be brought about by the introduction of acid, base, or a salt of polyvalent ions, into the cell system. Both phenomena are dependent upon the existence of an electrical double layer along the walls of the capillary pores.

In the process of electrical osmose, a difference of potential is enforced upon the cell system and is caused to be operative within the two solutions which bathe the two faces of the membrane; whereas in the process of anomalous osmose the difference of potential is self-induced, and it too may be assumed to function between the two faces of the membrane. The effects, resulting in a flow of solution through the membrane, are the same in either case.

Freundlich,[23] influenced by his own work on adsorption and by the theories of Perrin[24] regarding the analogies between the behavior of suspensions and the peculiarities of electrical osmose, was probably the first to point out clearly the intimate relations existing between adsorption and electrical osmose. Bancroft[25] has further contributed to our understanding of the relation between the sign of the charge on a membrane and the selective adsorption of anion or cation.

It is only a short step forward to apply to osmotic phenomena, which, as above stated, have been shown to be very similar fundamentally to electrical osmose, a definite theory based upon selective or preferential adsorption of ions.

Theoretical

In attempting to explain the osmose of electrolytes by an electrical theory similar to that used to account for electric osmose, two determining factors must always be considered: (1) the electric charge of the capillary pore wall in respect to the charge on the liquid layer bathing this wal (i. e., the Helmholtz electrical double layer), represented in Fig. I, which we shall refer to as the *capillary system;* and (2), the orientation of the electrical potential existing between the two faces of the membrane, represented in Fig. II, which we shall refer to as the *membrane system.*

Fig. I

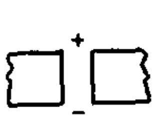

Fig. II

The magnitude of these two electrical factors is dependent upon the extent of diffusion of electrolyte through the membrane, upon the relative migration velocities of the ions and upon the extent of selective ion adsorption. These three factors are operative simultaneously and, since each factor affects to some degree the effect of the others, the result obtained is necessarily a differential one, it being the combined effect of all three factors; any one factor may play a predominating part in any particular case. The value of the electrical charges may be materially altered by even traces of acids or alkalis.

It has been pointed out by Bancroft[26] that adsorption is a specific process, the neutralization of the charge on a given colloid depending on the nature of the colloid, and upon the nature of both cation and anion. This harmonizes with the view of Freundlich,[27] Michaelis[28] and others that adsorption potentials are dependent upon the nature of the adsorbing material and upon the extent of selective ion adsorption. It seems probable, then, that the sign of the charge upon the capillary pore wall of an osmotic membrane is dependent mainly upon the relative adsorption of the cation and anion from the solution present in the capillary pore. An indication of the magnitude of the charge on the capillary wall may be obtained by reducing some of the membrane material to a fine suspension which can be placed in the solution in question and then subjected to the influence of a difference of potential (i. e., the process of cataphoresis). The direction and velocity of migration of the particle indicates the sign and magnitude of the charge upon it.

An application of the above concept brings out the fact that a complete cell system must exist in some one of nine different conditions of electrification. Each of the following diagrams (Fig. III) represents a single capillary pore extending

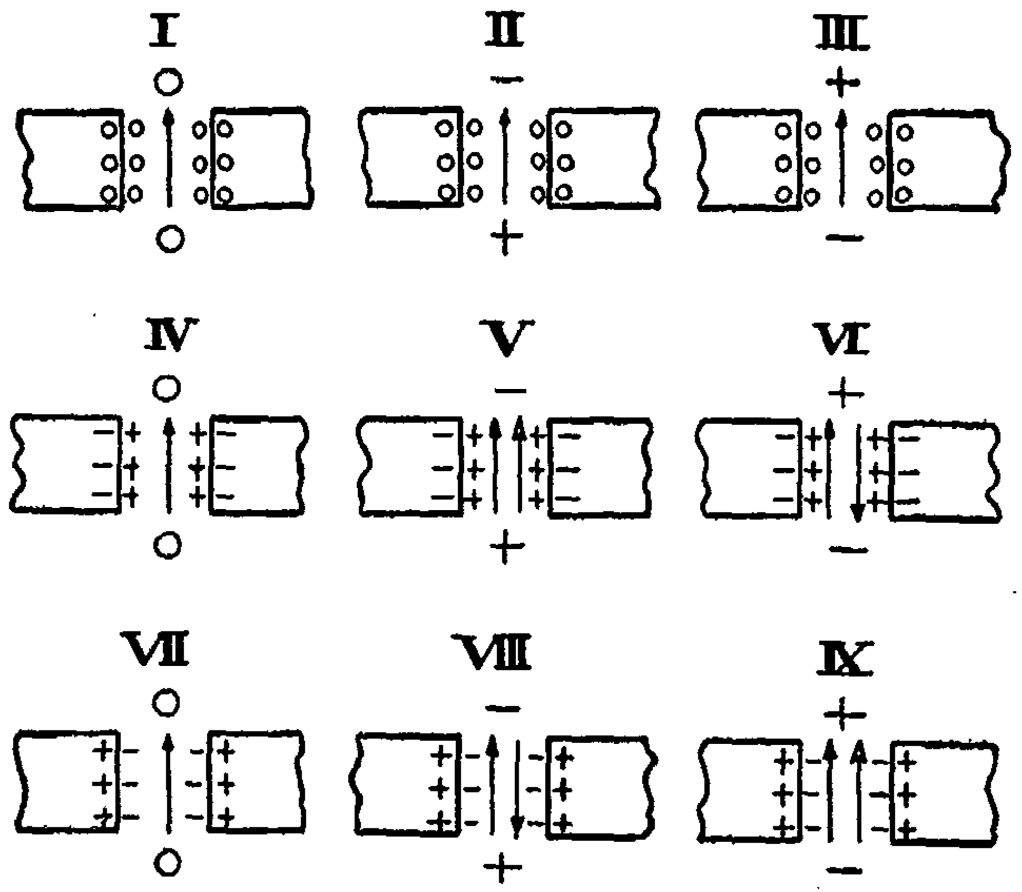

Fig. III

through a membrane; in connection with this pore there is indicated also the sign of the electrostatic charge on the membrane, the corresponding opposite charge of the liquid layer bathing the pore wall, and the electrical orientation of the membrane system. In each case the arrow on the left, pointing upward, represents the direction of the tendency to produce normal osmose, such for example, as would be obtained with sugar solution. The arrow on the right indicates the direction of the superimposed effect. The direction of this superimposed effect may be the same as, or opposite to, the normal osmotic effect. In the latter case negative osmose may result. The solution is understood to be on the upper side of the membrane, and water (or the more dilute solution), on the lower side. The osmose due to this superimposed effect, is assumed to be caused by the passage of a charged liquid layer along the walls of the capillary pores of the membrane under a driving force of potential which acts as though it were set up between the two faces of the membrane.[1]

If we consider all the cases in which it is possible for the cell systems to exist, we find, referring to diagrams in Fig.

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[1] The term *normal osmose* has been used throughout to designate that process which tends to produce an equilibrium difference of pressure, of magnitude expressible by the gas law formulations, when solution and solvent are separated by a membrane permeable to the solvent alone. In the present paper absolutely no attempt has been made to "explain" the phenomena of normal osmose. It has been assumed that a tendency to produce normal osmose does exist within a system whenever two aqueous solutions of unequal concentration—or a solution and water—are separated by a truly "semi-permeable" membrane. It is also assumed that, in case the membrane is not strictly semipermeable but is, instead, permeable to solute as well as solvent, the tendency to produce positive normal osmose still exists and will continue to exist until the solutions on the two sides of the membrane become of the same concentration. Further, it has been tacitly assumed that the rate of flow of liquid through the membrane in normal osmose should be very nearly the same with different kinds of solutions which are isotonically equal. In those cases in which the rate of flow of liquid through the membrane is different than the rate obtained as the result of normal osmose alone, it is assumed that some superimposed effect is operative within the system. The superimposed effect may act in conjunction with the force tending to produce normal positive osmose, resulting thereby in abnormally great positive osmose, or the superimposed effect may act in opposition to the normal osmotic tendency and may in some cases even become so great as to completely overcome the normal osmotic effects and produce as a result a flow of liquid from concentrated to dilute solution. This we have designated as *negative osmose*.

III, that in cases I, II, III, IV and VII, normal osmotic effects would be obtained; in cases V and IX abnormally high positive osmose would be produced; while in cases VI and VIII an abnormally low osmose would be produced, which osmose might even become negative.

Cases I, II and III represent a membrane which is iso-electric with the solution. This condition, even though a difference in potential might exist between the faces of the membrane, would produce normal osmose.

Case I would be obtained with a membrane electrically neutral, with a sugar solution. Cases II and III may be considered to exist when a membrane such as porcelain is in contact with a solution of an electrolyte at such concentration that the membrane material is at the iso-electric point.

Case IV represents a membrane such as porcelain (electro-negative) in a sugar solution. The membrane is negative to the sugar solution; however, owing to the fact that no polarization exists between the two faces of the membrane, only normal osmose would result.

Case V represents a membrane such as porcelain with a solution such as KNO_3; the membrane is electro-negative to the solution and the electrical orientation of the cell system is such that the solution side is electro-negative to the water side. This condition would result in an abnormally great positive osmose.

Case VI exists when a porcelain membrane is in contact with a dilute solution of a base within the cell. The membrane is negative to the solution, but owing to selective adsorption of ions and also to the more rapidly moving anion, the dilute solution side is electro-negative to the other side. An abnormally small, or even negative osmose would result.

Case VII represents a membrane such as aluminium oxide (electro-positive), with a sugar solution. The aluminium oxide is positive to the sugar solution, but since no polarization exists between the two faces of the membrane, only normal osmose would result.

Case VIII exists with a concentrated solution of HCl.

The capillary wall is positive to the solution as a whole, while the water or dilute solution side is electro-positive to the concentrated solution side. This condition would give an abnormally low or negative osmose.

Case IX is obtained with an $AlCl_3$ solution. The capillary wall is positive in respect to the solution, while the dilute solution side of the system is electro-negative, and would therefore result in an abnormally great positive osmose.

The anomalous osmosis due to the effect of electrolytes in general, used singly or in combination, and its relation to the equilibrium of emulsions, sols, jellies, blood coagulation, living plant and animal cells, etc., may be accounted for on the basis above outlined. This explanation is further confirmed by the various data obtained in connection with the action of electrolytes in many different physiological and biological systems. The same fundamental principles underlie all these inter-related phenomena.

Apparatus and Methods

The object of this investigation has been to study the osmotic effects produced by solutions of electrolytes with an animal membrane such as gold beaters skin, and to ascertain whether any parallelism exists between the observed osmotic effects produced, and the difference of potential associated with the same cell system.

The gold beaters skin used was of very fine grade and was of uniform texture. That we are justified in considering this membrane capillary in nature is evident from the work of Bigelow,[29] who found that Poiseuille's law for the passage of liquids through capillary tubes applies to the passage of water through collodion, parchment paper, and gold beater's skin.

It may be well to point out the fact that gold beaters skin membranes are far from being semi-permeable. From the beginning of an experiment to the end, there is a continual diffusion of solute from the more concentrated to the more dilute solution. This diffusion of solute, which results in a change in concentration, will continue until the solutions on the two sides of the membrane are of the same concentration. With a membrane of this type, we are unable to even approach the theoretical maximum osmotic pressure values.[1] What we actually have obtained in this work, is data showing the rate of flow of solution through the membrane. In some cases we have measured also the equilibrium pressure, expressed in terms of hydrostatic pressure, of the different solutions when the rate of flow of liquid through the membrane in one direction was just balanced by the rate of flow of liquid in the other direction. If the rate of flow of liquid was practically the same as that of a sugar solution of the same concentration, we have considered the rate of flow normal and have designated the process as normal osmose. If the rate of flow of liquid is far different from that of sugar solution, we have characterized the osmose as abnormal and the process as one of anomalous osmose. If the rate of flow of liquid was greater in the direction of the more concentrated solution, we have designated that as a positive osmotic flow or positive osmose, while if the rate of flow was greater in the direction of the more dilute solution, we have designated that as a negative osmotic flow, or negative osmose. It will readily be appreciated that a comparison of the rates of flow of different solutions is in no way an exact means of comparing the absolute osmotic activity of the different solutions. It does, however, give us a fairly accurate indication of the order of the maximum equilibrium pressures which may be obtained with these solutions. Furthermore, in those instances in which the direction of flow of solution is opposite to that obtained in normal osmose, there seems to be no logical argument against the view that some force must be operating in the system in addition to that tending to produce positive osmose. It is for the purpose of throwing some light on the nature and source of this additional force, or superimposed effect, that the work of this paper is directed.

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[1] It may be mentioned that this is quite the type of osmotic membranes we encounter in practically all living organisms, both animal and vegetable.

Osmotic experiments were carried out in a cell of two compartments, each half of which consisted of a glass L-tube of approximately 20 cc capacity—Fig. IV. The ends of the L-tubes in contact with the membrane were ground to make water-tight joints. The ends were covered with a thin coating of low-melting paraffin, which served as a protective cushion for the membrane when the cell was set up. The membrane was held in place by a piece of tightly fitting rubber tubing, which, in turn, was held firmly to the paraffined glass cell by means of tightly wound copper wires, the extensions of which served as legs to support the cell in an upright position. All the stoppers in the cell were coated with paraffin each time a cell was set up. As a result no difficulty was experienced from leakage. When concentrations of alkali greater than 0.01 M were used, it was necessary to protect the face of the rubber stoppers with paraffin. The outlet tubes, used to measure the osmotic effects, were of about 3 mm internal diameter. At the beginning of each experiment the cell was filled and the liquids were brought to the same height in both tubes. The temperature was kept at approximately 20° C. Readings were taken every two hours for twelve hours, at which time the cells had reached very nearly their maximum or minimum osmotic values. The main advantages of these cells are as follows: (1) Any leak in the cell is easily detected, (2) evaporation is practically eliminated, (3) temperature changes cause practically no alteration of the hydro-

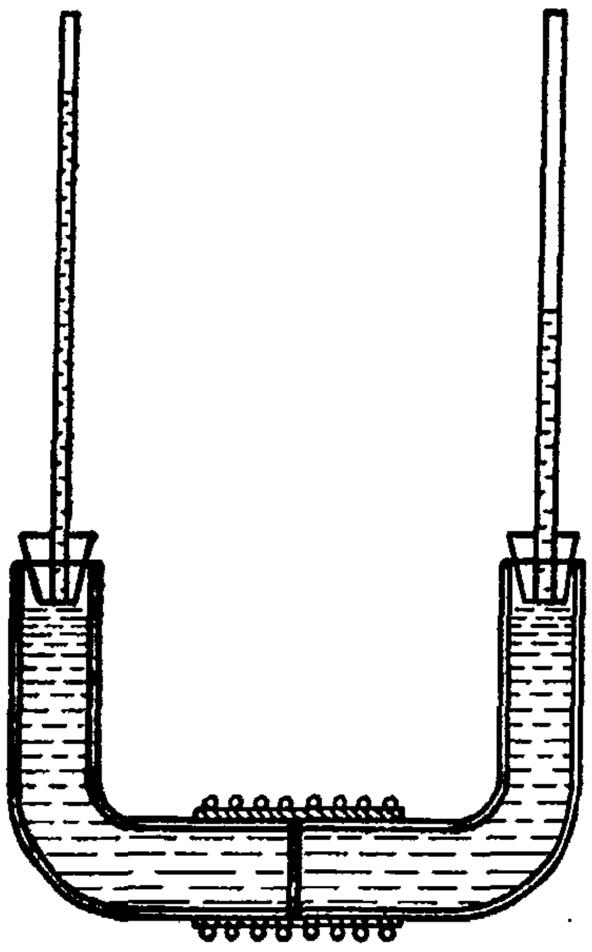

Fig. IV

static pressure on the membrane, since a change in temperature causes approximately the same rise in each of the outlet tubes, (4) no difficulty is experienced in working with solutions which must be protected from atmospheric contaminations, since both solutions are well enclosed, (5) any change in the concentration of the two solutions due to the dissolving of the membrane material is practically the same, (6) corrections due to the capillarity are negligible, since the effects are practically the same in the two outlet tubes, (7) the whole cell can easily be immersed in a constant temperature bath when quantitative measurements are desired.

Osmose of Chloride Solutions of Different Concentrations in a One-Compartment Cell

In the first series of experiments carried out, but one compartment of the above described cell was used, Fig. V.

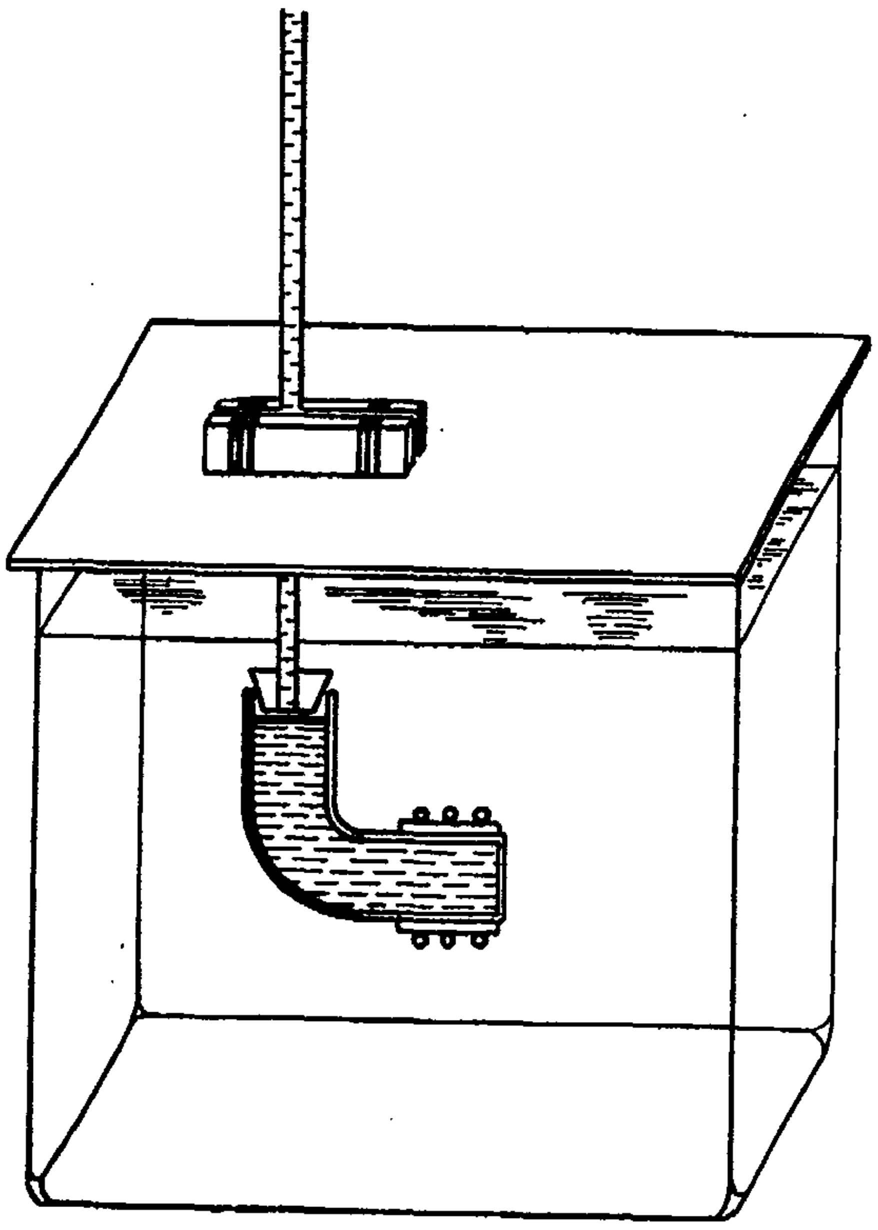

Fig. V

A membrane was fastened over one end of the glass L-tube and the whole was suspended in a vessel of water, about 1000 cc. With this set-up we determined the osmotic effect of the cell with a very large volume of water present. It was desired to compare osmotic effects obtained with large volumes of water present with those obtained when smaller volumes (about 20 cc) were present.

The following tables contain the results of the experiments on the osmose of chloride solutions of different concentrations, and of sugar solutions of the same concentrations as these, against a large volume of water. The data are given as rise in millimeters (from the original level of the meniscus). The height of the liquid in the outlet tubes was measured by means of a millimeter scale and estimated to 0.5 of a millimeter.

TABLE 1

Concentration 0.01 *M* Solutions of chlorides in cells

Time (hrs.)	KCl	NaCl	LiCl	$BaCl_2$	$MgCl_2$	$AlCl_3$	$ThCl_4$	Sugar
0	0	0	0	0	0	0	0	0
2	2	1.5	3	6	6	21	79	2
4	4	3	5	11	11.5	49	153	4
6	5	5	6.5	16	17	81	230	6
8	6	6.5	7	19	21	113	297	8
10	7	8	8	21	25	150	365	11
12	7	8	9	22.5	27	187	403	12

TABLE 2

Concentration 0.02 *M* Solutions of chlorides in cells

Time (hrs.)	KCl	NaCl	LiCl	$BaCl_2$	$MgCl_2$	$AlCl_3$	$ThCl_4$	Sugar
0	0	0	0	0	0	0	0	0
2	2.5	3	2.5	3	2	61	91	7
4	4	5	3.5	8	8	133	202	11
6	5	7	5	10.5	11	213	315	15
8	6	8.5	6.5	16	17	270	403	18
10	6.5	9	8.5	25	27	345	509	21
12	7.5	9	10	30	35	420	564	23

TABLE 3

Concentration 0.05 *M* Solutions of chlorides in cells

Time (hrs.)	KCl	NaCl	LiCl	$BaCl_2$	$MgCl_2$	$AlCl_3$	$ThCl_4$	Sugar
0	0	0	0	0	0	0	0	0
2	2	2	2.5	8	9	93	131	12
4	4	4	4	15	18	198	325	20
6	5	5.5	5.5	22	23.5	285	456	30
8	6	7	7	28	29	367	514	38
10	7	7.5	9	32	33	468	579	46
12	8.5	10	11	36	38	550	660	51

TABLE 4

Concentration 0.1 *M* Solutions of chlorides in cells

Time (hrs.)	KCl	NaCl	LiCl	$BaCl_2$	$MgCl_2$	$AlCl_3$	$ThCl_4$	Sugar
0	0	0	0	0	0	0	0	0
2	3	3.5	3.5	20	23	137	201	15
4	5.5	6	6.5	35	32	281	461	35
6	8	8.5	9	45	45	390	657	54
8	10	10	10	50	55	494	777	69
10	11	11.5	12	55	65	615	891	84
12	12	12.5	14	58	75	738	977	99

Osmose of 0.5 M Chlorides in Two-Compartment Cells

This set of experiments was made with the volumes of solution and solvent on opposite sides of the membrane, as nearly equal as possible. This was done, in contrast to the conditions in the previous experiments in which the volume of solution and solvent were made very unequal, in order to study the influence of the relative volumes of solution and water on the osmotic effect. For these experiments, likewise for those in which the effect of acid and alkali was studied, as also for those in which measurements were made of the E. M. F., the two-compartment type of osmotic cell previously described was employed. Using this type of cell, experiments were made to determine the osmose of 0.05 *M* chlorides. The results thus obtained are given in the following table:

TABLE 5

Concentration 0.05 M Solutions of chlorides in two-compartment cells

Time (hrs.)	KCl	NaCl	LiCl	$BaCl_2$	$MgCl_2$	$AlCl_3$	$ThCl_4$
0	0	0	0	0	0	0	0
2	9	3.5	5.5	27	42.5	112.5	91
4	20	8.5	10.5	42.5	66.5	129	112.5
6	25	15	19	55	84	152.5	150
8	28	21	27	62.5	97.5	147.5	166
10	29	27.5	31	61	107	142	170
12	29	31	36	61	112	137	169

The data contained in the preceding tables show that:

1. The order of osmose of the several salt solutions was the same with the double cell as with the single type of cell.

2. The osmose of the salt solutions of univalent and divalent cations was decidedly greater in the two-compartment cell than in the single cell.

3. On the other hand, the salt solutions containing polyvalent cations, as aluminium and thorium, gave decidedly smaller effects in the two-compartment cell than in the single cell.

The Osmose of Acid and Alkali Against Water

In these experiments nitric acid and sodium hydroxide were employed. Carbon dioxide-free water was used to make the solutions of alkali. The outlet tubes were closed with very small soda lime tubes to prevent the adsorption of carbon dioxide from the atmosphere.

A positive effect signifies a flow of liquid toward the side of the membrane in contact with the electrolyte, and a negative effect, indicated as (—), signifies a passage of liquid in the opposite direction. The osmose is expressed in terms of rise in mms of solution, which is half the actual hydrostatic pressure, or half the difference in level of the liquids in the two outlet tubes.

Concentrations of both acid and alkali varying from

0.0001 *M* to 0.5 *M* were employed, and the results of the tests are shown in Tables 6 and 7.

TABLE 6

The Osmose of Nitric Acid

Time (hrs.)	0.0001 *M*	0.001 *M*	0.01 *M*	0.1 *M*	0.2 *M*	0.5 *M*
0	0	0	0	0	0	0
2	0	0	3.5	—1.5	—7.5	—14.5
4	0.3	0.5	6.5	—2	—12	—22
6	0.5	1	9.5	—2.5	—14.5	—26
8	0.7	1.5	11.5	—2.7	—15.5	—27.5
10	1	2	13	—2.5	—16	—28
12	1	2.5	14.5	—2	—16.5	—28.5

From Table 6 it may be pointed out that:

1. Nitric acid gives both *positive* and *negative* osmose, depending on the concentration of the acid employed.

2. The osmose is positive at concentrations of 0.01 *M* or less, and negative at higher concentrations.

3. The osmose increases from 0.0001 *M* to 0.01 *M* as the concentration increases, but at 0.1 *M* concentration the osmose becomes slightly negative, and continues to become increasingly negative as the concentration of the acid is increased.

TABLE 7

The Osmose of Sodium Hydroxide

Time (hrs.)	0.0001 *M*	0.001 *M*	0.01 *M*	0.1 *M*	0.2 *M*	0.5 *M*
0	0	0	0	0	0	0
2	0	1.5	1	0	—4	—5
4	0.5	2	2	0	—3.5	—7
6	0.5	2	3	0	—2.5	—7.5
8	1	2	4	0	—2	—6
10	1.5	3	5	0.2	—2	—5.5
12	1.5	3	5	1	—2	—5.5

Table 7 shows that:

1. Sodium hydroxide also gives both positive and negative osmose.

2. The osmose is distinctly positive at concentrations of 0.01 *M* or less, but seems to be practically zero at 0.1 *M* concentration, and becomes increasingly negative as the concentration increases.

It is a peculiar and interesting fact that the turning point for both the acid and alkali is at about the same order of concentration, namely 0.01 *M* to 0.02 *M*. (See Fig. VI.)

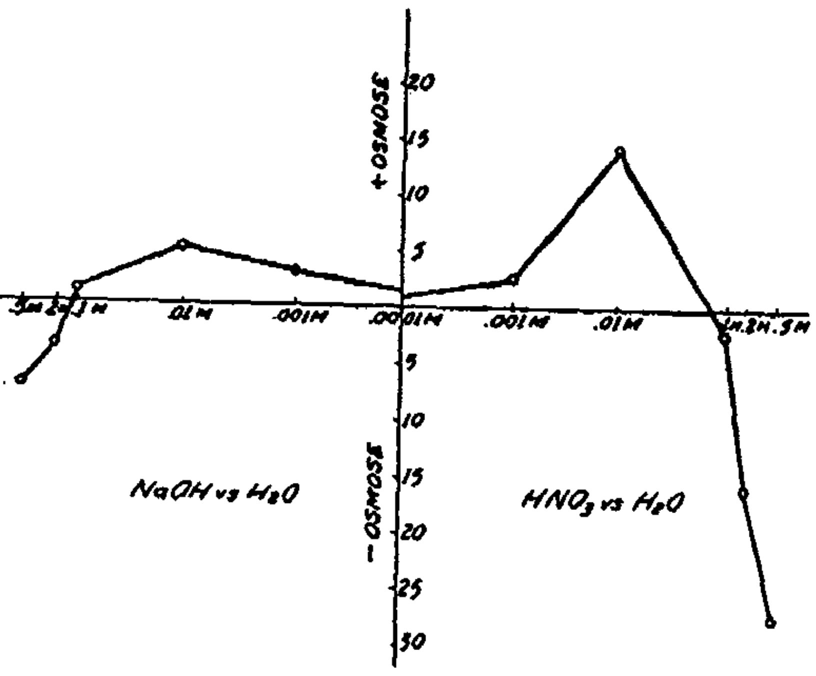

Fig. VI

In this same connection it may be noted that Bartell and Hocker,[30] in their work with porous porcelain membranes, make mention of a similar turning point in the case of hydrochloric acid and sodium hydroxide, but they did not observe negative osmose with the concentrations of acid used.

Measurement of Cell Potential

The relation of osmose to cell potential was studied by measuring the potential of the cell system when the cells were set up precisely as when measurements of osmose were to be made. These potential measurements were made by the compensation method, using calomel electrodes, a Wolff potentiometer, and a sensitive galvanometer. Two modified Hulett batteries connected in series served as a source of potential for the external balancing current. These batteries maintained a very good constancy. One electrode was brought in direct contact with the solution and the other electrode in similar contact with the water, giving the chain: Hg-Hg_2Cl_2-0.1 *M* KCl–solution-membrane–water-0.1 *M* KCl-Hg_2Cl_2-Hg. In the case of electrolytes used in combination, the chain was: Hg-Hg_2Cl_2-0.1 *M* KCl-solution A-membrane-solution B-0.1 *M* KCl-Hg_2Cl_2-Hg. Only the initial constant values were utilized since, as pointed out by Bayliss in his work with parchment paper,[31] they seem to be the more reliable for comparative data. However, a sufficient number of time measurements were taken to ascertain that the E. M. F. steadily falls after the cell has been set up for a time. This is due probably to diffusion of the electrolyte through the membrane, causing a change in concentration of the solutions bathing the faces of the membrane.

The Electromotive Force of 0.5 M Chlorides vs. H_2O

These and subsequent electromotive force measurements were made in an endeavor to ascertain whether there was any relation between the osmotic effect produced and the electromotive force of the same cell system. The measurements were carried out as previously described and are contained in the following table. The results given are the averages of two or more measurements, none of which varied more than two millivolts from the average value given. All the E. M. F. measurements were made within 5 minutes after the cell was set up.

TABLE 8

E. M. F. of 0.05 *M* Chlorides against H_2O

Solution	Potential Solution side Volt	Solution	Potential Solution side
KCl	+0.002	$MgCl_2$	+0.060
NaCl	+0.015	$AlCl_3$	+0.067
LiCl	+0.046	$ThCl_4$	+0.070
$BaCl_2$	+0.050		

TABLE 9

The E. M. F. of HNO_3 and NaOH against H_2O

Concentration HNO_3	Potential Solution side	Concentration NaOH	Potential Solution side
0.001 *M*	—0.050	0.001 *M*	+0.018
0.01 *M*	—0.092	0.01 *M*	+0.040
0.1 *M*	—0.110	0.1 *M*	+0.059

Summary of Results and Conclusions

1. The principal relationships found have been brought together in the following table:

Solution	Osmose		Sign of Potential Solution side	Sign of liquid layer	Osmotic Tendency
	Single cell (12 hrs.)	Double cell			
0.05 *M* Sugar	—	51	0.000		Normal (Positive)
0.05 *M* KCl	29	8.5	+0.002	+	Negative
0.05 *M* NaCl	31	10	+0.015	+	Negative
0.05 *M* LiCl	36	11	+0.046	+	Negative
0.05 *M* $BaCl_2$	61	36	+0.050	+	Negative
0.05 *M* $MgCl_2$	112	38	+0.060	+	Negative
0.05 *M* $AlCl_3$	137	550	+0.067	—	(Abnormally positive)
0.05 *M* $ThCl_4$	169	660	+0.070	—	(Abnormally positive)
0.001 *M* HNO_3	—	2.5	—0.050	+	(Abnormally positive)
0.01 *M* HNO_3	—	14.5	—0.092	—	(Probably near turning point)
0.1 *M* HNO_3	—	—2.0	—0.110	—	Negative
0.001 *M* NaOH	—	3	+0.018	+	Negative
0.01 *M* NaOH	—	5	+0.040	+	Negative
0.1 *M* NaOH	—	—1	+0.059	+	Negative

2. The osmose of sugar solutions indicate that the rate of osmose is very nearly proportional to the concentration of the solution.

3. It is noted that the direction and magnitude of flow of solution is, in practically every case, that which we would predict from the postulates above stated. If the solution

side of the membrane system is of the same electrical sign as the capillary liquid layer the resulting osmose will be abnormally low, or negative; whereas if these parts of the system are of opposite sign the resulting osmose will be abnormally high.

4. With salts of univalent and divalent cations the superimposed effect is found to work in opposition to normal osmose, with the result that the observed rate of osmose is less than normal.

5. With salts of Al and Th the superimposed effect works in conjunction with the normal osmose and the result is an abnormally great osmose.

6. Increase in concentration causes but slight increase in osmose of solutions of univalent cations, a marked increase in osmose of solutions of divalent cations and a decidedly greater increase in osmose of solutions of trivalent and quadrivalent cations. A logical explanation, for the facts just mentioned, seems to be that with dilute solutions of univalent and divalent cations, the charge of the membrane against the solution is at all times electro-negative which tends to produce an abnormally low osmose. In the case of the solutions of divalent cations there is a marked tendency to neutralize the negative charge of the membrane, with the result that with the more concentrated solutions the membrane approaches the iso-electric point and osmose now approaches the normal rate. In the case of solutions of trivalent and quadrivalent cations, the sign of the membrane is electropositive, even with the very dilute solutions; this results in an abnormally great positive osmose in every case.

7. With the two-compartment cells, the concentrations of the solutions on the two sides of the membrane are much more nearly equal than in the one-compartment cell. This is due to the small initial water volume, with the result that the E. M. F. of the *membrane system* is, in this case, much less than in the case of the one-compartment cell. Owing to the smaller potential difference between the two faces of the membrane, the resulting osmose is in all cases more nearly

normal. In the case of the solutions of univalent cations, there exists a lesser tendency toward negative osmose, whereas in the case of solutions of polyvalent cations, as Al and Th, there exists a lesser tendency for an abnormally great positive osmose.

8. In the case of dilute acid the tendency is toward an abnormally great positive osmose. As the concentration of acid is increased, the sign of the capillary system is changed (reversed), and the osmotic tendency passes from abnormally great positive to normal, then to abnormally small, and finally to negative osmose.

9. In the case of sodium hydroxide, a negative tendency persists throughout. At the higher concentrations the electrical factors of the system are such that negative osmose results.

10. Work with porcelain membranes showed somewhat similar results for the osmotic behavior of acids and alkalis. In some investigations it has been found that with certain concentrations of acid or alkali, (approx. 0.01 *M* conc.) positive osmose may be of a very considerable magnitude, whereas at still higher concentration of acid or alkali, negative osmose may result.

All these facts coincide with many physiological observations which up to the present time have received no satisfactory explanation.

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SOME FACTORS AFFECTING RHYTHMIC PRECIPITATION

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The phenomena of rhythmic precipitation, since Liesegang's[1] discussion of his discovery in 1898, have attracted considerable attention and created much interest. A very excellent historical account of the work of earlier writers is given by Stansfield,[2] so that it does not seem necessary to present this phase of the subject here. This paper gives the results of a number of experiments that throw some light on the conditions that affect the formation of rhythmic precipitates.

Most of the experiments described in this paper were performed with a gel prepared in the following way.[3] Equal volumes of a sodium silicate solution of 1.05 specific gravity and N/2 acetic acid were thoroughly mixed. The resulting mixture set within five minutes to a stiff gel. The sodium silicate solution was such that it was not quite acidified by an equal volume of half normal acid. It was found convenient to use normal acetic acid solution and to dilute it with an equal volume of water, K_2CrO_4 solution, or solutions of other substances whose effect on the rhythmic precipitation was to be studied. The gel was made $^1/_{80}$ molecular with respect to K_2CrO_4, and after it had set, a $^1/_2$ molecular solution of $CuSO_4$ was poured upon it.

If the $CuSO_4$ solution is poured upon the gel as soon as it has set, there will form within 24 hours, first, a dense band of basic copper chromate about one centimeter deep, in which there may often be distinguished many bands crowded close together. Then at intervals of 5 cm. or more there will be regular thin bands of the copper chromate. The intervals

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[1] "Chemical Reactions in Gelatine," Düsseldorf (1898).

[2] Am. Jour. Sci., [4] 43, 1 (1917).

[3] This procedure is somewhat similar to that described by Holmes: Jour. Am. Chem. Soc., 40, 1187 (1918).

between the bands increase toward the bottom of the test tube. The spacing is evidently logarithmic as has been shown by Okaya.[1] If the gel impregnated with K_2CrO_4 was allowed to stand for some time before pouring on the $CuSO_4$ solution, the bands that resulted were more and more irregular the longer the gel had stood. Finally, in a gel that had stood for a week or more, the copper chromate precipitate consisted of warped bands and fragments in all sorts of fantastic shapes. To all appearances the gel was as uniform as that which was freshly prepared. It seems likely that some change in the structure of the gel took place on standing open to the air that hindered the uniform diffusion of the interacting salts. This effect is shown in Fig. 1.

A remarkable effect on the rhythmic precipitation of the copper chromate is that of certain alcohols:—methyl, ethyl, propyl, and glycerin. Somewhat similar are the effects of urea and sugar. Photographs of some of these precipitates are shown in Fig. 2. Five cc of each of the liquids was added in place of the corresponding volume of water in the preparation of 50 cc of the gel. In all of these the most apparent effect was to make the bands of copper chromate more sharply defined. It also caused a difference in the distances between the bands. The alcohols and urea caused them to be closer together, whereas the sugar and glycerin caused them to be farther apart. The intervals between bands was especially large where the gel contained sugar. The test tubes containing the sugar were tightly corked and stood over the summer vacation. Then there were formed faint but very sharp layers between those of the copper chromate which had the appearance, as if the gel had been cut with a sharp knife and then put together again. It has not been ascertained what the substance of the secondary rings was. They will be mentioned again in another connection. The effect of concentration of the ethyl alcohol was studied from one to nine cc of the alcohol to 50 cc of the gel. The effect on the narrowing of the intervals between the bands was progressive with

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[1] Proc. Tokyo Math. Phys. Soc., [2] 9, 442 (1918).

increase in the concentration of the alcohol. With ten or more cc of alcohol the gel set too quickly, so that it could not be poured into test tubes before setting.

Fig. 1

19—$CuSO_4$ solution poured on 3 hrs. after the gel had set.
20—$CuSO_4$ solution poured on 5 days after the gel had set.
21—$CuSO_4$ solution poured on 10 days after the gel had set.

There are two things that these added substances may do, both of which would influence the distribution and sharpness of the bands. The presence in the gel of another substance would alter the rates of diffusion of the two reacting substances. This would bring the places, where sufficient concentration is reached for precipitation, either nearer together or farther apart according as the rates of diffusion are retarded or accelerated. Another important factor in the formation of the bands is the concentration of the reacting substances necessary for precipitation to begin. This would certainly be modified by the presence in the gel of a substance which would increase or decrease the solubility of the precipitating substance. The change in the spacing of the bands in the gel is then due to a combination of the two factors, the change in the rates of diffusion of the reacting substances and in the solubility of the resulting precipitate. As far as was possi-

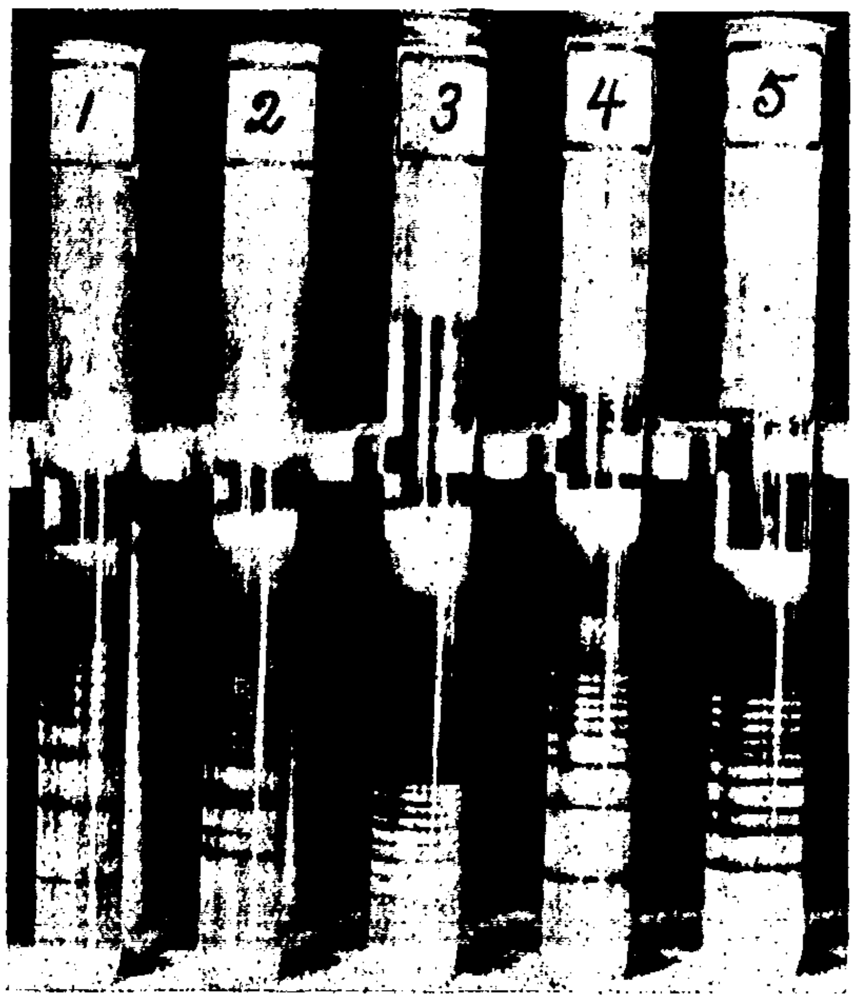

Fig. 2

Precipitations in silicic acid gel.
1—Precipitate formed by *m*/2 $CuSO_4$ and *m*/80 K_2SO_4, the latter being in the gel.
2—Same as 1 with 5 cc of C_2H_5OH per 50 cc of gel.
3—Same as 1 with 5 cc of C_3H_7OH per 50 cc of gel.
4—Same as 1 with 5 cc of CH_3COCH_3 per 50 cc of gel.
5—Same as 1 with 1 gm. of urea per 50 cc of gel.

ble to ascertain, there was no change in the nature of the precipitate.

In a gel where 5 cc of ethyl acetate were present in 50 cc, there resulted in place of sharp uniform bands of copper chromate, all sorts of fragmentary bands and queer scraps of precipitate. Some of these were remarkably symmetrical in outline and some bent and curled into fantastic shapes. There is often in this case and in others, a tendency to form beautiful spirals that wind about in the test tube like the threads of a screw. It was found that the ethyl acetate did not all dissolve in the acidified silicate solution and was present both within the resulting gel and on its surface in the form of small globules. The drops on the surface were lifted off by the $CuSO_4$ solution, thus giving it an uneven surface from which diffusion started. In fact, this etching of the surface was plainly visible. The droplets within the body of the gel caused an uneven distribution of the interacting salts. The result was that there were very irregular bands and pieces of bands bent into various strange shapes, the nature of which can be seen in the photograph in Fig. 3. The mere mutilation of the surface from which the diffusion takes place did not necessarily result in a deformation of the bands. So it would seem that the enclosed droplets are the chief cause of these deformations.

Gels containing 0.2 to 0.3 gm of finely powdered kaoline, $BaSO_4$, PbO_2, flowers of sulphur, charcoal, coke, bone black, and pumice in 50 cc were prepared. These gave sharp uniform bands provided the powder was fairly uniformly distributed in the gel. This was best accomplished by soaking the powders for some time in water before mixing with the silicate and acid. If the dry powders were stirred up with the mixture, it was easy to see that they were not uniformly distributed in the resulting gel. In these cases, the bands of copper chromate were always very irregular and broken up. This was especially true of charcoal, bone black, and kaolin where adsorption would make the diffusion all the more irregular. Sapo venetus was very effective in producing irregular bands, for this produced little centers where the $CuSO_4$ was used up in the formation of insoluble soap. This was evident by the dots of the deep blue copper soap scattered irregularly through the gel. It was also noticed that when the mixture of water-glass solution and acid was shaken for some time and poured just before it would set, then there were streaming cloud-like precipitates with curved bands of the copper chromate running parallel to their outer boundaries. Some of these are shown in Fig. 4. In all these cases where either some added substance or the structure of the gel interferes with the uniform diffusion of the reacting substances, there result irregularities in the rhythmic bands that are formed.

Fig. 3
Copper chromate precipitate where 5 cc of ethyl acetate was added to 50 cc of the gel.

Stansfield[1] has made a considerable number of experiments to show the effects of the relative concentrations of the reacting substances and their relative rates of diffusion on the phenomena of rhythmic precipitation. He comes to the conclusion that the greater the difference in the rate of diffusion of the two interdiffusing substances the farther apart will be the bands of precipitate. This difference in the rates of diffusion may be due to the nature of the substances, the

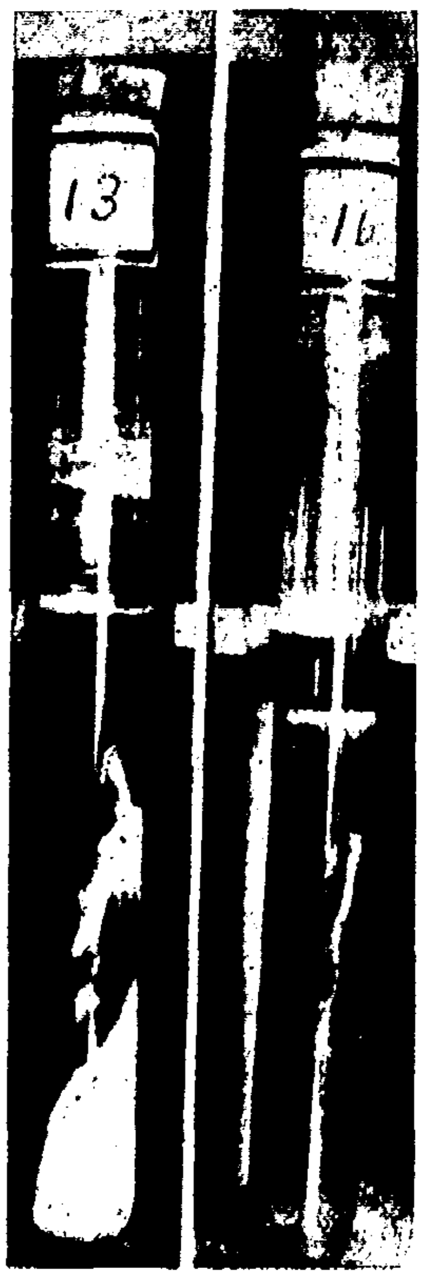

Fig. 4
Copper chromate precipitate in a gel that was poured just before it set.

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[1] Am. Jour. Sci., [4] 43, 1 (1917).

medium in which they move, and their relative concentrations. This can be illustrated by allowing a copper sulphate solution to diffuse into a slightly alkaline silicic acid gel containing various amounts of potassium chromate. The smaller the concentration of the chromate the farther apart will be the bands of copper chromate. If the amount of potassium chromate in the gel is kept constant, the bands become closer together as the concentration of the overlying copper sulphate solution is decreased. When the concentrations of the $CuSO_4$ and the K_2CrO_4 become nearly equimolecular, the bands come so close together as to form a continuous precipitate and finally as the concentration of the $CuSO_4$ is farther decreased there is no precipitate in the gel at all. This is true in the case of other combinations of precipitate forming solutions. These experiments are best done in the following way: The acidified water-glass containing the K_2CrO_4 is sucked up into ordinary glass tubes. After the gel has set, the tube is cut into convenient lengths and put into the solution of $CuSO_4$. The bands are very sharp in such tubes and are convenient for comparison and measurement. Stansfield shows how all these phenomena may be explained by the ordinary laws of diffusion.

The following experiments are given because they are certainly due to simple diffusion and precipitation and their study throws light on the things that take place in the rhythmic precipitation of substances in gels.

When a liter flask of hydrochloric acid gas is connected with a similar flask of ammonia gas by means of a glass tube several meters long and about 4 mm internal diameter, the NH_4Cl formed is deposited in a series of sharp bands on the wall of the tube. These bands run around the tube at right angles to the direction of the diffusion. They vary in width from 0.5 mm to 5 mm. Between them is a faint deposit of NH_4Cl with an occasional sharp clear band. At the bottom of the tube the loose NH_4Cl gathers into little heaps and valleys like the cork dust in a vibrating tube. The bands are always built toward the gas that diffuses less rapidly.

The formation of the bands may be explained thus. Suppose that we were to start with the two flasks containing equal volumes of ammonia and hydrochloric acid at the same temperature and pressure. The gases diffuse out into the air of the connecting tube till they meet. In the case cited this would be a little beyond the middle of the connecting tube nearer the hydrochloric acid containing flask. They will diffuse into each other till the concentration is such that solid NH_4Cl is formed. The sharp heavy band is deposited where the ammonia and hydrochloric acid have the greatest concentration. Small amounts of HCl and NH_3 on either side of the band rise to the light fog that is between the bands of NH_4Cl. The space for some distance is cleared of the interacting gases. They again diffuse toward each other and meet at some point nearer the less rapidly diffusing gas, the HCl in this case. They diffuse into each other. The point of greatest concentration will be where they met the second time and here the second ring will be deposited with its thin fog on either side. And so the process continues.

When H_2S and Cl_2 were put into the flasks and connected by a tube as before, the bands of sulphur formed were very wide, 20 to 30 cm, and shaded off gradually into the intermediate clear space. This is probably due to the fact that these gases react more slowly than the HCl and NH_3 and require a greater concentration before the precipitation of sulphur occurs. With SO_2 and H_2S there was no distinct banding of the precipitated sulphur because their rate of reaction is still slower than that of the Cl_2 and H_2S.

NH_3 and HBr make very sharp bands as also do NH_3 and HF. In the latter case the NH_3 was at a lower concentration than the HF. The flask containing the HF was lined with paraffin but the connecting tube was left uncovered. It showed no evidence of having been etched by the HF.

When the flasks containing the NH_3 and HCl were connected by tubes in a vertical position, the bands were always built downward whether the NH_3 or the HCl was in the upper flask. The flasks may also be placed side by side and connected by a tube bent back on itself, that is into a long U-tube. This offers the most convenient form for keeping the two flasks at the same temperature conditions. A farther study of these phenomena is in progress.

These experiments show that the chief factor in the formation of rhythmic precipitates is a difference in the velocity of diffusion of the interacting substances. It is not necessary to assume, as is suggested by Holmes,[1] that the precipitate formed acts as a retarding membrane. In fact, it is evident from the examination of a large number of different substances that were deposited as rhythmic bands, that the precipitated substance occupies only a small portion of the cross-section of the gel.

Another important factor in the formation of banded precipitates, is the relative concentration of the reacting substances that must be attained before the solid phase is deposited. In the case of the interaction of gases, the rate of the reaction that forms the solid and in the gels, the degree of supersaturation that may obtain, also play important roles. These factors have not been studied to any extent from a quantitative standpoint. The differences in the precipitation of the NH_4Cl and sulphur, described in this paper, are illustrations of the effects of the precipitation concentration and the speed of interaction of the substances brought together. An interesting example of the effect of supersaturation is the following: A half molecular $CuSO_4$ solution was allowed to diffuse into a slightly alkaline silicic acid gel, prepared as described before and containing 1 cc of pyridine in 50 cc of the gel. The progress of the $CuSO_4$ could be readily followed by the deep blue color resulting from its combination with the pyridine. The gel remained clear for some weeks. Then bands of greenish blue crystals of the copper sulphate-pyridine compound were formed, which became more distinct as the crystals grew at the expense of the compound which was in solution in the gel. It is possible that the forma-

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[1] Jour. Am. Chem. Soc., 40, 1187 (1918).

tion of the secondary bands between those of copper chromate in the gel containing cane sugar, mentioned elsewhere in this paper, may have a similar explanation. In a gel that was very nearly neutral and which contained $^1/_{80}$ molecular K_2CrO_4, the bands of copper chromate were always formed in the midst of the gel which was already blue with the $CuSO_4$. That is, the $CuSO_4$ had already penetrated a considerable distance beyond the place where the formation of a band of copper chromate took place, and where the gel was most supersaturated with respect to copper chromate.

Summary

A number of experiments are described which show that the uniformity of the bands formed in rhythmic precipitation is influenced by the structure of the gel. This non-uniform structure may be brought about by allowing the gel to stand for some time before the solution is poured upon it or by pouring the mixture of sodium silicate and acid just before it sets.

The bands of the precipitate may be modified by the presence in the gel of substances such as alcohols, urea and sugar, which modify the rates of diffusion of the reacting substances and the solubility of the precipitated substances.

The rhythmic bands may be broken up more or less by the presence in the gel of various inert powders unevenly distributed and by the presence of small particles of soap, all of which tend to interfere with the uniform diffusion of the reacting substances.

A series of experiments on the formation of rhythmic bands by the interaction in narrow tubes of such gases as NH_3 with HCl, HBr, or HF; and H_2S with Cl_2 or SO_2, have been described and their relation to the phenomena in gels pointed out.

In addition to the effects of diffusion and the factors that modify it, there are also the effects of the concentrations necessary for precipitation to take place, the velocity of the reaction that takes place which forms the precipitate, and the degree of supersaturation which the resulting substance may reach in a given medium, before precipitation takes place.

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THE SCATTERING OF LIGHT BY DUST-FREE LIQUIDS.

BY W. H. MARTIN

1. Historical

If a strong beam of light be concentrated in a flask of water and viewed in a direction at right angles to that of the beam against a black background, the path of the light through the liquid is clearly visible. The cause of this "light cone" in carefully distilled liquids has been a subject for controversy at least since 1869, when Lallemand and Soret disagreed as to its cause. Lallemand[1] thought it a property of the liquid itself, while Soret[2] attributed it wholly to particles suspended in the liquid.

Some years later the problem was attacked and apparently settled by two different experimenters: Spring[3] described the preparation of "optically empty" water by two different methods, while Tyndall described the preparation of optically empty air by filtration through cotton-wool. Lobry de Bruyn and Wolff[4] confirmed Spring's work, preparing dilute solutions of sodium chloride and other salts, which they said scattered no light. They found, however, that solutions of saccharose, raffinose and phosphomolybdic acid could not be made optically empty by the methods used. "Nous croyons pouvoir tirer de nos recherches la conclusion, qu'il faut répondre affirmativement à la question posée comme titre de cette communication, et que par conséquent les solutions 'véritables' de substances à poids moléculaire elevé sont susceptibles de provoquer la diffraction de la lumière. Ce résultat indique donc la continuité entre les solutions vraies et les pseudo-solutions."

Several years ago, when some experiments on the be-

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[1] Comptes rendus, **69**, 1294 (1869).

[2] Ibid., **69**, 1192 (1869).

[3] Rec. Trav. chim. Pays.-Bas., **18**, 153, 233 (1899). See also **19, 24, 25, 29.**

[4] Ibid., **23**, 155 (1904).

havior of solutions of partially miscible liquids at the saturation point were being carried out in this laboratory by W. J. Fawcett,[1] it was suggested that the reason for the difficulty in supersaturating such solutions was that dust particles served as nuclei for the formation of the second phase. The author of the present paper, in the winter of 1912–13, attempted to remove the dust from liquids by Spring's method, but found it impossible to obtain optically empty liquids either by this or by other methods, and came to the following conclusion:[2]

"The general result was that the light beam in water and in aqueous alcohol—the two liquids most thoroughly investigated—consists of two parts; a part which is removed by each of the methods of purification and a part which is not removed by any of the methods and which *is constant in intensity irrespective of the method of purification used.* This permanent part is faint and is plane-polarized, and can be seen only if the room is dark, the light beam very intense, and the vessel clean and free from striae."

As far as I am aware, this is the first conclusive evidence for the scattering of light by pure liquids—or indeed by solids and gases. This paper was presented at the meeting of the Royal Society of Canada in May, 1913. Almost at the same time Le Blanc and Kangro, in a preliminary communication,[3] presented to the Deutsche Bunsen-Gesellschaft in August, 1913, and elaborated later[4] describe their attempts to repeat Spring's preparation of optically empty liquids. They found they could still see the light cone if all foreign light was excluded; that strong solutions scattered more light than weak; and that solutions of colloids scattered more light than solutions of crystalloids. Finally they described an elaborate method of distillation, which, however, did not

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[1] Proc. Roy. Soc. Canada, **7**, III, 219 (1913).

[2] The Tyndall effect in liquids. Proc. Roy. Soc. Canada, **7**, III, 219 (1913); Chem. Abs., **8**, 3739 (1914).

[3] Zeit. Elektrochemie, **19**, 794 (1913).

[4] Zeit. phys. Chem., **87**, 257 (1914).

give optically empty water. The authors were nevertheless unwilling to grant that the dust-free liquids might scatter light. "To attribute the scattering to the dissolved salt molecules is a belief for which no chemist or physicist is ready. It is much less far-fetched and more plausible to ascribe the scattering to fine suspended particles * * * * "

In 1915 Cabannes[1] observed the scattering of light in dust-free air, and a short time later R. J. Strutt[2] carried out some experiments—the results of which are discussed later in this paper—in which he measured the relative intensity and the polarization of the light scattered by a number of gases.

The conception that dust-free liquids and gases scatter light is one which seems to have been gradually forced on the experimenters more or less against their will, largely because Tyndall and Spring, by their classical researches on the removal of dust particles, had left such a strong impression that the scattered light was entirely due to this dust.

The very noticeable light scattered by many organic liquids (see p. 487) was observed by Lobry de Bruyn, who, however, called it fluorescence,[3] apparently because he noted that a picric acid filter cut off the light. In this conclusion he appears to have disregarded the fact, experimentally shown by Tyndall, that very small particles scatter to an appreciable extent only the short wave lengths of light. Spring,[4] too, observed that the cyclic organic compounds showed this faint blue "fluorescence" to a much greater extent than did aliphatic compounds. There can be no doubt that these two men, and probably many others, have observed the scattering of light; but, lacking any strict definition of fluorescence, they failed to distinguish between the two phenomena.

The work begun in 1912–13 by the author, was interrupted

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[1] Comptes rendus, 160, 62 (1915); see also 168, 340 (1919).

[2] Proc. Roy. Soc., 94A, 453 (1918); 95A, 155, 476 (1919); Nature, 104, 412 (1919).

[3] Rec. Trav. chim. Pays-Bas, 23, 163 (1904).

[4] Ibid., 16, 1 (1897).

at that time to be taken up again recently. In view of the increased interest attached to the early results by reason of the later developments in the study of light-scattering, it is thought best to include in the present paper a more complete account of some of the results then obtained.

2. Preparation of Dust-Free Liquids

Three methods for removing the suspended motes were used: distillation, envelopment, and cataphoresis.

A. *Distillation of Water.*—The method of distillation in vacuum with the special form of apparatus (Fig. 1) was found to be much more convenient and more generally applicable than the other methods, and later was used entirely for the removal of motes from liquids of various kinds. Ordinary distillation of water in air or even in vacuum with boiling removes very few of the motes. With the apparatus shown the distillation can be conducted at a temperature far below the boiling point of the liquid and *without ebullition.*

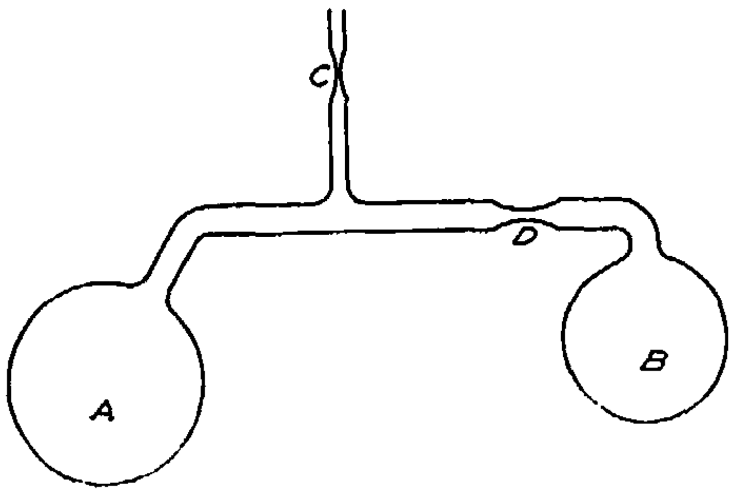

Fig. 1

Sufficient water is put into the bulbs to more than half fill each of them. By heating or by the use of an air pump the liquid in the bulbs is boiled until about one-third has been evaporated, after which the apparatus is sealed off at C, care being taken that no air is left in the bulbs. By keeping the bulb A 10° warmer than B a distillation without boiling is effected in a few hours. The first distillates are shaken back from B to A so as to wash back the dust. In most cases the motes were all removed after four distillations. The tube T serves as a reflux condenser in which there is continuous condensation of the liquid. After distillation is completed the bulb B is sealed off at D.

After the fourth distillation of water there remain no motes, but still there is visible a light cone or opalescence. It is a bluish haze, faint but very definite, and repeated distillations up to ten times do not lessen its intensity. Distillations with the bulb A at 100° and B at 90°, and again with A at 20° and B at 0° give distillates with the same opalescence.[1]

Fractional Distillation

By using an apparatus consisting of four bulbs of decreasing size all connected and sealed off with vacuum, and by properly adjusting the temperatures of the various bulbs some water was fractionated three times, but no difference whatever between any of the fractions could be observed.

Distillation in Quartz

Since glass is measurably soluble in water, it was thought possible that the light was scattered by some siliceous suspension from the walls of the vessels. If so it seemed unlikely that quartz and soft glass would give rise to the same amount of light scattering. When a pair of quartz bulbs (Fig. 1) was used, the distillate showed the same amount of light-scattering as in the glass bulbs. The apparatus afterwards constructed to measure quantitatively the light-scattering showed this to be true within the limits of experimental error. The error was, however, larger here than for other measurements, since the quartz had air inclusions which reflected a good deal of light and made it difficult to get consistent results.

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[1] In these experiments as in all those described in my former paper, the intensity of the light-scattering by different liquids was judged by passing the same beam of light alternately through the two bulbs held side by side. The quantitative method used in Section 3 of this paper had at that time not been developed.

After the measurements had been taken the 40 cc of water in the quartz bulb B was distilled back again to A so that any dissolved quartz might collect where the last drop evaporated. It proved impossible to find any residue even with a microscope, although one drop of distilled water evaporated on glass leaves a residue visible to the naked eye. The only evidence that there was any residue in the quartz bulb was the fact that, when condensation first occurred on the dry bulb, a ring formation of droplets was seen at the place where the last drop of water had evaporated. The solubility of quartz must then be negligible compared to the solubility of glass, and it seems, therefore, certain that the scattered light can not be attributed to any suspended siliceous material from the glass.

B. *Envelopment.*—Using Spring's method; gelatinous precipitates of aluminium, cadmium, and zinc hydroxides were precipitated from dilute solutions of their sulphates by addition of slight excess of potash. Solutions were prepared of

Aluminium sulphate,	7 g. per litre
Zinc sulphate,	20 g. per litre
Cadmium sulphate,	5 g. per litre

These were precipitated in each case in corked Erlenmeyer flasks by slight excess of potash, shaken and left to settle for a week. The resulting liquids in a condensed beam of light were found to be free from motes, but in every case the blue opalescence remained equal to that of pure water.

C. *Cataphoresis of Water.*—The apparatus consisted of a glass bulb with two side tubes containing platinum electrodes separated from the bulb by parchment partitions. The whole was filled with distilled water and a potential of 110 volts was maintained over the terminals for several weeks.

Experiments showed that in five days the motes were all removed and that the opalescence was then the same as that of the best water obtained by distillation in vacuum. Two months additional cataphoresis made no further reduction in the opalescence. That the dust had not settled from long standing alone was shown by comparing with a similar bulb of water left standing for the same time undisturbed.

It seemed, therefore, certain that the light-scattering observed in water and other distilled liquids was not caused by foreign particles, but was a property of the liquids themselves, and quantitative measurements of its intensity, were therefore, undertaken.

3. Measurement of the Scattered Light

A. *Preparation of the Liquids.*—All the liquids investigated, ranging in boiling points from —10° (sulphur dioxide) to 250° (monochloronaphthalene) were freed from motes by the method of distillation in vacuum described above. No special precautions were taken to free the liquids of dissolved volatile impurities, as is proved later (see page 487) that in general liquids with high light-scattering power, with the possible exception of carbon bisulphide, have high formula weights and proportionately high boiling points. Consequently these could not be present in large amounts in the distillate unless the latter were itself a high-boiling liquid, and in this case its light-scattering power would be but slightly affected by the presence of impurities.

Kahlbaum's chemicals were used in all cases except methyl alcohol and benzene, which were Baker's C. P., chloronaphthalene which was Eastman's, and sulphur dioxide which was the commercial article from a steel cylinder.

Before sealing off the distillation apparatus about one-third of the liquid was allowed to boil away, and after the distillation about one-third of the liquid remained in the large bulb; so that the distillation was a fractional one in which the middle fraction alone was used.

B. *Apparatus for Measuring the Intensity of the Light-scattering.*—A parallel beam of light from a carbon arc (about 60 V, 12 A) passed through a narrow horizontal slit S and was focused by a lens L in the middle of the bulb B of the liquid to be studied; then, after traversing a cell C of ammoniacal copper sulphate solution to make its color comparable with that of the scattered light, it fell on a piece of white paper at the back of the box. A quinine sulphate filter Q was used to prevent any possible fluorescence, although it made no noticeable difference. A small section (about 1 cm) of the beam of light passing through the liquid was observed through T, and appeared as an oblong of light about 1.5 mm wide. It was found that the lens L made this oblong brighter and its edges more definite. The image of the slit R, illuminated by light from the paper P, was reflected in the mirror M and was seen in focus beside the oblong of light. The whole box and its contents except the bulb of liquid were painted dead black, and the tube T was stopped down with several black diaphragms to prevent reflection from its sides.

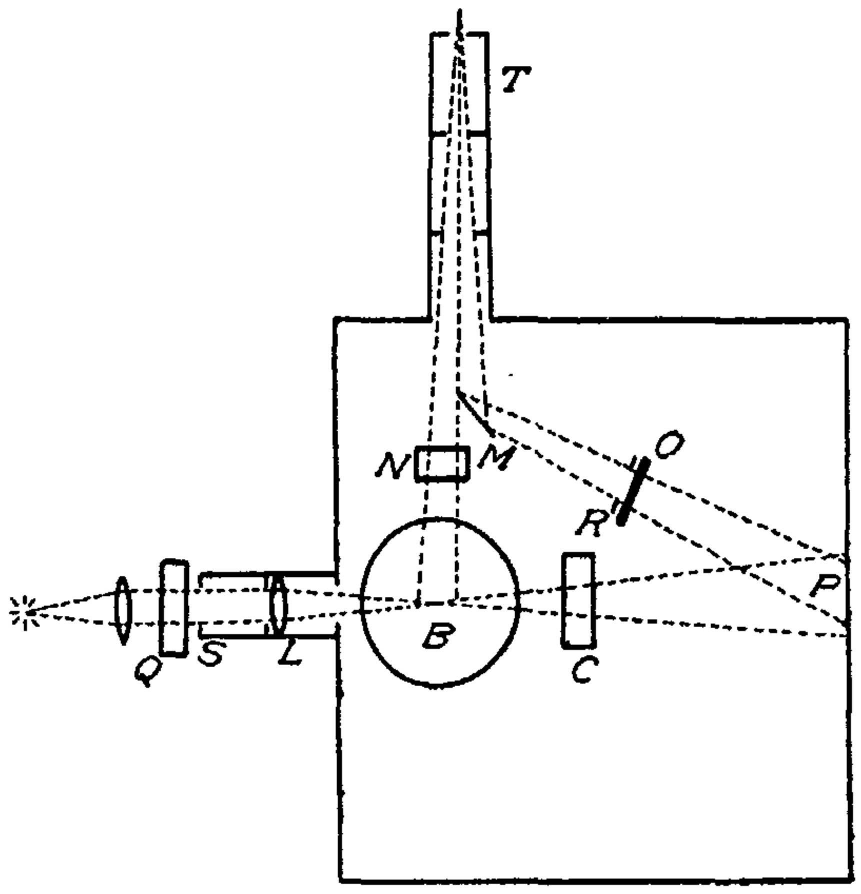

Fig. 2

By means of an optical wedge O of transmission 1 to 1/10 calibrated with an accuracy of about one percent, and supplemented by a number of uniformly fogged photographic plates of a transmission measured photometrically to the same accuracy, the light from the back of the box was matched with the scattered light from the bulb. In this way a comparison of the intensity of the light scattered by the various liquids was obtained. For measuring the extent of the polarization a Nicol was placed at N and readings of the intensity were taken with the Nicol in two positions at right angles to one another. A very little light was reflected from the glass bulbs containing the liquids, but not enough to seriously interfere with the measurements.

C. *The Relative Intensity of the Scattered Light.*—The following results are calculated from the averages of a great many readings, generally 18 or 24, made in sets of 6, each set made on a different occasion and with new adjustments. Very few results calculated from individual measurements differed by more than 10 percent from the average result thus obtained. A typical set of scale readings, in which a decrease of 1 in the scale reading corresponds to an increase in the light-scattering power by a factor 1.176, is as follows:

Heptane—13.3, 12.5, 13.8, 13.6, 13.4, 13.3. Average, 13.3.

The relative intensities of the scattered light (toluene = 1) calculated from three such sets of readings as the above are as follows:

Heptane—0.390, 0.384, 0.348.[1] Average, 0.374.

Table of the relative intensities of the light scattered by different liquids:

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[1] The agreement between the individual measurements would warrant the expectation of a much better agreement between the results calculated from the averages of the sets of 6 measurements. The variation in these results was found to be largely attributable to the variation in the illuminated area at the back of the box, caused by the slight difference in size and shape of the bulbs. It would probably be better to use parallel light and vessels with plane sides.

Liquid	Formula weight	Relative intensity of scattered light (toluene = 1)	$\frac{\text{R liquid}^{1}}{\text{R toluene}}$
Inorganic Compounds:			
Water	18	0.060	0.074
Sulphur dioxide	64	0.400	0.276
Aliphatic Compounds:			
Methyl alcohol	32	0.160	0.162
Ethyl alcohol	46	0.180	0.279
Ether	74	0.236	0.467
Ethyl acetate	88	0.210	0.488
Isobutyl chloride	93	0.375	
Heptane (mixture of heptanes)	100	0.374	
Isobutyl butyrate	144	0.320	
Aromatic Compounds:			
Benzene	78	0.91	0.864
Toluene	92	1.00	1.00
Chlorobenzene	112	1.52	1.09
Ethyl benzoate	150	1.55	1.39
Chloronaphthalene (alpha)	162	4.30	2.19

It is evident from the above results that there is a relation between the formula weight and class of substance on the one hand, and the intensity of the scattered light on the other hand:

(1) Aliphatic compounds scatter relatively little light; Benzene and its derivatives scatter decidedly more light; Chloronaphthalene, a compound with two benzene rings in its formula, scatters light to a still greater extent.

(2) The intensity of the scattered light with certain exceptions increases with increasing formula weight for the same class of compounds.

A great many physical properties, of course, bear some relation to the formula weight and chemical formula of the compound. For example the refractive index is found to be considerably greater for benzene and its derivatives than for aliphatic compounds, and greater still for naphthalene and its derivatives.

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[1] See page 488 for meaning of R liquid.

Lord Rayleigh, before any experiments on light-scattering by dust-free gases and liquids had been made, formulated a relation between the index of refraction of the medium and the light-scattering caused by particles in the medium. According to his equation[1] the intensity of the scattered light for different media and for any given wave length of light is proportional to $\frac{(\mu - 1)^2}{n}$, where μ is the index of refraction and n the number of scattering particles per unit volume. This relation was deduced to apply to the light-scattering by any suspension of spherical particles of dimensions small compared to the wave-length of light. Its application to dust-free media would rest on the assumptions that the media are "discontinuous" and that there are present in the media secondary and spherical sources of light.

R. J. Strutt[2] has shown that, within the limits of his experimental error, the relation given above, where

$$n = \frac{\text{Density}}{\text{Formula weight}},$$

held true for the gases investigated.

In the case of liquids, by giving n[3] the same meaning, the relative values of (R liquid =) $\frac{(\mu - 1)^2}{n}$ have been listed in the above table for the various liquids, the value R toluene being taken as unity. It appears from the table that, although the relation does not hold so well for liquids as for gases, there is, nevertheless, some agreement between the observed and calculated values.

D. *The Polarization of the Scattered Light.*—Readings of the intensity were taken with the Nicol in two positions at right angles to one another. It was found that in every case the vibrations of the scattered light were transverse to the direction of the exciting beam. The results are given in

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[1] Phil. Mag., 47, 375 (1899); Collected Works, Vol. 4, 397, Equation 14.

[2] Proc. Roy. Soc., 95A, 155 (1919).

[3] In assigning a value to n the ordinary formula weight derived from the formula has been used. There is no generally accepted way of defining the formula weight of a pure liquid.

Column I of the following table. Column II gives the values obtained by R. J. Strutt for the corresponding gases:

Liquid	I $\frac{\text{Intensity in plane of pol'n} \times 100}{\text{Intensity in plane at right angles}}$	II Results for the gaseous phase (R. J. Strutt)
Inorganic Compounds:		
Water	6.7	
Sulphur dioxide	22.0	
Aliphatic Compounds:		
Methyl alcohol	7.0	
Ethyl alcohol	7.1	
Ether	9.3	1.7
Ethyl acetate	22.8	
Isobutyl chloride	18.0	
Heptane	13.4	
Isobutyl butyrate	17.3	
Aromatic Compounds:		
Benzene	54	6.0
Toluene	54	
Chlorobenzene	52	
Ethyl benzoate	55	
Chloronaphthalene (alpha)	78	
Carbon bisulphide[1]	70	12.0
Colloidal silica solution	0.25	

It appears from the above results:

(1) That for those substances which scatter very little light, the polarization is fairly complete; and that the polarization decreases as the light-scattering power increases.

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[1] Experiments on carbon bisulphide and solutions of carbon bisulphide and methyl alcohol of various strengths gave results which seemed unreliable on account of the evident discoloration of the carbon bisulphide in the light. They seemed to indicate, however, that carbon bisulphide, a liquid with an extremely high refractive index, scatters a great deal of light which is but slightly polarized. On the other hand, alcoholic solutions of carbon bisulphide scattered about the amount of light one would expect from their dilution, but the scattered light was, contrary to expectation, very largely polarized and the amount of polarization increased with the dilution.

(2) That the scattered light is much less completely polarized by the liquid than by the corresponding gas. (It is noteworthy, however, that where data for both liquid and gaseous form are at hand—namely, for benzene, ether and carbon bisulphide—the order of these three substances when arranged according to their polarization is the same for both phases.)

(3) That the light scattered by any of the liquids studied is very much less completely polarized than that scattered by a colloidal silica solution.

E. *May the Phenomenon be Called Fluorescence?*—The light scattered by all liquids is sky-blue in color when the light of the carbon arc is the exciting source. This means that the shorter wave lengths of light are scattered to a much greater extent than the long (according to Lord Rayleigh's relation[1] the light scattering varies inversely as the fourth power of the wave length).

The scattered light was too faint to observe visually with a spectroscope, but by the help of some Wratten monochromatic light filters, which excluded all the exciting light except a narrow band of the spectrum, the following results were obtained for all the liquids tried:

(1) Exciting light of any color in the visible spectrum, from faintest violet to the beginning of the yellow, was scattered; with exciting light of wave length longer than yellow no scattering could be observed.

(2) The scattered light always had the same color as the exciting light whatever the color of the latter.

(3) A quinine sulphate cell in the path of the exciting light did not noticeably change the intensity nor the polarization of the scattered light.

Previous work by R. J. Strutt showed that for gases and for the one liquid investigated—ether containing dissolved water—the scattered light has the same spectrum as the exciting light.

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[1] Phil. Mag., 47, 375 (1899); Collected Works, Vol. 4, 397.

From the information at hand it would appear, therefore, that taking the generally accepted criterion of fluorescence as being alteration in wave length, the light emitted by the liquids studied—which has been sometimes looked upon as fluorescent—is really scattered light. The author contemplates the spectroscopic examination of the emitted light to obtain further data for the various liquids.[1]

Many esters and other high-boiling compounds showed before purification a distinct blue-green fluorescence. This was removed by vacuum distillation in the case of ethyl benzoate, the only one studied, and must, therefore, have been due to some impurity.

F. *The Effect of Change of Temperature.*—Measurements of the light scattered by water and toluene were made at 20° and again at 60°, but the variation in the intensity of the scattered light, if any, was within the experimental error of the readings.[2]

Summary.

(1) A method of preparing dust-free liquids by simple distillation in a vacuum is described.

(2) Liquids were found to scatter light; the short wave lengths being scattered to a much greater extent than the long.

(3) A relation, formulated by Lord Rayleigh and verified in the case of gases by R. J. Strutt, connecting the index

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[1] Since this paper was sent in a photograph of the spectrum of the light scattered by chloronaphthalene has been taken and shows only the line spectrum of the glass mercury lamp used as the source of light. There is no sign of continuous spectrum. Since moreover chloronaphthalene is the liquid which one would most suspect from its formula of showing fluorescence there can be no doubt that the phenomenon observed is true scattering.

[2] Since the intensity of the light-scattering was found to vary approximately as $\frac{(\mu - 1)^2}{n}$, any considerable change in light-scattering with temperature would necessitate a change in n and, therefore, in the formula weight. Ramsay and Shields' surface tension measurements on a great many liquids (Zeit. phys. Chem., 12, 433 (1893)) led them to postulate for many liquids a formula weight which was independent of temperature, and for a few liquids—one of which was water—a formula weight which varied greatly with temperature.

of refraction of the medium and its light-scattering power, showed some agreement in the case of the liquids investigated.

(4) The scattered light is largely plane-polarized in the case of liquids which scatter very little light; and the polarization in different liquids decreases as the relative intensity of the scattered light increases. The polarization is much less complete for liquids than for gases.

(5) Evidence is given that the phenomena observed are due to scattering and not to fluorescence.

This research was begun at the suggestion of Professor F. B. Kenrick, and has been carried out under his direction.

Chemical Laboratory,
University of Toronto,
April, 1920

NEW BOOKS

The Engines of the Human Body. *By Arthur Keith. 23 × 15 cm; xii + 284. Philadelphia: J. B. Lippincott Company, 1920. Price: $3.00.*—This extraordinarily interesting book is the outcome of Christmas lectures at the Royal Institution in which the author presented the knowledge of the anatomists and physiologists from the view-point of the mechanical engineer. So far as possible, I shall let Professor Keith tell his story in his own words, pp. 29, 32, 59, 76, 84, 86, 89, 116, 175, 187, 222, 254, 261.

The muscles are to be considered as internal combustion engines. "In the engine of the motor cycle we saw that there was a pipe—the inlet pipe—which conveyed to the cylinder the explosive mixture made up of fine particles of petrol diffused through eight or nine times the same weight of air; then we saw another pipe—the exhaust pipe—which carried away from the cylinder the gases formed when the charge was exploded. Now there is not one pipe but several which enter the biceps muscle, only we name them not pipes but arteries, and they convey to the muscle not petrolised air but red arterialised blood. Then there are pipes which issue from the muscle and carry away from it, not waste gases, but dark venous blood. Only we do not call these vessels exhaust pipes, but veins. Then, too, we saw that a wire ended in the combustion chamber of the cylinder and carried an electric current which fired the explosive mixture and set the engine in motion. A cable of most peculiar 'wires' also enters the muscle; we call the cable a nerve, and the current or messages which it conveys to the engine are not electric but of a different kind, yet they serve the same purpose; they set the muscle in motion.

"If we look more closely we shall find that not only have the engines of the motor cycle and of the human machine pipes of a corresponding kind, but that through these pipes there passes a circulation which serves a similar purpose. Petrolised air is pumped through the circulatory system of the engine of the motor cycle; arterialised blood is pumped through the corresponding system of the muscular engines of the human machine. But the system of pumping employed in muscular engines is by far the superior. We have seen that in the 4-cycle internal-combustion engine only one stroke in four is really effective; the other three are spent on pumping or circulating the explosive mixture. The first stroke we saw drew in petrolised air and thus charged the cylinder with an explosive mixture; the second compressed the mixture into the combustion chamber; the third stroke, which is the only effective or driving one, is caused by the explosion; the fourth one sweeps out the waste gases through the exhaust. Thus three strokes out of every four are used to keep up the circulation of petrolised air through the engine. So far as driving power is concerned these three strokes are lost or wasted. Engineers are trying hard to make each stroke of the engine an effective or driving one. Dr. Dugald Clerk has succeeded in getting rid of two of them. He managed to do this in a very simple manner. He attached a pump to the engine in such a way that it forced a charge of petrolised air into the combustion chamber just when the piston had swept all the waste gases through the exhaust and was ready to begin a new stroke. Thus the first or suction stroke and the second or compression stroke became unnecessary;

in this way two strokes were saved. Many millions of years before man had thought about motor cycles, Nature had invented a method of making each stroke of the muscular engine effective. She did this by means of a wonderfully contrived pump called the heart. It is this pump which maintains a constant circulation through the muscular engine we are now considering—the biceps. Through the arteries it pumps into the muscle blood which contains both fuel and air—an 'explosive mixture'; the blood returns by the veins laden with waste products. The biceps does not look at all like the engine of a motor cycle, but when we look beneath the surface we see that they have corresponding parts."

In order to be sure that the biceps really acts as an internal combustion engine we must find out whether our muscles are supplied with an explosive mixture. "We can see that the blood which is being pumped into them through the arteries is bright red; that is because the millions of microscopic discs or red corpuscles, which float in the fluid or plasma of the blood, are charged with minute loads of oxygen. In the plasma there is a hydrocarbon compound—a kind of sugar—which serves as fuel or petrol for the muscle. Thus we find that the blood pumped into a muscle through its arteries is laden with the ingredients of an explosive mixture. The blood leaving by its veins has lost its bright color and is laden with waste products, especially carbon dioxide. The harder a muscle is made to work the quicker becomes the current of blood which passes through it, and the greater is the output of products of combustion. Heat also is generated. All these are signs that muscles act as internal-combustion engines, just as the engine of a motor cycle. But there is one important difference. In the motor cycle engine carbon dioxide is produced at the instant when the explosion occurs and the piston gives its driving stroke. This is not the case in the muscular engine. Sir Walter Fletcher and Prof. F. G. Hopkins found out that the carbon dioxide (CO_2) is not thrown off at the moment of contraction but afterwards. A process of combustion or oxidation therefore does take place in the muscular engine, only it does not occur as an explosion but in a slower and better regulated way. Yet it is clear that the muscle is an internal-combustion engine of a peculiar sort, very different and much superior to any kind which man has yet invented. Apparently the muscular engine builds up the materials supplied to it into a particular kind of fuel, which it can store and use when needed.

"There is another point in which a muscular engine like the biceps is greatly superior to mechanical engines. With the biceps we can give what length of stroke we will. We can make it move the forearm with a stroke which is only a twentieth of an inch in length, or we can make it bend the elbow through its full range from complete extension to comple flexion. We can make it work the forearm backwards and forwards at any point of its range of movement, quickly or slowly, gently or strongly. It is true that engineers can alter the strength and rate of the stroke of a mechanical engine by opening or closing the throttle valve, thus regulating the amount of explosive mixture admitted; but there is only one length of stroke—that to which the engine is set. Think for a moment what our case would be if the biceps had only one length of stroke. We should set it, I suppose, so that it could just reach the mouth in feeding. To make a delicate or short movement at the elbow would be impossible. We should have to bring the hand as far as the mouth or not at all. In the muscle-engine a method has been discovered of regulating the rate of combustion as well as length of stroke. Work is not performed by a series of unregulated explosions as in a motor engine, but by a regulated process of oxidation which we do not rightly understand as yet."

In a muscle like the biceps we have an engine which is made up of tens of thousands of microscopic cylinders, with combustion chambers which are so minute that the most powerful microscope has never revealed them. The essential difference between a muscle engine and a metal engine is that the former is a pull machine and the latter a push machine. Flesh engines exert their power by pulling, and changing their shape all the time; they have flexible piston rods which we call tendons or sinews.

"We must look closely at the foot lever if we are to understand it. It is arched or bent; the front pillar of the arch stretches from the summit or keystone, where the weight of the body is poised, to the pad of the foot or fulcrum; the posterior pillar, projecting as the heel, extends from the summit to the point at which the muscular power is applied. A foot with a short anterior pillar and a long posterior pillar or heel is one designed for power, not speed. It is one which will serve a hill-climber well or a heavy, corpulent man. The opposite kind, one with a short heel and a long pillar in front, is well adapted for running and sprinting—for speed. Now, we do find among the various races of mankind that some have been given long heels, such as the dark-skinned natives of Africa and of Australia, while other races have been given relatively short, stumpy heels, of which sort the natives of Europe and of China may be cited as examples. With long heels less powerful muscular engines are required, and hence in dark races the calf of the leg is but ill developed, because the muscles which move the heel are small. We must admit, however, that the gait of dark-skinned races is usually easy and graceful. We Europeans, on the other hand, having short heels, need more powerful muscles to move them, and hence our calves are usually well developed, but our gait is apt to be jerky.

"If we had the power to make our heels longer or shorter at will, we should be able, as is the case in a motor cycle, to alter our 'speed-gear' according to the needs of the road. With a steep hill in front of us we should adopt a long, slow, powerful heel, while going down an incline a short one would best suit our needs. With its four-change speed-gear a motor cycle seems better adapted for easy and economical travelling than the human machine. If, however, the human machine has no change of gear, it has one very marvellous mechanism—which we may call a *compensatory* mechanism, for want of a short, easy name. The more we walk, the more we go hill-climbing, the more powerful do the muscular engines of the heel become. It is quite different with the engine of a motor cycle; the more it is used the more does it become worn out. It is because a muscular engine is living that it can respond to work by growing stronger and quicker."

"In 1867 Professor Culmann, a famous Swiss engineer and mathematician, paid the bone builders of the neck of the femur a great compliment. The design they employed, he found, was exactly similar to that applied in the Fairbairn crane—the most perfect of all levers which man has invented for the lifting of heavy weights. Every beam of bone in the neck of the femur, he said, had been given the shape, thickness, and position which ensured the greatest economy of material. Everywhere in the body we find the same perfect design in the work of bone-builders."

The lubricating system is discussed with special reference to the ankle-joint. "The mechanism is a simple one. The rubbing surfaces of the two opposed bones are coated with a thin layer of cartilage, less than an eighth of an inch in thickness.....When one presses on the cartilage it yields or flattens, but when the pressure is withdrawn it springs out again, showing that the cartilage which lines joints is elastic and can serve as a buffer. Its surface, too, is always covered by a film of substance named synovia, which is not unlike white of egg in appearance, but so slippery that cartilage slips through our fingers should we try to grasp a bone by its articular end."

"Many men and women pass through life and never have cause to know that the easy movement of the human machine is dependent on a lubricant system—so perfectly does it serve their needs. Even at the age of seventy human axles and bearings may be as fresh and unworn as in the hey-day of youth. That bug-bear of the motor-driver—the sudden 'seizing' of joints—never troubles the drivers of the human machine. And yet to many people—especially as years crowd over them—a peculiar kind of 'seizing' does happen. From some cause we have not yet discovered, the lubricant system fails—in one joint or in several. Then the one cartilage plate begins to rub stiffly on its opponent, there is friction, and the articular plate wears in patches. The cartilage-builders, in place of melting down and becoming a slippery lubricant, remain obdurate and fibrous. The cartilage plates become leathery in consistence and ultimately worn through in places. The neighboring bone-builders, which are saved from all forms of friction in healthy joints, become disturbed by the grating in the articular plates and build wildly, throwing out knarled outgrowths of bone round the affected joints. With each movement a distinct creaking sound can be heard. This is the condition which we call chronic rheumatism; it is a veritable 'seizing' of the joints, because the lubricant system has broken down and we have not yet learned how to set it right again. The fault lies with the cartilage-builders. They grow as before and seek to make good the waste that arises from wear, but fail us in their final sacrifice. Instead of disappearing into oil, they turn to a stiff leathery residue which clogs and wears the surfaces of joints."

It is estimated that in a man of medium size the locomotive system weighs about eighty pounds, the bones weighing twenty pounds and the muscles about sixty. "This mass of machinery can be kept going only if it is supplied with certain materials; the muscular engines need to be continually stoked, while the masons in the bones and the lubricators at the joints must have their stores constantly replenished. Nature has met that need by adopting another contrivance—one which man discovered for himself long ago and with which we are all familiar—the pump. The heart of the human body is a pump—one which in the ingenuity of its construction, the delicacy of its regulation, and the effectiveness of its work far surpasses any model of man's invention."

When the body is in action, the heart has to pump at a much greater rate, and the heart always responds; it can increase its output to eight times or more the amount thrown out when the body is at rest.

"There is, however, another mechanism, beside that of increasing the output of the heart, which is employed to keep up the head of blood-pressure in the aorta. The terminal arteries leading to parts which are not required in severe bodily exercise, such as the organs of digestion and the brain, are constricted, thus economising the blood supply for the benefit of the muscles. When the muscles are set in motion their vascular stopcocks are turned on, while others are turned off. If the human machine were not supplied by this elaborate stopcock system, it would be impossible, as Dr. Leonard Hill has shown, to regulate the distribution of blood to the various parts of the body. Everyone knows how difficult it is to do head work immediately after a meal. The stomach and organs of digestion have then their vascular stopcocks turned full on; the needs of the stomach take precedence then to those of the brain. The brain, if it pushes hard enough, may obtain a blood-supply at the expense of that rightfully designated for the organs of digestion, but it is certain to have to pay for its greed sooner or later by headache. Every time we alter our posture—when we lie down, stand up, or sit upright—there is a slight and automatic switching of the tens of thousands of vascular stopcocks of the body. We are so unconscious of this silent activity that we find it difficult to believe that it actually occurs. A moment's reflection will show that this switching on and off must take place. When we rise from bed in the morning our feet and legs, were it not for the automatic turn-cocks, would draw all the blood from the head, for they have the advantage of gravity. Our hands would be engorged, while our shoulders would starve for blood; the organs in the upper part of the body would bleed into those in the lower part. The moment we stand up the vascular controlling centres in the spinal cord—being nerve exchange centres, receiving and giving thousands of messages of which we are unconscious—come into action and regulate the distribution of blood by turning off and on the vascular stopcocks of the body. This machinery may break down under certain circumstances, particularly after we have been kept standing in a hot stuffy room in a crowd of people. We may then have a sudden faint and collapse on the floor, because the vascular stopcock machinery has been over-taxed or broken down. The blood has been drained from the brain; hence the unconsciousness."

"In the contrivance of the pharynx we have one of the most remarkable examples of Nature's reflex or 'touch-the-button' mechanisms. Modern life has made us familiar with inventions of this kind, but they were discovered by Nature long ago. We press a button at the door of a high building, thereby setting an electric current flowing and a bell ringing in a chamber in its upper story, with the result that a bolt is drawn and the door opens to let us enter. In the hall we find a lift or elevator provided with a row of buttons—one for each story. We press one, an electric motor sets the lift in motion, and we stop at the desired landing. The lining membrane of the pharynx is studded with 'nerve-buttons' or transmitters. The breath passes and repasses without influencing them, but the instant a bolus of food, a mouthful of water, or the root of the tongue, which forms a piston for the pharynx as well as for the mouth, comes in contact with or touches them, then a stream of messages is thereby dispatched which flows upwards in the nerves until certain busy nerve exchanges are reached in the medullary part of the brain stem. From these exchanges relays of orders are issued which reach the muscular engines controlling the doorways of the pharynx; those leading to the larynx, to the nose, and to the mouth are promptly shut, while the sphincter engine, which guards the opening to the oesophagus, is ordered to relax. At the same time the muscular walls of the pharynx are thrown into action; the pharynx then becomes a force-pump;

all its openings are closed save one, and it is through that one that the bolus is forced within the upper end of the oesophagus. How essential the machinery of the pharynx is to life we learn when we see men or women in whom disease has damaged the controlling nerve centres in the medulla; all attempts at swallowing end in choking and spluttering. The reflex or 'touch-the-button' mechanisms of the pharynx have broken down. That such people may live food must be poured directly into the oesophagus by means of a tube attached to a funnel or filler."

"Although the stomach has all the outward appearance of being simply a soft-walled double-mouthed bag, yet when we look more closely it turns out, in reality, to be a great chemical factory. Food, the raw material from which tissue-fuel is prepared, occupies its great chamber; into its wall are built not only the miniature retorts which are to furnish the solution or juice needed nor chemical treatment of the food, but also myriads of microscopic engines which bring the retorts in contact with the food, and subsequently discharge such contents as are fit to be passed on to the next factory, the duodenum. When we begin a meal, even before food has actually reached the stomach, the miniature retorts all over the inner wall begin to manufacture and pour out a juice or solution that exercises a digestive action on the food exposed to it. The mechanism which sets secretion going is not of the 'touch-button' kind, for food applied directly to the lining membrane of the stomach does not excite the flow of gastric juice. The nerve exchange which controls the stomach is placed in the medulla, and the nerve messages which set it in operation are received from the mouth (nerves of taste), from the nose (nerves of smell), and from the eye (nerves of sight). It is strange that Nature should have adopted such means to set in operation the chemical factory which produces our gastric juice. She has, however, taken good care to protect her contrivance from abuse. For the controlling centre is fully excited only when there is need of food—when there is hunger and appetite. Hunger is the result of hard physical work, and therefore a price has to be paid in the form of labour before the stomach has sauce ready for another meal."

"That the human body was provided with a quick-acting or telegraphic system, medical men have known for hundreds of years. From its brain and spinal cord—the G. H. Q. of the human machine—they could see great cables of nerves issuing in all directions, linking the various members to the controlling centres. They knew that messages sped along the wires of the nerve cables, carrying orders and information from and to the commander-in-chief and the various departments of his staff. It is surprising to think that it is only in quite recent years that we began to suspect that the human body was also provided with a postal system. Our previous blindness was all the more remarkable because we knew that great colonies of simple units, such as make up living corals and sponges, did communicate with and control each other, and yet, as was well known, these colonies were unprovided with nerve systems. We were also aware that among primitive peoples, like the aborigines of Australia, there were neither postal nor telegraphic systems; one tribe communicated with another by sending out a messenger carrying a stick on which certain symbols were rudely carved. We ought to have suspected that, in the evolution of the human body, a postal system would precede a telegraphic one. That was not so, however. The first clear recognition that the human body possessed a postal as well as a telegraphic system was made by Professor Starling in 1904. Professor Bayliss and he found that the pancreas began to form and pour out its digestive juice upon the receipt of certain missives which were posted by the living units lining the upper part of the duodenum. The arrival in the duodenum of the acid contents of the stomach caused the dispatch of secretin, the substance or hormone which acts as a missive for stimulating the pancreas to action. Secretin is posted in the nearest letter-boxes or capillaries in the duodenal wall and is carried away in the general blood circulation, which serves for all kinds of postal traffic. In a postal system where there are no sorters and which must be conducted by an automatic mechanism, letters or missives cannot be addressed in the usual way. Their destination is indicated not by their inscription but by their shape. The molecules of secretin may be regarded as ultramicroscopic Yale keys sent out to search for the locks of letter-boxes which they can fit and enter. They fit and can enter only the letter-boxes of the pancreatic molecules, and hence they must circulate round the body until they automatically find their destination. What is still more wonderful in this system is that the letter-boxes, or we may call them locks, have a positive attraction for the key-missives which are destined for them.

"To such key-missives as are posted in and delivered by the general circulation, Professor Starling gave the name of hormones. The muscular engines of the body use the carbon dioxide which they cast into the circulation as a hormone or missive to inform the respiratory centre in the medulla of their needs and to stimulate it to action. The harder the muscles work the more is their need for oxygen and the greater is the quantity of carbon dioxide which has to be got rid of; the respiratory bellows must meet their requirements by ventilating the lungs more rapidly. The more the carbon dioxide accumulates in the circulation, the more acid becomes the reaction of the blood; and the more the blood becomes acid in reaction, the greater becomes its power to stimulate the respiratory centre. In this instance the carbon dioxide missives deliver their message while on their way to a final destination—the lungs. As our knowledge increases we see that a postal system is extensively used in the control or management of the human body."

"One example will suffice to illustrate how extensive the telephone service of the body is. A particle of dust is blown into the eye; its arrival is immediately announced to two exchanges; through one of these the incoming messages are transmitted to a central station some distance off, occupied by the driver units which can shut the eyelids. These driver units keep the eyelids shut as long as irritant messages come through from the eye; when the foreign particle is removed the messages cease and the driver cells sink into their usual state of wakeful quiescence. The particle of dust also sets up another group of messages, one which is transmitted to a small local exchange in communication with the lachrymal gland. The messages thus transmitted send the lachrymal gland into a state of activity; tears stream across the eye with the intention of washing away the offending particle of dust. Even when that has been got rid of, if damage has been done, the flow of tears continues as long as the irritation lasts. Thus Nature employs a kind of telephonic system for many and diverse purposes in carrying on the work of the human machine."

"Let us see how trunk calls are managed in the nerve system of the human body. A sharp fragment of stone falls within a shoe and presently works its way under the foot. With each step it presses against some of the transmitters in the sole and sets up messages, at first giving a mere feeling of discomfort, but afterwards becoming more urgent, giving a sense of intolerable pain. The brain is set into operation, with the result that the movements necessary for unlatching the shoe are undertaken and the offending body is discovered and removed. The instance is not unlike that which we have been following in connection with an epidemic in a country town. In the human body, however, the wire which carries messages from the sole of the foot does not pass through the local exchange in the spinal cord; it sends off merely a side branch to one, two, or more spinal exchanges and passes up the spinal cord until it reaches the first great exchange of the body—one which is situated where the spinal cord becomes continuous with the brain stem. Here the messages from the sole of the foot are automatically switched on to main trunk cables which carry them to a second exchange centre—one situated in the great masses of grey matter placed within the cerebral hemishere. It is in these grey masses that the messages from the sole rise up into the field of consciousness as painful senastions. The executive exchanges or departments of the brain lie still further on; they are spread out in the grey matter which forms the cortex or rind of the cerebral hemispheres. Hence the messages which have reached the basal masses and given rise to the sensation of pain have to be transmitted by a third relay or wires to the cortex of the brain before steps can be taken by the executive departments. To obtain relief the 'driver' cells of the cortex have to be set in motion. We have already seen that the 'driver' units, which exercise a direct control over muscular engines, are grouped round the local exchanges of the spinal cord. These driver cells we meet with in the cortex of the brain are 'master drivers'; they control the driver units in the local exchanges, and combine their actions so that the muscular engines carry out the movements which are determined on by operations effected within the exchange systems of the cortex. The cortex of the human brain is by far the most elaborate central exchange in creation.

"It is into this exchange, then, that messages dispatched from the sole of the foot pass, after being switched through two great exchanges and having travelled over three relays of nerve cables. Arriving in the cortical exchange they set going a machinery which leads to the master driver cells taking charge of the movements of the body. It was they which controlled the driver units of the local centres during the body movements which led to the removal of an offending stone from the shoe."

It would have been interesting to have quoted more passages but we must stop somewhere. This book is one in a thousand. It is fascinating from beginning to end. Books like this one are milestones in the life of a reviewer and life seems to be measured chiefly in Scotch miles. *Wilder D. Bancroft*

Inbreeding and Outbreeding. *By Edward M. East and D. F. Jones 21 X 15 cm; pp. 285. Philadelphia: J. B. Lippincott Company, 1919. Price: $2.50.*—The authors have discussed the important controlled experiments on inbreeding and outbreeding. The subject is presented under the following headings: introduction; reproduction among animals and plants; the mechanism of reproduction; the mechanism of heredity; mathematical consideration of inbreeding; inbreeding experiments with animals and plants; hydrid vigor or heterosis; conceptions as to the cause of hybrid vigor; sterility and its relation to inbreeding and cross-breeding; the rôle of inbreeding and outbreeding in evolution; the value of inbreeding and outbreeding in plant and animal improvement; inbreeding and outbreeding in man and their effect on the individual; the intermingling of races and national stamina.

On p. 137 the authors draw the conclusion that "inbreeding has but one demonstrable effect on organisms subject to its action—the isolation of homozygous types. The diversity of the resulting types depends directly upon the number of heterozygous heredity factors present in the individuals with which the process is begun; it is likely, therefore, to vary directly with the amount of cross-breeding experienced by their immediate ancestors. The rapidity of isolation of homozygous types is a function of the intensity of the inbreeding."

Inbreeding is not injurious merely by reason of the consanguinity, p. 139. "The only injury proceeding from inbreeding comes from the inheritance received. The constitution of the individuals resulting from a process of inbreeding depends upon the chance allotment of characters pre-existing in the stock before inbreeding was commenced. If undesirable characters are shown after inbreeding, it is only because they already existed in the stock and were able to persist for generations under the protection of more favorable characters which dominated them and kept them from sight. The powerful hand of natural selection was thus stayed until inbreeding tore aside the mask and the unfavorable characters were shown up in all their weakness, to stand or fall on their own merits.

"If evil is brought to light, inbreeding is no more to be blamed than the detective who unearths a crime. Instead of being condemned it should be commended. After continued inbreeding a cross-bred stock has been purified and rid of abnormailties, monstrosities, and serious weaknesses of all kinds. Only those characters can remain which either are favorable or at least are not definitely harmful to the organism. Those characters which have survived this 'day of judgment' can now be estimated according to their true worth. As we shall see later, vigor can be immediately regained by crossing. Not only is the full vigor of the original stock restored, but it may even be increased, due to the elimination of many unfavorable characters. If this increased vigor can be utilized in the first generation, or if it can be fixed so that it is not lost in succeeding generations, then inbreeding is not only not injurious but is highly beneficial. As an actual means of plant and animal improvement, therefore, it should be given its rightful valuation."

In regard to cross-breeding the authors say, pp. 141, 193: "Whether or not inbreeding in a race of plants or animals results injuriously depends primarily, as we have attempted to show, upon the hereditary constitution of the organism. The beneficial effect of crossing, heterosis, is a more wide-spread phenomenon. It may be expected when almost all somewhat nearly related forms are crossed together. Even plants or animals which show no harmful results of inbreeding are frequently improved thus in a remarkable way. *Moreover, this stimulating effect is immediately apparent in the individuals resulting from the cross. It is then at a maximum.*"

"In general, therefore, it can be said that differences in uniting germ plasms, when not too great, may bring about both more efficient development and increased fertility. Beyond that critical point of difference both fertility and vigor may be decreased, but fertility is usually the first to suffer—even complete sterility often being coupled with rampant growth. Nature thus steps in before a germinal heterogeneity which will endanger the health of the hybrid organism has been reached, and prevents multiplication entirely. This is an important physiological provision, since when great germinal differences exist there is reduced growth as well as sterility. Groups are thus set apart which may evolve within themselves by putting to good use heterosis and Mendelian recombination. What apparently happens is this: As germinal differences increase a point is reached at which the precise and complex machinery governing gametogenesis cannot do its work in the normal manner and sterility results, although under the same conditions developmental cell division goes on as usual. Beyond this degree of difference in the uniting germ plasms, even somatic cell division is affected."

In the chapter on the value of inbreeding and outbreeding in plant and animal improvement, p. 210, the authors say: "The origin of our more important domestic animals and cultivated plants is a matter on which there is no direct evidence. Among animals the ostrich is the only example of modern domestication; among plants not a single species of great economic worth has been brought into cultivation within historic times. If one must have a theory concerning their genesis, and what one of us does not delight in theorizing, the weight of evidence is in favor of a poly-phyletic origin in nearly every case. There is more than one wild species related to our modern dogs, cattle, swine and sheep, our wheats, barleys, apples and grapes; and these species will cross together and yield partially fertile hybrids. The wild relatives of the domestic forms were variable, so variable that many species were differentiated by natural causes; yet these species groups remained so well adapted to each other germinally that their hybrids are not completely sterile. What seems more reasonable than to suppose the original domestic races to have been produced by uniting two or more wild types and following this union of diverse germ plasms with more or less close inbreeding and selection?

"Such procedure, at least, has been the method whereby the clearly distinct and highly valuable breeds of the present day have originated. Take the draft horses as an example. In the early days of Europe native breeds were developed in every country for military purposes. Just how they originated we cannot say. The obvious fact is that none of them developed outstanding merits except the Flemish horse. Then improvement became rapid and steady. With an infusion of Flemish blood came the remarkable development of the Clydesdale in Scotland, the Shire in England, and Belgian in the low countries. Adding the Arabian blood which came in with the defeat of the Saracens in 732, and the wonderful Percheron of France came into being.

"Similarly the origin of all modern breeds of coach, light harness and saddle horses may be traced. To the native breeds of Europe were added the blood of the Barb or its derivatives, the Turk and the Arabian. In France, in Spain, in England and in Russia the history is the same—hybridization, then close breeding and selection. . . .

"While there has always been a certain amount of inbreeding as a necessary adjunct in building up breeds of livestock because of the necessity of mating near relatives in order to establish uniformity, the opinions of breeders have differed and still differ as to how long or how close intermating can be practiced with safety. Yet some of the most noted modern livestock strains owe their excellence to a close and continuous inbreeding that would be looked upon with misgivings by the majority of animal raisers. In fact, the inbreeding actually practiced was due more to enforced isolation, or the expenses or difficulty of securing unrelated animals with desirable characteristics, than to a firm belief in the desirability of the method. This might be said of the Shetland pony, the Angora goat, the Merino sheep in America, and of many breeds of dogs.

"Notwithstanding these facts, it would be a mistake not to recognize how great an amount of continuous and extended inbreeding has been practiced intentionally with the best of results after the general characteristics of a breed have been established. This is true as a generalized statement for the modern trotting horse and saddle horse which have shown so much speed; for the Shorthorn and Hereford, the most famous English breeds of beef cattle; for the Southdown and the other famous sheep breeds, the Shropshire, the Oxford and the Hampshire, to which it has given rise; and for almost all of the more famous breeds of dogs, not even excepting the large types, the mastiff, the St. Bernard, and the Newfoundland, which are derived from the Tibetan dog, *Canis niger*, as a foundation stock.

"Perhaps the most notable examples of conscious use of intense inbreeding in developing breeds of marked excellence are the dairy cattle of the channel islands, the Jersey and the Guernsey. One does not need to describe or to eulogize these strains. What they are and what they have accomplished in producing milk and butter fat are known throughout the world. Starting with the cattle of Normandy and Brittany as foundation stock, these two breeds have been built up by persistent use of a more intense system of inbreeding than is recorded in the history of any other strain of livestock. In fact, since 1763 rigidly enforced laws have prevented landing any live cattle whatsoever on either island except for slaughter. When one realizes that the larger of these two islands, that of Jersey, is but eleven miles long by six miles wide, he can appreciate the amount of inbreeding these laws have promoted."

Wilder D. Bancroft

James Cutbush. *By Edgar F. Smith. 15 × 10 cm; pp. 94. Philadelphia: J. B. Lippincott Company, 1919. Price: $0.50.*—In the preface the author says: "There is nothing thrilling in the following pages. They contain the story of the life-work of a very modest man deeply interested in and enamored with the science of chemistry, who sought also to inspire others and to familiarize the general public of his time with the intimate connection of chemistry with manufactures and things which enter so largely into every-day occupations. He was an active member of a small group of chemists who, in the early years of eighteen hundred, caused thousands of the laity to give thought to the possibilities of chemistry, and in addition was a pioneer in pyrotechnics, on which account he is deservedly entitled to every recognition."

James Cutbush was born in 1788 and was certainly a pharmacist in Philadelphia and probably a manufacturing chemist. He was also a Professor of Chemistry, Mineralogy and Natural Philosophy at St. John's College in Philadelphia and one of the first men to give extension lectures in chemistry. In 1809 the Chemical Society of Philadelphia had gone out of existence when Woodhouse died. In 1811 the Columbian Chemical Society was founded with Cutbush as its first president. In 1813 Cutbush published two volumes entitled "Philosophy of Experimental Chemistry." In 1814 he was appointed assistant apothecary general in the United States Army, in 1820 chief medical officer at West Point, and seventeen months later acting professor of chemistry and mineralogy at West Point. While at West Point, Cutbush did a great deal of work in pyrotechny, writing a book which appeared in 1825 after his death under the title of "A System of Pyrotechny."

While Cutbush made no discoveries comparable with those of Hare, for instance, he was influential in interesting the public in chemistry and was, therefore, a honorable member of that early group of Philadelphia chemists, about whom Dr. Smith has written so eloquently. The following extract from an article by Cutbush, written in 1811, shows his point of view: 'Thus chemistry is become an entirely new science. It is no longer confined to the laboratory of the arts; it has extended its flights to the sublimest heights of philosophy, and pursues paths formerly regarded as impenetrable mysteries. Placed forever in the elevated rank it now holds, rich with all its new conquests, it is to become the science most adapted to the sublime speculations of philosophy, the most useful in advancing all the operations of the arts, and the most rational for scientific amusement. Exact in its process, sure in its results, varied in its operations, without limit in its applications and its views, severe and geometrical in its reasoning, there is scarcely any human occupation which it does not enlighten, and upon the perfection of which it may not have great influence. It bestows great enjoyment to every class of individuals: and who would not be ambitious of becoming acquainted with a science which enlightens almost every species of human knowledge." *Wilder D. Bancroft*

Il trattamento termico preliminare degli acciai dolci e semi-duri per costruzioni mechaniche. *By Federico Giolitti. 23 × 16 cm; pp. xx + 621. Milano: Ulrico Hoepli, 1918. Price: 28 lire.*—The book is divided into five sections: the phenomena of diffusion in primary mixed crystals; the effects of the phenomena of diffusion on the course of the secondary crystallization; general remarks on the technical application of the phenomena of diffusion in mixed crystals as regards the preliminary heat treatment of steels; the preliminary heat treatment of cast steel; the preliminary heat treatment of rolled steel. The photomicrographs are from the author's laboratory with one exception.

The preliminary heat treatment of low-carbon steel is to produce homogeneity while the final heat treatment, as the author uses the term, is to give quality. The preliminary heat treatment is intended to overcome the liquation which may arise when the gamma iron separates and to control the distribution of the solid phases in the cast or rolled steel. While this is an interesting book and well worth reading, it seems to the reviewer at any rate that the author is not definite enough. It is not that the author does not know his subject, because he does. He does not make his points clearly and concisely and one gets the presumably erroneous impression of a man who believes firmly that a scientific study of the behavior of iron is of the greatest importance; but who is not quite certain why it is important. *Wilder D. Bancroft*

HYDROUS OXIDES. II

BY HARRY B. WEISER

Hydrous Aluminum Oxide

In a recent communication[1] an account has been given of the effect of various factors on the physical character and chemical properties of hydrous ferric oxide. Hydrous aluminum oxide which resembles hydrous ferric oxide in a number of respects, will next be considered.

COMPOSITION AND PROPERTIES OF PRECIPITATED ALUMINA

A number of hydrates of aluminum oxide have been described; but for the most part these are amorphous in character and have been prepared or analyzed under such conditions that their percentage composition just happened to approach that of a definite hydrate. Thus Mitscherlich[2] obtained a product nearly agreeing in composition with the formula assigned to the mineral diaspore, $Al_2O_3.H_2O$, by heating amorphous alumina with water between 260° and 305°. Becquerel[3] claimed to get $Al_2O_3.H_2O$ by suspending a solution of $CrCl_3$ contained in a tube covered with parchment paper, in a solution of gelatinous alumina in caustic potash. Ramsay[4] ascribed the same formula to the precipitated oxide dried at 100°.

Amorphous bauxite is assigned the formula $Al_2O_3.2H_2O$. Löwe[5] obtained a substance having approximately the same formula by drying at 100° the precipitate formed by the action of ammonium chloride on a solution of alumina in potassium hydroxide. Péan de St. Gilles[6] obtained a substance having approximately the same composition by boiling gelatinous aluminum oxide in water for several days and drying the resulting product at 100°. Crum[7] likewise assigned the

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[1] Weiser: Jour. Phys. Chem., **24**, 277 (1920).

[2] Jour. prakt. Chem., **83**, 468 (1861).

[3] Jahresberichte, 87 (1868).

[4] Jour. Chem. Soc., **32**, 395 (1877).

[5] Zeit. für Chemie, **3**, 247 (1864).

[6] Ann. Chim. Phys., (3) **46**, 57 (1856).

[7] Liebig's Ann., **89**, 156 (1853).

formula $Al_2O_3.2H_2O$ to the precipitate obtained by digesting a solution of aluminum acetate at 100° from 30 to 36 hours.

Amorphous aluminum oxide precipitated in the cold and dried at 100° is usually considered to be $Al_2O_3.3H_2O$[1] corresponding to the mineral gibbsite. Cossa[2] claimed to get an amorphous compound of this composition by the action of water on aluminum amalgam. Bonsdorff[3] first prepared a crystalline hydrate by saturating a sodium hydroxide solution with gelatinous aluminum oxide and allowing the solution to stand in a closed vessel. After a few days the bottom of the vessel was covered with small granular crystals having the composition $Al_2O_3.3H_2O$. A similar compound was obtained by the slow action of carbon dioxide in the air on the saturated solution of hydrous alumina in potassium hydroxide. These observations of Bonsdorff have been confirmed by van Bemmelen,[4] Bayer,[5] Ditte,[6] Allen,[7] and Russ.[8] Mitscherlich[9] heated precipitated alumina for twelve hours at 60°, dried it on a water bath for 1/2 hour and analyzed. The composition approximated that of a trihydrate.

Zanino[10] obtained a product which he described as a voluminous grayish spongy mass, by the action of moist air on aluminum that had previously been dipped in mercury. This mass he claimed was essentially $Al_2O_3.5H_2O$. Ramsay[11] found that the oxide precipitated at 100° and dried at ordinary temperatures contained Al_2O_3 and H_2O in the approximate ration of 1 to 5.

Schlumberger[12] obtained a precipitated alumina to which

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[1] Cf. Allen: Chem. News, **82**, 75 (1900).

[2] Zeit. für Chemie, **13**, 443 (1873).

[3] Pogg. Ann., **27**, 275 (1833).

[4] Rec. Trav. chim. Pays-Bas, **7**, 75 (1888).

[5] Chem. Zeit., **12**, 1209 (1889).

[6] Comptes rendus, **116**, 183 (1893).

[7] Loc. cit.

[8] Zeit. anorg. Chem., **41**, 216 (1904).

[9] Jour. prakt. Chem., **84**, 468 (1861).

[10] Gazz. chim. ital., (1) **30**, 194 (1900).

[11] Loc. cit.

[12] Bull. Soc. chim. Paris, (3) **13**, 41 (1895).

he assigned the formula $Al_6O_{14}H_{10}$ and which he called meta tri-aluminum hydroxide. It might be considered to be $3Al_2O_3.5H_2O$.

From the above survey one might conclude that at least four well-defined hydrates of alumina had been prepared. However, a study of the dehydration of precipitated alumina by Carnelley and Walker[1] led them to the conclusion that: "Ramsay's and our own results show either that there are no definite stable hydrates of aluminum or what is more probable that a very large number of hydrates exist, but so unstable that the smallest rise in temperature is sufficient to convert a higher into a lower." The results of Carnelley and Walker were confirmed by van Bemmelen;[2] but the latter did not feel compelled to postulate the existence of an indefinite number of unstable hydrates to account for the behavior of the precipitated oxide on drying. He concluded that there is no definite ratio between the number of oxide molecules and the molecules of water and hence, that there are no definite hydrates formed by drying precipitated alumina. He showed that at constant temperature the precipitated oxide takes up or gives off water until the vapor tension of the substance is the same as that of the surroundings; hence, change in temperature causes a continuous change in the water content of the substance by changing its vapor tension. He showed further that the vapor tension of the hydrous oxide varies with variation in the conditions of precipitation and in the subsequent treatment of the precipitated oxide. Thus an oxide precipitated from a very dilute solution of aluminum chloride retains and adsorbs water more strongly than one precipitated from a more concentrated solution. Moreover, the precipitated alumina becomes more sparingly soluble in acids and alkalis in proportion to the quantity of water which it loses when heated; and after heating the oxides at various temperatures they adsorb smaller quantities of water when placed in a saturated atmosphere and they retain less

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[1] Jour. Chem. Soc., 53, 87 (1888).

[2] Loc. cit.

in dry air in proportion to the loss of water which has occurred. By standing under water the capacity to adsorb water and the solubility in acids and alkalis alters in proportion to the time of standing.

Tommasi[1] first called attention to the fact that ordinary hydrous alumina precipitated by ammonia from a solution of alum, possessed different properties after it had stood for three months under water. Whereas the newly formed oxide was quite soluble in acids and alkalis, the aged product was sparingly soluble. Moreover, the old oxide was not peptized by aluminum chloride or as Tommasi puts it, did not combine with aluminum chloride to form an oxychloride. To both the new and the old oxide he assigned the same formula, $Al_2O_3.3H_2O$; and attributed the difference in properties to a molecular change in the newly formed hydrate which took place on standing. Tommasi called the insoluble hydrous oxde δ to distinguish it from the ordinary oxide, α, the mineral gibbsite, β, and the Graham colloidal oxide, γ. As is well known, the newly formed gelatinous oxide is readily soluble in caustic alkalis from which solution a granular, difficultly soluble oxide precipitates on standing. These facts have led to the quite general recognition of at least two allotropic or isomeric modifications of hydrated alumina.[2] Russ designates the usual soluble form by α and the more insoluble form by β.

In the light of van Bemmelen's experiments it is evident that the hydrous alumina formed by precipitation of an aluminum salt contains no definite hydrates. Moreover, it is altogether unnecessary to postulate the existence of an indefinite number of definite hydrates to account for the behavior of the gelatinous oxide when subjected to various conditions of temperature and vapor pressure. Just as we may have an indefinite number of hydrous oxides varying all the way from the most highly hydrous to the anhydrous; so an indefinite number of hydrous oxides may be prepared that show a con-

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[1] Comptes rendus, 91, 231 (1880).

[2] Bayer: Ditte, Russ, Loc. cit.

tinuous variation in their solubility in acids and alkalis. The so-called ordinary and meta, or α and β modifications, may represent the two extremes of solubility; but there is no definite temperature of inversion from the α to β form. Accordingly, between these two extremes one may have all possible variations in the degree of solubility. As above pointed out, van Bemmelen has shown that there is a close connection between the solubility of the partly dried hydrous oxide and the extent and method of the drying. The solubility falls off as the water content decreases and as the size of the particles increases; the same is true of the mordanting action.

The evidence seems to indicate that but one definite crystalline hydrate has been prepared, the trihydrate, formed by spontaneous precipitation from the solution of gelatinous alumina in sodium or potassium hydroxide. Russ claims that the product which he obtained even in this way showed no crystalline structure at a magnification of 500 diameters, although it was distinctly granular in character.

PREPARATION AND PROPERTIES OF COLLOIDAL SOLUTIONS OF ALUMINA

Since it is possible to prepare an indefinite number of hydrous aluminas differing in the size of the particles and in the amount of water they contain, so it should be possible to obtain colloidal solutions of alumina having widely varying properties depending on the method of preparation.[1] Two general methods are employed in the preparation of colloidal solutions of hydrous alumina; hydrolysis of aluminum salts; and peptization of the gelatinous oxide by acids and salts. These will now be considered.

I. Colloidal Aluminum Oxides Prepared by Hydrolysis

Hydrolysis of Aluminum Acetate.—Colloidal alumina was first prepared by Crum[2] by the hydrolysis of an aluminum acetate to which he assigned the formula $Al(OH)_3(OCOCH_3)_2$. "A solution of aluminum acetate so highly diluted that it con-

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[1] Cf. Bancroft: Jour. Phys. Chem., **19**, 232 (1915).

[2] Liebig's Ann., **89**, 168 (1854).

tained not more than 1 part of alumina to 200 parts of water was placed in a stoppered bottle and the latter was immersed up to the neck in boiling water where it was kept continuously for ten days and nights. By this time it had almost entirely lost the astringent alum taste and had acquired that of acetic acid. The liquid was now placed in a wide, flat vessel filling it to a depth of $^1/_4$ inch; and by heating the solution so strongly that it boiled actively over the entire surface, the acetic acid was driven off in about $1^1/_2$ hours so that the liquid no longer reacted to litmus paper. In this operation the liquid must contain not more than 1 part of alumina to 400 parts of water and the water lost by evaporation must be replaced continuously.

"The liquid so obtained is almost as transparent and clear as before the acid was driven off. Longer boiling of the solution, particularly if it is concentrated, causes it gradually to assume a gummy consistency which property can be partly taken from it again by the addition of acetic acid.

"If one gram of sulphuric acid (SO_3) in 1000 grams of water is mixed with 8000 grams of the solution which contains 20 grams of alumina, the whole thing sets to a solid transparent gel. By compressing it in a bag, the liquid part of the gel can be readily separated from the solid, the volume of which in the compressed condition is but $^1/_{60}$ to $^1/_{70}$ that of the gel. On investigation I found that the solid part of the coagulum contained almost all the sulphuric acid, something like 1 equivalent of H_2SO_4 to 15 of Al_2O_3.

"One formula weight of citric acid (tribasic acid) coagulated it just as effectively as 3 formula weights of sulphuric acid; and 1 formula weight of tartaric acid (dibasic acid) just as effectively as 2 formula weights of sulphuric. Two formula weights of oxalic acid showed nothing like the same activity as 1 formula weight of sulphuric acid. With hydrochloric and nitric acid must be used not less than 300 equivalents in order to have the same effect as 1 equivalent of sulphuric acid. * * * * * "

"One gram of potassium hydroxide in 1000 grams of water coagulates 9000 grams of the solution, which is in about the proportion of 1 equivalent of KOH to 20 of Al_2O_3. The mixture reacts weakly alkaline. The hydroxides of sodium, ammonium and calcium react equally strongly. The coagulum brought down by the hydroxides is partly dissolved again by neutralizing with acetic or hydrochloric acid. The resulting salts make the solution appear somewhat oily. A boiling solution of potassium or sodium hydroxide dissolves the coagulum and at the same time changes it into the ordinary modification of alumina which separates out as the ordinary hydrate with three atoms of water, when the alkali is neutralized."

"Concentrated sulphuric acid likewise dissolves the solid portion of the coagulum even after drying, especially if the acid is hot. Strong hydrochloric acid acts in the same way at the boiling temperature, although less readily; and there results the ordinary sulphate and chloride of aluminum. A large amount of acetate can be added to the colloid before coagulation takes place. When the solid portion of the coagulum thrown down by a concentrated solution of sodium acetate has been freed from this salt by compressing the precipitate, the latter dissolves again in pure water and the solution may be recoagulated by the addition of another portion of this salt. Investigations with potassium acetate gave the same results. Nitrates and chlorides coagulate it with difficulty. Solutions of the sulphates of sodium, magnesium and calcium, bring down the coagulum just as quickly as a solution which contains the same amount of sulphuric acid in the free state. On investigating such a mixture, sulphate was again found in the solid part of the coagulum and the liquid reacted neutral."

"A small teaspoonful of the liquid placed in the mouth immediately becomes solid by the action of the saliva.

"A digested alumina solution from which the acetic acid has not been removed by boiling requires for coagulation something like double the amount of sulphuric acid required to precipitate the boiled solution.

"One of the characteristic properties of the solution changed by digestion of the acetate is its inability to act as a mordant. As is known, the ordinary acetates form a yellow opaque precipitate with a quercitron extract. The solution of the digested acetate is coagulated by such a mordant but the color of the latter is changed but little and the coagulum remains transparent. The same results were obtained by using an infusion of logwood or Brazilwood."

Crum's experiments carried out more than three-quarters of a century ago are particularly interesting and important since they bring out so many facts of a general nature in connection with colloidal oxides. Thus, it is evident that his colloid is positive since anions are chiefly concerned in precipitating it. Anions of high valency have a high precipitating power and are carried down to a considerable extent by the gelatinous precipitate; univalent anions have a low precipitating power and in these cases the precipitation is reversible on account of the ease with which the precipitating agent is washed out. The conditions of formation, namely prolonged digestion at a high temperature with subsequent boiling, are conducive to the formation of larger and less hydrous particles than would be obtained in the cold. Accordingly the precipitated oxide is not very soluble in acids and alkalis and has no mordanting action. In general, it corresponds to the oxide formed by long standing of ordinary precipitated alumina. The Crum colloid has many properties in common with the Péan de St. Gilles[1] colloidal ferric oxide prepared in a similar way.[2]

Graham[3] prepared a colloid having properties similar to Crum's by heating an acetate solution for several days and dialyzing in the cold.

Hydrolysis of Aluminum Chloride and Aluminum Nitrate.—Graham failed to obtain colloidal aluminum oxide by the intermittent dialysis of the chloride. Since a $^1/_{1000}$ molar solu-

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[1] Comptes rendus, 40, 568, 1243 (1855).

[2] Weiser: Jour. Phys. Chem., 24, 277 (1920).

[3] Phil. Mag., (4) 23, 290 (1862).

tion of the salt is but 4.5% hydrolyzed[1] at 25°, one should expect the yield of colloid to be low. By the continuous dialysis of a $^1/_3$ molar solution of the salt Neidle[2] found that 2 percent was transformed into colloid in 15 days. Since the temperature coefficient of the hydrolysis is quite high[3] a better yield should result if the solution were heated during the dialysis. Neidle confirmed this conclusion by showing that 9.5 percent of the salt was transformed into colloid when a 0.05 molar solution was dialyzed for 37 hours at a temperature of 75° to 80°.

Biltz[4] attempted to prepare colloidal alumina by dialysis of aluminum nitrate, but was unsuccessful, as almost all the salt diffused through the dialyzer undecomposed.

II. Colloidal Aluminum Oxides Prepared by Peptization

(1) *Peptization of Aluminum Oxide by Aluminum Chloride.*—Graham[5] peptized freshly prepared and thoroughly washed hydrous aluminum oxide in a solution of aluminum chloride and then dialyzed out the excess of the peptizing agent in the cold. In this way he prepared a colloid that differs in many respects from the colloid prepared by continued boiling of the acetate. "Soluble alumina is one of the most unstable of substances,—a circumstance which fully accounts for the difficulty of preparing it in a state of purity. It is coagulated or pectized by portions so minute as to be scarcely appreciable, of sulphate of potash and, I believe, by all other salts; and also by ammonia. A solution containing 2 or 3 percent of alumina was coagulated by a few drops of well water, and could not be transferred from one glass to another unless the glass was repeatedly washed out with distilled water, without gelatinizing. Acids in small quantities also cause coagulation; but the precipitated alumina

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[1] Ley: Zeit. phys. Chem., 30, 249 (1899).

[2] Jour. Am. Chem. Soc., 39, 71 (1917).

[3] Bjerrum: Zeit. phys. Chem., 59, 343 (1907).

[4] Ber. deutsch. chem. Ges., 35, 4432 (1902).

[5] Liebig's Ann., 121, 41 (1862).

readily dissolves in an excess of acid. The colloids, gum and caramel, also act as precipitants.

"This alumina is a mordant and possesses indeed all the properties of the base of alum and the ordinary aluminous salts. A solution containing 0.5 percent of alumina may be boiled without gelatinizing, but when concentrated to half its bulk it suddenly coagulated. Soluble alumina gelatinizes when placed upon red litmus paper, and forms a faint blue ring about the drop, showing a feeble alkaline reaction. Soluble alumina is not precipitated by alcohol or by sugar. No pure solution of alumina, although dilute, remained fluid for more than a few days."

On account of the similarity in properties between the oxide precipitated from true solution by ammonia and the oxide prepared by the method of Graham, the latter considers that his colloid is ordinary colloidal alumina while the Crum colloid is colloidal meta-alumina, an allotropic modification that is "no longer a mordant and forms when precipitated a jelly that is not dissolved by an excess of acid." It is evident that the difference in the properties of the two colloids is the same as distinguished the so-called α and β oxides. Moreover, the colloids prepared by the two methods differ from each other in much the same way as the colloidal hydrous ferric oxide prepared by the method of Péan de St. Gilles differs from that prepared by the method of Graham.[1] Analogous to the case of the colloidal ferric oxides, the difference in the properties of the two aluminas is due to the difference in the degree of hydration and the size of the colloidal particles. Peptization of highly gelatinous alumina in the cold favors the formation of small and highly hydrous particles that are more soluble than the larger, less hydrous particles formed during prolonged boiling.

The peptization of a gel of alumina by aluminum chloride does not take place very readily; but a modification of Graham's method was proposed by Hantzsch and Desch[2] which

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[1] Cf. Weiser: Jour. Phys. Chem., **24**, 277 (1920).

[2] Liebig's Ann., **323**, 30 (1902).

affords a very simple method of preparing the colloid. They added a dilute solution of ammonium hydroxide to a solution of aluminum chloride until the precipitate first formed no longer dissolved on standing. This solution was then dialyzed, giving a clear, colorless liquid that gave no test for chloride ion. By evaporating on the water bath a glassy mass was formed which dissolved in water, forming an opalescent colloidal solution. The evaporation to dryness obviously resulted in the formation of larger particles, giving the colloid a cloudy appearance that was not characteristic of the original preparation.

Neidle[1] carried out the dialysis of the solution of hydrous aluminum oxide prepared by the method of Hantzsch and Desch, at a temperature of 75° to 80° and obtained a slightly opalescent colloid.

(2) *Peptization of Aluminum Oxide by Hydrochloric and Nitric Acid and by Certain Chlorides and Nitrates.*—Schneider[2] first studied the behavior of pure gelatinous aluminum oxide in the presence of varying amounts of hydrochloric acid. With quite dilute acid an opalescent solution was obtained. The solution containing 7 moles of hydrochloric acid to 1 of aluminum oxide was clear, although it contained both colloidal alumina and aluminum chloride. This was proven by adding to the perfectly clear solution a small amount of dilute sulphuric acid which threw out a gelatinous precipitate. The amount of alumina in colloidal solution was greater the more dilute the acid employed and the longer the original oxide precipitated with ammonia was allowed to stand in contact with the mother liquor before filtering and treating with acid. Schneider used acid of sufficient concentration that a portion of the oxide was always converted to the chloride. He found that 0.17 gram of Al_2O_3 as the gelatinous oxide was entirely converted to chloride by 20 cc of concentrated hydrochloric acid, as the addition of sulphuric acid gave no precipitate.

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[1] Loc. cit.

[2] Liebig's Ann., **257**, 359 (1890).

Schneider carried out some interesting experiments with the colloid obtained by peptization with relatively dilute acid. He showed that the colloid could be evaporated several times to a thin transparent film which was almost entirely soluble in water, forming an opalescent colloidal solution. The colloid which undoubtedly contained chlorine gave no test with silver nitrate in the cold; on heating, however, a precipitate of silver chloride was obtained but no colloid was precipitated. Schneider believed that nitrate ion simply displaced chloride ion. With silver oxide he observed not only the appearance of silver chloride, but the coagulation of the colloid.

The above results involve more than the simple displacement of one ion by another. Since chloride ion is usually adsorbed as strongly as nitrate, I doubt whether this factor is of prime importance. Ruer[1] has shown that hydrous ferric oxide has a distinct protective action on silver chloride. Accordingly a small amount of chloride ion in the presence of a large amount of hydrous ferric oxide will not be detected by the addition of silver nitrate since the protective action does not allow the particles of chloride to become large enough to cause turbidity. Now it has been found that hydrous aluminum oxide has a very good protective power;[2] hence we might expect to get no test for chloride ion in the cold in the presence of an excess of this oxide although considerable of the ion was present. On heating the solution, the usual test was obtained due to partial agglomeration of the silver chloride. The colloid was not precipitated in this case since it is stabilized by preferential adsorption of the strongly adsorbed hydrogen and aluminum ions and the addition of a small amount of the weakly adsorbed nitrate ion is altogether inadequate to neutralize the adsorbed ions which give the colloid its stability. The addition of silver oxide, however, introduces the strongly adsorbed hydroxyl ion which neutralizes the

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[1] Zeit. anorg. Chem., 43, 85 (1905); cf. Weiser: Loc. cit.

[2] Zsigmondy: "Chemistry of Colloids," translated by Spear, 1917, 105; Biltz: Ber. deutsch. chem. Ges., 37, 1095 (1904).

charge on the particles precipitating the colloidal oxide together with silver chloride.

Schneider found that gelatinous alumina was peptized by solutions of ferric chloride and ferric nitrate, giving a colloid with properties similar to the solution of hydrous alumina in dilute hydrochloric acid. With these colloids the coagulum obtained with sulphuric acid contained both ferric and aluminum oxide and both iron and aluminum were present in the filtrate. Ferric sulphate acted differently on the gelatinous oxide than the chloride and nitrate. Solutions of the former salt under 2 percent in the cold and more concentrated solutions when heated deposit what are usually called basic salts of varying composition; but which we now know to be solid solutions of ferric oxide, sulphuric acid and water.[1] This dissociation was hastened by the presence of alumina owing to the neutralization of a part of the sulphuric acid. Accordingly when a dilute solution of ferric sulphate was boiled with hydrous alumina all the iron precipitated out, leaving only aluminum in the filtrate.

On account of the strong hydrolysis of ferric salts their solutions will contain both ferric and hydrogen ions, the amount of each depending on the concentration and the temperature. Since we might expect hydrous alumina to show a strong adsorption for both of these ions and since chloride and nitrate ions are not strongly adsorbed, the peptization by these salts is readily understood. The colloidal solutions will, of course, contain both hydrous ferric oxide and hydrous aluminum oxide. With ferric sulphate, however, the adsorption of the cations is cut down by the strongly adsorbed sulphate ion and no colloid whatsoever results.

Müller[2] has confirmed and extended the investigations of Schneider. Equal quantities of hydrous alumina containing 1.224 grams of Al_2O_3 were suspended in 250 cc of water and peptized by the smallest possible amount of hydrochloric acid, ferric chloride, thorium nitrate and chromic nitrate.

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[1] Cameron and Robinson: Jour. Phys. Chem., 11, 641 (1907).

[2] Zeit. anorg. Chem., 57, 311 (1908).

Dilute solutions of the salts were added in small quantities (1 cc to 2 cc) at a time and after each addition the contents of the flask were boiled 10 to 15 minutes, replacing the water as it evaporated. This was repeated until the oxide was completely converted into a homogeneous colloidal solution. For complete peptization of 1.224 grams of aluminum oxide were required 19.6 cc of 0.050 *N* hydrochloric acid; 1 cc of 1.115 *N* ferric chloride; 10.4 cc of 0.385 *N* thorium nitrate; and 4.5 cc of 0.574 N chromic nitrate. Calculating these values to cubic centimeters of normal solutions required, we find: 0.98 cc of hydrochloric acid; 1.15 cc of ferric chloride; 3.99 cc of thorium nitrate and 2.58 cc of chromic nitrate are necessary for complete peptization. To convert 1.224 grams of Al_2O_3 to $AlCl_3$ it would be necessary to use 72.8 cc of normal hydrochloric acid. Thus only $^1/_{73}$ of the acid necessary for forming $AlCl_3$ was needed for peptization. The stability of the colloid is quite high, probably owing to the presence of a comparatively large amount of peptizing agent. "Dilute univalent acids and salts with univalent anions can be added without appreciable change. Acids with polyvalent anions and their salts (*e. g.*, sulphuric acid and sulphates) cause coagulation of the colloid in quite low concentration."

From the above results it will be noted that ferric chloride is almost as good a peptizer for hydrous alumina as is hydrochloric acid. In discussing Müller's observations Taylor[1] says: "These results are not necessarily at variance with Lottermoser's theory [that a peptizer must contain one, or, in some cases, either of the ions of the disperse phase] for it is quite probable that the first action between ferric chloride and aluminum hydroxide is the formation of some ferric hydroxide and aluminum chloride. Or ferric chloride, like all the above salts, is hydrolyzed into basic hydroxide and free acid which is thus in a position to act on the aluminum hydroxide with the production of $Al^{\cdot\cdot\cdot}$. It is rather curious that hydrochloric acid and ferric chloride are apparently equally effective in peptizing aluminum hydroxide."

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[1] "Chemistry of Colloids," 1915, 205.

It seems to me altogether unnecessary to postulate the formation of aluminum ions in solution to account for the peptizing action of certain acids and salts. Lottermoser[1] made the interesting and important observation that substances show a strong preferential adsorption for their own ions; and that peptization may result from this preferential adsorption. This does not exclude peptization of a substance by preferential adsorption of ions other than its own. This is what happens with hydrous aluminum oxide. Hydrogen ion and the multivalent cations $Fe^{\cdot\cdot\cdot}$, $Cr^{\cdot\cdot\cdot}$ and $Th^{\cdot\cdot\cdot\cdot}$ are adsorbed more strongly than the univalent anions NO_3' and Cl'. Peptization, therefore, results and the solution containing the most readily adsorbed cation peptizes in the lowest concentration. Since dilute ferric chloride is completely hydrolyzed at 100°, hydrogen ion plays the chief rôle in this case. Aluminum chloride is not so strongly hydrolyzed and it is a pity that Müller did not carry out some experiments with this salt in order to get the relative effects of aluminum ion and hydrogen ion. For the purpose of making this comparison, the following experiments were carried out:

Experiments on Peptization of Hydrous Alumina

An aluminum chloride solution was prepared containing 25 grams of Al_2O_3 per liter. Fifty cubic centimeters of this solution were diluted to 150 cc, heated to boiling and precipitated with a slight excess of ammonia. After boiling 5 minutes the mixture was transferred to 250 cc bottles and the precipitate thrown down in a centrifuge making 2000 r. p. m. After centrifuging for 5 minutes, the supernatant liquid was poured off and the inside of the bottle rinsed; after which 150 cc of water was added and the precipitate thoroughly shaken up. The centrifuging was then repeated. On the third washing by this process it was found that the removal of electrolyte was so complete that a part of the precipitate went into a colloidal solution that could not be thrown down by centrifuging for 30 minutes. Accordingly, the precipitate

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[1] Zeit. phys. Chem., 62, 359 (1908); Zeit. Kolloidchemie, 3, 31 (1908).

was washed but twice, after which it was transferred to an Erlenmeyer flask, suspended in 250 cc of water, and the suspension heated to boiling. To this suspension *N*/5 hydrochloric acid was added in 1 cc portions, boiling the solution for 10 minutes between each addition. The behavior was similar to that observed by Müller, but it was very difficult to tell when all the oxide had gone into colloidal solution. Even after peptization was apparently complete, a considerable quantity of oxide was thrown down by centrifuging. Moreover, as has been pointed out, the oxide went into colloidal solution if the washing was carried too far. If the precipitate washed until it started to become colloidal, was suspended in water, a considerable amount would be carried up. Hence, comparable results would be obtained only in case each sample was washed to exactly the same extent. To avoid these obvious sources of error the following method was employed for comparing the peptizing action of different electrolytes: Four 50 cc portions of the standard aluminum chloride solution were precipitated and washed as above described. The precipitates were transferred to a 1000 cc flask and shaken with water until the mass was entirely free from lumps. The suspension was made up to 1000 cc and 150 cc portions were transferred to 250 cc Erlenmeyer flasks, stirring the suspension all the while to ensure uniformity. The contents of the flask were heated to boiling on an electric hot-plate and the electrolytes added; after which the boiling was continued for 1 hour, replacing the water as it evaporated. After boiling, the solutions were transferred quantitatively to bottles and centrifuges for 10 minutes at 2000 r. p. m. The supernatant colloid could be readily poured off from the precipitate which was subsequently transferred to a quantitative filter and washed, using hot water, containing a little ammonium chloride. The weights of ignited oxide that were not peptized gave at once the relative peptizing power of different electrolytes, providing the same amount of electrolyte was used in each case. Two series of experiments were made with different samples of oxide and with different amounts of electrolytes. In Table I are given the results using 5 cc of *N*/5 electrolytes in 155 cc; in Table II the results using 10 cc of *N*/5 electrolytes in 160 cc. The electrolytes are arranged in the order of peptizing power beginning with the greatest:

TABLE I

Peptization of Aluminum Oxide (1)

Electrolyte *N*/5	Amount added cc	Aluminum Oxide Grams		
		Treated	Remaining	Peptized
HNO_3	5	0.750	0.164	0.586
HCl	5	0.750	0.170	0.580
$FeCl_3$	5	0.750	0.178	0.572
$AlCl_3$	5	0.750	0.191	0.559
$HC_2H_3O_2$	5	0.750	0.242	0.508
	None	0.750	0.313	0.477

TABLE II

Peptization of Aluminum Oxide (2)

Electrolyte *N*/5	Amount added cc	Aluminum Oxide Grams		
		Taken	Remaining	Peptized
HNO_3	10	0.750	0.088	0.662
HCl	10	0.750	0.097	0.653
$FeCl_3$	10	0.750	0.104	0.646
$AlCl_3$	10	0.750	0.130	0.620
$HC_2H_3O_2$	10	0.750	0.207	0.543
	None	0.750	0.296	0.454

As shown in the above tables, the electrolytes arrange themselves in the same order in both series of experiments. It is interesting to note the marked peptization of the precipitated oxide resulting from washing out the precipitating agent. The peptizing action of nitric acid is slightly greater than hydrochloric acid, indicating that nitrate ion is somewhat less strongly adsorbed by hydrous alumina than chloride ion. This is actually the case. Ferric chloride acts almost like hydrochloric acid since it completely decomposes at 100°. Contrary to what one might expect from Lottermoser's theory, aluminum chloride apparently does not act so strongly as either hydrochloric acid or nitric acid. Some might attribute this difference to the solvent action of the acids. At the dilution used this solvent action is comparatively slight, however, since the supernatant liquid left after coagulating 50 cc of the colloid (from HCl) with potassium sulphate gave no tests whatsoever for aluminum ion. The results indicate that the formation of aluminum ion is not a necessary step in the peptization of gelatinous alumina by acids and salts.

(3) *Peptization by Acetic Acid.*—Bentley and Rose[1] precipitated hydrous alumina and after thorough washing dissolved it in acetic acid. On the addition of hydrochloric acid to this solution, a gelatinous precipitate was obtained. In the light of the investigation of Crum, Graham, Schneider, Hantzsch and Desch and Müller above referred to, it would seem that Bentley and Rose were dealing merely with peptization of alumina by acetic acid although they state: "We were unable to find anything in the literature available which threw light on this phenomenon. * * * * " Apparently the similarity of this solution to the colloidal solutions prepared by Graham's method was not recognized although they note that: "The appearance of the precipitate indicated a colloidal nature and suggested that an hydrosol was formed by the action of acetic acid and that this was coagulated by the hydrochloric acid added." Bentley and Rose carried out experiments to determine the best concentration of acid to use. It is very interesting to note the similarity between these experiments and the earlier ones of Schneider on the action of hydrochloric acid on hydrous alumina: "Equal portions of a specimen of the hydrated oxide containing about four molecules of water, were treated with equal volumes of acetic acid varying by tens from 99.8 percent acid down to 40 percent and by ones down to one percent. It was found

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[1] Jour. Am. Chem. Soc., 35, 1490 (1913); cf. Rose: Zeit. Kolloidchemie, 15, 1 (1914).

that above 40 percent acid scarcely any hydrosol was formed, since hydrochloric acid did not produce coagulation. Normal aluminum acetate was the product formed. From 40 percent down, the amount of hydrosol steadily increased as did the ease with which the material dissolved until a 4 percent acid was reached. Below 4 percent the material dissolved only partly, the remainder swelling up to an almost transparent mass which, after prolonged treatment, formed an opalescent and most easily coagulated solution. For practical purposes we consider about 8 percent acid the most favorable strength."

Unfortunately, the quantity of alumina used in the above experiments was not given and so one has no way of judging the peptizing power of acetic acid. This was determined in the manner previously described. By referring to Tables I and II it will be noted that the peptizing action of acetic acid is much less than the same concentration of hydrochloric and nitric acids. This is what one might expect on account of the low concentration of hydrogen ion in the acetic acid solutions.

The colloid used by Bentley and Rose was prepared by adding precipitated alumina to hot concentrated acetic acid until no more would dissolve. This colloid was not very stable, since, "if the solution was submitted to prolonged boiling without the addition of any reagent, coagulation occurred on centrifuging and sometimes simply by allowing the material to stand." The precipitation value of hydrochloric acid was comparatively high. Quantitative data showed, "that enough hydrochloric acid must be added to make the solution $N/5$ in this acid in order to produce coagulation. When the solution was 0.8 normal in hydrochloric acid, 90 percent of the alumina was found in the coagulum."[1] The colloid was not precipitated by acetic acid. "We have, however, been able to coagulate the solution by adding sodium acetate and the coagulum thus formed dissolved in water and was capable of reprecipitation by potassium sulphate.

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[1] Rose: Loc. cit.

We have also been able to secure the same results by adding aluminum sulphate, thus indicating that ions of aluminum were capable of precipitating this colloid."[1] Rose has extended the investigations of Bentley and Rose on the precipitation of colloidal alumina: "Experiments on the addition of normal aluminum chloride and nitrate to the acetic acid colloid have shown that the latter is not coagulated by these salts and also not by sodium acetate. On the other hand, aluminum chloride produces reversible coagulation in a colloid prepared with hydrochloric acid but not with one prepared with nitric acid; while aluminum nitrate coagulates a colloid prepared with nitric acid but not one prepared with hydrochloric acid. These observations prove, without doubt, that for obtaining reversible coagulation, the coagulating agent must at least possess an ion common to the phase in colloidal solution."

Potassium sulphate coagulated the acetic acid colloid readily and the precipitate could not be washed into colloid solution again. For some unknown reason Bentley and Rose did not obtain coagulation with sulphuric acid. "Various acids were substituted for hydrochloric acid but only one other,—nitric acid behaved like hydrochloric acid and produced coagulation. Sulphuric acid not only produced no turbidity but cleared the solutions coagulated by hydrochloric and nitric acids."

The observations above recorded were so unusual in certain respects that further consideration seemed necessary. On account of the low ionization of acetic acid, I should not expect this acid to coagulate alumina peptized by acetic acid; but sodium acetate should cause coagulation as observed by Bentley and Rose, but apparently not confirmed by Rose. Since I have shown that the peptizing action of hydrogen ion and aluminum ion is almost the same and since hydrochloric acid and nitric acid precipitate the colloid, it would seem that aluminum chloride and aluminum nitrate should cause coagulation. Furthermore, since potassium sulphate

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[1] Bentley and Rose: Loc. cit.

precipitates the colloid readily, one would certainly expect sulphuric acid to do the same. Finally, since nitrate ion and chloride ion are usually adsorbed to about the same extent, it seems altogether unlikely that aluminum nitrate but not aluminum chloride would cause reversible precipitation of a colloid prepared by peptization of alumina with nitric acid; and that aluminum chloride but not aluminum nitrate would cause reversible precipitation of a colloid prepared with hydrochloric acid. To settle these points the following experiments were carried out:

Experiments on Coagulation of Colloidal Alumina

(1) *Coagulation of Colloidal Alumina prepared with Acetic Acid.*—The colloid used in these experiments was prepared by the method of Bentley and Rose. Hot aluminum chloride solution was precipitated with a slight excess of ammonia and the oxide was washed thoroughly, making use of the centrifuge in the manner above described. A considerable excess of the oxide was added to hot 8 percent acetic acid and the mixture was allowed to stand for an hour with frequent stirring. The resulting colloid was then centrifuged for 15 minutes to remove the excess of alumina. The sol was cloudy and quite viscous; but was fairly stable. To 5 cc portions of the colloid in test tubes were added 1, 3 and 5 cc portions of 25 percent solutions of sodium acetate, aluminum chloride and aluminum nitrate. Coagulation took place in every case, the solution being so concentrated that a jelly was formed. After standing over night, the contents of the tubes were centrifuged for 10 minutes, the supernatant liquid drained off and water added. It was found that the coagulation was reversible in every case, the partial removal of the precipitating electrolyte resulting in the reformation of a colloidal solution. A small amount of dilute sulphuric acid likewise caused coagulation. These results were confirmed by a dilute colloid prepared by a modification of Crum's method.

(2) *Coagulation of Crum's Colloidal Alumina.*—It will

be recalled that Crum prepared colloidal alumina by heating a solution of aluminum acetate for 10 days, followed by removal of the acetic acid by boiling. This time-consuming method has been successfully modified by following the same procedure used in the preparation of colloidal ferric oxide from ferric oxide peptized by acetic acid.[1] Sufficient aluminum chloride to make 2 grams of Al_2O_3 was precipitated with a slight excess of sodium carbonate and thoroughly washed with the aid of the centrifuge, until the precipitate started to go into colloidal solution. To this oxide was added 100 cc of warm acetic acid containing only about one-third of the acid necessary to form normal aluminum acetate. The solution was kept at approximately 50° until all the oxide was taken up. The almost clear solution was filtered, diluted to 1500 cc and boiled vigorously for 24 to 36 hours, replacing the water as it evaporated. By this process almost all the acetic acid was removed. The colloid was almost clear, was odorless and the sour taste of acetic acid was lacking. Five cubic-centimeter portions of this dilute colloidal alumina were treated with sodium acetate, aluminum chloride and aluminum nitrate. The colloid was precipitated by all three, sodium acetate precipitating in lowest concentration and aluminum nitrate requiring the highest concentration. The precipitate was thrown down in the centrifuge, the supernatant liquid poured off and replaced with distilled water. On shaking up the solid, a colloidal solution was reformed. The precipitation value of sulphuric acid was exceedingly low and the coagulation was irreversible.

(3) *Coagulation of Colloidal Alumina prepared with Hydrochloric and Nitric Acids.*—The colloids were prepared by Müller's method above described, taking the precaution to centrifuge out the excess suspended alumina. To 5 cc portions of each of the colloids were added 1, 3 and 5 cc portions of 25 percent aluminum chloride and aluminum nitrate. Observations made after 10 hours showed that both electrolytes precipitated both colloids. As observed, pre-

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[1] Weiser: Jour. Phys. Chem., 24, 277 (1920).

viously, aluminum nitrate has a higher precipitation value than aluminum chloride: the 1 cc portion of the former failed to precipitate either colloid while the 1 cc portion of the latter precipitated each of them. The precipitation was reversible.

The series of experiments above described give results in exact accord with what one might expect with a colloid peptized by preferential adsorption of cations; and indicate some source of error in certain observations of Bentley and Rose, and of Rose.

The Composition of the Colloids

In the literature is described a number of solid amorphous substances designated as basic salts of aluminum. In most cases these substances have been prepared by methods similar to the peptization methods above given for the preparation of colloidal alumina; and have led certain investigators to conclude that colloids prepared by this method are in reality colloidal basic salts of varying composition. Thus Ordway[1] prepared what he termed basic salts of aluminum by digesting the hydrous oxide with normal salts and evaporating the solution so obtained to dryness. Tommasi[2] prepared certain solutions with properties strikingly similar to colloidal alumina produced by the Graham method. He allowed aluminum to act on cupric chloride solution and claimed to get "oxychlorides" the composition of which depended on the concentration of copper. solution. With a certain concentration of copper chloride, he obtained a substance to which he assigned the formula $AlCl_3.6Al(OH)_3.6H_2O$. This substance was taken up by water and hydrous alumina was precipitated from the solution on the addition of certain salts such as the sulphates of sodium, potassium, magnesium, ammonium, zinc, copper and iron; but it was not precipitated by boiling with the chlorides of potassium, sodium, ammonium, copper and barium, by potassium iodide, potassium bromide, ammonium nitrate or potassium nitrate.

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[1] Am. Jour. Sci., (2) 26, 196 (1858).

[2] Bull. Soc. chim. Paris, (2) 37, 443 (1882).

This similarity in behavior to the Graham colloid suggests either that the latter is made up of basic salts of varying composition or that Tommasi's "oxychlorides" are merely mixtures. In my paper on hydrous ferric oxide[1] I have pointed out that there is little or no evidence for the existence of any basic salt of iron; and that it is unnecessary to postulate the existence of an indefinite number of basic or complex salt of varying composition to account for the behavior of the colloidal hydrous ferric oxides under widely varying conditions.[2] Similarly conclusive evidence of the formation of definite basic aluminum salts by any method is also lacking, although some are referred to in the literature. Thus Hautefeuille and Perrey[3] prepared a number of amorphous products containing chlorine, by passing aluminum chloride and oxygen over heated alumina; but their composition varied so widely with the conditions of formation that there is no indication of the formation of definite compounds. From a study of the hydrolysis of aluminum chloride, Wood[4] likewise suggested that a basic salt was formed in accord with the following reaction: $AlCl_3\ H_2O = Al(OH)Cl_2HCl$. This could not be proven on account of the impossibility of isolating and analyzing the substance. The further suggestion was made but, of course, not proven, that a solution of aluminum chloride might contain both normal and basic chlorides of varying composition in varying proportions.

It is claimed that a basic acetate is obtained by evaporation of a solution of normal aluminum acetate. If rapid evaporation occurs at low temperatures by spreading it out in thin layers on glass or porcelain, a gummy mass perfectly soluble in water is formed to which is assigned the formula $Al_2(C_2H_3O_2)_4O$;[5] but if left to evaporate slowly at ordinary temperature it is said to deposit insoluble basic salts. It is extremely doubtful whether definite compounds are obtained

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[1] Loc. cit.

[2] Cf. Fischer: Zeit. anorg. Chem., 66, 37 (1910).

[3] Comptes rendus, 100, 1219 (1885).

[4] Jour. Chem. Soc., 93, 411 (1908).

[5] Beilstein: "Handbuch der organischen Chemie."

in this way. Bentley and Rose[1] claim that the colloid prepared by peptization of hydrous alumina with acetic acid contains basic acetates and that the precipitate which is thrown out by centrifuging the colloid is likewise a basic salt. Since the precipitate went into colloidal solution on washing, they analyzed it by the usual indirect method: The colloid was analyzed for aluminum and acetic acid before centrifuging and the supernatant liquid after centrifuging; the results were expressed in grams per liter. The difference, they considered to represent the composition of the precipitate. Unfortunately, this indirect method can give correct results only in case the precipitate absorbs no water, a condition that hardly obtains even with a crystalline precipitate.[2] Failure to take this into account with a bulky gelatinous mass like precipitated aluminum oxide probably introduced a very considerable error. Although no high degree of accuracy was claimed they conclude that the solution consists of a basic acetate mixed more or less with the normal acetate. "As to the precipitate the formula which is apparently nearest in correspondence with the above figure is

$$(AlOC_2H_3O_2)_2(Al_2O_3)_3.$$

This would yield alumina and acetic acid in the ratio 3.407 : 1 while our ratio as determined is 3.116 : 1."

Bentley and Rose thought at first that the precipitate formed by adding hydrochloric acid to the acetic acid colloid was a basic acetate chloride similar to the crystalline chromi- and ferriacetate chlorides (double salts) described by Weinland.[3] However, when they analyzed the precipitate thrown down by hydrochloric acid and washed with water containing a little hydrochloric acid they found no acetic acid and so concluded that the hydrochloric acid converted the basic acetate to a basic chloride which was subsequently precipitated by the addition of more acid.

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[1] Loc. ct.

[2] Leighton: Jour. Phys. Chem., **20**, 32, 188 (1916); cf. Weiser and Middleton: Ibid., **24**, 30 (1920).

[3] Chem. Ztg., **35**, 7 (1906).

The experimental evidence cited is insufficient to substantiate the existence of any definite basic salts of aluminum. It is altogether improbable that the colloids prepared by peptization of gelatinous alumina are made up of basic salts of varying composition. When the peptizing agent is hydrochloric, nitric or acetic acid the colloid may contain some normal aluminum salt in true solution, particularly if the peptization is carried out at a high temperature and the acid concentration is fairly high. The colloid, however, is hydrous alumina, stabilized by preferential adsorption of hydrogen ions and aluminum ions. When this colloid is precipitated it carries down with it both positive and negative ions in amounts depending on the conditions.

The Reversibility of Precipitation of Hydrous Aluminum Oxide

The view expressed in the preceding paragraph, that a precipitated alumina varied in composition depending on the degree of adsorption, was suggested by Bentley and Rose and promptly rejected by them since they could not account for reversibility of precipitation, starting with this assumption. "An obvious suggestion as to the identity of the precipitate would be that it was simply alumina holding back some acetic acid in the form of normal aluminum acetate or in some other form and that the amount of acetic acid thus retained was accidental rather than definite. This view we reject because the precipitate dissolved when treated with a considerable quantity of water as described. It seems impossible, or at least unlikely, that an indefinite mixture should dissolve in this way. This investigation confirms the conclusion that the cause of the reversibility of coagulation is accomplished by the crystalloidal soluble salt (either the basic or the normal) of the acid used for the formation of the colloid."

There is nothing new in the observation that "the precipitate dissolved when treated with an excess of water." The analytical chemist is frequently confronted with this difficulty. Thus, a silver halide precipitated with excess halide and filtered at once will run through the filter when the excess of halide is washed out. Stannic oxide must be washed with dilute nitric acid to prevent its going into colloidal solution. Zinc sulphide readily washes into colloidal solution if the wash water contains no electrolytes. Rose[1] amplifies his explanation of the nature of the colloid formed with alumina and acetic acid and of the cause of the reversibility of precipitation: "The following conclusions may be drawn from the results of the experiments above described: 1, that the phase in colloidal solution in the hydrosol is composed of basic compounds of aluminum with the acid used; 2, that the molecules which constitute the colloidal particles are ionized to a certain extent; and 3, that the reversible coagulation represents a phase of the well established law of mass action applied to the solubility product. A search through the literature with reference to this has shown that several investigators consider their solutions weakly ionized. It is quite clear, however, that none of the accepted theories can explain the reversible character of these hydrosols.

"From the experiments on the washing and ultimate dissolving of the coagulum obtained by centrifuging of the hydrosol, it was clear that the solution, little by little, became further hydrolyzed by each new addition of pure water until the substance approached pure aluminum hydroxide. Likewise it appeared evident that the addition of dilute hydrochloric acid instead of water gradually displaced the acetic acid from the hydrosol until the latter was completely removed. From these considerations it must follow that we are dealing here with a series of colloidally dissolved complex compounds which in some respects are like the complex weakly ionized crystalline compounds such as are described by A. Werner, R. F. Weinland and their pupils. As was previously pointed out, the investigations of Weinland on the hydrated ferri- and chromiacetate chlorides are of particular interest in this connection."

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[1] Loc. cit.

The above explanation of the nature of colloidal alumina is open to a number of objections. In the first place, as previously pointed out, there seems to be no very good reason for postulating that the different colloidal aluminas are complex basic salts of widely varying composition depending on the method of preparation, particularly since there is no conclusive evidence of the existence of any definite basic salt of aluminum. It seems to me that there is a wide difference between the definite crystalline double salts prepared by Weinland and hypothetical complex basic aluminum salts. Moreover, by hydrolysis of a dilute solution of aluminum acetate and boiling off the acetic acid, it is possible to prepare a colloidal solution in which the ratio of alumina to acetic acid is so large that it is inconceivable that the disperse phase is a basic salt. And yet, the colloid prepared by long boiling of the acetate is quite similar to the Bentley and Rose colloid.

The theory that the reversibility of the colloid is due to the variation in the concentration of the soluble aluminum salt of the acid used in its formation in agreement with the mass action law, is likewise not in accord with the facts. I have pointed out that Rose's observation is incorrect, namely that aluminum chloride but not aluminum nitrate causes reversible coagulation in a colloid prepared with hydrochloric acid; and that aluminum nitrate but not aluminum chloride causes reversible coagulation in a colloid prepared with nitric acid. Moreover, contrary to Rose's observation, it has been shown that *sodium* acetate readily precipitates a colloid prepared with acetic acid and alumina.

There is an apparent disposition on the part of Bentley and Rose to regard the precipitation by potassium sulphate as distinctly different than the precipitation by hydrochloric and nitric acids: "The substance is, however, different from that formed by either of the other precipitants investigated for this coagulum will not dissolve in water even though it is washed repeatedly. It has appeared to us that this precipitation is like that which usually occurs when a colloidal solution is precipitated by an electrolyte."

In the work carried on in this laboratory on the adsorption of precipitating ions by hydrous oxides we have found that reversible precipitation usually occurs with electrolytes having univalent ions, altogether irrespective of the physical character of the precipitate.[1] On the other hand, with electrolytes having multivalent anions, the precipitation is nearly always irreversible. This is what one should expect. Electrolytes with univalent anions precipitate the positive hydrous oxides only at high concentration on account of the weak adsorption of the anions. The weakly adsorbed anions are, of course, readily washed out and so the precipitates go into colloidal solution when washed with pure water. On the other hand, electrolytes with multivalent anions precipitate in extremely low concentration as a rule and the strongly adsorbed anions are not readily removed, so that under these circumstances the precipitates are not carried back into colloidal solution by washing. From this point of view the observations on the colloid formed by peptizing alumina with acetic acid are readily interpreted. When gelatinous alumina is added to dilute acetic acid, a portion of the alumina is dissolved, the amount varying with the concentration of the acid, the temperature and the method of procedure followed; and a portion is peptized by preferential adsorption of hydrogen ions and aluminum ions. If the solution so obtained is highly diluted and boiled until acetic acid can be no longer detected, a stable colloid is obtained that will stand indefinitely without coagulating. However, if the colloid is prepared by saturating an 8 percent solution of acetic acid with hydrous alumina, and filtering, it is too concentrated to possess the high degree of stability of a dilute colloid; hence, a portion will settle out on standing. The precipitate carries down with it acetate ion and an equivalent amount of aluminum and hydrogen ion. The addition of an excess of an acid or salt having a univalent anion causes agglomeration and the precipitating anion is carried down in the precipitate. When these precipitates are washed the weakly adsorbed anion is

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[1] Weiser: Jour. Phys. Chem., 24, 277 (1920).

removed, together with an equivalent amount of cation until the concentration of the precipitating agent is so low that the entire precipitate goes into colloidal solution again. The precipitate that can be obtained with a trace of potassium sulphate is not reversible since sulphate ion is too strongly adsorbed to be removed by washing with pure water.

The Action of Alkalis on Gelatinous Aluminum Oxide

In considering the peptization of hydrous alumina some mention should be made of the action of alkalis on the newly-formed oxide. It is known, for example, that chromic oxide is peptized by caustic alkali and that no chromite is formed.[1] Similarly, beryllium hydroxide,[2] and to a certain extent, hydrous copper oxide,[3] cobalt oxide[4] and stannic oxide[5] are peptized by sodium and potassium hydroxide. In these cases peptization is caused by preferential adsorption of hydroxyl ion, resulting in the formation of a negative colloid. Certain authors[6] have supported the view that hydrous aluminum oxide is carried into colloidal solution in this way by sodium hydroxide and potassium hydroxide. However, the bulk of the evidence[7] seems to indicate that peptization plays but a slight rôle in the process and that definite aluminates are formed. The composition of the aluminates is $KAlO_2$ or $NaAlO_2$ or some multiple thereof. Allen and

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[1] Fischer and Herz: Zeit. anorg. Chem., **31**, 352 (1902); Nagel: Jour. Phys. Chem., **19**, 331, 569 (1915).

[2] Hantzsch: Zeit. anorg. Chem., **30**, 289 (1902).

[3] Loew: Zeit. anal. Chem., **8**, 463 (1870); Fischer: Zeit. anorg. Chem., **40**, 39 (1904).

[4] Tubandt: Zeit. anorg. Chem., **45**, 368 (1905).

[5] Varga: Kolloidchem. Beihefte, **11**, 1 (1919).

[6] Mahin, Ingraham and Stewart: Jour. Am. Chem. Soc., **35**, 30 (1913).

[7] Prescott: Jour. Am. Chem. Soc., **2**, 27 (1880); Lyte: Chem. News, **51**, 109 (1885); Noyes and Whitney: Zeit. phys. Chem., **15**, 694 (1894); Herz: Zeit. anorg. Chem., **25**, 155 (1900); Hantzsch: Ibid., **30**, 289 (1902); Rubenbauer: Ibid., **30**, 331 (1902); Fischer and Herz: Ibid., **31**, 355 (1902); Slade: Jour. Chem. Soc., **93**, 421 (1908); Zeit. anorg. Chem., **77**, 457 (1912); Hildebrand: Jour. Am. Chem. Soc., **35**, 864 (1913); Blum: Ibid., **35**, 1499 (1913); **36**, 2383 (1914); Slade and Polack: Trans. Far. Soc., **10**, 150 (1914).

Rogers[1] have prepared crystals of potassium aluminate having the composition $K_2Al_2O_4.3H_2O$. The hydrolysis of the aluminates in solution results in the formation of colloidal alumina which then settles out in the slightly hydrous, difficultly soluble, granular form.

The Physical Character of Precipitated Alumina

Hydrous aluminum oxide is ordinarily precipitated in an extremely gelatinous form that is very difficult to filter, a property distinctly more marked with this oxide than with the corresponding iron oxide. Taylor[2] claims that the oxide is less gelatinous if the precipitation is carried out at 66° instead of at 100°. I have compared the precipitates obtained at the two temperatures and find that both are quite voluminous. As pointed out in the preceding section, colloidal alumina is formed by the hydrolysis of alkali aluminate and from this solution it precipitates in a slightly hydrous granular form. Under these conditions the precipitation is relatively slow and takes place in a medium having a solvent action. As I have shown in the case of colloidal hydrous ferric oxide,[3] these are the conditions under which one would expect to get granular precipitates. The explanation of this behavior with colloidal solutions has been considered in the paper referred to above and need not be discussed here. Although colloidal ferric oxide may be precipitated in a distinctly granular form under suitable conditions, the coagulation of positive colloidal alumina always results in a highly gelatinous precipitate. Analogous to the observations with hydrous ferric oxide, it seemed probable however, that colloidal alumina coagulated by an acid having some solvent action might produce a less voluminous precipitate than is obtained with a neutral salt. Since dilute sulphuric acid possesses a slight solvent action on the colloid prepared by hydrolysis of aluminum acetate and since potassium sulphate solution

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[1] Am. Chem. Jour., 24, 304 (1900).

[2] Chem. News, 103, 169 (1911).

[3] Jour. Phys. Chem., 24, 277 (1920).

possesses no such action, some experiments were carried out to determine whether the precipitate obtained with the acid is less voluminous than that obtained with the salt. Unfortunately, the precipitate obtained with both electrolytes was so hydrous that it settled very slowly indeed; and so the comparison could not be made by the same method used with colloidal ferric oxide. However, the following procedure was found to be satisfactory: Twenty-five cubic centimeter or fifty cubic centimeter portions of a colloid containing 2 grams Al_2O_3 per liter were precipitated with an equal volume of the electrolytes and the solutions allowed to stand for an hour, after which they were centrifuged for three minutes at 2000 r. p. m. The supernatant liquid was poured off, the precipitates transferred quantitatively to graduated test tubes and the centrifuging repeated. By subjecting all solutions to the same procedure, comparable results were obtained. The results of the two series of experiments are given in Table III.

TABLE III

Solutions mixed		Volume of precipitate cc
Colloid	Electrolyte	
25 cc	0.25 cc of *N* K_2SO_4 in 25 cc	2.8
25 cc	0.5 cc of *N* H_2SO_4 in 25 cc	2.7
25 cc	10.0 cc of *N* H_2SO_4 in 25 cc	1.8
25 cc	25.0 cc of *N* H_2SO_4 in 25 cc	1.7
50 cc	0.5 cc of *N* K_2SO_4 in 50 cc	5.1
50 cc	0.5 cc of *N* H_2SO_4 in 50 cc	5.0
50 cc	5.0 cc of *N* H_2SO_4 in 50 cc	4.4
50 cc	10.0 cc of *N* H_2SO_4 in 50 cc	4.0
50 cc	25.0 cc of *N* H_2SO_4 in 50 cc	3.9

From the results of the two series of experiments above recorded it is evident that the precipitate obtained with a fairly high concentration of acid is less voluminous than that obtained with a small amount of acid or salt. The difference could not be due to the removal of alumina by the formation of aluminum sulphate since the supernatant liquids after centrifuging were tested for aluminum by making them slightly alkaline with ammonia and allowing them to stand; in only one case was a test obtained: Experiment number four, Table III. Though less marked, the results are quite similar to those obtained with colloidal hydrous ferric oxide.

The results of this investigation may be summarized as follows:

(1) Aluminum oxide forms but one definite hydrate, the trihydrate, precipitated from the solution of the oxide in caustic alkali. The so-called hydrates formed by precipitating soluble aluminum salts with ammonia are not definite compounds but are hydrous oxides prepared or analyzed under such conditions that their percentage composition just happened to approach that of a definite hydrate.

(2) Analogous to ferric oxide, it is possible to prepare any number of hydrous aluminum oxides differing in the size of the particles and in the amount of water they contain. The larger and less hydrous the particles the smaller is the solubility in acids and alkalis. There is no temperature of inversion from the ordinary oxide which is soluble to the so-called meta oxide which is insoluble. Accordingly, an indefinite number of hydrous oxides are possible that show a continuous variation in their solubility in acids and alkalis.

(3) Any number of colloidal aluminas may be prepared which show a continuous variation in properties. The colloidal oxide prepared by prolonged digestion of aluminum acetate at a high temperature is insoluble in acids and alkalies and has no mordanting action; the colloid prepared by peptizing gelatinous alumina with aluminum chloride and dialyzing in the cold, is soluble in acids and possesses a mordanting action. By suitable variation in the conditions, colloids with intermediate properties are readily formed.

(4) Colloidal alumina is a positive colloid and so is stabilized by preferential adsorption of cations. The relative peptizing power at 100° of certain acids and salts on gelatinous alumina has been determined. The order is: nitric acid > hydrochloric acid > ferric chloride > aluminum chloride >

acetic acid. The peptizing power of ferric chloride is almost the same as of hydrochloric acid since dilute solutions of the former are completely hydrolyzed at 100° with the formation of colloidal ferric oxide and hydrochloric acid. It is probably incorrect and altogether unnecessary to assume the formation of aluminum ion as an intermediate step in the peptization of aluminum oxide by acids and salts.

(5) The colloids formed by peptization of gelatinous alumina are not composed of basic salts of varying composition. Moreover, there is no necessity for postulating the formation of a series of hypothetical complex salts in order to account for the properties of the colloid.

(6) The coagulation by electrolytes of colloidal aluminas prepared by different methods has been studied. Strong acids with univalent anions and their salts precipitate the colloid but only in high concentration. The precipitation with these electrolytes is reversible on account of the weak adsorption of the anion which is readily removed by washing. Acids with multivalent anions and their salts precipitate the colloids in very low concentration and the precipitation is irreversible since the strongly adsorbed multivalent anions can not be removed by washing.

(7) Rose's explanation of the cause of the reversibility of precipitation of colloidal alumina has been shown to be theoretically and experimentally unsound.

(8) Gelatinous alumina dissolves in caustic soda or caustic potash with the formation of an aluminate that is unstable. The decomposition of the aluminate forms a colloidal hydrated alumina which separates out in a granular, difficultly soluble form.

(9) Observation of the effect of the nature of the coagulating agent on the physical character of the precipitated oxide confirms the conclusions previously reached from the investigations on colloidal hydrous ferric oxide.

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A RELATION BETWEEN THE VOLUME AND THE VELOCITY OF SOME ORGANIC IONS

BY HOMER W. SMITH

Investigation discloses that the velocity of an organic ion is independent of the mass of the ion, and independent of its configuration. It depends essentially upon two factors:

First—The specific nature of the nucleus or polar group to which the ion owes its chemical properties.

Second—The total volume of the ion.

In any series of ions having a common ionic nucleus, and no other (viz., $—COO'$*,* $—NH_3'$*,* $—NH'$*, etc.), and apart from certain well-defined disturbing influences, the velocity is an inverse exponential function of the volume.*

In 1894, G. Bredig[1] published a lengthy treatise on the velocities of organic ions, in which he pointed out all of the salient facts, considering the phenomena involved in terms of molecular weights. He recognized the numerous parallels and exceptions, and treated them from an additive point of view. Since Bredig's publication, more light has been thrown on the volume of the atoms and atom-groups comprising the organic molecule, and it is the purpose of this paper to point to the regularity in the behavior of these ions when considered on a basis of volume, rather than mass.

The Determination of Ionic Velocity.—The equivalent conductance of a dissolved salt increases with dilution, at first rapidly, then more slowly, and as very great dilutions are reached it approaches a maximum. This increasing conductance with dilution is supposed to be the result of increasing ionization, and the equivalent conductance is, therefore, the greatest at a dilution where the salt is completely ionized.[2]

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[1] Zeit. phys. Chem., 13, 191 (1894).

[2] The failure of salts of strong acids and bases to obey the mass law in the matter of ionization has been explained on the hypothesis that such substances are completely ionized, even in concentrated solutions, and that the decrease in the conductance ratio is to be attributed wholly to a decrease in ionic mobility, arising from interionic attractions (secondary valence (H. W. S.)) and not to

This maximum value is sometimes determined by direct measurement at great dilution, but more often by extrapolation to zero concentration from several determined dilutions. The equivalent conductance of a salt at infinite dilution will be the combined conductance of the two ions, and to obtain the conductance of either ion alone, it is necessary to combine this value with the transference number of one of the ions as determined by other methods. Thus it is known that in a dilute solution of sodium chloride, the sodium ion carries 41.2 percent of the current, and the chlorine ion 58.8 percent. Since at infinite dilution the equivalent conductance of sodium chloride is 119.4 (25°), the equivalent conductance, Λ, of the sodium ion is 49.2, and that of the chlorine ion is 70.2. Having once determined the equivalent conductance of the sodium ion or the chlorine ion, at 25°, we need only to subtract that value from the equivalent conductance of any sodium salt or chloride similarly determined for infinite dilution and at the same temperature, to obtain the equivalent conductance of the other ion. Since each ion carries a unit, or some multiple of a unit charge, it is supposed that the variations observed in the equivalent conductance of various ions are attributable to differences in the velocity with which they move through the solvent, and the terms "equivalent conductance" as applied to ions are used interchangeably with the terms "ionic velocity."

The values for the ionic velocity given here are quoted directly from Bredig's paper. For Λ_{Na}, he used 49.2; for Λ_{Cl}, 70.2. All of his work was done at 25°, and is expressed in the Siemens unit.

The Calculation of Ionic Volume.—The conception that a molecule occupies a definite and well-defined space which no other molecule can occupy simultaneously is founded upon

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the association of ions into true molecules. (Milner: Phil. Mag., **35**, 214, 354 (1918); Ghosh: Jour. Chem. Soc., **113**, 449, 627 (1918); Bjerrum: Zeit. Elektrochemie, **24**, 321 (1918); Noyes: Jour. Am. Chem. Soc., **30**, 335, 353 (1908); and Noyes and MacInnes, Ibid., **42**, 239 (1920).) Langmuir carries this idea a step further, saying, "*According to this theory* all salts are completely ionized even before they are brought into solution." Jour. Am. Chem. Soc., **42**, 274 (1920); cf. p. 292.

the apparent fact that a gram-molecule of any substance possesses a well-defined volume, specific for that substance at a certain temperature and pressure. From an analysis of the gram-molecule volumes of a number of liquid chemical compounds, it has been shown that each atom contributes a definite share to this volume, just as each atom contributes a definite share to the total mass, though the calculation of the total volume of the molecule is by no means as simple as the calculation of its total mass. The difficulties inherent in the former arise from the facts that the volume of an atom may vary under different conditions—the volume of oxygen, for example, varying by more than 100 percent—and that interactions take place between groups which result in a shrinkage in the total volume of the molecule.

For the purposes of calculating molecular and ionic volumes, the rules of Le Bas[1] have been observed. They are briefly summarized here, but for the details the original monograph must be consulted. The figures given are based upon the study of liquid chemical compounds at the normal boiling point, and represent the volume in cubic centimeters. No hard and fast rules can be set down for the calculation of molecular volumes, and it is always best wherever possible to work from a compound of known volume. The principal atomic and group volumes are as follows:

C	14.8		$—CH_3$	26.0
H	3.7		$—C_2H_5$	48.0
Cl	21.6	Terminal	$—C_3H_7$	70.0
	24.6	Medial	$—C_4H_9$	92.3
	21.6	On the ring		
Br	27.2		—OH	10.0
I	37.9		$—NH_2$	17.8
S	25.6	Mercaptans and Thioethers	—CO	22.0
N	27.0	Ring and —SCN	—CHO	25.9
			—CN	30.4
			$—NO_2$	32.0
	10.5	Primary amines	—COOH	37.8
	12.0	Secondary-Tertiary amines	—SCN	52.0
	(15.2)	(Quaternary)		
P	27.0		$—C_6H_5$	92.8

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[1] The Molecular Volumes of Liquid Chemical Compounds: Longmans, Green and Co. (1915).

Oxygen:
6.4 Alcohols
9.9-11.0 Ethers
7.4 Aldehydes and ketones

12.0 CO in acids

We have used these values for the hydrocarbon radicals when in combination with N.

$—CH_3$	(25.2)
$—C_2H_5$	(46.8)
$—C_3H_7$	(67.9)
$—C_4H_9$	(89.0)
$—C_5H_{11}$	(109.7)

The polar groups interact, causing contractions as indicated:

$—Cl$, $—Br$, $—I$, $—OH$, $—NH_2$, $—NO_2$, $—COOH$......

αα	—0.0			
αβ	—3.0	On the ring,		
αγ	—4.5		Ortho	—2.2
αδ	(—6.0)		Meta	—1.1
αε	(—7.5)		Para	(—0.5)
αζ	(—9.2)			

—CO...... ±0.0

For every *iso* group............ —0.5

$—H_2C:CHX$ —1.7

$—XHC:CHX$ —1.7

The formation of a ring is accompanied by large contractions:

Three members	— 6.5	Seven members	—20.0
Four members	— 8.5	Eight members	—25.5
Five members	—11.5	Eleven members	—26.0
Six members	—15.0	Twelve members	—30.0
Eighteen members	—48.0		

In estimating the contraction of a ring, every atom which enters into each ring is counted, even though some atoms may be counted two or three times. Thus, in naphthalene, there are two rings, each of which contain six members, so the contraction would be —30.0, in pyridine, —15 (six members), etc. This contraction is shared alike by every atom in the ring, as well as the attached hydrogens. Therefore, the value of hydrogen in benzene is 3.2, rather than 3.7.

When a polar group is attached to the benzene ring, there are further contractions:

—CH$_3$, etc.	—0.5	—NO$_2$	—2.7
—COOC$_2$H$_5$, etc.	—0.5	—COOH	—3.9
—OH	—0.9	—NH$_2$	—4.3
—COOCH$_3$	—1.5	—CH$_2$X	As indicated for X
—Cl, —Br, —I, OCH$_3$......	±0.0		

(The figures in parenthesis are not given by Le Bas, but are my own extrapolations from the available data, and are given merely to indicate the values used in such cases.) The nitrogen derivatives present the greatest difficulty. The influence of the nitrogen atom upon the hydrocarbon complex is such as to greatly diminish its value in the lower members. The values given are derived by simply subtracting the figure given by Le Bas for —NH$_2$ from the observed values of the amines.

Attention is called to the fact that the molecular volume calculated by this method represents the gross volume of the molecule when surrounded by a thermo-dynamic environment of an homologous nature; no allowance has been made for any changes in volume which might follow its introduction into a dissimilar environment. There is sufficient evidence to indicate that the volume of an ammonium molecule may not be the same when in aqueous solution as it is when it is surrounded by nothing but ammonia molecules. It has been tacitly assumed that the molecular volumes will parallel molecular-solution volumes, and that for the purpose of comparing the behavior of different molecules under similar conditions, the latter may be neglected. The results obtained indicate that this assumption is well founded, and that Le Bas' method of calculation will lead to the uncovering of some very nice relationships involving the volume of the molecule.

The Comparison of Ionic Velocity on a Basis of Volume

The Nitrogen Derivatives.—These compounds may be divided into four principal groups according to the nature of the polar group which carries the open valence, or the ionic-polar group:

1—Primary Nitrogen
2—Secondary Nitrogen
3—Tertiary Nitrogen
4—Quaternary Nitrogen
—Pyridine Nitrogen (possibly)

These groups are identified by two characteristics: (1) a fairly smooth curve can be drawn through each group when volume is plotted against velocity; (2) each successive group

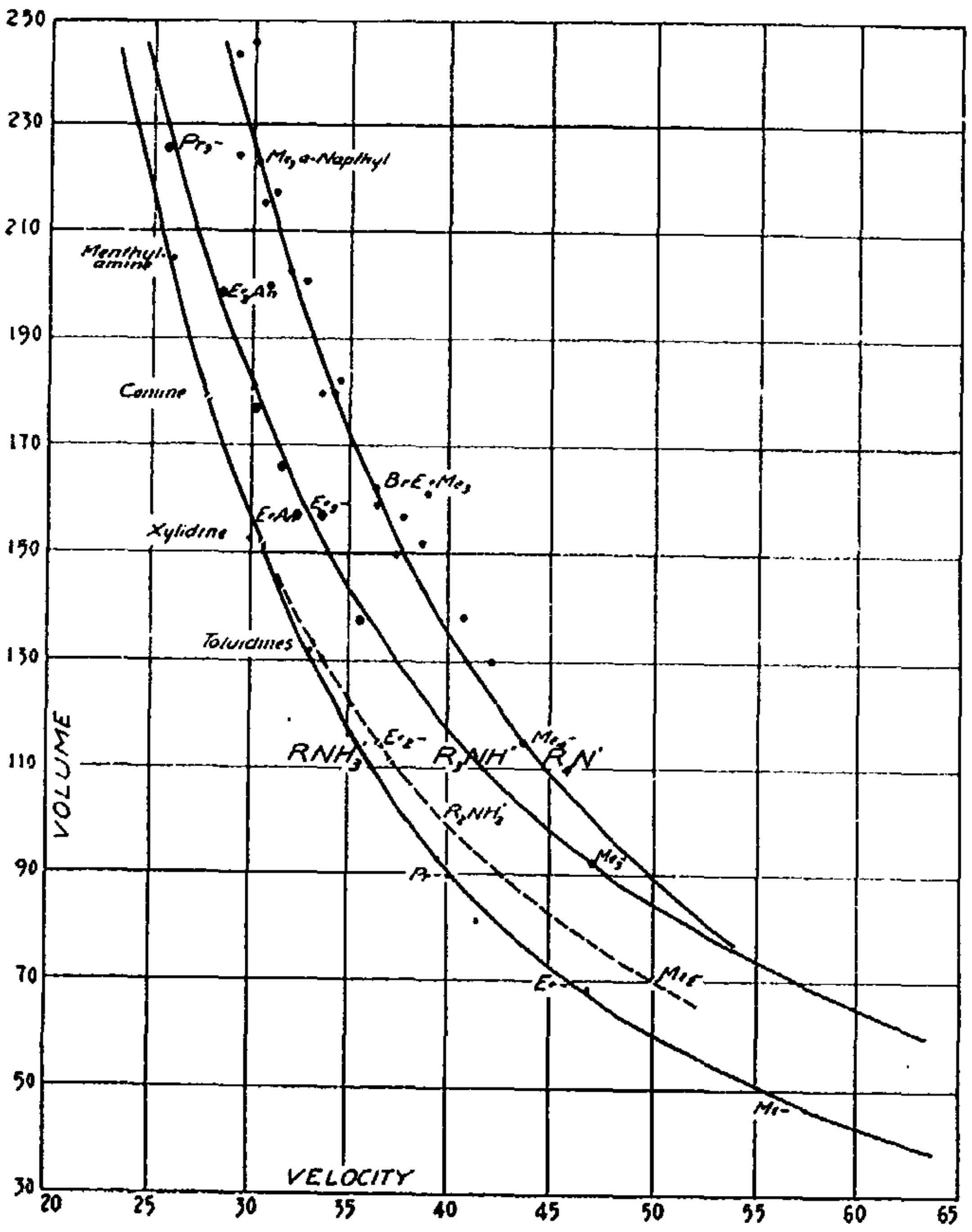


Fig. 1

as named shows a greater velocity at a given volume than the preceding group. (See Fig. 1.) We will consider each group separately.

Primary Nitrogen

TABLE I

		V_i	Λ	$\sqrt[1.85]{V_i}\,\Lambda$
Ammonia	NH_4'	30.6	70.4	447
Methylamine	$MeNH_3'$	46.7	57.6	462
Ethylamine	$EtNH_3'$	68.3	46.8	460
Allylamine	$C_3H_5NH_3'$	82.2	41.5	450
iso-Propylamine	$(Me)_2CHNH_3'$	88.9	40.0	452
β-Bromoethylamine	$BrCH_2CH_2NH_3'$	88.8	39.4	445
Propylamine	$PrNH_3'$	89.4	40.1	457
iso-Butylamine	$(Me)_2CHCH_2NH_3'$	110.0	36.3	460
Aniline	$PhNH_3'$	110.3	35.9	455
o-Toluidine	$MeC_6H_4NH_3'$	130.4	33.5	464
iso-Amylamine	$(Me)_2CH(CH_2)_2NH_3'$	130.7	33.9	470
Benzylamine	$PhCH_2NH_3'$	131.1	34.2	475
m-Toluidine	$MeC_6H_4NH_3'$	131.5	32.8	458
p-Toluidine	$MeC_6H_4NH_3'$	132.6	33.0	464
Xylidene, 1:3:4	$(Me)_2C_6H_3NH_3'$	152.3	30.0	456
Menthylamine	$C_{10}H_{19}NH_3'$	204.7	26.0	463

We see that these compounds show a constantly decreasing velocity, when arranged in the order of increasing volume. The necessity of considering *volume*, rather than *mass*, is apparent in this group, though not as striking as in some of the later ones. The formation of a ring compound is accompanied by a large contraction in volume, this contraction being shared by each atom of the ring.

	M.W.	V_i	Λ
Hexylamine	101.19	151.1	—
Benzylamine	107.15	131.1	34.2
iso-Amylamine	87.14	130.7	33.9

Thus benzylamine, which has a mass equivalent to hexylamine, has a volume equivalent to that of amylamine, which it also approximates in velocity.

Again, bromoethylamine has a mass twice as great as propylamine, but their volumes and velocities are respectively nearly identical.

Propylamine	59.13	89.4	40.1
β-Bromoethylamine	124.03	88.8	39.4

The comparison might be extended by numerous instances; the result of the introduction of a ring, a halogen, a hydroxyl group, a nitro group, etc., into a simple aliphatic compound is evidently a change in velocity proportional to the change in volume, and not in mass.

With each group is given an empirical equation which yields approximately a constant: $\sqrt[y]{V_iA} = K$. It is not assumed that this equation represents the exact interpretation of the relation between velocity and volume, but it serves as a check for the graphical picture and enables us to compare various compounds in each group. No attempt has been made to secure ultimate accuracy for y; a slight variation one way or the other might be said to fit the facts just as well.

Though the significance will not be evident as yet, we will call attention to the fact that the ring-containing compounds, aniline, the toluidines, xylidene and menthylamine, do not show sufficient deviation from the group constant to warrant our assigning to the ring any specific influence upon the nitrogen nucleus.

Secondary Nitrogen

TABLE II

		V_i	A	$\sqrt[1.6]{V_iA}$
Dimethylamine	$(Me)_2NH_2'$	70.0	50.1	711
Piperidine	$C_5H_{10}NH_2'$	112.5	35.8	684
Diethylamine	$(Et)_2NH_2'$	113.0	36.1	691
Methylaniline	$PhNH_2'Me$	133.3	35.0	747
Dipropylamine	$(Pr)_2NH_2'$	155.2	30.4	712
Conimine	$PrC_5H_9NH_2'$	179.3	28.0	718
Ethylaniline	$PhNH_2'Et$	155.3	30.5	714

Only a very few compounds containing secondary nitrogen are available for study. There is no question, however, but what they form a separate group, because the velocity of the lower members is greatly increased over that of the former group. The difference in velocity between primary and secondary nitrogen becomes less marked as the volume

Tertiary Nitrogen

TABLE III

	V_i	Λ	$\sqrt[1.5]{V_i}\Lambda$
Trimethylamine, $(Me)_3NH'$	91.7	47.0	957
Methyldiethylamine, $(Me)(Et)_2NH'$	134.5	35.8	942
Triethylamine, $(Et)_3NH'$	156.3	32.6	945
Tripropylamine, $(Pr)_3NH'$.	226.2	25.6	950
			Mean, 948

	V_i	Λ obs.	Λ calc.	Δ
Dimethylaniline, $PhN(Me)_2H'$	156.1	33.8	32.7	+1.1
Methylethylaniline, $PhN(Me)(Et)H'$	177.6	30.4	30.1	+0.3
Diethylaniline, $PhN(Et)_2H'$	198.4	28.6	27.9	+0.7
Pyridine, C_5H_5NH'	93.2	44.1	45.5	—1.4
α-Picoline, MeC_5H_4NH'	115.4	39.1	40.3	—1.2
Collidine, $(Me)_3C_5H_2NH'$	156.2	34.8	33.0	+1.8
Lepidine, MeC_9H_6NH'	166.0	31.6	31.3	+0.3
Morphine, $C_{17}H_{19}O_3NH'$	(280.6)	23.0	(22.4)	+0.6
Codeine, $C_{18}H_{21}O_3NH'$	(302.1)	23.2	(21.2)	+2.0

increases, and dipropylamine shows but slightly greater velocity than that which would be calculated for hexylamine. The constants as given here generate curves which cross at V_i = 164.0, but it is possible that if more data were available, the secondary curve would be found to be tangential to the primary. With the exception of the methyl compound, the aniline derivatives compare favorably with the amines.

The tertiary nitrogen nucleus has been considered more in detail, for the results regarding the influence of the ring are somewhat conflicting. The aliphatic amines do not themselves give very satisfactory agreement, but the average value of the constant derived from them has been used in comparing the behavior of the other members of the group.

It will be seen that the variation of the aniline and pyridine derivatives is not consistent, and considering the difficulty of obtaining accurate conductivity data with these compounds, it may possibly be said to lie within the experimental error. The quaternary pyridine derivatives show a consistent diminution in velocity, and coupled with the diminution observed in pyridine and α-picoline, this fact suggests that pyridine-nitrogen cannot be classed with either group. Nitrogen in, or adjacent to the ring (pyridine or aniline), shows chemically quite a different nature from aliphatic nitrogen, and if there is a difference made evident in this phenomenon in one case, we would expect it in the other. But in this as in previous groups, anilido-nitrogen shows no deviation from the group behavior.

This group affords us an excellent opportunity of checking our interpretation of velocity in terms of volume. It is clear that no comparison can be made in terms of mass or of spatial configuration, for we find here every sort of organic arrangement. As a group, the velocity is clearly determined by the volume of the molecule. The ones which we would expect to show the greatest deviation, show the least, and vice versa. It is unlikely that the error lies in the determination of the equivalent conductance, though it is possibly in the calculation of the volume. Empirical rules have been

Quaternary Nitrogen

TABLE IV

	V_i	Λ	$\sqrt[1.85]{V_i}\Lambda$
Tetramethylammonium, Me_4N'	116.0	43.6	572
Vinyltrimethyl ammonium, $(C_2H_3)(Me_3)N'$	131.9	41.8	570
Trimethylethyl ammonium, $(Me_3)(Et)N'$	137.6	40.4	575
Iodomethyltrimethyl ammonium, $(CH_2I)(Me_3)N'$	150.2	37.2	556
Trimethylallyl ammonium, $(Me_3)(C_3H_5)N'$	151.2	38.1	575
β-Chloroethyltrimethyl ammonium, $(C_2H_4Cl)(Me_3)N'$	152.5	37.3	567
β-Bromoethyltrimethyl ammonium, $(C_2H_4Br)(Me_3)N'$	158.1	36.2	562
Trimethylpropyl ammonium, $(Me_3)(Pr)N'$	158.7	36.2	560
Dimethyldiethyl ammonium, $(Me_2)(Et_2)N'$	159.2	38.2	592
Trimethyl*iso*butyl ammonium, $(Me_3)(C_4H_9)N'$	179.3	33.9	562
Trimethylphenyl ammonium $(Me_3)(Ph)N'$	179.3	34.3	568
Methyltriethyl ammonium, $(Me)(Et_3)N'$	180.8	34.4	570
Trimethyl*iso*amyl ammonium, $(Me_3)(C_5H_{11})N'$	200.0	30.8	538
Dimethylethylphenyl ammonium, $(Me_2)(Et)(Ph)N'$	200.9	32.9	578
Tetraethyl ammonium, $(Et_4)N'$	202.4	32.2	568
Iodomethyltriethyl ammonium, $(CH_2I)(Et_3)N'$	215.0	30.8	560
Triethylallyl ammonium, $(Et_3)(C_3H_5)N'$	216.1	31.5	572
Triethylpropyl ammonium, $(Et_3)(Pr)N'$	223.5	29.5	550
Trimethyl-α-naphthylamine, $(Me_3)(C_{10}H_7)N'$	230.4	30.6	583
Trimethyl-β-napthylamine, $(Me_3)(C_{13}H_7)N'$	230.4	30.4	579
Triethyl*iso*butyl ammonium, $(Et_3)(C_4H_9)N'$	244.1	29.1	570
Triethyl*iso*amyl ammonium, $(Et_3)(C_5H_{11})N'$	264.8	26.3	540

followed, and it is entirely possible that in the quaternary compounds, where we have no experimental data upon which to rely, there occur contractions or expansions of considerable magnitude. Certainly there is no exaltation here to be associated with the ring.

The Quaternary Pyridine Derivatives

TABLE IVa

	V_i	Λ obs.	Λ calc.	Δ
Ethylpyridinium, $(C_5H_5)(Et)N'$	139.5	38.7	39.5	—0.8
Methylpicolinium, $(C_6H_7)(Me)N'$	140.1	38.9	39.4	—0.5
Methyllutidinium, $(C_7H_9)(Me)N'$	161.1	35.2	36.8	—1.6
Ethylpicolinium, $(C_6H_7)(Et)N'$	161.7	35.1	36.7	—1.6
Methylmorphine, $(Me)(C_{17}H_{19}O_3)N'$	(305.3)	23.9	25.8	—1.9

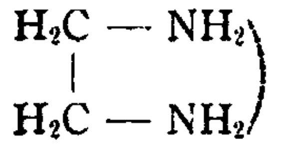
These compounds show a consistent decrement in comparison with the quaternary nitrogen curve. Pyridine and picoline showed a similar decrement in comparison with the tertiary nitrogen curve. This leads one to believe that pyridine nitrogen is to be differentiated from other types, but not anilido-nitrogen.

The Diamines

TABLE V

	V_i	Λ	$\sqrt[3]{V_i}Λ$
Ethylenediamine, $NH_3'(CH_2)_2NH_3$	82.4	75.9	330
Trimethylenediamine, $NH_3'(CH_2)_3NH_3'$	103.5	70.6	332
β-Chlorotrimethylenediamine, $NH_3'CH_2CHClCH_2NH_3'$	121.4	63.8	316
Tetramethylenediamine, $NH_3'(CH_2)_4NH_3'$	123.2	65.4	326
Pentamethylenediamine, $NH_3'(CH_2)_5NH_3'$	142.0	61.4	322
β-Methyltetramethylenediamine, $NH_3'(CH_2)_2CH(CH_3)CH_2NH_3'$	144.6	61.1	321

Too few compounds are given here to tell us much. The general velocity is greatly increased by their divalent nature, and the exponent *y* is higher than in any other group. The chlorine compound is a little slow; the behavior of the rest would indicate an exponent slightly lower than the cube root. The diamines have been shown to suffer condensation, (cf. Le Bas):



$$\left.\begin{array}{l} H_2C - NH_2 \\ \ \ | \\ H_2C - NH_2 \end{array}\right)$$

and allowance must be made for the consequent contraction in the calculation of their volumes. The fact that this condensation takes place, shows that there is a mutual attraction between two amino polar groups, though it is difficult to say what the net result of this interaction is on the ionic velocity.

The Quaternary Phosphonium Compounds

TABLE VI

	V_i	Λ	$\overset{(2)}{\sqrt{V_i}}\Lambda$
Tetramethylphosphonium, Me_4P'	127.8	39.6	446
Tetraethylphosphonium, Et_4P'	214.2	30.6	448
Methyltriphenylphosphonium, $(Me)(Ph)_3P'$	330.6	24.1	438
Ethyltriphenylphosphonium, $(Et)(Ph)_3P'$	352.2	23.4	438
Propyltriphenylphosphonium $(Pr)(Ph)_3P'$	373.2	22.8	440
Triphenylbenzylphosphonium, $(Ph)_3(Bz)P'$	414.9	22.4	456
iso-Amyltriphenylphosphonium, $(C_5H_{11})(Ph)_3P'$	414.5	21.2	435
Tetrabenzylphosphonium, $(Bz)_4P'$	465.0	(22.0)	(474)

Like the nitrogen nucleus, the phosphorus nucleus does not seem to be affected by the benzene ring, though there are too few compounds here to show this conclusively. The italics for the last member of the group are Bredig's.

The Acids

The Aliphatic Monobasic Acids

TABLE VII

	V_i	Λ	$\sqrt[2.5]{V_i\Lambda}$
Formic acid, $HCOO'$	37.8	51.2	(219)
Acetic acid, $MeCOO'$	60.3	39.3[1]	203
Glycollic acid, $OHCH_2COO'$	61.9	37.6	196
Acrylic acid $CH_2 : CHCOO'$	74.2	34.8	201
Propionic acid $MeCH_2COO'$	81.6	34.3	199
Lactic acid $MeCH(OH)COO'$	85.0	32.9	195
Tetrolic acid, $MeC : CCOO'$	89.3	35.7	(214)
iso-Crotonic acid, $HMeC : CHCOO'$	96.2	32.2	200
Crotonic acid, $MeHC : CHCOO'$	96.7	32.0	199
iso-Butyric acid, $(Me)_2CHCOO'$	103.6	30.9	198
Butyric acid, $Me(CH_2)_2COO'$	104.1	30.7	197
Tiglic acid, $MeHC : C(Me)COO'$	118.4	29.6	200
Angelic acid, $MeCH_2HC : CHCOO'$	118.9	29.4	199
Valeric acid, $Me(CH_2)_3COO'$	126.3	28.8	199
Hydrosorbic acid, $MeCH_2CH : CHCH_2COO'$	141.4	28.8	(209)
Caproic acid, $Me(CH_2)_4COO'$	148.8	27.4	203

Unlike the nitrogen derivatives we cannot include in one group those acids which are unsubstituted and those

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[1] The ionic velocity of acetic acid is given by Bredig as 38.3, a figure which is apparently too low. The figure 39.3 is obtained from Kohlrausch (Kohlrausch and Holborn: Leitvermögen der Elektrolyte (1898)) and gives a very good agreement with the rest of the group.

which contain the benzene ring or other polar groups. The unsubstituted aliphatic monobasic acids, when considered by themselves, give excellent agreement, but there are no

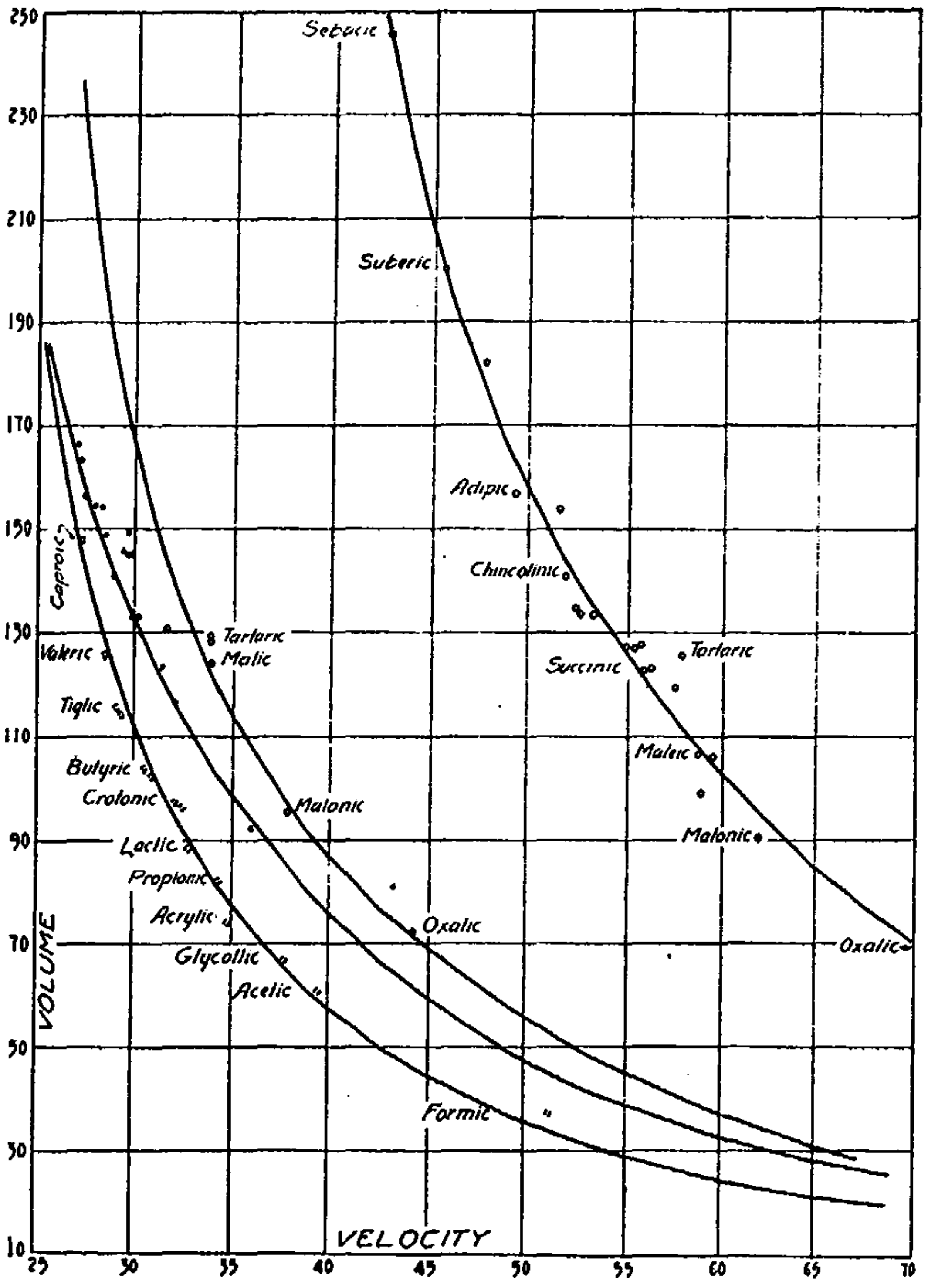

Fig. 2

groups here which cause large changes in volume. (See Fig. 2.) Formic acid has much too high a velocity but no explanation can be advanced for its behavior. There are two points of extreme interest to be found in this group. First, that the ethylene linkage should have no effect upon the velocity. This is of interest because of the behavior of the benzene ring, consideration of which follows this. Out of seven acids containing double linkages, five behave quite regularly. The other two show exaltation:

	Λ obs.	Λ calc.	Δ
Tetrolic acid	35.7	33.0	+2.7
Hydrosorbic acid	28.8	27.6	+1.2

Two out of seven cases are hardly sufficient to establish any positive influence of one double linkage upon the carboxyl group. In calculating the volumes of these acids, I have not allowed for any shrinkage from an interaction of this sort; the only possible change is a shrinkage, and that would result in giving the observed velocity too low a value rather than too high a one. Therefore, I conclude that such an interaction does not take place. The second point of interest is the behavior of the hydroxy acids. The discussion of these will be deferred, however, until we take up the dibasic group, when there will be more evidence.

The carboxyl group is characterized by its sensitivity to other polar groups. Especially interesting is the phenyl radical, the introduction of which in the carboxylic anion results in the formation of an entirely new group, the general velocity being considerably greater than that of the aliphatic group. The negative exponent y is reduced from 2.5 to 2.0, and as a result the aromatic curve crosses the aliphatic curve ($V_i = 182$) in much the same manner as the secondary nitrogen curve appeared to cross the primary. This, however, is a more certain matter, and there is no doubt but what aromatic acids above this volume have a lower velocity than the aliphatic acids of corresponding volume. For this reason this group could hardly be related to the previous one by differences.

We concluded that the nitrogen nucleus (and probably

The Aromatic Monobasic Acids

TABLE VIII

	Λ_i	Λ	$\sqrt{V_i}\Lambda$
Nicotinic acid, C_6H_4NCOO'	116.5	31.9	344
Benzoic acid, C_6H_5COO'	123.2	31.2	346
o-Amidobenzoic acid, $C_6H_4'NH_2)COO'$	131.3	29.8	342
m-Amidobenzoic acid, $C_6H_4(NH_2)COO'$	132.4	29.9	344
Phenylglycolic acid, $C_6H_5CH(OH)COO'$	148.5	28.0	341
Mandelic acid, $C_6H_5CH(OH)COO'$	148.5	28.3	345
Phenylpropiolic acid, $C_6H_5C:CCOO'$	150.6	27.5	338
Cinnamic acid, $C_6H_5CH:CHCOO'$	159.0	27.3	344
Atropic acid, $C_6H_5C(CH_2)COO'$	161.2	27.1	344
Phthaluric acid, $C_6H_4(CONHCONH_2)COO'$	196.3	24.6	345

phosphorus, too) was not disturbed by the proximity of the benzene ring or other polar groups. In view of this fact, the formation of a new group when the ring and the carboxyl are associated would indicate that some very extensive rearrangement of secondary valence had taken place. Moreover, the carboxyl (at least when it is on the ring) seems to be much more sensitive to the influence of other polar groups than is the nitrogen nucleus. From the preceding table it will be seen that the amino group does not cause much exaltation, but the hydroxyl group does:

	V_i	Λ obs.	Λ calc.	Δ
o-Hydroxybenzoic acid	126.9	32.2	30.5	+1.7
m-Hydroxybenzoic acid	128.0	33.6[1]	30.4	+3.2
p-Hydroxybenzoic acid	128.6	32.7[1]	30.4	+2.3

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[1] Obtained by extrapolation of data from Scudder: Conductivity and Ionization Constants: Longmans, Green and Co. (1915).

This exaltation is reduced by methylation, as would be expected:

p-Methoxybenzoic acid	152.1	28.6	27.9	+0.7

The methyl group, which is only slightly polar, shows an exalting power in the toluic acids:

o-Toluic acid	143.3	29.9	28.8	+1.1
m-Toluic acid	144.5	30.0	28.6	+1.4
p-Toluic acid	145.6	29.6	28.5	+1.1
α-Toluic acid	144.5	29.8	28.6	+1.2
2,3,4-Trimethylbenzoic acid	187.8	24.6	25.2	—0.6
2,4,6-Trimethylbenzoic acid	187.8	25.5	25.2	+0.3

The nitro group is also active in this respect:

o-Nitrobenzoic acid	147.1	29.8	28.4	+1.4
p-Nitrobenzoic acid	148.8	30.1	28.2	+1.9

And so are the halogens:

o-Chlorobenzoic acid	139.6	30.8	29.2	+1.6
m-Bromobenzoic acid	146.1	30.7	28.5	+2.2

In every case the exaltation appears to be greater in the meta and para positions than in the ortho. The halogens produce distinct exaltation when on the chain; the increase here is questionably in favor of the alpha position.

	V_i	Λ abs.	Λ calc.	Δ
Chloroacetic acid	74.3	37.3	35.5	+1.8
Bromoacetic acid	80.8	36.2	34.6	+1.6
α-Chloro*iso*crotinic acid	113.0	31.9	30.2	+1.7
β-Chlorocrotonic acid	112.0	31.9	30.3	+1.6
β-Chloro*iso*crotonic acid	111.5	31.7	30.4	+1.3
β-Iodopropionic acid	115.0	30.8	29.8	+1.0
Dichloroacetic acid	93.5	35.4	32.6	+2.8
Trichloroacetic acid	115.8	32.8	29.6	+3.2
Trichlorolactic acid	134.8	28.4	28.2	+0.2

The Dibasic Acids

TABLE IX

	V_i	Λ	$\sqrt[2.5]{V_i}\Lambda$
Oxalic acid, $(COO')_2$	68.2	71.1	(386)
Malonic acid, $CH_2(COO')_2$	90.4	62.2	376
Succinic acid, $COO'(CH_2)_2COO'$	112.6	56.2	373
Pyrotartaric acid, $COO'(Me)CHCH_2COO'$	134.2	52.7	374
Glutaric acid, $CH_2(CH_2COO')_2$	134.8	52.5	373
Adipic acid, $(CH_2)_4(COO')_2$	157.0	49.6	375
Pimelic acid, $(CH_2)_5(COO')_2$	179.2	48.0	383
Suberic acid, $(CH_2)_6(COO')_2$	201.4	46.0	382
Sebacic acid, $(CH_2)_8(COO')_2$	245.8	42.8	388

	Λ obs.	Without ring formation			With ring formation		
		V_i	Λcalc.	Δ	V_i	Λcalc.	Δ
Acetylenedicarboxylic acid, $COO'C:CCOO'$	59.1	97.8	59.7	−0.6	91.8	61.4	−2.3
Maleic acid, $COO'CH:CHCOO'$	59.6	105.2	58.0	+1.6	99.2	59.3	+0.3
Fumaric acid, $COO'CH:CHCOO'$	58.9	105.2	58.0	+0.9	99.2	59.3	+0.4
Diglycolic acid, $O(CH_2COO')_2$	56.2	122.6	54.5	+1.7	115.1	56.0	+0.2
Mesaconic acid, $COO'C:(Me)CHCOO'$	55.0	126.9	53.9	+1.1	120.9	54.8	+0.2
Citraconic acid, $COOCHC:(Me)COO'$	55.5	126.9	53.9	+1.6	120.9	54.8	+0.7
Itaconic acid, $COO'CH_2C(:CH_2)COO'$	55.3	126.9	53.9	+1.4	120.9	54.8	+0.5
Ethylmalonic acid, $CH(C_2H_5)(COO')_2$	53.5	134.2	52.5	+1.0	129.7	53.4	+0.1

	V_i	Λ obs.	Λ calc.	Δ
Thiodiglycollic acid, $S(CH_2COO')_2$	141.9	56.4	51.6	+4.8
Phthalic acid, $C_6H_4(COO')_2$	148.2	51.9	50.5	+1.4
Quinolinic acid, $C_5H_3N(COO')_2$	141.3	52.3	51.7	+0.6
Phenylpyridinedicarboxylic acid, $COO'C_6H_4C_5H_3NCOO'$	222.3	45.2	43.0	+2.2
α-Truxilic acid, $C_{16}H_{14}(COO')_2$	309.6	39.4	37.7	+1.7
β-Truxilic acid, $C_{16}H_{14}(COO')_2$	309.6	39.8	37.7	+2.1
o-Nitrophthalic acid, $C_6H_3NO_2(COO')_2$	171.6	51.0	47.9	+3.1

In calculating the volumes of the dibasic acids, the question arises as to the pseudo-ring formation from the interaction between the terminal polar groups. It will be remembered that the diamines have been shown to double up into a ring, and such evidence as is available indicates that the dibasic acids do too. But the ring so formed is not a true one like the benzene ring, and the resulting contraction is not as great, and rather uncertain. As a preliminary step, no contraction was admitted, and it is these uncorrected figures which are given in the first part of the preceding table. With the introduction of a double linkage, there appears an exaltation of irregular value. Thinking that this might be the result of the bending of the molecule, a comparison was made on the basis of contractions in volume as indicated in the first part of the paper for two polar groups in the αβ, αγ,αδ, etc., positions, applying the correction to all of the compounds progressively; this did not change the relative picture one bit, the exaltation from the double linkage being just as great as ever. It is perhaps significant that the exaltation practically disappears, if we admit of a condensation in those compounds having double linkages, and not in the others. Such a treatment is perhaps not in accord with the chemistry of these compounds, for they probably all form anhydrides, with equal ease, but it raises an interesting question concerning the flexibility of a molecule in connection with double linkages. Without such an assumption, it may be rather difficult to explain an exaltation from a double linkage in the dibasic acids, when no exaltation is observed in the monobasic. However, for the time being, the question will be left open, and the figures given for volume must be considered as tentative.

Though the hydroxyl group produced a marked exaltation when on the ring, its effect in the aliphatic acids is very uncertain, averaging about nil.

	V_i	Λ obs.	Λ calc.	Δ
Glycolic acid, $OHCH_2COO'$	61.9	37.6	38.4	−0.8
Lactic acid, $MeCHOHCOO'$	85.0	34.3	33.8	+0.5
Oxy*iso*butyric acid, $(Me)_2COHCOO'$	107.0	31.0	30.8	+0.2
Malic acid, $COOHCH_2CHOHCOO'$	115.1	34.0	34.9	−0.9
Tartaric acid, $COOH(CHOH)_2COO'$	119.9	34.0	34.5	−0.5
Mesotartaric acid $COOH(CHOH)_2COO'$	119.9	34.0	34.5	−0.5
Malic acid, $COO'CH_2CHOHCOO'$	111.4	57.6	56.7	+0.9
Tartaric acid, $COO'(CHOH)_2COO'$	116.2	57.9	55.7	+2.2
Phenylglycolic acid, $C_6H_5CHOHCOO'$	148.5	28.0	28.2	−0.2
Mandelic acid, $C_6H_5CHOHCOO'$	148.5	28.3	28.2	+0.1

The absence of exaltation in this case raises another perplexing question. The whole situation may be summed up in the statement that we do not know what happens to any of these polar groups when they are put upon the benzene ring, and any conjecture in this direction would be premature until we know more concerning the nature of that peculiar molecular aggregation.

In this respect, it is interesting that the benzene ring should have no effect upon the sulphonic acid anion:

The Sulphuric Acids

TABLE X

		V_i	Λ	$\sqrt{V_i}\Lambda$
Sulphuric acid	SO_4''	58.8	73.5	(563)
Methylsulphuric acid	CH_3O_4S'	84.8	44.7	412
Ethylsulphuric acid	$C_2H_5O_4S'$	106.8	41.6	430
Propylsulphuric acid	$C_3H_7O_4S'$	128.8	36.1	410
Benzolsulphonic acid	$C_6H_5O_3S'$	143.5	34.3	399
iso-Butylsulphuric acid	$C_4H_5O_4S'$	152.3	32.3	399
Nitrobenzolsulphonic acid	$NO_2C_6H_4O_3S'$	169.1	32.8	427
Naphthylenesulphonic acid	$C_{10}H_7O_3S'$	193.4	30.2	419
ψ-Cumolsulphonic acid	$C_9H_{11}O_3S'$	209.2	27.2	405

The empirical method of analysis which has been applied to this problem has disclosed evidence that in dealing with the relations between the solute and the solvent we need not be concerned with the incommensurate factors of symmetry and configuration. Furthermore, this evidence has emphasized the necessity of the consideration of the volume of the molecule, rather than the mass. The rôle of volume in the velocity of the organic ions is clearly not only a matter involving frictional or viscosity relations with the solvent, but it is intimately associated with the mechanism which binds the molecules of the solute to the molecules of the solvent. This supposition is based not only on the behavior of the different polar groups, but also on the well-known fact that particles of large dimensions move with a velocity of the same order of magnitude as that of ions. It is to be assumed that in such cases, the affinity between the particles under observation and the surrounding medium is negligible. As the degree of dispersion approaches molecular dimensions the decreasing influence of volume is offset by the appearance of forces of a fundamental nature which bind the dispersed phase to the containing phase and thereby give rise to a restraining influence which at molecular dimensions becomes of considerable magnitude. It is rather to be expected that the complex of the velocity of the organic ions can be resolved into two factors, the volume of the ion and the secondary valence which binds it to the solvent. With the inorganic ions the situation is more confusing, for not only is the problem complicated by hydration (that is, the permanent and nonlabile addition of one or more molecules of solvent) but each ion is presumably a distinct and different polar group, and there is nothing upon which to base a correlation. With the organic ions, the polar group which gives the ion its characteristic velocity can be kept constant, and the remainder of the ion modified at will. What we have observed in the effects of substituent polar groups is here, as elsewhere, only an expression of the net result of interactions of undetermined nature and for the present at least, offer little information on the fundamental mechanism involved.

But as more and more material becomes available for analysis, it becomes more and more evident that the characteristic behavior of any molecular species in aqueous or other solution is going to be primarily determined by the volume of the molecule and the nature and intensity of the secondary valence which it possesses.

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TOXICITY AND CHEMICAL POTENTIAL

BY W. LASH MILLER

In 1895 Scheurlen[1] discovered that the addition of sodium chloride to solutions of phenol increased their toxicity towards anthrax spores and towards staphylococcus; he explained his discovery by a hydrate theory. The discovery was confirmed and the theory rejected by Beckman;[2] and in 1897 Scheurlen[3] discarded his theory in favor of another one, viz., that the degree of dissociation of phenol in solution is affected by the addition of salt. In the meantime, Paul and Krönig[4] had published the results of an extensive series of experiments in which they showed that a number of other salts shared the power of sodium chloride to affect the toxicity of phenol; their conclusions were summed up in the words "In general, organic salts seem to have less influence than inorganic salts, and sodium salts are more effective than those of potassium, but we are not able to offer a satisfactory explanation."

While writing a paper "On the Second Differential Coefficients of Gibbs' Function ζ,"[5] at about the time this toxicological work was coming out, it occurred to me that the increase in the chemical potential of the phenol due to addition of salt to its aqueous solution might well account for its increased action on bacteria; if this were so, a solution of phenol to which salt had been added would have the same toxic effect as the (more concentrated) solution of phenol in pure water which has the same phenol potential; that is, two phenol solutions, with or without salt, which were in equilibrium with the same solution of phenol in some immiscible solvent, would prove to be isotoxic.

This conclusion was supported by the observations of

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[1] Arch. f. exp. Path. u. Pharm., **37**, 74 (1895).
[2] Centrlbl. f. Bakteriologie, **20**, Abt. I, 577 (1896).
[3] Münch. Med. Wochenschr., **44**, 81 (1897).
[4] Zeit. phys. Chem., **21**, 414 (1896).
[5] Jour. Phys. Chem., **1**, 633 (1897).

Paul and Krönig that a 4 percent solution of phenol in absolute alcohol (with which phenol is miscible in all proportions), and a 4 percent solution of phenol to which an equivalent amount of sodium hydrate has been added, are neither of them toxic to anthrax; while "acid. carbol. liquef.," containing about 90 percent phenol, is if anything, less toxic than a 5 percent solution of phenol in water.

The "Biological Lift" and the "Machine"

No opportunity to test this theorem further presented itself until the winter of 1902–3, when Prof. J. J. Mackenzie undertook the necessary bacteriological experiments. It was decided to work with anthrax, but instead of using spores dried on threads or garnets, as did Paul and Krönig, it seemed better to infect the phenol solutions from a suspension of the spores by means of a platinum loop.

Experiments with 30 percent sulphuric acid, however, showed that the volume of liquid lifted by a given loop, as determined by titration, was a very variable quantity. When the plane of the loop was kept parallel with the surface of the liquid, and lifted out with a sharp turn of the wrist (the "biological lift"), the volume of $^1/_{26}$ normal potassium hydrate needed to neutralize the loopful of acid varied from 1.14 to 1.61 cc. When the plane of the loop was kept perpendicular to the surface, the amount fell to 0.29–0.42 cc if taken from the middle of the vessel, and to 0.16 if taken from the edge of the meniscus. A quick lift, moreover, might remove 40 percent more acid than a slow one. A platinum tube was then made by winding fine platinum wire around a pin, heating, hammering, and dissolving out the pin with nitric acid; this was lifted perpendicularly, it removed acid equivalent to 1.34–1.40 cc potash if lifted quickly, 0.94–0.97 if lifted slowly.

The factors on which uniformity depends having thus been discovered, a "machine" was constructed, consisting of a balanced beam to one end of which the platinum wire with loop or tube was attached by a set screw (binding post), the other end being somewhat overweighted by a piece of chain, whose end hung down to the table. In using this apparatus, the loop was immersed in the acid till just covered, and a trigger was sprung; the weight of the chain lifted the tube perpendicularly through the centre of the meniscus at a fixed speed; and then as the loop rose and the length of chain on the table increased, the whole came gently to rest, without jolting out the drop. With this device the volume of acid lifted depended only on the depth to which the tube was immersed; if attention were paid to this matter uniform results were attained, the deviation between greatest and least of six successive determinations never exceeding five percent of a total volume of about 0.005 cc.

This machine was used in all the work with anthrax and staphylococcus referred to below, and gave good satisfaction; but it soon became apparent that equal volumes of the same suspension of spores or cocci were far from containing an equal number of cells; even when the suspension had been thoroughly centrifuged to remove clumps, two 10 cc portions of agar infected by two successive loopfuls would often differ by 20 percent in the number of colonies they would produce.

Determination of the Equivalent Solutions

Toluene was selected as immiscible solvent, and 50 cc of aqueous solutions of phenol of various known concentrations, with or without salt, were placed with 10 cc toluene in stoppered bottles in a thermostat at 25° C and shaken repeatedly. When the two layers had finally separated, a glass tube with a thin bulb blown on the lower end was passed through the upper layer, the bulb crushed against the bottom of the bottle, and a portion of the lower (aqueous) layer pipetted out for analysis. The concentration of phenol in the upper layer was calculated by difference.

In analyzing the solutions, at first Koppeschaar's method[1] was used (it depends on the action of bromine on phenol); but his procedure was found most unsatisfactory, duplicate

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[1] Zeit. anal. Chem., 15, 233 (1876).

analyses often differing by as much as two percent. The trouble was found to lie in the formation of tribrom-phenol-brom; Mr. S. J. Lloyd studied the rate at which this interfering chemical was produced,[1] and established conditions under which accurate determinations could be made. Lloyd's method of analysis[2] was used in all subsequent work.

The following are the results of the determinations with solutions of phenol in water, and with solutions containing 2 percent of salt as well as phenol. By "percent" is to be understood number of grams phenol (or salt) in 100 cc solution.

No Salt

Aqueous layer	0.21	0.45	0.76	0.97	1.13	1.34	1.42	1.70	1.88% phenol
Toluene layer	0.34	0.88	1.69	2.22	2.65	3.24	3.80	4.93	5.73% phenol

2.0% Salt

Aqueous layer	0.20	0.44	0.58	0.79	1.00	1.25	1.49	2.00% phenol
Toluene layer	0.38	0.98	1.37	1.98	2.75	3.75	5.38	9.02% phenol

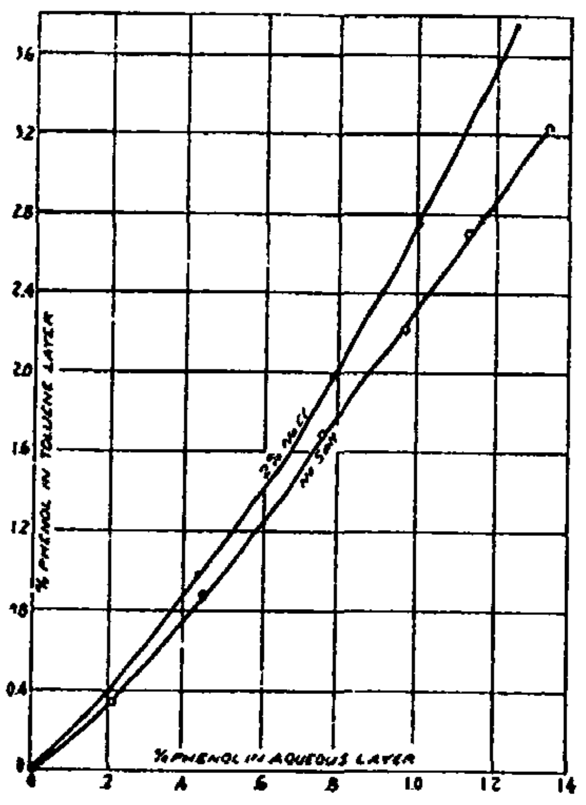

Fig. 1

These results are plotted in the accompanying figure, in which the abscissas of points on the two curves which have the same ordinate give the percentage of phenol in "chemically equivalent" solutions, one with no salt, the other containing 2.0 percent salt in addition to the phenol. Thus, solutions containing 0.6, 0.7, 0.8 and 1.0 percent phenol without salt are chemically equivalent to, i. e., have the same chemical potential of phenol as, solutions containing 2.0 percent

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[1] Jour. Am. Chem. Soc., 27, 7 (1905).

[2] Ibid., 27, 16 (1905).

salt and 0.54, 0.63, 0.72 and 0.88 percent phenol, respectively; and on the assumption made, these solutions should be isotoxic each to each. The same numerical results can, of course, be obtained without the graph, by arithmetical interpolation from the experimental results given above.

A large number of determinations were also made with higher concentrations of phenol and of salt; but for the purpose in hand toluene proved a very unsuitable solvent, as the ratio between the concentration of phenol in toluene and that in the aqueous phase increases rapidly with the concentration. The hydrocarbon known as coal-oil, or kerosene, is freer from this objection; Mr. J. S. Laird, and after him Mr. C. G. Fraser made use of it for the determination of equivalent solutions, and Mr. E. I. Fulmer extended the experiments with toluene; the results obtained with the two solvents are in good agreement.

Experiments with Anthrax Spores and with Staphylococcus

Prof. Mackenzie's first experiments with anthrax and solutions of phenol and salt showed that in general the order of toxicity of the solutions is that of the concentration of their chemically equivalent phenol solutions, and a note to that effect was published.[1] They were continued in 1905–6 under his supervision by Dr. J. S. Lemon, and extended to include experiments with staphylococcus as well. No further work was done with anthrax, and that with staphylococcus was brought to a conclusion by Mr. Laird, working in the chemical laboratory through the winter of 1909–10, and by Mr. Burgess in 1913–14.

The results of these experiments, which are published in detail in the following papers, show that in general the toxicity of the solutions studied, (viz., phenol with various concentrations of sodium chloride, phenol with a fixed concentration of each of ten other salts) is in each case the same as that of the chemically equivalent solution of phenol in water; one or two exceptions were met with that may be

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[1] Trans. Roy. Soc. Canada, Sec. III, 51 (1903).

ascribed to toxicity of the salt itself, and one (viz., acetic acid and phenol) that needs further study. In dilute solutions, osmotic pressure less than 1.75 atmos., it was shown that staphylococci were killed by plasmolysis, without regard to the toxicity of the solutions employed; and that the resistance of the cocci to this attack is variable, and depends on their previous history.

The experience gained in this work brought out the weak points in the technique employed; apart from the difficulty of infecting the solutions with a constant number of cells—a minor matter—the trouble lies in the variability of the microbes employed as test objects. It proved quite useless to compare the death-rate of a given culture in a phenol solution with that of another culture in the equivalent phenol-salt solution; comparisons could be made only between two solutions infected at the same time from the same suspension. It was, therefore, impossible to cut down the work by determining once for all the toxicity of a set of phenol solutions and using the results as a standard.

This same variability of the microbes was the cause of another and even greater loss of time in the laboratory. It was never safe to assume, from the result of previous experiments, that the cells would all be killed after the poison had acted for a certain number of minutes, or that action of the poison for less than another (shorter) time would have a negligible effect; so in order to guard against the danger of having to repeat the whole series, it was always necessary to prepare and incubate many more plates than in the end proved useful, and each wasted plate took just as much time to prepare, and occupied just as much space in the incubator, as one that in the end proved worth while.

Experiments with Saccharomyces: a Convenient Criterion of Death

In view of the necessarily slow progress of the work under such circumstances, a search was made for some criterion of death that could be applied quickly and that would obviate the three or four days' delay involved in waiting for the surviving cells to grow into countable colonies on agar; and it was also decided to select some one organism for the subsequent work and try to find conditions under which a more or less standard strain could be developed. A couple of almost adventures with anthrax and staphylococcus emphasized the desirability of working with a non-pathogenic form, and in the end the choice fell upon yeast.

Mr. C. G. Fraser, after experimenting with a number of other dyes, found that under certain conditions methylene blue was without action on living yeast cells, but rapidly stained dead cells, whether they had died a natural death or had been killed by heat or by poison. Comparison with the results of plating experiments showed that while the two criteria of death are not identical—a cell may be poisoned enough to lose its power of reproduction, without being dead enough to stain—yet they are so nearly alike that a few minutes with the microscope enables one to decide whether it is or is not worth while to pour a plate. This aid has proved of great assistance in all our subsequent work; the difference between the two criteria is being made the subject of further study.

He then compared the toxicity of phenol solutions towards yeast with that of the equivalent solutions containing phenol and salt, both by staining and by plating; and paid particular attention to the differences between the results obtained by the two methods. With low concentrations of salt the equivalent solutions are slightly more toxic, this difference increases with increase in the concentration of the salt; concentrated salt solutions themselves proved toxic. Similar results with phenol and alcohol were obtained by Mr. Fulmer.

Standard Conditions for Yeast Culture

This problem was taken up by Mr. E. I. Fulmer, who studied the resistance towards phenol exhibited by yeast cells taken from a culture in wort at varying intervals after inoculation. He found conditions under which yeast cells comparable from a toxicological point of view could be grown;

and traced the abnormal behavior of older cells to the influence of the alcohol generated in the wort. A number of experiments showing the regular rate of increase in the number of cells, and in the evolution of carbon dioxide under these standard conditions, were carried out by Mr. N. Clark.

As an interesting outcome of this work on variability, Mr. Fulmer was led to study the adaptability of yeast to ammonium fluoride, and its loss of resistance when grown in solutions free from that salt. Details of all these experiments will shortly be published.

The results of this work, carried out at intervals over many years as opportunity offered, may be summed up in the statement that the toxicity of a solution containing phenol and an indifferent salt depends primarily on the chemical potential of the phenol in the solution; two solutions have the same toxicity if they are such as to be in equilibrium with the same solution of phenol in an immiscible solvent (toluene or kerosene). Complications may arise from the toxicity of the salts themselves, or in dilute solutions from plasmolysis of the cell independent of the toxicity of the solutions employed. One or two individual cases which do not seem to fall under either of these two heads deserve further study.

The observation of Paul and Krönig, that solutions of mercuric chloride in aqueous alcohol show a maximum of toxicity when the ratio of alcohol to water in the solution is as 1 to 3, affords another illustration of the same principle; for Laird has shown that the solubility of mercuric chloride in aqueous alcohol passes through a minimum at the same ratio.

The University of Toronto
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THE TOXICITY TOWARDS ANTHRAX AND STAPHYLOCOCCUS, OF SOLUTIONS CONTAINING PHENOL AND SODIUM CHLORIDE

BY J. S. LEMON

The following experiments were carried out in the pathological laboratory of the University of Toronto in the winter of 1905–6, under the supervision of Prof. J. J. Mackenzie, with solutions supplied by Prof. W. Lash Miller.

Cultures of the "potato bacillus" (*B. mesentericus*) of anthrax (*B. anthracis*) and of *Staphylococcus pyogenes aureus* were grown on agar, the colonies washed off the agar, without breaking its surface, by 0.6 percent salt solution, and the suspension let stand (sometimes centrifuged) so that clumps might settle to the bottom. A second measured portion of the 0.6 percent salt solution was then infected by from one to three loops taken from the upper portion of the suspension; this constituted the "second suspension," in the case of potato spores and anthrax spores it was heated to 70° C to destroy vegetative forms. In the poisoning experiments, 10 cc of the toxic liquid was inoculated with a loopful of this "second suspension" and the time noted; to ensure that a good average sample should be removed for the inoculation, a mixing-rod was kept in the suspension tube, and the liquid was thoroughly stirred before a loopful was removed. The poison was then left to stand at room temperature, or in an incubator, and at measured intervals of time a loopful from it was added to 10 cc agar jelly, which had been melted and kept at 45° C; this was poured into a petri dish, allowed to solidify, and put away in the incubator. The number of colonies that grew on a measured area of the plate was taken as a measure of the number of cells left living in the poison at the time the agar was infected.

The usual precautions were taken against accidental infection—tubes and instruments were sterilized, tubes plugged with cotton wool which was "flamed" before removing, etc., and the loopfuls of suspension were measured out with the "machine."[1] "Neutral agar" holding 1.5 percent agar-agar was employed, and the cultures were in all cases grown on the same agar as that used for the plates, for fear there might be some difference in the preparations made up at different times—although in every case the same recipe was followed. Koch has shown the need for this preacution in his experiments with iodine, which he found would act well in a neutral medium containing a trace of albumin, but not nearly so actively in an alkaline medium containing more albumin.

Preliminary experiments were, of course, necessary in order that the number of colonies grown on a plate might be suitable for counting. In the case of staphylococcus, for instance, one cc of 0.6 percent brine was added to a 24-hour-old pure culture and shaken; the second suspension was made by adding three loops of the first to 5 cc of the brine, and 10 cc agar was infected with one loop of this second suspension. The plates were so thickly sown that a count could not be made. The procedure was varied by using 5 cc salt solution for the first suspension and 10 cc for the second, but the plates were still too thickly sown. Finally, by using 10 cc for the first and 10 cc for the second, a satisfactory count of 7300 colonies was obtained; the plates had an area of 63 to 64 square centimeters, and the number of colonies on 12 cm^2 of each plate was counted.

The spores were used instead of the vegetative forms of anthrax and potato bacillus because the former are much more resistant to phenol, and thus enabled the experiments to be made with higher concentrations of the poison. It was hoped that the innocuous potato spores might be used instead of the virulent anthrax, and preliminary experiments showed that insofar as their resistance is concerned, this is quite feasible; but it proved too difficult to prepare a uniform constant culture, while the very characteristic colonies of the anthrax made it easy to procure and maintain a pure strain, and in the end work with the potato bacillus was abandoned.

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[1] Lash Miller: Jour. Phys. Chem., 24, 563 (1920).

Spores of the potato bacillus were obtained from a pure culture on agar, by incubating at 34° C over night and then leaving four days at room temperature (19-20° C); anthrax spores by incubating the culture for 16 hours (when, according to Koch spores begin to form) and then letting stand at room temperature for 48 hours. This procedure worked well in practice, though some observers place the optimum for spore production (anthrax) at 31° C and others at 24-35° C.

Resistance of the Spores to High Temperature

To compare their resistance to high temperatures, capillary tubes were filled with the second suspensions of potato spores, and anthrax spores respectively, their ends were sealed, and they were plunged into boiling water. After a measured interval they were removed, broken into sterile broth, and the growth noted. In the case of the potato spores there was a heavy growth after 2 minutes at 100° C, a smaller growth after 4 minutes, and a slight growth after 6 minutes, but none after 8, 10 or 15 minutes; in the case of anthrax, also, some were found alive after 6 minutes immersion in the boiling water.

Effect of Temperature on the Rate of Poisoning by Phenol

That the resistance of the potato spore to phenol is much the same as that of anthrax, may be seen by comparing the following measurements with those given later for anthrax spores; the immediate object of this set, however, was to ascertain how much effect the temperature of the poison bath had on the time it took the potato spores to die. Solutions were made up containing 2.5, 3.0, and 3.5 percent of phenol, respectively, and 10 cc of each of them was inoculated with one loop of the potato spore suspension, and kept at room temperature for two weeks, plates being poured each day. As a control, one loop of the same suspension was added to 10 cc of 0.6 percent salt solution at the same time as the others. Counts of plates made immediately after inoculation showed no less numbers than the control. On the second day, a very slight reduction in the number of colonies was observed on plates from the 3 percent and 3.5 percent phenol; on the third day the decrease was more marked, and there was also noticeable a decrease in the number of colonies on the plate from the 2.5 percent phenol. On the fourth day, all the plates still showed colonies, but many fewer than the control, especially in those infected from the 3 and 3.5 percent phenol. For seven days the numbers continued to fall off, but even after the poisons had acted for fourteen days, plating showed that some of the cells had survived.

The experiment was then repeated, using 0.6 percent salt, 3.5 percent phenol and 4.75 percent phenol, but keeping the poison tubes in the incubator at 34° C instead of at room temperature. The results were as follows (20 cm^2 counted on each plate):

B. mes. in poison	1	2	3	4	5	6	7	8	23	hours
3.5% phenol	121	108	58	57	46	38	15	9	0	colonies
4.75% phenol	25	13	13	2	3	1	0	2	0	colonies
0.6% NaCl	282	—	—	288	—	—	—	-	287	colonies

Thus a phenol solution that will not completely kill potato spores in fourteen days at 19–20° C will kill all but a few stragglers in eight hours at 34° C, and even these most resistant individuals in twenty-three hours.

With staphylococcus similar results were obtained (culture No. 6 used):

Staph. in poison	9.5	19.5	20.5	31.5	45	55	60	minutes
0.6% phenol at 35.5° C	3093	0	0	0	0	0	0	colonies
0.6% phenol at 24.5° C	15064	—	3984	280	0	0	0	colonies
0.8% phenol at 35.5° C	—	0	—	0	0	0	0	colonies
0.8% phenol at 24.5° C	—	112	—	4	0	0	0	colonies
1.0% phenol at 35.5° C	0	0	0	—	—	—	—	colonies
1.0% phenol at 24.5° C	3	0	0	—	—	—	—	colonies
0.6% NaCl at 35.5° C	23419	—	—	—	—	—	22783	colonies

Another series with staphylococcus, culture No. 7, gave analogous results:

Staph. in poison	2	5	7	10	20	30	35	40	50	min.
0.7% ph. at 34–35° C	—	752	0	0	0	0	0	—	—	col.
0.7% ph. at 21–22° C	—	—	—	21000	11264	4582	936	199	10	col.
0.8% ph. at 35° C	17883	47	22	—	0	—	—	—	0	col.
0.8% ph. at 21–22° C	—	—	—	14892	508	3	1	0	0	col.
1.0% ph. at 33–34.5° C	1	0	0	0	—	—	—	—	—	col.
1.0% ph. at 21.5° C	—	—	—	2	(12 min. 2 col., 15 m. 0 col.)					

Effect of Salt on the Toxicity of Phenol towards Anthrax Spores

In the following tables the solutions are arranged in the order of the concentrations of the solutions of phenol in toluene with which they are in equilibrium; the numbers in brackets give the composition of the chemically equivalent solution of phenol, that is, the composition of the solution of phenol in water (without salt) which would be in equilibrium with the same toluene solution. For instance, after "1.9 percent ph. 5 percent NaCl" the number "(2.6)" signifies that a solution containing 2.6 grams of phenol, and no salt, per hundred cc, and a solution containing 1.9 g phenol and 5.0 g salt per hundred cc, would be in equilibrium with the same solution of phenol in toluene.

In the first set of experiments the poison tubes were inoculated from a suspension of anthrax spores that had been heated to 70° C for 30 minutes:

B. anth. in poison	18 m.	1	2	3	4	5	6	7	8	hours
1.9% ph. + 5% NaCl (2.6)	8	4	3	3	2	1	1	1	0	colonies
3.0% phenol	6	3	2	1	3	1	1	0	0	colonies
3.5% phenol	4	2	1	3	1	1	0	0	0	colonies
2.5% ph. + 5% NaCl (3.6)	4	3	2	0	0	0	0	0	0	colonies
1.9% ph. + 10% NaCl (3.9)	7	2	1	0	0	0	0	0	0	colonies
4.5% phenol	6	0	0	0	0	0	0	0	0	colonies
2.5% ph. + 10% NaCl (5)	5	2	0	0	0	0	0	0	0	colonies

As it seemed probable that the low counts might be due to the prolonged heating at 70° C, in the next and in all subsequent work the suspensions were heated to 70° C for 20 minutes only. The counts so obtained were much higher; but that may be due in part at least to a change in the way of counting, for in the first series colonies growing at a depth in the agar had not been counted, they differed in appearance from those on the surface and it was feared that the culture was not pure.

B. anth. in poison	25 m.	1	2	3	4	5	6	7	hours
1.9% ph. + 5% NaCl (2.6)	153	75	130	55	57	77	104	49	colonies
3.0% phenol	182	174	101	88	97	89	75	56	colonies
3.5% phenol	195	—	125	40	87	83	36	36	colonies
2.5% ph. + 5% NaCl (3.6)	78	103	103	35	35	31	39	48	colonies
1.9% ph. + 10% NaCl (3.9)	137	118	60	21	45	25	11	21	colonies
4.0% phenol	103	107	118	44	30	50	35	25	colonies
2.5% ph. + 10% NaCl (5)	72	46	3	5	1	0	1	0	colonies

In the third series the suspension was thoroughly centrifuged after heating:

B. anth. in poison	20 m.	1	2	3	4	5	6	7	8 hours
1.9% ph. + 5% NaCl (2.6)	142	134	114	84	46	18	13	23	6 colonies
3.0% phenol	124	81	109	73	34	15	18	17	9 colonies
3.5% phenol	119	107	90	48	12	17	10	5	0 colonies
2.5% ph. + 5% NaCl (3.6)	145	154	90	112	15	15	14	10	3 colonies
1.9% ph. + 10% NaCl (3.9)	115	92	41	51	7	5	7	2	0 colonies
4.0% phenol	124	110	110	53	19	18	13	15	2 colonies
2.5% ph. + 10% NaCl (5)	78	52	9	5	0	0	0	0	0 colonies

The fourth set were carried out under the same conditions as the third; the temperature of the incubator varied from 37.5° C to 42° C.

B. anth. in poison	15 m.	1	2	3	4	5	6	7	8 hours
1.9% ph. + 5% NaCl (2.6)	179	78	72	31	70	59	48	42	40 colonies
3.0% phenol	118	184	149	79	61	52	75	75	55 colonies
3.5% phenol	170	163	118	90	54	27	42	48	45 colonies
2.5% ph. + 5% NaCl (3.6)	179	78	72	31	70	59	48	42	40 colonies
1.9% ph. + 10% NaCl (3.9)	122	40	31	10	10	4	1	4	2 colonies
4.0% phenol	169	115	58	64	10	24	16	17	11 colonies
2.5% ph. + 10% NaCl (5)	90	16	0	0	0	0	0	0	0 colonies

Comparison of these four sets, shows that even when working with every care, duplicate results are not to be expected; the trouble lies, no doubt, in the uneven distribution of the spores in the suspensions from which measured volumes are taken for inoculation and for culture. The results, however, leave no doubt that the toxicities of the phenol-salt solutions are about equal to those of their salt-free equivalents.

A fifth set was undertaken, including 1.22 percent phenol with 10, 15 and 20 percent salt. In this case the culture after 16 hours in the incubator was kept for 6 days at room temperature, the growth washed off as usual with 10 cc 0.6 percent brine, heated in the tube of a centrifuge for 30 minutes to 70° C, agitated to break up clumps, and then centrifuged at high speed. Two loops of this (first) suspension were used to inoculate 10 cc of each of the poisons, and after standing in a water bath (whose temperature varied from 38° C to 44° C) for the time noted, one loop was used to infect the 10 cc of agar; the "machine" was used, and the same small platinum tube that was used in the experiments with staphylococcus.

With the exception of the solution containing 1.22 percent phenol and 15 percent salt, the order of toxicity is that of the equivalent solutions; the results obtained with this exceptional solution are abnormal also in the relatively large count after one hour, followed by a rapid decrease to zero.

B. anth. in poison	1(?)	2	3	4	5	6	7	8	hours
1.22% ph. + 10% NaCl (2.1)	1141	872	700	445	310	381	274	255	colonies
2.5% phenol	675	220	257	357	171	120	98	82	colonies
3.0% phenol	381	142	186	124	78	55	40	36	colonies
1.22% ph. + 15% NaCl (3.0)	117	40	10	2	3	0	0	0	colonies
3.5% phenol	140	106	41	25	25	16	13	11	colonies
4.0% phenol	58	14	34	32	16	8	8	—	colonies
3.0% ph. + 5% NaCl (4.1)	50	5	4	1	3	1	0	0	colonies
1.22% ph. + 20% NaCl (7+)	3	0	0	0	0	0	0	0	colonies

Effect of Salt on the Toxicity of Phenol towards Staphylococcus

This form was chosen for the experiments with lower concentrations of phenol. Colonies on agar, 24 hours old, were washed off with 0.6 percent brine, and suspensions made as already described; of course, the heating to 70° C was omitted. All infections were made with the "machine," using a small platinum tube as "loop." The poison acted at room temperature; 0.6 percent NaCl was used as control; the various cultures are distinguished by numbers.

Preliminary experiments with 1.0 percent phenol showed that the time required to kill all the cells was the same whether the poison was infected by a large or a small number of cells, and that a culture 47 hours old gave about the same results as one 24 hours old.

Staph. in poison	5	10	15	20	25	30	35	minutes
1.0% ph., cult. No. 4, 27° C	5	2	0	0	0	0	0	colonies
1.0% ph., cult. No. 5, 24.5° C	8	2	0	0	0	0	0	colonies
1.0% ph., cult. No. 6, 24.5° C	1402	29	0	0	0	0	0	colonies
1.0% ph. ,cult. No. 7, 24.5° C	512	5	0	0	0	0	0	colonies
1.0% ph., cult. No. 9, 24.5° C	2963	4	0	0	0	0	0	colonies
0.6% NaCl, cult. No. 7, 24.5° C	20491	18073	16514		15102	—	—	colonies
0.6% NaCl, cult. No. 9, 24.5° C	15082	15948	13048		—	—	—	colonies

With cultures Nos. 4 and 5, the machine was used; with the others the "biological lift," giving a much heavier infection. Culture No. 9 had been grown on agar for 47 hours; all the others in this paper for 24 hours only.

Experiments were then made to find the range of phenol concentrations within which poisoning takes place at a convenient rate; next the effect of sodium chloride, without phenol, was tested, and then comparison was made of the toxicity of 0.8, 0.7 and 0.6 percent phenol solutions with their chemical equivalents, viz., solutions containing 2.0 percent salt and 0.72, 0.63 and 0.54 percent phenol, respectively.

It soon became evident that experiments carried out under what were intended to be identical conditions, gave very different results. One cause of variation lay in the fact that equal volumes removed from the same suspension contain varying numbers of cocci—for instance, three plates prepared at the same time each from 10 cc of the same agar, infected in each case with the same volume of suspension (one loop taken with the machine), gave 5335, 5791, 6173 colonies, respectively, being a variation of 16 percent from the highest to the lowest. The principal cause, however, obviously lies in the variability of the staphylococcus itself, with culture No. 29 for instance, the time required for complete sterilization by 0.6 percent phenol was nearly twice as long as with culture No. 22, although in the first case the temperature was, if anything, a little higher.

In order to compare the toxicity of different solutions, therefore, it was necessary in every case to carry out simultaneous experiments with the same suspension; and as but little guidance could be obtained from previous experiments with the same poison but a different culture, a great many plates were poured which, on incubation, turned out to be sterile. All this added greatly to the amount of work and time required to obtain results; and if work of this kind is to be undertaken on any considerable scale, it will be necessary first to find some criterion of death which involves less delay than the plating method, and second to find conditions under which the microbes experimented with can be grown "true to type" from the toxicological point of view. In comparison with the loss of time caused by the lack of these requisites, an uncertainty of 20 percent or so in the number of cells introduced into the poison is of little moment; and it is obvious that a more accurate regulation of temperature during the action of the poison can easily be attained by the use of a suitable thermostat.

SELECTION OF THE RANGE OF CONCENTRATIONS

Staph. No. 8 in poison	0	5	10	15	20	30	40	50	70 min.
0.25% phenol, 24.5° C	—	—	44077	—	—	55315	—	42995	59630 col.
0.50% phenol, 24.5° C	—	—	43084	—	51039	55032	49741	48129	— col.
1.0% phenol, 24.5° C	—	16927	73	0	—	—	—	—	— col.
0.6% NaCl, 24.5° C	39711	—	—	—	—	49724	—	—	43046 col.

Staph. No. 10 in poison	40	60	70	80	90	100	110	120 min.
0.25% phenol, room temp.	—	—	7000	—	7573	—	6427	— col.
0.5% phenol, room temp.	10500	7509	—	6637	—	6205	—	2418 col.
0.6% NaCl, room temp.	6045	—	—	—	—	7064	—	— col.

Staph. No. 10 in poison	130	140	150	160	170 min.
0.25% phenol, room temp.	5727	—	8591	—	7955 col.
0.50% phenol, room temp.	—	1527	—	1209	— col.

In the experiments with culture No. 10, the room temperature varied from 20° C to 24° C, but as the tubes stood close together, and plates were poured from them alternately, the results are comparable.

Comparison of 0.80% Phenol with Its Chemical Equivalent

The equivalent contained 0.72 percent phenol and 2.0 percent salt. After "control" is given the number of colonies counted on plates from a 0.6 percent salt solution infected at the same time as the poison liquids; usually one plate from this salt solution was poured immediately after inoculating, and another towards the close of the poison experiments.

Culture No. 17; temp. 22° C. Control: 7128, 8173 col.

Staph. in poison	5	6	10	11.5	15	16	20	21	30	40	50	67 min.
0.80% phenol	—	8210	—	7191	—	6084	—	2864	734	44	0	0 col.
Equivalent	7058	—	5728	—	1819	—	2149	—	742	0	0	0 col.

Culture No. 18; temp. 20° C. Control: 8546 after 3 min., 10882 after 5 min.

Staph. in poison	5	10	15	20	30	40	55	60	70 min.
0.80% phenol	10426	8400	6428	3755	350	6	0	—	— col.
Equivalent	10927	10692	6199	5543	2864	293	11	8	3 col.

Culture No. 29; temp. 24–27° C. Control: 10500 col.

Staph. in poison	5	10	15	20	30	40	55	70 min.
0.80% phenol	3309	309	1	0	0	0	0	0 col.
Equivalent	2546	55	38	4	0	0	0	0 col.

Towards culture No. 17, the phenol and its equivalent proved equally toxic; but towards Nos. 18 and 29, the "equivalent" was less toxic than the pure phenol solution.

Comparison of 0.70% Phenol with Its Chemical Equivalent

The equivalent contained 0.63 percent phenol and 2.0 percent salt.

Culture No. 14; temp. 21° C. Control: 7828, 6555, 6491 col.

Staph. in poison	10.5	15	23	24.5	33	35	44	45	(11 more, to 98)	min.
0.70% phenol	3384	—	674	—	142	—	3	—	0	col.
Equivalent	—	2262	—	970	—	82	—	3	0	col.

The following experiment was carried out at the same time, with the same culture and controls, to compare the effect of 0.6 and 0.7 percent phenol.

Staph. in poison	10	22.5	31	42	52.5	62.5	72.5	80	86.5	96.5 min.
0.60% ph.	5409	4975	3134	3039	2095	914	419	41	25	13 col.

Culture No. 14;

Staph. in poison	14	15	23.5	24	34.5	35	44	45	etc., to 66	min.
0.70% phenol	—	1994	51	—	0	—	0	—	0	col.
Equivalent	1980	—	—	311	—	9	—	0	0	col.

Culture No. 16; temp. 22° C. Control: 5489 after 4 min., 5441 after 6 min.

Staph. in poison	10	20	30	40	50	60	70	85	100	min.
0.70% phenol	2896	980	22	2	0	0	0	0	0	col.
Equivalent	2694	2198	1604	1591	680	135	66	5	0	col.

Culture No. 27; temp. 23–24° C. Control: avg. 9673 colonies

Staph. in poison	11	21	30	40	50	60	75	90	min.
0.70% phenol	1273	11	0	0	0	0	0	0	col.
Equivalent	167	40	0	0	0	0	0	0	col.

Culture No. 30; temp. 19–25° C. Control: avg. 10163 colonies

Staph. in poison	10	20	30	40	50	60	75	90	105	min.
0.70% phenol	7937	1400	37	0	0	0	0	0	0	col.
Equivalent	1273	19	0	0	0	0	0	0	0	col.

The five experiments with culture No. 14 were carried out at the same time and under the same conditions; those with Nos. 27 and 30, together with the experiments on 0.60 percent phenol given below. Towards cultures 14 and 27 the phenol solution and its equivalent are equally toxic; towards No. 16 the equivalent was very much less toxic, while towards No. 30 the equivalent seems to be somewhat more toxic than the pure phenol solution, though the unsteadiness of the temperature renders this conclusion uncertain. In comparison with the difference between the death rates with 0.7 percent and 0.6 percent phenol, however, the 0.7 percent phenol and its chemical equivalent come very close together, except in the experiments with culture No. 16.

Comparison of 0.60% Phenol with Its Chemical Equivalent

The equivalent contained 0.54 percent phenol and 2.0 percent salt. Owing to the unexpected results obtained, a large number of experiments were made in the course of which fresh solutions were made up and the old ones were re-analyzed, the tubes, etc., used in the experiments were exchanged for others, and every precaution taken to avoid accidental contamination; but the same general results were always obtained.

Culture No. 15; temp. 21° C. Control: 7471 after 2.5 min., 6627 after 5.5 min.

Staph. in poison	10	20	30	40	50	60	70	82	97	117	min.
0.60% phenol	5844	5791	5955	3914	2810	2535	1889	1623	616	57	col.
Equivalent	7955	6351	7573	6151	5388	5476	5371	4484	1209	728	col.

Culture No. 19; temp. 23–27° C. Control: 3882, 5037 colonies

Staph. in poison	10	20	30	40	50	71.5	87.5	102.5	min.
0.60% phenol	576	0	0	—	0	0	0	0	col.
0.60% equivalent	3293	1591	1389	—	647	371	109	30	col.
0.70% equivalent	1718	1256	627	84	1	1	0	0	col.

Culture No. 20; temp. 23.5. Control: 5728, 6713 colonies.

Staph. in poison	10	20	30	40	50	60	75.5	91	105	121	min.
0.60% phenol	4035	858	6	2	0	0	0	0	0	0	col.
Equivalent	6762	5473	3500	3946	3755	1909	1972	1095	389	170	col.

Culture No. 21; temp. 23.5° C. Control: 6619, 7636 colonies.

Staph. in poison	10	20	30	40	50	60	75	90	105	120	min.
0.60% phenol (1)	1284	585	74	22	0	0	0	0	0	0	col.
0.60% phenol (2)	—	763	—	1	0	0	0	0	0	0	col.
Equivalent	7319	5728	4811	4694	4137	3710	1654	1600	1336	332	col.

Culture No. 22; temp. 22–24° C. Control: avg. 6470 colonies

Staph. in poison	12	20	30	40	50	60	75	90	105	120	min.
0.60% phenol	5728	2482	338	3	0	0	0	0	0	0	col.
Equivalent	7433	6364	5855	5454	5465	5091	4614	2800	2609	1146	col.

Culture No. 23; temp. 23–27° C. Control: avg. 6250 colonies

Staph. in poison	10	20	30	40	50	60	75	90	105	120	min.
0.60% phenol (1)	4391	1745	1	0	0	0	0	0	0	0	col.
0.60% phenol (2)	3882	1852	317	2	0	0	0	0	0	0	col.
Equivalent	6619	5537	4968	4960	4028	3946	—	1728	1209	440	col.

Culture No. 24; temp. 22.5–25° C. Control: 9835, 10424 colonies

Staph. in poison	10	20	30	40	50	60	75	90	105	120	min.
0.60% phenol (1)	5727	4646	1146	104	2	0	0	0	0	0	col.
0.60% phenol (2)	7637	—	2819	—	40	1	0	0	0	0	col.
0.54% phenol	5307	4072	2545	500	3	0	0	0	0	0	col.
0.60% equivalent	8057	4455	—	1464	272	21	5	0	0	0	col.

Culture No. 25; temp. 20.5–24.5° C. Control: avg. 11137

Staph. in poison	10	20	30	40	50	60	75	90	105	120	min.
0.60% phenol	9164	7510	2927	305	1	0	0	0	0	0	col.
0.60% equivalent	8782	8591	4136	955	83	1	0	0	0	0	col.
0.54% phenol	8973	8591	7700	5918	580	109	5	0	0	0	col.

Culture No. 27; temp. 23–24° C. Control: avg. 9673 colonies

Staph. in poison	11	21	22	30	40	50	60	75	90	105	min.
0.60% phenol	9037	—	7828	6619	1856	1044	425	1	0	0	col.
Equivalent	7700	5155	—	2757	1686	636	283	63	29	0	col.

Culture No. 30; temp. 19–25° C. Control: avg. 10163 colonies

Staph. in poison	10	20	30	40	50	60	75	90	105	min.
0.60% phenol	10100	7541	6746	2227	573	127	4	0	0	col.
Equivalent	10100	5300	2227	11	39	15	1	0	0	col.

Towards Culture No. 30, where the unsteadiness of the temperature renders conclusions uncertain, the equivalent solution was more toxic than the 0.60 percent phenol. In every other case, the equivalent proved less toxic—often very much less toxic—than the pure phenol solution. In the case of No. 19, the solution containing 0.60 percent phenol was even more toxic than a solution containing more phenol and salt as well, viz., "the 0.70 percent equivalent" 0.61 percent phenol + 2.0 percent salt; similarly with No. 24, a solution containing 0.54 percent phenol proved more toxic than one containing 0.54 percent phenol + 2.0 percent salt, but with No. 25, the reverse was the case. Towards culture No. 25, the 0.60 percent phenol was distinctly more toxic than the 0.54 percent phenol solution, while towards No. 24 there was no great difference, in the behaviour of the two solutions.

Summary

My experiments with anthrax spores show that the increased toxicity observed on adding salt to a phenol solution is in accordance with the assumption that two solutions of phenol, with or without salt, are equally toxic if their compositions are such that both would be in equilibrium with the same solution of phenol in toluene. The experiments with staphylococcus, however, in which lower concentrations of phenol were employed, show that while the asumption is fairly in accord with the behaviour of 0.80 percent phenol, in the case of 0.60 percent phenol the chemically equivalent solution containing salt is much less toxic; 0.70 percent phenol occupies an intermediate position.

Every care has been taken to avoid accidental contamination of the vessels, and accidents in making up the solutions; and in view of the large number of corroborative experiments, the general result must be regarded as well established; but I have had no time to look farther into its cause.

The University of Toronto
June, 1920

NEW BOOKS

The Application of the Coal Tar Dyestuffs. *By C. M. Whittaker. 22 × 15 cm; pp. xii + 214. New York: D. Van Nostrand Company, 1919. Price: $3.00.*—This is one of a new series on industrial chemistry, edited by Samuel Rideal. In the general preface the editor says: "The rapid development of Applied Chemistry in recent years has brought about a revolution in all branches of technology. This growth has been accelerated during the war, and the British Empire has now an opportunity of increasing its industrial output by the application of this knowledge to the raw materials available in the different parts of the world. The subject in this series of handbooks will be treated from the chemical rather than the engineering standpoint. The industrial aspect will also be more prominent than that of the laboratory. Each volume will be complete in itself, and will give a general survey of the industry, showing how chemical principles have been applied and have affected manufacture. The influence of new inventions on the development of the industry will be shown, as also the effect of industrial requirements in stimulating invention. Historical notes will be a feature in dealing with the different branches of the subject, but they will be kept within moderate limits. Present tendencies and possible future developments will have attention, and some space will be devoted to a comparison of industrial methods and progress in the chief producing countries. There will be a general bibliography, and also a select bibliography to follow each section. Statistical information will only be introduced in so far as it serves to illustrate the line of argument....

"To the advanced student the books should be especially valuable. His mind is often crammed with the hard facts and details of his subject which crowd out the power of realizing the industry as a whole. These books are intended to remedy such a state of affairs. While recapitulating the essential basic facts, they will aim at presenting the reality of the living industry. It has long been a drawback of our technical education that the college graduate, on commencing his industrial career, is positively handicapped by his academic knowledge because of his lack of information on current industrial conditions. A book giving a comprehensive survey of the industry can be of very material assistance to the student as an adjunct to his ordinary text-books, and this is one of the chief objects of the present series. Those actually engaged in the industry who have specialized in rather narrow limits will probably find these books more readable than the larger text-books when they wish to refresh their memories in regard to branches of the subject with which they are immediately concerned."

The subject is discussed under the following general headings: general survey of dyeing; the varied uses of the basic dyestuffs; the application of the acid dyestuffs; the Turkey red industry, and other uses of the alizarine dyestuffs; the application of the direct cotton dyestuffs, including those which develop on the fiber; the azo-coloring matters and their special use in dyeing; the properties of the resorcine dyestuffs; the application of the sulphur dyestuffs; the application of the vat dyestuffs; the dyeing of union materials, including garments; colors produced on the fiber by the oxidation of coal tar products; other uses of coal tar dyestuffs; dyestuffs other than coal tar dyestuffs still in use; the valuation and detection of dyestuffs.

In regard to fastness the author says, p. 6: "Passing on to the question of fast and loose dyestuffs, it is necessary to thoroughly grasp the fact that there is no such thing as absolute fastness as applied to dyes, yet I have been repeatedly asked in the course of business if a certain shade is absolutely fast. It is essential to realize that fastness is purely relative, not absolute. If experience has proved that a dyestuff during the lifetime of a fabric withstands all influences to which that fabric is subjected, then the dyer designates that dyestuff as fast for that particular class of goods. The range of fastness for which dyers have to cater is extraordinarily wide and varied, and it is this fact which makes all terms of fastness *re* dyestuffs purely relative. This may be illustrated by choosing two extreme instances. A lady's ball dress is never exposed to daylight, and the only process through which it may be passed is drycleaning, therefore the most fugitive dyestuffs may safely be termed fast for ball fabrics: on the contrary, a naval uniform is exposed to the severest conditions extant, viz., sunlight and exposure to sea air, therefore the fastest obtainable colors must be used for this purpose—in fact, indigo is used, but even this gradually suffers under these influences. One is justified in saying that the nearest approach to absolute fastness is made by some of the modern vat dyestuffs, in that they will last longer than the cotton on which they are usually dyed, i. e., the fabric perishes before the color has faded: yet these dyestuffs will not withstand boiling under pressure with caustic soda without bleeding on the adjacent white."

It is interesting to read, p. 104, that the sulphur in sulphur blacks is present in three forms: as mechanically free sulphur which can be extracted with carbon bisulphide; to the extent of 20–25 percent as easily oxidizable, chemically active sulphur which goes over readily into sulphuric acid; to the extent of 50–75 percent as firmly combined sulphur only oxidizable by strong oxidizing agents.

On p. 114 we read that "Sulphur dyestuffs possess a great affinity for basic dyestuffs; in fact, they may almost be said to act as a mordant for them. The resulting shades possess quite a good fastness to washing. This process is therefore frequently used for beautifying sulphur colors. Since the war this process has been the means of enabling millions of yards of navy blue to be dyed, which the trade would otherwise have been unable to dye due to lack of dyestuffs. The navy blue for munition workers' overalls has been dyed by topping a medium shade of sulphur black with methylene blue and methyl violet. The operation must be carried out carefully, because the sulphur colors have a strong affinity for basic colors, which consequently have a tendency to rush on unevenly."

The author points out, p. 131, that with the anthracene series "the curious thing is that a light shade requires just as much caustic soda as a heavy shade, for which I have never yet seen an adequate explanation, though as a hard practical fact it is indisputable. The caustic soda plays a most important part and requires to be calculated on the volume of liquor employed and not on the amount of dyestuffs." What this really means is that a definite hydroxyl concentration is necessary in order to get good results. If the dye is in colloidal solution, this result would not be surprising.

With wool and cotton union fabrics in which it is not very important that the cotton should be of exactly the same shade as the wool, the wool is usually dyed with acid colors and the cotton is then filled with direct colors in a cold alkaline bath, p. 140. "This is the method commonly used in shoddy dyeing, the cotton being afterwards filled up by means of sumac and iron in the case of blacks, blues and heavy browns, or with some suitable direct cotton color dependent on the shade of the wool. It is also used in pile fabrics with a cotton warp back, and goods that are likely to crimp if dyed in a neutral Glauber's salt bath, such as wool and cotton unions with artificial silk effect threads. Its advantage is that one can get brighter shades on the wool by this method than by the single-bath method. For filling up the cotton a large range of direct cotton dyestuffs are available which leave the wool unstained at low temperatures whilst having a strong affinity for cotton. This dyeing of the cotton should not be carried out absolutely cold, because experiment has shown that the temperature at which it is carried out has a very distinct influence on the fastness to rubbing on the cotton. The higher the temperature at which the filling up of the cotton is carried out, the faster to rubbing is the cotton; thus, if the filling up is carried out cold, the cotton will be liable to rub, but if carried out at 50°–60° C, the cotton will be found quite fast to rubbing; moreover, the higher the temperature employed, the better the value obtained from the dyestuffs. This operation is usually carried out on the washing machine, which enables a very short liquor to be used, and in which the heavy roller plays an efficient part in squeezing the color into the centre of the material."

On p. 155 the author says: "The results of indigo and sulphide blacks dyed in the hydrosulphite vat are most striking in that indigo practically does not dye faded flannel at all, whilst sulphur blacks dye the faded flannel heavier than the non-faded. These absolutely contradictory results show how difficult it is to build any theories on exactly what happens to the wool fiber on exposure to the atmosphere."

This is a very interesting book: it furnishes a great deal of material for anybody wishing to develop the theory of dyeing. The author is quite frank about admitting that his own knowledge of dyeing is absolutely empirical.

Wilder D. Bancroft

Metallography. *By Samuel L. Holt. Part I: The Principles of Metallography. 23 × 15 cm; pp. x + 256. New York: McGraw-Hill Book Company, 1920. Price: $3.00.*—The present volume deals with the general principles of metallography and with some of the more important methods which are used to carry out general investigations in the metallographic laboratory. It is to be followed by a volume dealing with the metallography of the more important metals and alloys, including steel, cast iron, and the special steels; and by a third volume which will contain the applications of metallography to the metallurgical and engineering industries. The chapters in this volume are entitled: constitution diagrams; the preparation of metallic alloys; metallic microscopy; microstructure of metals and alloys; pyrometry and thermal analysis; physical properties; mechanical properties.

There are a number of nice things in the book. The statement in regard to apochromatic objectives is excellent, p. 85. "In the achromatic objectives light of only one wave length, the brightest color to the eye, passes through without producing spherical aberration. This means that perfectly sharp images are secured with only one color and that other images are blurred so as to form color fringes and to cast a general haze over the entire field. This is lack of complete correction and is due to the 'chromatic difference of spherical aberration.' The apochromatic objectives, on the other hand, produce images which are nearly equally distinct for all colors so that the quality of the image is independent of the light used for illumination. Furthermore, the color correction in achromatic objectives is adequate only in one zone and the definition falls off toward the centre and the margin, while in the apochromatic objectives the color correction is uniform over the entire field. Chromatic aberration in achromatic objectives is corrected for two colors—red and violet—by using appropriate combinations of optical glass and lenses. This leaves a 'secondary spectrum' of apple-green which limits the aperture which can be employed. However this correction is perfect only within the limited zone. The apochromatic objectives produce coincident images with three different colors and this is true for the entire field, so that the various images, besides being individually perfected, are brought more nearly coincident in the same focal plane to produce uniform and sharply defined images. For these reasons the apochromatic objectives combine, very satisfactorily, a high resolving power, superior definition and a wide range of magnification; and this is true whether the illumination is vertical or oblique or with colored or with white light."

The discussion of grain size is good, p. 104; the paragraphs on eutectic structure are admirable, p. 116; and the reviewer was interested in the statement in regard to surface tension, p. 119. "The usual effect of surface tension on the shape of the primary crystals is to produce dendrites with rounded surfaces, which shows that the surface tension is greater than the resistance of the material. The diamond has been cited as an example of this effect. On the other hand, if the strength of the material exceeds the force of surface tension, the dendrite is able to assume its more natural shape, often characterized by sharp angles."

The author refers, p. 178, to the experiments of Fink on coarse and fine powders of thoria and tungsten. He is very clear, p. 198, as to the theoretical conditions for measuring the electromotive force of an alloy as a reversible alloy, though he is evidently not clear at all as to the way in which such measurements are to be used, because the cut on p. 199 is worse than useless to anybody primarily interested in alloys, who wished to use electromotive force measurements to determine the constitution of an alloy. It should also have been stated that the method is of no value except in the simplest possible cases, where it is superfluous. On the other hand the discussion of the change of tensile strength and ductility of annealed and hard-drawn copper with changing temperature, p. 239, is excellent.

What is said in regard to hardness, p. 240, is so good as to be worth quoting: "The property of hardness is another one which is difficult to define and equally difficult to measure. Our simplest conception of a hard substance is one which cannot be readily scratched. This is the use of the term as accepted by mineralogists and is the basis of the well-known scale of Mohs. However applicable this test may be in mineralogical determinations, it is not capable of rendering quantitative results which would be serviceable in the physical testing of materials. For our purposes we may take hardness as the resistance of a material to abrasion or to cutting by a hard substance, or to penetration by another (harder) substance. In some form or another, this is the property (or better, combination of properties, for we have no conception of hardness which permits us to classify it as a single property) which is measured by the methods commonly employed. The different kinds of hardness are brought out by the different methods which are used to test for hardness, and, as a corollary, it is necessary to select the method with due regard for the particular kind of hardness which is to be measured. As a matter of fact 'hardness' which means resistance to cutting is in reality a combination of hardness with some other property, such as toughness. Other kinds of 'hardness' may be regarded as similar combinations. The term 'hardness' is often incorrectly used to signify strength or even brittleness. Inasmuch as this usage is not justified by the definitions of the terms and can only lead to confusion, it should be discarded."

While the book is admirable in most respects, it seems misleading to speak, p. 36, of a binary eutectic separating from a ternary melt along the boundary curve leading from the binary eutectic to the ternary eutectic. The relative masses of the two phases separating along the boundary curve are not necessarily the same as the binary eutectic and are not so represented in the cut. On p. 190 the reviewer is by no means clear what actually happens to the magnetic transformation when the field strength is varied and consequently he cannot state to what extent there is even an apparent discrepancy with the phase rule. The matter is complicated by the fact that the author has evidently forgotten that on the first page he excluded magnetic forces explicitly.

Wilder D. Bancroft

The Physical Chemistry of Metals. *By Rudolph Schenck. Translated and annotated by R. S. Dean. 24 × 16 cm; pp. viii + 239. New York: John Wiley and Sons, 1919. Price: $3.00.*—The German edition appeared in 1908; but the translator has revised the text so as to bring it up to date so far as possible. In the introductory chapter the author discusses the properties of metals including melting-points, transition points, densities, heats of fusion, conductance, reflecting power and metallic lustre, thermo-electric force, and passivity. The second chapter deals with metallic solutions and alloys, and the third with the alloys of metals with carbides, oxides and sulphides. Iron and steel come in this chapter. The fourth chapter is devoted to oxidation and reduction, while the decomposition of carbon monoxide and the blast furnace process form the subject of the fifth chapter. The reactions of sulphides are taken up in the sixth chapter, in other words, the roasting of sulphide ores.

The book contains a great deal of interesting information and the photomicrographs are well reproduced, though the connection between the text and the cuts is not always as close as one would like. The sample of fuchsin paper on p. 27 is very striking. In the discussion on passivity, p. 37, it is stated that if a conductor is once made passive, changing the magnetic field would have no effect. The work of Nichols and Franklin is referred to in support of this view; but the reviewer's recollection is that iron which had become passive in nitric acid became active when the magnetic field was applied. Also, the experiments of Bennett and Burnham made it probable that this effect of the magnetic field had nothing to do with electrons. On p. 44 it seems a pity only to note from

Ramsay's experiments on the vapor pressures of mercury solutions of metals that there is proportionality between concentration and depression and that most of the metals are monatomic. To most people the striking thing was the molecular weight of 19 for calcium, 76 for barium, 18 for sodium, and 30 for potassium.

On p. 48 it is stated that the Parkes process and the shaking out of organic substances with ether "depend on the fact that the third substance distributes itself between the layers according to a definite ratio." The constancy of the ratio is not important at all and probably does not occur in most cases. The essential thing is that the ratio shall be satisfactory and not that it shall be constant. We cannot even lay down a hard and fast rule as to what constitutes a satisfactory ratio.

In the case of a compound, AB, which forms no eutectic point with component B, it is at least a question whether one should speak of the solid mass rich in B as consisting of AB and the eutectic of B and AB, p. 64. There is a vagueness about the following sentence, p. 68, which undoubtedly existed in the German: but which might well have been eliminated in the translation: "It is clear, that an alloy with the most homogeneous possible structure, which has the same components as another, containing interstratified large crystals, will excel in tensile and compressive strength."

The facts in regard to the dissociation of metallic oxides are given clearly, the reduction by carbon monoxide is discussed in detail, and the chapter on the roasting of sulphide ores is helpful. *Wilder D. Bancroft*

The Microbiology and Microanalysis of Foods. *By Albert Schneider. 24 × 17 cm; pp. x + 262. Philadelphia: P. Blakiston's Son and Co., 1920. Price: $3.50.*—In the introduction the author says: "During our participation in the World War and since the declaration of the armistice and the demobilization subsequent thereto, numerous reports of extensive outbreaks of severe enteritis in army encampments, in barracks, and on transports have been made by privates, mess sergeants, camp cooks and by officers. All of the reports were quite uniform as to the symptoms of the food intoxications. Generally a severe enteritis with great prostration, lasting from three to five days. In one aviation barrack, housing about 5,000 men, fifty percent were thus stricken after an evening meal. No thorough investigation was made. The mess sergeant laid the trouble to bad meat. In one large training camp severe and extensive outbreaks of enteritis developed with some regularity, usually at the close of the week, suggesting to the men that they were given a periodic purgative with the food. A committee of privates called on the commanding officer and asked if this were so, and, if so, urged that the dose be much reduced as the effects were too severe. The officer declared that there was nothing to the surmise of the men. No special investigation was made and the conclusion reached was that the attacks were caused by bad food, coupled with the increase in unsanitary conditions of the mess toward the close of the week. Several extensive outbreaks of enteritis appeared in the S. A. T. C. barracks of one of our large universities. No thorough investigation was made. Reports of the kind cited could be multiplied many times. They serve to emphasize the importance of army sanitation as well as the importance of properly inspecting and testing the food supplies intended for the men.

"A most serious drawback to the cause of purer and better foods is the inability on the part of many, if not most, food bacteriologists to get away from the plate culture method for determining food decomposition, and also because many, if not most, laboratory analysts have such limited practical experience in food inspection, food production and preparation, etc., as to make it impossible for them to make proper use of the organoleptic tests. There are many technically experienced food analysts who assert that a direct bacterial count is of little value as indicator of the quality of the food article, whereas in fact it is the most valuable analytical factor now in use. Particularly is this the case in the examination of all foods which are much handled or which are long stored. The direct microscopical examination is the only means we have for determining the pre-processing conditions of canned foods, of dried foods and of frozen foods. Food materials in cans may be entirely decomposed and yet the plating results may be wholly negative. In these cases the direct microscopical examination will reveal billions of dead bacteria per cc or per gram. The direct bacterial count is the simplest and the most practical means for determining the quality of sausages of all kinds, of pastes, of minced meats, of potted fish and other meats, of gelatine, of dried, smoked, kippered and otherwise preserved meats and of frozen and cold storage meats, of dried milk, dried eggs, albumen, etc. In every case the organoleptic tests must be very carefully made and intelligently interpreted. The relationship of the direct count and the plating methods, as far as field work is concerned, may be summarized as follows: The direct count is all-important and the plating methods (and other special cultural methods, including special staining methods) are quite secondary in significance; and the direct count must be supplemented by the organoleptic tests."

The subject is presented under the following heads: introduction; decomposition changes in food; the principal groups of organisms concerned in food spoilage; subdued and retarded food decompositions; foods especially liable to be harmful or dangerous; food substances not likely to undergo microbic decomposition; food analysis in the field; food adulterations; general and special micro-analytical methods; micro-analytical rating of food products; legal standards of purity; diet table.

There is an occasional statement which is open to question. It is certainly not true that pears are better when ripened on the tree, p. 53, and many people would deny that the relish for the so-called gamey flavor in birds indicates a perverted taste. Under canned goods, p. 41, the enthusiastic reader can learn what swells, springers, flippers, and flat sours are.

It is interesting to read, p. 91, that "one of the most remarkable crazes which originated among civilians of the United States during the World War, was the notion that broken glass was added to flours, breads, sugar and other food stuffs. For a time a considerable number of the entire personnel of the food laboratories were kept busy examining materials which were suspected to contain broken or powdered glass. Of the thousands upon thousands of food products that were examined for broken glass not one was ever found which actually contained this substance. The suspicion was found to be either entirely groundless, or the suspected material proved to be a trace of sand, of pebbles and in a number of instances, granulated sugar."

On p. 22 there is a paragraph on the new method of transporting fish.

"Abiosis is a form of suspended animation due to freezing. Certain animals may be completely frozen, with apparent complete suspension of all life functions, and on careful thawing out will again be restored to life. This discovery has recently been made use of commercially. The Pictet procedure as applied to fish is carried out as follows: The fish in a tank of water are supplied with oxygen which is admitted to the water and which permits the drawing off of most of the water, whereupon the vessel packed with the fish is run into a refrigerating tank, and the entire mass (of water and fish) frozen into one solid block. This block, with suitable covering to prevent thawing, may now be shipped to any desired place. Upon arrival at the destination, the frozen block is put through a slow thawing process, lasting for about ten hours, whereupon the fish again assume their normal activities when placed in a suitable water supply. This method for shipping live fish is said to be simple and cheap. It is asserted that the state of abiosis through freezing has been induced in animals much higher in the scale of evolution than fish, as sheep and dogs; however, no practical application has as yet suggested itself in these cases."

The reviewer is not competent to speak as to the real value of the book; but he has found it interesting and helpful. *Wilder D. Bancroft*

La Matérialisation de l'Énergie. *By Louis Rougier. 19 × 12 cm; pp. xii + 148. Paris: Gauthier-Villars et Cie, 1919.—Price: 3.50 francs.*—This book is apparently written by a professor of philosophy and not of physics; but it is one of the best presentations of modern physics to be found anywhere. The author has read and mastered the work in regard to energy, quantum theory, and relativity; and the book can be recommended very highly. The subject is presented under the headings: duality of matter and energy; mass and the principle of relativity; electromagnetic dynamics; the electronic theory of matter; the inertia of energy; the weight of energy; the structure of energy; conclusions. It is to be hoped that this book may be translated into English before long.

Wilder D. Bancroft

Die Welt der vernachlässigten Dimensionen. *By Wolfgang Ostwald. Fourth edition. 23 × 15 cm; pp. xii + 222. Dresden and Leipzig; Theodor Steinkopff, 1920. Price: $1.00.*—The English translation of the first edition was reviewed two years ago (**22**, 380). While the fourth German edition has been revised and contains some new matter, the book as a whole has not been changed materially and consequently an extended review is not called for.

Wilder D. Bancroft

ANOMALOUS OSMOSIS WITH GOLD BEATERS SKIN MEMBRANES. CHLORIDE SOLUTIONS IN THE PRESENCE OF ACIDS AND BASES[1]

BY F. E. BARTELL AND O. E. MADISON

In our previous studies of the relation of osmose of solutions of electrolytes to the electrical states of the membrane system, we concluded that the nature and magnitude of the resulting osmose was dependent largely upon two factors: (1) the electrical orientation of the membrane system, and (2) the electrical orientation of the capillary wall system. The four conditions responsible for abnormal osmose may be represented by the following diagrams, Fig. I.

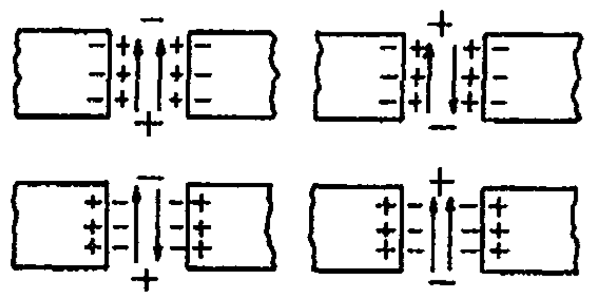

Fig. 1

With conditions represented in A and D, an abnormally great positive osmose would be obtained; while with conditions represented in B and C, an abnormally low, or even negative, osmose would result.

Gold beaters skin in pure water is electro-negative to the water. With dilute salt solutions of univalent cations, the solution side of the membrane system is electro-positive to the other side (case B), which should give as a result a

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[1] Practically all the data given in this paper had been obtained prior to December, 1917. Certain minor phases of the investigation as originally planned have not been completed owing to the fact that both authors entered war service and have not, up to the present time, found it possible to continue the experimental work of this problem. The work is, however, so nearly completed that it seems desirable to publish the results at this time.

tendency to produce an abnormally low osmose. In our experimental work we have found that this prediction correctly represents the facts.

With salt solutions of polyvalent cations as aluminium and thorium, the membrane becomes electro-positive to the solution. The solution side of the membrane is electro-positive (case D). The resulting osmose should be abnormally positive. The experimental results were entirely in accord with this prediction.

It is well known that small amounts of acids or bases play an important rôle in adsorption, and that comparatively small amounts of these substances tend to alter greatly the sign of the charge of any adsorbing materials placed in such solutions.

It was our aim in the present investigation to study the effect of the presence of different concentrations of acids and bases upon the osmose of different salt solutions. If our fundamental hypothesis is correct, we should be able, by altering the sign of the charge of the membrane by having present acids or bases, to greatly alter the osmotic effects of the different salt solutions. For example, those salt solutions which show an abnormally great osmose in neutral solution should be caused to show an abnormally low or even negative osmose when the electrical sign of the system is properly altered by the presence of acid or alkali. Solutions of chlorides of K, Na, Li, Ba, Mg, Al and Th (the same salts that were used in our earlier investigation), of 0.05 concentration, were used.

Three series of experiments were run in which were used both HNO_3 and NaOH solutions of different concentrations. The acid or alkali was used (1) throughout the cell system, (2) on the solution side of the membrane with distilled water on the opposite side, and (3) on the side of the membrane opposite to that of the solution.

The apparatus and methods used were the same as those described in the previous paper. The results obtained are shown in the following tables.

TABLE 1

Concentration of 0.05 *M*. Solutions of Chlorides in Two-compartment Cells

Time (hrs.)	KCl	NaCl	LiCl	$BaCl_2$	$MgCl_2$	$AlCl_3$	$ThCl_4$
0	0	0	0	0	0	0	0
2	9	3.5	5.5	27	42.5	112.5	91
4	20	8.5	10.5	42.5	66.5	129	112.5
6	25	15	19	55	84	152.5	150
8	28	21	27	62.5	97.5	147.5	166
10	29	27.5	31	61	107	142	170
12	29	31	36	61	112	137	169

TABLE 2

Acid throughout the Cell System

Concentration of Acid 0.0001 *M*. 0.05 *M* Chlorides in Cells

Time (hrs.)	KCl	NaCl	LiCl	$BaCl_2$	$MgCl_2$	$AlCl_3$	$ThCl_4$
0	0	0	0	0	0	0	0
2	9.5	12.5	16	22.5	64	72	42
4	16	21	29.5	36	112	90	49
6	20	27.5	39	44.5	142	81	40
8	22.5	33	42	49	162	72	33
10	25	34.5	44	55.5	174	56	27
12	27	37	46	60	182	46	24

TABLE 3

Acid throughout the Cell System

Concentration of Acid 0.001 *M*. Solutions of Chlorides in Cells

Time (hrs.)	KCl	NaCl	LiCl	$BaCl_2$	$MgCl_2$	$AlCl_3$	$ThCl_4$
0	0	0	0	0	0	0	0
2	17	29.5	35	82	116	105	14
4	32	33	71	150	204	112	12
6	43.5	44	91	202	306	100	10.5
8	50	54	108	251	380	92	8
10	53	57	118	271	414	81	4.5
12	55	68	121	312	466	71	3

Table 4

Acid throughout the Cell System
Concentration of Acid 0.01 *M*. 0.05 *M* Solutions of Chlorides in Cells

Time (hrs.)	KCl	NaCl	LiCl	$BaCl_2$	$MgCl_2$	$AlCl_3$	$ThCl_4$
0	0	0	0	0	0	0	0
2	14	26.5	32	49	93.5	61	11
4	23.5	35	51	99	178	50	9
6	29	38	60.5	144	270	40	7
8	34.5	40	62	173	336	35	5
10	38	46	52	208	392	29	3
12	42	48	50	227	429	23	3

Table 5

Acid throughout the Cell System
Concentration of Acid 0.1 *M*. 0.05 *M* Solutions of Chlorides in Cells

Time (hrs.)	KCl	NaCl	LiCl	$BaCl_2$	$MgCl_2$	$AlCl_3$	$ThCl_4$
0	0	0	0	0	0	0	0
2	3.5	7.5	9.5	25	26.5	21	6.5
4	5.5	10	12.5	44	43	36	5
6	7	16	19	62	63	31	4
8	9	19	26.5	72	78	25	1
10	10	20.5	30	81	93	21.5	0
12	10	22.5	31.5	91	105	16	0

Table 6

Acid on Solution Side; Distilled Water on Other Side
Concentration of Acid 0.0001 *M*. 0.05 *M* Solutions of Chlorides in Cells

Time (hrs.)	KCl	NaCl	LiCl	$BaCl_2$	$MgCl_2$	$AlCl_3$	$ThCl_4$
0	0	0	0	0	0	0	0
2	7	8	10.5	23	41	71	80
4	11	17	29	38	102	155	170
6	13	20	44	37	155	213	250
8	12	17.5	54	26	195	247	275
10	11	14	66	19	227	256	282
12	9	9.5	72	12	242	252	270

TABLE 7

Acid on Solution Side; Distilled Water on Other Side
Concentration of Acid 0.001 *M*. 0.05 *M* Solutions of Chlorides in Cells

Time (hrs.)	KCl	NaCl	LiCl	$BaCl_2$	$MgCl_2$	$AlCl_3$	$ThCl_4$
0	0	0	0	0	0	0	0
2	22	31	36	52	96	162	175
4	46	53	72	49	196	291	300
6	58	69	103	37	285	343	350
8	68	76	121	21	359	353	376
10	71	81	135	13	429	347	355
12	74	80	144	8	483	334	330

TABLE 8

Acid on Solution Side; Distilled Water on Other Side
Concentration of Acid 0.01 *M*. 0.05 *M* Solutions of Chlorides in Cells

Time (hrs.)	KCl	NaCl	LiCl	$BaCl_2$	$MgCl_2$	$AlCl_3$	$ThCl_4$
0	0	0	0	0	0	0	0
2	20	25	29	75	75	120	142
4	37	46	61	61	163	240	265
6	54	59	85	57	246	337	374
8	61	67	110	43	316	392	422
10	67	69	125	30	380	432	461
12	70	71	132	18	436	455	500

TABLE 9

Acid on Solution Side; Distilled Water on Other Side
Concentration of Acid 0.02 *M*. 0.05 *M* Solutions of Chlorides in Cells

Time (hrs.)	KCl	NaCl	LiCl	$BaCl_2$	$MgCl_2$	$AlCl_3$	$ThCl_4$
0	0	0	0	0	0	0	0
2	18	25	26	61	63	77	98
4	31	38	51	111	133	156	240
6	41	44	70	156	190	232	280
8	50	54	85	189	215	289	340
10	56	55	99	235	263	333	400
12	51	62	109	252	287	274	445

TABLE 10

Acid on Solution Side; Distilled Water on Other Side
Concentration of Acid 0.05 *M*. 0.05 *M* Solutions of Chlorides in Cells

Time (hrs.)	KCl	NaCl	LiCl	BaCl$_2$	MgCl$_2$	AlCl$_3$	ThCl$_4$
0	0	0	0	0	0	0	0
2	8	13	14	35	43	101	105
4	13.5	24	27	81	92	216	228
6	16.5	36	37	116	130	244	262
8	15.5	39	41	138	151	275	294
10	15.5	44	47.5	157	167	306	324
12	15.5	48	51	172	184	340	360

TABLE 11

Acid on Solution Side; Distilled Water on Other Side
Concentration of Acid 0.1 *M*. 0.05 *M* Solutions of Chlorides in Cells

Time (hrs.)	KCl	NaCl	LiCl	BaCl$_2$	MgCl$_2$	AlCl$_3$	ThCl$_4$
0	0	0	0	0	0	0	0
2	4	9	9.5	25	24	41	54
4	7	15	17	44	42	78	86
6	8.5	21	23	62	62	124	142
8	10	25	28	74	76	158	186
10	10.5	28	32	86	90	193	245
12	11.5	30	35.5	95	100	221	282

TABLE 12

Acid on Solution Side; Distilled Water on Other Side
Concentration of Acid 0.2 *M*. 0.05 *M* Solutions of Chlorides in Cells

Time (hrs.)	KCl	NaCl	LiCl	BaCl$_2$	MgCl$_2$	AlCl$_3$	ThCl$_4$
0	0	0	0	0	0	0	0
2	1.5	4	4	10	10	19.5	24
4	2.5	7	8	20	20	39	48
6	3	11	12.5	30	32	70	88
8	3.5	12.5	13.5	35	38	84	116
10	4	13	17	42	46.5	107	132
12	3.5	15	19	46.5	52.5	122	146

TABLE 13

Acid on One Side; Solution on the Other Side
Concentration of Acid 0.0001 *M*. 0.05 *M* Solution of Chlorides in Cells

Time (hrs.)	KCl	NaCl	LiCl	$BaCl_2$	$MgCl_2$	$AlCl_3$	$ThCl_4$
0	0	0	0	0	0	0	0
2	9.5	7.5	19.5	39	49	69	25
4	13	12	33.5	56.5	98	140	17
6	15.5	14.5	38	63.5	124	70	14
8	17	16	41	64	136	15	10
10	18	19	41	62	142	15	7
12	18	22	41	59	141	15	4

TABLE 14

Acid on One Side; Solution on the Other Side
Concentration of Acid 0.001 *M*. 0.05 *M* Solutions of Chlorides in Cells

Time (hrs.)	KCl	NaCl	LiCl	$BaCl_2$	$MgCl_2$	$AlCl_3$	$ThCl_4$
0	0	0	0	0	0	0	0
2	24	29	31	76	22	80	67
4	42	59	53	80	30	144	87
6	54	78	68	84	29	152	137
8	61	94	87	64	27	162	125
10	64	104	102	54	26	167	110
12	66	109	114	49	25	167	90

TABLE 15

Acid on One Side; Solution on the Other Side
Concentration of Acid 0.01 *M*. 0.05 *M* Solutions of Chlorides in Cells

Time (hrs.)	KCl	NaCl	LiCl	$BaCl_2$	$MgCl_2$	$AlCl_3$	$ThCl_4$
0	0	0	0	0	0	0	0
2	28	33.5	35	81	11.5	147	275
4	48	66	71	92	12.5	200	350
6	61	89	90	104	11	222	425
8	69	106	113	80	11	222	500
10	73	121	123	72	11	222	525
12	75	130	133	63	11	222	540

TABLE 16

Acid on One Side; Solution on the Other Side
Concentration of Acid 0.1 *M*. 0.05 *M* Solutions of Chlorides in Cells

Time (hrs.)	KCl	NaCl	LiCl	$BaCl_2$	$MgCl_2$	$AlCl_3$	$ThCl_4$
0	0	0	0	0	0	0	0
2	2	20	24	45	47.5	51	220
4	2	27	38.5	54	60	65	310
6	2	30	44	60	68	71	340
8	2	28	47	48	68	74	355
10	2	26	47	45	66	76	350
12	2	26	47	45	66	75	350

TABLE 17

Alkali throughout the Cell
Concentration of Alkali 0.0001 *M*. 0.05 *M* Solutions of Chlorides in Cells

Time (hrs.)	KCl	NaCl	LiCl	$BaCl_2$	$MgCl_2$	$AlCl_3$	$ThCl_4$
0	0	0	0	0	0	0	0
2	2	4	5	13	15	97	101
4	3	5	7	24	23	176	186
6	4	7	11	29	27	225	240
8	6	9	14	33	32	256	262
10	9	12	17	33	35	280	290
12	11	14	18	33	35	285	310

TABLE 18

Alkali throughout the Cell
Concentration of Alkali 0.001 *M*. 0.05 *M* Solutions of Chlorides in Cells

Time (hrs.)	KCl	NaCl	LiCl	$BaCl_2$	$MgCl_2$	$AlCl_3$	$ThCl_4$
0	0	0	0	0	0	0	0
2	2.5	10	11	7	8	35	85
4	4.5	17	20	9.5	11	40	90
6	7	22	25	10.5	13	39	65
8	7.5	25	28	9.5	17	39	44
10	9	27	30	9.5	16	32	40
12	11	29	33	9.5	16	32	38

TABLE 19

Alkali throughout the Cell

Conc. of Alkali 0.01 *M*. 0.05 *M* Solutions of Chlorides in Cells

Time (hrs.)	KCl	NaCl	LiCl
0	0	0	0
2	2	3	3·5
4	3	4	5
6	4	6	7
8	6	8	9
10	7	12	14
12	7	15	18

TABLE 20

Alkali throughout the Cell

Conc. of Alkali 0.1 *M*. 0.05 *M* Solutions of Chlorides in Cells

Time (hrs.)	KCl	NaCl	LiCl
0	0	0	0
2	0	2	3
4	1	4	4·5
6	2	5	6
8	2	5	7
10	3	5	9
12	4	5	10

The Electromotive Force of 0.05 M Chlorides with Nitric Acid and with Sodium Hydroxide throughout the System.— In order to study the effect of the presence of acid on the E. M. F. of the neutral salt solutions, and to compare this effect with the effect the acid exercised on the osmose of the same salt solutions, measurements were made of the cell potential of 0.05 *M* chlorides when different concentrations of nitric acid were used throughout the system. The concentrations of acid used were 0.001 *M*, 0.01 *M*, and 0.1 *M*.

A study similar to that made with nitric acid was made with sodium hydroxide. The following tables give only the results obtained when either the acid or alkali was present throughout the entire system. The + or — sign indicates the sign of potential on the solution side of the membrane.

TABLE 21

E. M. F. of 0.05 M Chlorides with Nitric Acid throughout the Cell

Concentration	KCl	NaCl	LiCl	$BaCl_2$	$MgCl_2$	$AlCl_3$	$ThCl_4$
0.001 M	+0.0061	+0.0165	+0.0270	+0.0287	+0.0321	+0.0245	+0.0142
0.01 M	+0.0010	+0.0020	+0.0024	+0.0065	+0.0079	+0.0190	+0.0105
0.1 M	—0.0025	—0.0028	—0.0032	—0.0050	—0.0053	—0.0063	—0.0067

TABLE 22

E. M. F. of 0.05 M Chlorides with Sodium Hydroxide throughout the Cell

Concentration	KCl	NaCl	LiCl	$BaCl_2$	$MgCl_2$	$AlCl_3$	$ThCl_4$
0.001 M	+0.0020	+0.0065	+0.0144	+0.0268	+0.0328	+0.0417	+0.0436
0.01 M	+0.0010	+0.0026	+0.0040	—	—	—	—
0.1 M	+0.0005	+0.0010	+0.0021	—	—	—	—

Summary of Results

Summary of Results.—A summary of the results obtained when acid or alkali are present throughout the cell system is best shown by the curves in Figs. 2 and 3.

From the above data it is shown conclusively that the presence of acid or alkali does have a marked effect upon the osmose of salt solutions.

It is also clearly shown that the presence of acid or alkali may alter not only the electrical sign of the capillary wall system but also may alter, or even reverse, the electrical sign of the membrane system.

A study of the results obtained brings out the fact that the direction of osmose, as also its magnitude, is closely related to the electrical orientation of the cell system. Although different salt solutions with cations of the same valence do not behave exactly alike under all conditions, they all do show similar effects which may be considered to be characteristic for the solutions of that class. For the purpose of simplifying the analysis of results, we may select the potassium salt as being representative of those with univalent cations, magnesium salt as being representative of those with divalent cations, and thorium salt as being representative of salts with cation with a valence of three and above.

Osmosis of Salt Solutions with Acid or Alkali throughout Cell. Potassium Chloride.—The osmose of neutral KCl solution is abnormally small; its cell system is represented by case B.

In the presence of 0.001 *M* acid to 0.01 *M* acid the electrical orientation of the cell system is represented by case D, which is productive of an abnormally high positive osmose.

When the system contains acid of 0.1 *M* concentration or greater, the electrical orientation of the system is represented by case C, which is productive of abnormally low or even negative osmose.

When the system contains alkali throughout, the membrane is in every case electro-negative and the electrical orientation of the cell system is represented by case B, which is productive of abnormally low, or negative, osmose.

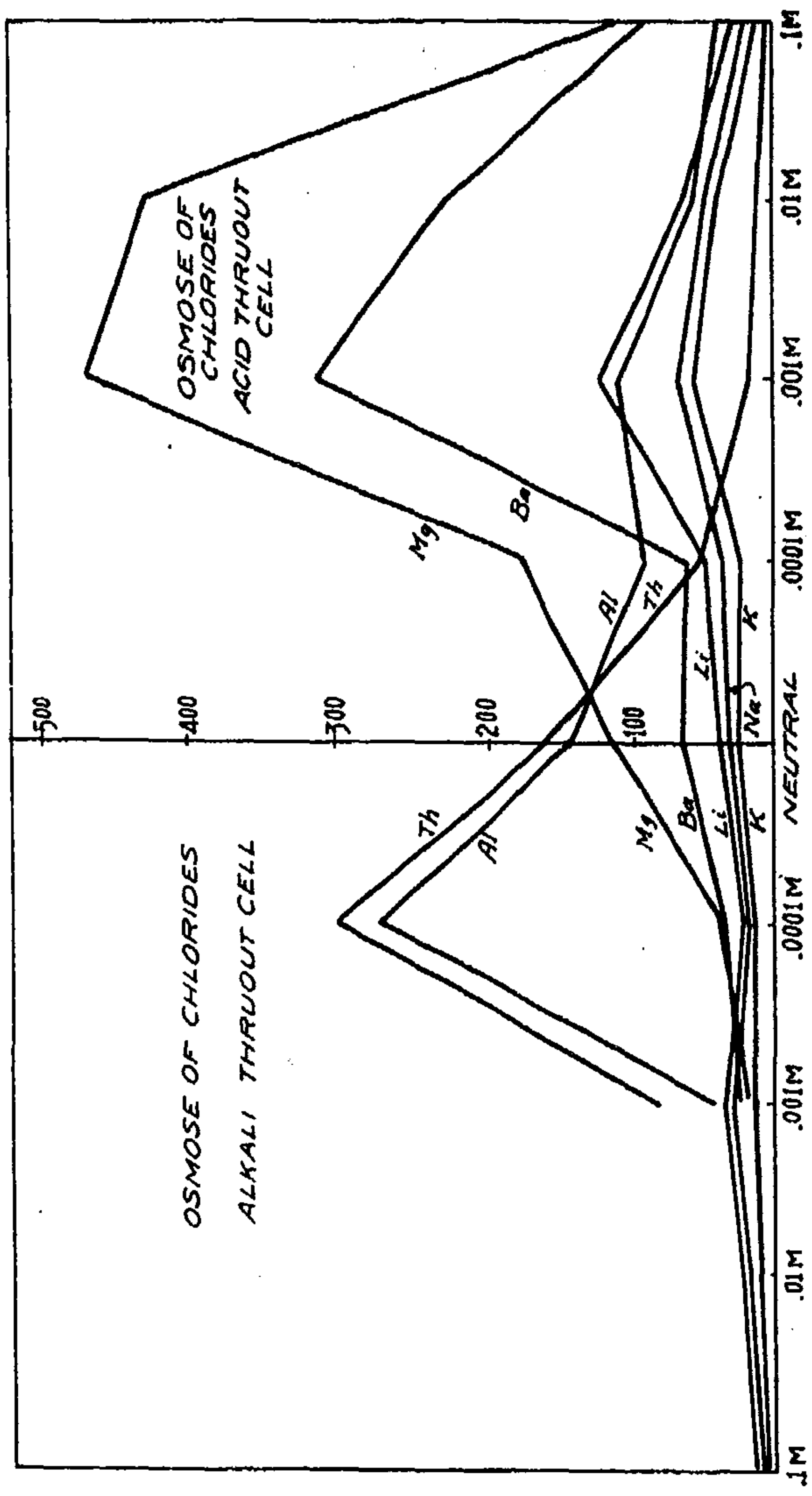
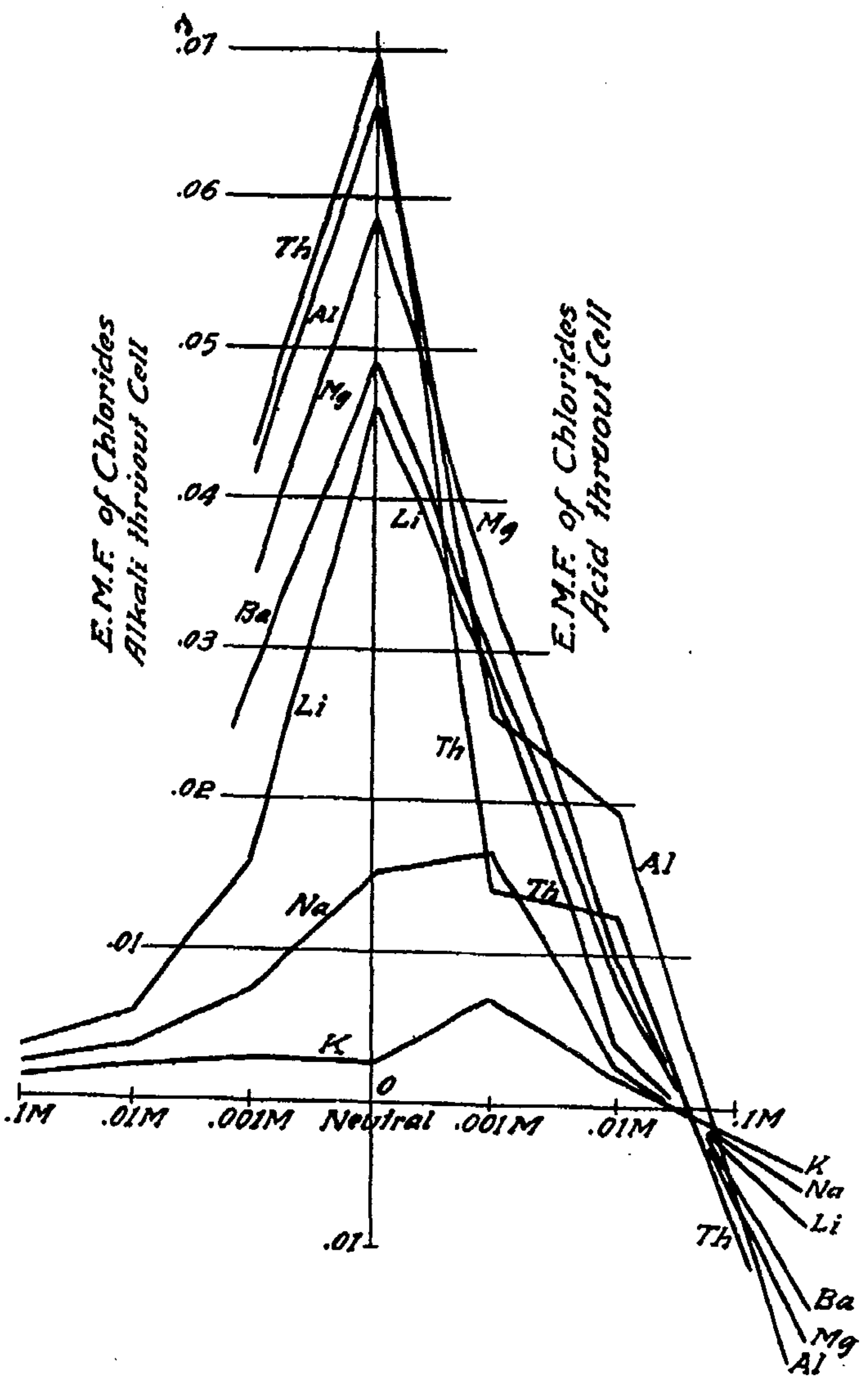

OSMOSE OF CHLORIDES ACID THRUOUT CELL
OSMOSE OF CHLORIDES ALKALI THRUOUT CELL
500
400
300
200
100
.1M
.01M
.001M
.0001M
NEUTRAL
.0001M
.001M
.01M
.1M
Mg
Ba
Al
Th
Li
Na
K
Th
Al
Mg
Ba
Li
K

Fig. 2


.07
.06
.05
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E.M.F. of Chlorides Alkali throout Cell
E.M.F. of Chlorides Acid throout Cell
Th
Al
Mg
Ba
Li
Na
K
Li
Mg
Th
Al
Th
0
.1M
.01M
.001M
Neutral
.001M
.01M
.1M
K
Na
Li
Th
Ba
Mg
Al

Fig. 3

Magnesium Chloride.—The factors governing the osmose of magnesium chloride are identical with those governing the osmose of potassium chloride. The same explanations given for the results obtained with potassium chloride solutions apply throughout to those obtained with magnesium chloride.

Thorium Chloride.—The osmose of neutral thorium chloride solutions is abnormally great and is accounted for by the fact that the electrical orientation of the cell system is represented by case D.

An exceedingly small amount of acid present in the cell system lowers the potential of the membrane interface system which, as a result, tends to lower the abnormally great positive osmotic tendency of thorium chloride solutions.

A still greater concentration of acid throughout the system (0.1 *M* and above) reverses the electrical orientation of the membrane system giving as a result conditions represented in case C. The resulting osmose now becomes abnormally low or even negative.

With a low concentration of alkali (0.0001 *M*) throughout the system the membrane is still electro-positive due to the pronounced effects of the quadrivalent cation of the salt solution. The conditions are represented by case D, and an abnormally great positive osmose results.

With somewhat higher concentrations of alkali throughout the system, the sign of the membrane material becomes electro-negative; the conditions are represented by case B. An abnormally low or negative osmose results.

It was mentioned above that the sign of the gold beaters skin membrane to water is electro-negative. The iso-electric point of this membrane is reached with comparatively low concentrations of acid, approximately 0.0001 *M*. In the presence of different salt solutions with the acid, the iso-electric point comes at a somewhat different concentration with each of the different salts. It is quite likely that the distinct breaks noted in the various curves (Fig. 2), which come at about 0.0001 *M* acid concentration, may be accounted for by the fact that at these points the membrane is near, or is passing through the iso-electric point.

It is hardly necessary for the writers to further analyze the results obtained with the various solutions under the different conditions of the above experiments. The same general principles apply throughout. It may be stated that many experiments in addition to those reported in this paper have been carried out in this laboratory during the past eight years in which this investigation has been in progress, and in practically every case the results obtained may be explained when the factors above described are determined and the principles above given are applied. Experiments similar to the above have been carried out with other types of membranes. Considerable work has been done with membranes of collodion; with this material we have been able to vary the diameter of the pore spaces as well as the thickness of the membrane. Both of these factors are important in the consideration of anomalous osmose.

In a subsequent paper we shall attempt to point out the relation of the principles discussed in this paper to colloidal processes, including the swelling of gels and various biological phenomena which, up to the present time, have received no satisfactory explanation.

University of Michigan

ELECTROLYTIC PREPARATION OF SODIUM PERMANGANATE

BY C. O. HENKE AND O. W. BROWN

Manganese, used as an anode in an alkaline solution, gives permanganate, manganate, manganese dioxide and manganous hydroxide, the particular product and the current efficiency depending upon the concentration of the alkali, the temperature of the electrolyte, and the current density. In this investigation we studied the effect of temperature, current density, and concentration of the alkali upon the production of sodium permanganate.

The formation of permanganate at a manganese anode in alkaline solutions was first discovered by Lorenz.[1]

Müller[2] studied the anodic behavior of manganese in solutions of sodium sulphate and sodium di-hydrogen phosphate, with and without the addition of sodium hydroxide. He showed by polarization measurements that hydroxyl ions produced passivity.

White[3] states that ferromanganese anodes in sodium hydroxide solutions form manganous hydroxide at low current densities. He found that this could be readily oxidized electrolytically to manganese dioxide but not to permanganate. Neither was he successful in oxidizing the manganese dioxide electrolytically to permanganate. From this he concluded that the electrolytic formation of permanganate is a direct reaction not involving manganous hydroxide or manganese dioxide as intermediate steps. At 95° C he secured the green manganate.

Wilson and Horsch[4] state that they secured the best current yields of sodium permanganate from ferromanganese anodes in sodium carbonate solutions, at low temperatures and

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[1] Lorenz: Zeit. anorg. Chem., 12, 393 (1896).

[2] Müller: Zeit. Elektrochemie, 11, 755 (1905).

[3] White: Jour. Phys. Chem., 10, 502 (1906).

[4] Wilson and Horsch: Trans. Am. Electrochem. Soc., 35, 371 (1919).

with a current density of about 13 amperes per square decimeter, but they give no quantitative results to show the effect of temperature and current density. The major portion of their article is concerned with the development of a commercial process, the object being to secure a pure solution of the permanganate to meet the Government's requirements, as impurities caused serious deterioration in the resulting soda-lime.

Thompson[1] gives the results of some experiments carried out on a large scale. He used ferromanganese anodes in a 24 percent potassium carbonate solution and secured a current efficiency of 17 percent.

In our experiments we used a manganese anode containing 92.0 percent manganese, the impurities being for the most part iron, silicon and carbon. The anode was made by reducing pyrolusite with coke in an electric arc furnace. Connection with the anode was made by soldering a copper wire onto one edge of it. The anode had a surface of 30 square centimeters on each side. In calculating the current density 45 square centimeters or $1^1/_2$ times the area of one side was used, since there was only one cathode on one side of the manganese anode. The electrolysis was carried out in a beaker $8^1/_2$ cm in diameter by $11^1/_2$ cm high. This was kept within two degrees of the indicated temperature by placing in a water bath. To secure the lower temperatures a cooling coil was also used, which was placed inside the vessel. The cathode consisted of a perforated platinum plate having a surface of 10 square centimeters counting both sides. The electrolyte was in each case 350 cc. The amount of current used was indicated by an ammeter, slight variations being noted. Before each electrolysis the manganese anode was scrubbed with an iron wire brush, in order to have it in as nearly the same condition as possible at the start of each experiment.

The amount of permanganate formed was determined by pipetting out a portion of the electrolyte, which was acidi-

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[1] Thompson: Chem. Met. Eng., 21, 680 (1919).

fied with sulphuric acid, heated to 65° C and then reduced by a known amount of a standard solution of oxalic acid, an excess being added which was titrated with a standard solution of potassium permanganate. Since the manganese is oxidized to a valence of seven, one ampere hour should produce 0.7566 gram of sodium permanganate which is equivalent to 265.5 cc of a decinormal solution of oxalic acid.

In some preliminary experiments a porous cup was used. This worked nicely for a time but soon the resistance of the cup would begin to increase and the voltage would rise to a prohibitive figure. On breaking the cup the walls were found to contain a deposit of a brownish black oxide of manganese. Morse and Olsen[1] encountered the same difficulty in making permanganic acid. This led us to attempt the formation of the permanganate without the use of a diaphragm. The electrolyte was a solution of caustic soda containing 10 grams of sodium hydroxide per liter. Using a current of 3.5 amperes (current density 7.7 amperes per square decimeter), at 25° C for one hour the current efficiency was 16.4 percent, while in a similar electrolysis, except with the addition of an excess of calcium hydroxide, the current efficiency was 32.8 percent. That is, under these conditions, the addition of an excess of lime increased the current efficiency about 16 percent. There was a great deal of difference in the appearance of the platinum cathode under the two conditions. Without the lime it was covered with a coating of a black oxide of manganese, probably manganese dioxide, while with the addition of the calcium hydroxide the coating on the cathode was very similar in color to that of manganese. It seems as though the calcium hydroxide formed a film over the cathode which acted as a diaphragm. In the following experiments no diaphragm other than that formed by the calcium hydroxide was used.

The results of Table I are plotted in Plate I. The current efficiency, which is plotted in Curve A, rises rather rapidly

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[1] Morse and Olsen: Am. Chem. Jour., 23, 431 (1900).

Table I

Effect of Current Density on Current Efficiency
Temperature 25° C
Electrolyte—350 cc of NaOH solution containing 10 grams NaOH per liter. To this an excess of $Ca(OH)_2$ was added
Time of passage of current—one hour

Current strength amperes	Current density amperes per sq. dcm	Bath tension volts	Anode discharge potential volts	$NaMnO_4$ formed grams	Current efficiency in percent of theory
0.75	1.66	3.4	—1.157	0.0250	4.4
1.52	3.38	4.0	—1.239	0.2351	20.5
2.62	5.82	5.3	—1.415	0.5547	28.1
2.98	6.66	5.5	—	0.6774	30.1
3.5	7.78	5.9	—1.445	0.8593	32.5
3.83	8.52	6.3	—	0.9795	33.8
4.7	10.43	7.0	—1.445	1.1844	33.4
5.7	12.68	7.8	—1.445	1.4626	34.2
6.9	15.33	8.6	—1.485	1.6288	31.2

with increase in current density up to 6 amperes per square decimeter and then less rapidly up to 12.7 amperes per square decimeter, after which it declines slightly. In Curve 8 the anode discharge potential is plotted. This was measured after the current had been passing half an hour. In calculating the discharge potential the voltage of the calomel half-cell was taken as —0.56 volt. The results show that the discharge potential increases with increase in current efficiency calculated from the formation of permanganate. In the case of lead anodes[1] in sodium hydroxide solutions the corrosion decreased when the anode discharge potential increased.

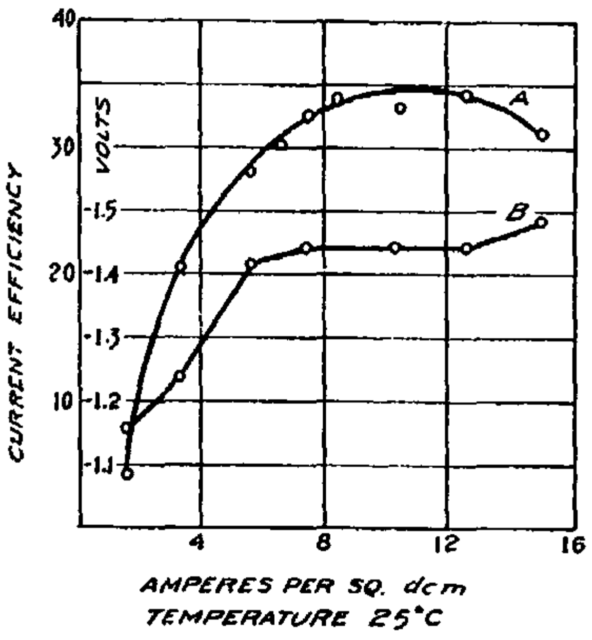

Plate I

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[1] Brown, Henke and Smith: Jour. Phys. Chem., 24, 367 (1920).

The results of Table II are plotted in Plate II. Curve A shows the decrease in current efficiency with increase in temperature. The efficiency decreases from 38.6 percent at 8° C to 8.1 percent at 60° C. Besides the decrease in efficiency the color of the solution was different at 60° C. The color indicated that there was a large amount of manganate along with the permanganate. Also at 40° and 60° C the platinum cathode was covered with a black coating probably manganese dioxide, even though there was an excess of calcium hydroxide present. At the lower temperatures there was no black coating on the cathode. This indicated that the lime did not make as good a diaphragm at the high as at the low temperatures. Curve B shows the decrease in anode dis-

Table II

Effect of Temperature on Current Efficiency

Current density 12.7 amperes per square decimeter

Electrolyte—350 cc of NaOH solution containing 10 grams NaOH per liter. To this an excess of $Ca(OH)_2$ was added

Time of passage of current—one hour

Current strength amperes	Temperature degrees centigrade	Anode discharge potential volts	$NaMnO_4$ formed grams	Current efficiency in per cent of theory
2.93*	8	—	0.8548	38.6
2.78*	16	—1.445	0.7518	35.8
5.70	25	—1.445	1.4726	34.2
5.63	40	—1.363	0.8548	20.1
5.70	60	—1.211	0.1342	3.1

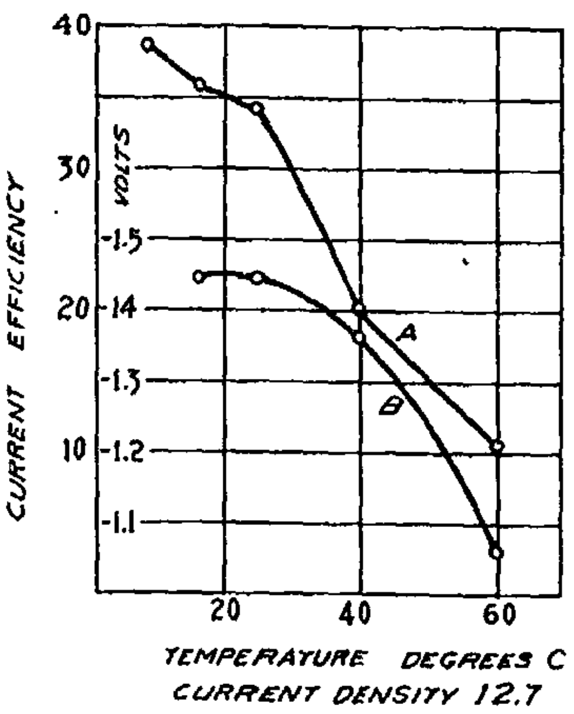

Plate II

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* Only one-half of the anode was immersed in the electrolyte.

charge potential with temperature, the discharge potential decreasing with the current efficiency as it did in Plate I, Curve B.

TABLE III

Effect of Concentration of Sodium Hydroxide on Current Efficiency
Temperature 25° C
Current density—12.7 amperes per square decimeter
Electrolyte—350 cc of NaOH solution of concentration indicated in column two below. To this an excess of $Ca(OH)_2$ was added
Time of passage of current—one hour

Current strength amperes	Concentration of NaOH in grams per liter	Bath tension volts	Anode discharge potential volts	$NaMnO_4$ formed grams	Current efficiency in percent of theory
5.70	10	7.8	—1.445	1.4726	34.2
5.68	30	3.4	—1.234	0.8424	19.6
5.70	75	2.9	—1.114	0.7167	16.6
5.70	112.5	3.0	—1.076	0.8802	20.5
5.75	150	3.0	—1.034	1.0900	25.0
5.75	180	2.9	—1.034	1.0924	25.1
5.85	225	2.8	—1.005	1.1347	25.7
5.82	300	2.9	—1.005	1.2315	28.0

The results of Table III are plotted in Plate III. Curve A shows the effect of concentration of the sodium hydroxide

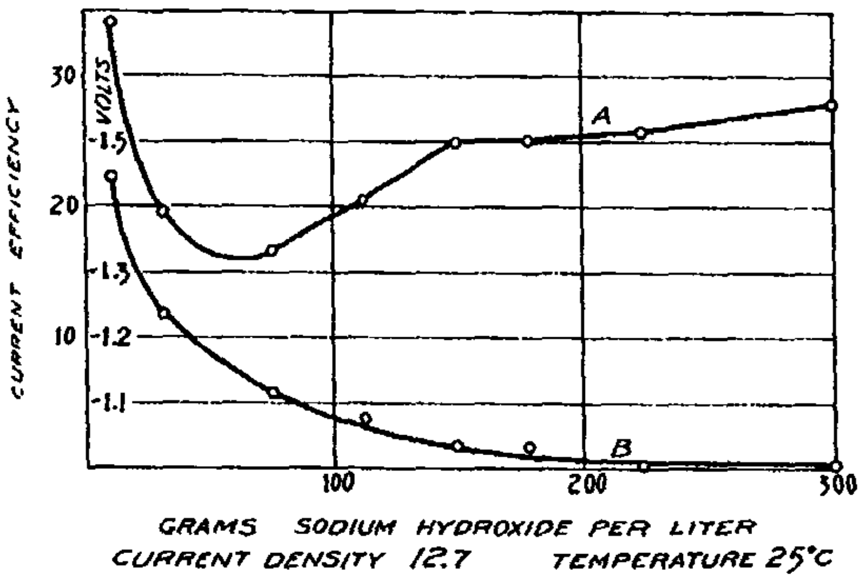

Plate III

on the current efficiency. The shape of this curve is peculiar in that there is a minimum with maxima on either side.

Thus at a concentration of 10 grams of sodium hydroxide per liter the efficiency is 34.2 percent and at 150 grams per liter the efficiency is 25 percent, while with 75 grams sodium hydroxide per liter the efficiency is only 16.6 percent. At the low concentration permanganate is formed while at the high concentration of sodium hydroxide manganate is formed. So it may be possible that the curve shown in the figure consists of the branches of the two curves, one where the formation of manganate predominates along with some permanganate, and the other where the formation of the permanganate predominates along with some manganate, and that these two curves intersect at the low point in the curve, that is, at a concentration of about 65 grams sodium hydroxide per liter.

At the higher concentrations of the sodium hydroxide the black coating on the cathode was formed. In an attempt to secure a substance that would give a better diaphragm than calcium hydroxide and thus prevent this reduction, we tried the hydroxides of magnesium, strontium and barium, thinking that the solubility of the hydroxide would determine its efficiency as a diaphragm. However, with the concentration of the sodium hydroxide at 150 grams per liter, the efficiency was practically the same with the different alkali earth hydroxides, that is, about 25 percent, although with the strontium hydroxide we got 26.9 percent current efficiency.

Curve B, which shows the effect of concentration of sodium hydroxide on the anode discharge potential, drops continuously from —1.445 to —1.005 volts, although during the latter part of the curve the current efficiency is increasing. In the other two plates the discharge potential increased when the current efficiency increased. In the first part of the curve in Plate III that is also true, but after the minimum in the current efficiency curve is passed the discharge potential continues to decrease although the current efficiency increases. But during the last increase the amount of manganate in proportion to the permanganate formed increases until at a concentration of 300 grams sodium hydroxide per liter the manganate with practically no permanganate is formed.

This would seem to indicate that when the manganese goes into solutions as permanganate the discharge potential is higher than when it goes in solution as manganate. That is, the discharge potential is higher when the manganese goes into solution with a valence of seven than it is when it goes in solution with a lower valence, which would be six in the case of manganate. A similar occurrence is found when lead is used as an anode in sodium hydroxide solutions.[1] Lead dissolves as a bivalent metal and the discharge potential is low. When dark spots of lead peroxide begin to appear the lead stops corroding properly and the discharge potential increases. Hence it appears that the higher the valence to which the metal is oxidized the higher the discharge potential becomes.

This is further indicated by the following experiment: A solution of sodium carbonate containing 150 grams per liter was used as electrolyte. The current density was 12.7. A porous cup diaphragm was used, the catholyte being a 11 percent sodium hydroxide solution. The temperature was 25° C. The current efficiency was 37.1 percent and the anode discharge potential was —1.61 volts. With strong solutions of the carbonate the permanganate is formed while with strong solutions of sodium hydroxide the manganate is formed. This is also borne out by the discharge potentials. With the carbonate solution permanganate is formed and the anode discharge potential is —1.61 volts, while with the hydroxide solution, containing the same number of grams per liter, considerable manganate is formed and the discharge potential is only —1.034 volts. That is the higher the valence to which the manganese is oxidized the higher the discharge potential.

Conclusions

1. We secured high current efficiencies in the formation of sodium permanganate without the use of a diaphragm.

2. The current efficiency was highest at a current density of about 13 amperes per square decimeter.

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[1] Loc. cit.

3. The current efficiency increased with decrease in temperature to over 38 percent at 8° C, and indications are that it would have been still higher at lower temperatures.

4. The higher the valence at which the metal goes into solution the higher the discharge potential.

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THE SURFACE TENSION OF CERTAIN SOAP SOLUTIONS AND THEIR EMULSIFYING POWERS

BY MOLLIE G. WHITE AND J. W. MARDEN

Introduction

This investigation was stimulated by questions of students in General Chemistry regarding the cleansing action of soap. Students who have gone no further in chemistry than the first course, frequently point out the untenability of the theory which is included in many of the older text-books, that soap hydrolyzes in aqueous solutions liberating free alkali and that the cleansing power is due to this free alkali of hydrolysis. The student frequently asks if this is true why a very dilute solution of sodium hydroxide will not serve for cleansing purposes as well as soap itself.

It has been suggested by various authors on the cleansing power of soap (1) that the free alkali liberated by the soap when it dissolves in water acts on free fats and oils to saponify them; (2) that the alkali of hydrolysis acts in such a way as to allow contact of water with the substance to be cleaned; (3) that the alkali liberated acts as a lubricant, or (4) that the alkali of hydrolysis acts on greases to emulsify them so that they can be washed away in suspensions with other impurities.

Hillyer[1] has considered all of these theories and found them to be untenable. He has accumulated data, however, which serves as the basis for a more comprehensive theory, showing that aqueous liquids having the greatest power of forming emulsions were those with the lowest surface tensions.

Bancroft[2] quoting Hillyer, says, "The conclusion arrived at is that emulsification is due largely to the small surface tension between the oil and the emulsifying agent which allows the emulsifying agent to be spread out into thin films, separating the oil droplets. The surface tension is not strong

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[1] Jour. Am. Chem. Soc., 25, 511, 524, 1256 (1903).

[2] Jour. Phys. Chem., 16, 177, 345, 475 (1912); 17, 501 (1913).

enough to withdraw the film from between the droplets except slowly and, if the emulsifying agent has great internal viscosity or if great superficial viscosity is shown between the liquids, the thinning of the film becomes so slow that the emulsion is permanent. Hillyer's views correspond very closely with those of Donnan,[1] except that Hillyer lays more stress on the importance of viscosity or of surface viscosity."

Smith[2] restates the theory that the cleansing power of soap is due to the fact that soap solutions have a low surface tension compared to the surface tension of pure water but of approximately the same order as that of many oils. When two liquids are mixed having somewhat the same surface tension they do not separate because of the fact that the tendency to unite to form larger droplets is no greater in one case than in the other. The separation of oil and water is brought about largely by the high surface tension of water. The droplets of water combine to form larger drops with greater force than droplets of oil; they collect together with such force that the oil is pushed away and freed so that it forms a separate layer.

In the present work there has been an attempt to measure accurately the surface tensions of several soap solutions in the hope that the data obtained would give additional proof of the above theory and would help to clear up some of the questions yet unanswered on the subject.

Experimental Work

The Soap Solutions.—Two purified soap solutions were prepared, sodium palmitate and sodium stearate. The method of preparation was as follows: Purified palmitic acid having a melting point of 62.45° C was dissolved in 95 percent alcohol and sodium carbonate added in slight (calculated) excess, after having first been dissolved in boiling distilled water. This solution was evaporated to dryness, the residue dissolved in 95 percent alcohol filtered to remove any excess of sodium

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[1] Jour. Am. Chem. Soc., 25, 1215 (1903).

[2] "Intermediate Chemistry," Century Co., N. Y. (1918).

carbonate and again evaporated to dryness. The resulting residue was again dissolved in alcohol and filtered. The filtrate upon evaporation at ordinary temperature formed pure sodium palmitate which after standing at laboratory temperature for some days was found free of alcohol, but still containing some moisture.

Pure sodium stearate was made in exactly the same manner, starting with stearic acid, melting point 69.0° C and purified sodium carbonate.

These soaps contained some water, and were therefore carefully analyzed for the fatty acids. The following method was employed. About 0.12 to 0.25 gram of soap were weighted out into beakers, dissolved in water and the solution warmed gently with an excess of dilute sulfuric acid until the

TABLE I

Analysis of Soap Solutions

Number sol. used	I Sodium palmitate	II	III	IV
Grams of soap taken	0.2509	0.2509	0.1323	0.1323
Weight of fatty acid, uncorrected (dried 1 hour at 110° C)	0.2222	0.2205	0.1170	0.1174
Weight of fatty acid, corrected	0.2242	0.2225	0.1180	0.1184
Percent of soap	97.0	96.3	96.8	97.0
Average, percent	96.8			

Number sol. used	V Sodium stearate	VI	VII	VIII
Grams of soap taken	0.2571	0.2571	0.1260	0.1260
Weight of fatty acid, uncorrected (dried 1 hour at 110° C)	0.2303	0.2307	0.1130	0.1130
Weight of fatty acid, corrected	0.2230	0.2335	0.1143	0.1143
Per cent of soap	97.6	97.8	97.7	97.7
Average, percent	97.7			

fatty acids separated. It was found that too much heating caused the fatty acids to stick to the sides of the beaker. When they had separated, they were filtered on to Gooch crucibles and dried at 110° C in small beakers in an electric oven. Both of these fatty acids lose weight on being heated to 110° C and therefore it was necessary to make corrections for the loss in weight during the drying of the crucibles. Palmitic acid loses 0.0009 g per 0.1 g per hour while 0.1 g stearic acid loses 0.0012 g per hr at 110° c. The following table shows the weight of soap taken and weight of fatty acids obtained (corrected) and also the percent of pure sodium palmitate or stearate.

TABLE II
Concentrations of Soap Solutions

Series	Wt. soap taken	Corrected weight of soap	g per 100 cc
Volume of Solution, 600 cc E			
E (sodium palmitate)	1.0120	0.9796	0.1632
E_1 (100 cc E diluted to 200 cc)	—	—	0.0816
E_2 (100 cc E_1 diluted to 200 cc)	—	—	0.0408
E_3 (100 cc E_2 diluted to 200 cc)	—	—	0.0204
E_4 (100 cc E_3 diluted to 200 cc)	—	—	0.0102
Volume of Solution, 400 cc F			
F (sodium stearate)	0.6212	0.6069	0.1517
F_1 (100 cc F diluted to 200 cc)	—	—	0.0758
F_2 (100 cc F_1 diluted to 200 cc)	—	—	0.0379
F_3 (100 cc F_2 diluted to 200 cc)	—	—	0.0189
F_4 (100 cc F_3 diluted to 200 cc)	—	—	0.0094
Volume of Solution, 400 cc G			
G (sodium palmitate)	0.5075	0.4912	0.1223
G_1 (100 cc G diluted to 200 cc)	—	—	0.0614
G_2 (100 cc G_1 diluted to 200 cc)	—	—	0.0307
G_3 (100 cc G_2 diluted to 200 cc)	—	—	0.0153
G_4 (100 cc G_3 diluted to 200 cc)	—	—	0.0076

The solutions used for the determinations of the surface tension were made up by dissolving carefully weighed out samples of the above soaps in distilled water. Three such solutions were prepared and then diluted in series as shown in Table II.

The Measurement of the Surface Tension.—The surface tension of the soap solutions was measured by the rise in capillary tubes, the solution being in contact with air. By means of a cathetometer accurate measurements were secured of the distance between the lowest part of the meniscus in the tube and the surface of the solution to be measured. The surface tension was measured in dynes per centimeter, the formula for making the calculations being, $\frac{r\,h\,d\,g}{2}$ = surface tension, where

r = radius of the capillary tube,

h = height to which the liquid rises,

d = density of the solution at the temperature of measurement, and

g = gravitational acceleration in cm/sec^2.

These calculations give correct results only if the meniscus shows an even curvature and is hemispherical, forming thus an angle of 0° with the walls of the tube. In these measurements correction for the angle made by the liquid and the wall of the vessel was made by adding $r/3$ to the height in each reading because the volume occupied by the meniscus (estimated by means of a meniscus drawn on cross-section paper and counting the number of squares) occupies approximately one-third the entire volume of the tube between the highest and lowest portions of the meniscus.

For these experiments, capillary tubing of six different sizes was secured. Three tubes were cut from each size of tubing and marked definitely as No. 1 of set I, etc., up to and including set VI. A micrometer microscope was used for measuring the inside diameter of the tubes, its calibration constant being obtained by determining the number of turns of a transverse screw (near the upper end of the instrument), necessary to carry the cross-hairs across the distance between the divisions on the image of a scale divided into half millimeters. The number of turns is easily read by means of a comb-like arrangement with its notches being indicated in hundredths on the circular head of the screw. The average of several readings multiplied by two gives the calibration constant or the number of turns of the transverse screw per mm, which was fourteen for this microscope. Measurements of the capillary bore at both the top and bottom of each tube were made and the average calculated. This average, divided by the calibration constant of the micrometer microscope, gave the diameter of the tube in millimeters. Table No. III shows the values thus obtained.

TABLE III

Diameters of Capillary Tubes

Tube No. I	Top	Bottom	Average	Diameter mm
1st set	10.02	10.58	10.30	0.735
2nd set	20.58	28.08	27.83	1.98
3rd set	29.655	30.25	29.95	2.14
4th set	42.16	42.609	42.384	3.027
5th set	45.619	45.14	45.374	3.24
6th set	10.49	10.17	10.33	0.736
Tube No. II				
1st set	10.13	10.11	10.12	0.721
2nd set	27.80	27.37	27.565	1.968
3rd set	30.32	29.97	30.145	2.153
4th set	42.36	42.684	32.52	3.037
5th set	46.41	46.71	46.56	3.325
6th set	10.56	10.75	10.655	0.761
Tube No. III				
1st set	9.635	10.22	9.927	0.709
2nd set	27.33	27.77	27.55	1.967
3rd set	30.38	30.47	30.425	2.173
4th set	42.635	42.64	42.637	3.045
5th set	45.04	45.029	45.035	3.216
6th set	10.48	10.22	10.35	0.739

In order to test the accuracy of the tube measurements and to insure that all of the apparatus for the measurements of the surface tensions was satisfactory, several liquids (which wet the surface of capillary tubes dipped into them) were measured in contact with air and the capillary rise recorded. Table IV shows the surface tensions calculated from these data compared with data by other observers.

TABLE IV

Surface Tensions of Several Liquids

Liquid	H_2O (distilled)	C_2H_5OH (95%)	$CHCl_3$ (C. P.)	CH_3COCH_3 (C. P.)
Temp.	27.5° C	20.0° C	20.0° C	24.5° C
Density	—	0.788	1.483	0.795
No. of trials	4	2	3	8
Av. surf. tension (dynes per cm)	72.00	21.74	28.20	22.80
Other values	71.4[1]	21.7[1]	26.7[1]	23.3[1]
Temp.	30° C	20° C	20° C	17.6° C

The Surface Tension of Solutions of Sodium Palmitate and Sodium Stearate.—The following tables show the values obtained for the surface tensions of the solutions prepared as described above.

TABLE V

Surface Tensions of Solutions of Sodium Stearate at 25 Degrees Series F

Sol. used	F	F_1	F_2	F_3	F_4
Gm/100 cc	0.1517	0.0758	0.0379	0.0189	0.0084
Density	1.00038	1.00300	1.000256	1.00020	1.00017
No. of trials	8	9	8	8	6
Average, surface tension (dynes per cm)	21.97	26.28	30.65	34.98	39.33

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[1] Smithsonian tables.

TABLE VI
Surface Tensions of Solutions of Sodium Palmitate at 25 Degrees
Series E

Sol. used	E	E_1	E_2	E_3	E_4
Gm/100 cc	0.1632	0.0816	0.0408	0.0204	0.0102
Density	1.0004	1.00023	1.00017	1.00013	1.00010
No. of trials	9	8	8	8	7
Average, surface tension (dynes per cm)	20.22	26.86	31.97	43.23	49.69

TABLE VII
Surface Tensions of Solutions of Sodium Palmitate at 25 Degrees
Series G

Sol. used	G	G_1	G_2	G_4
Gm/100 cc	0.1228	0.0614	0.0307	0.0076
Density	1.00032	1.00026	1.00019	1.00010
No. of trials	7	5	6	7
Average, surface tension (dynes per cm)	21.30	29.14	34.60	46.43

The combined data on sodium palmitate are shown below in Curve I, the points taken from Table VI marked in circles and the points from Table VII in crosses, where the gram per 100 cc are plotted against the surface tension. In Curve II the surface tension of sodium stearate has been plotted against the concentration in like manner.

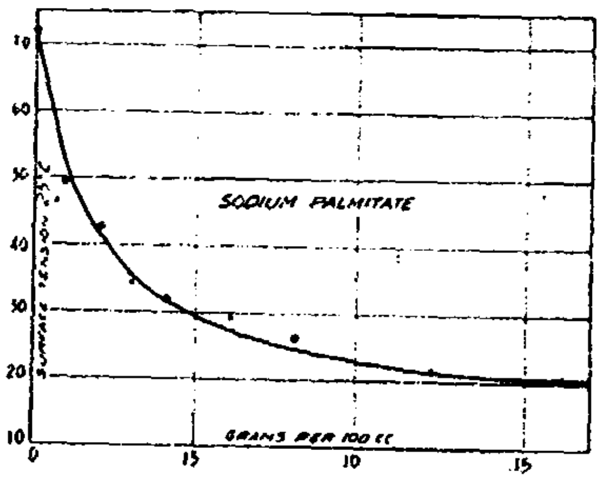

Fig. 1

The Comparative Emulsifying Powers of Soap Solutions.—The surface tensions of the various soap solutions were compared as to their emulsifying powers. To obtain the data for this, several trials were made to secure a method of making uniform emulsions. It is difficult to get uniform and satisfactory results by stirring and it was finally decided that shaking by hand for a specified time would be the best method. Twenty-cubic-centimeter graduated cylinders fitted with rubber stoppers were used for the containers. Three trials were made for each soap solution of which the surface tension had been measured. Ten cubic centimeters of the solution were placed in the cylinder and two cubic centimeters of linseed oil or other oil added. The mixture was then shaken by hand for five minutes, following which the time of noticeable separation on standin was observed and recorded. The trials were repeated using five cubic centimeters of the linseed or kerosene oil instead of two cubic centimeters.

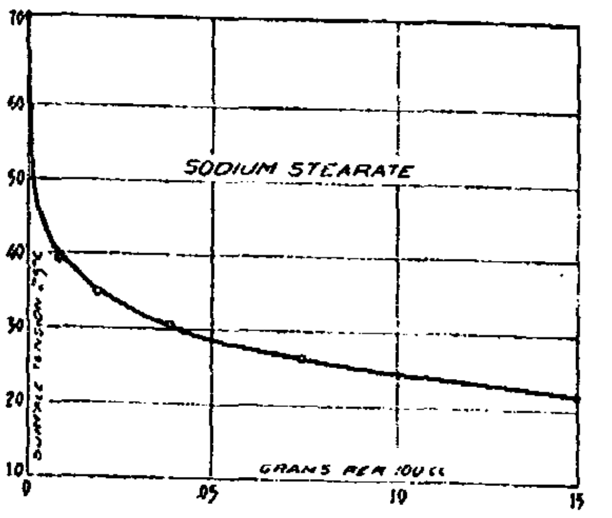

Fig. 2

Table VIII shows the data for the emulsifying power of solutions of sodium stearate, shaken with kerosene, specific gravity 0.813. The time of noticeable separation is the average of three readings in each case at 25 degrees C.

Table VIII

Kerosene and Sodium Stearate Emulsions

Soap sol. used	F	F_1	F_2
Vol. soap sol.	10 cc	10 cc	10 cc
Surface tension (dynes per cm)	21.97	26.28	30.65
Time shaken	5 min.	5 min.	5 min.
Time of noticeable separation—2 cc kerosene	18.02 min.	10.85 min.	1.66 min.
Time of noticeable separation—5 cc kerosene	16.35 min.	8.29 min.	0.66 min.

Curve III shows the time of noticeable separation of emulsions of kerosene and sodium stearate solutions plotted against the surface tension.

Table IX shows data for the emulsifying power of solutions of sodium palmitate, shaken with kerosene, specific gravity 0.813. The time of noticeable separation is the average of three observations in each case at 25 degrees C.

Table IX

Kerosene and Sodium Palmitate Emulsions

Soap sol. used	E	E_1	E_2
Vol. soap solution	10 cc	10 cc	10 cc
Surface tension dynes per cm	20.22	26.86	31.97
Time shaken	5 min.	5 min.	5 min.
Time of noticeable separation—2 cc kerosene	5.11 min.	3.90 min.	3.10 min.
Time of noticeable separation—5 cc kerosene	0.64 min.	0.51 min.	0.44 min.

Using 5 cc kerosene gives almost immediate separation showing that probably the critical saturation point of the sodium palmitate had been exceeded.

Table X shows data for the emulsifying power of solutions of sodium stearate, shaken with linseed oil, specific gravity 0.923 The time of noticeable separation is given as the average of these three observations in each case, at 25 degrees C.

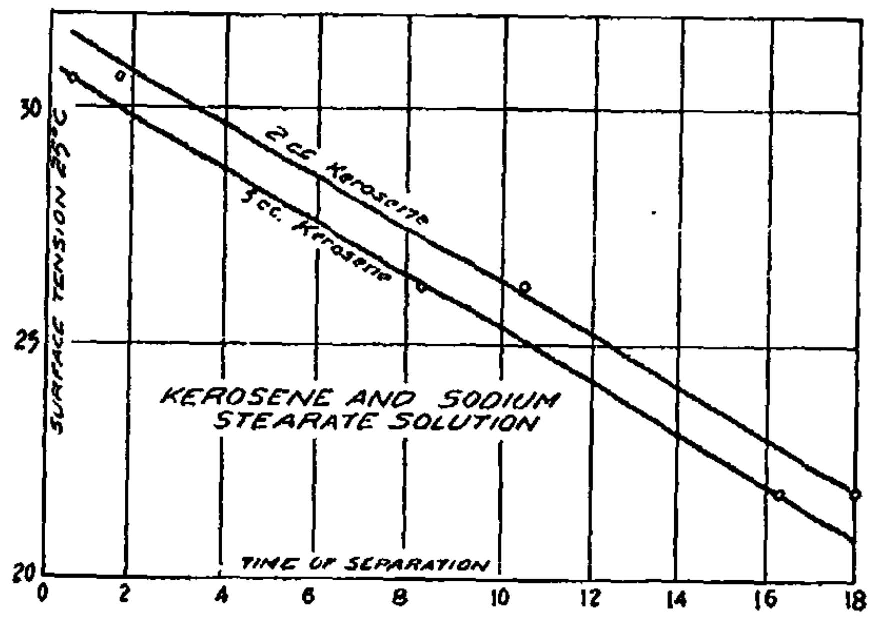

Fig. 3

TABLE X

Linseed Oil and Sodium Stearate Emulsions

Soap sol. used	F	F_1	F_2
Vol. soap solutions	10 cc	10 cc	10 cc
Surface tension (dynes per cm)	21.97	26.28	30.65
Time shaken	5 min.	5 min.	5 min.
Time of noticeable separation—2 cc linseed oil	9.76 min.	5.08 min.	1.47 min.
Time of noticeable separation—5 cc linseed oil	18.0 min.	5.10 min.	1.67 min.

Table XI shows data for the emulsifying power of solutions of sodium palmitate shaken with linseed oil, specific gravity, 0.923. The time of noticeable separation is given as the average of observations in each case at 25 degrees C.

TABLE XI

Linseed Oil and Sodium Palmitate Emulsions

Sol. used	G	G_1	G_2
Amount used	10 cc	10 cc	10 cc
Surface tension (dynes per cm)	20.22	26.86	31.97
Time shaken	5 min.	5 min.	5 min.
Time of noticeable separation—2 cc linseed oil	4.51 min.	2.22 min.	1.77 min.
Time of noticeable separation—5 cc linseed oil	19.60 min.	7.76 min.	2.06 min.

Curve IV shows the time of noticeable separation of linseed oil and sodium palmitate solution plotted against the surface tensions of the sodium palmitate solutions.

The Effect of Foreign Substances on the Surface Tension. —An effort was made to determine the effect of an added foreign substance such as sugar and glycerine on the surface tension of the soap solutions.

To a measured amount of solution F, the surface tension of which was found to be 21.97 dynes per cm, there was added enough sugar to make a ten percent solution. The surface tension of the resulting solution was found to average 30.45

dynes per cm. On the other hand, solution F_1 whose surface tension was 26.28 upon the addition of enough glycerine to form a ten percent solution then had a surface tension of 26.02 dynes per cm. The addition of sodium carbonate increased the surface tension.

A little work was done on solutions of Ivory soap to see if the data secured would be comparable to those secured from solutions of pure sodium palmitate and pure sodium stearate. A sample was shaved into a beaker and dried for some time at 65 degrees C. From this a solution was prepared which showed upon analysis and average value of 0.2161 g fatty acid per 100 cc of solution. The average surface tension of this soap solution was found to be 19.39 dynes per cm at 25 degrees C. This is about the same value that either sodium stearate or sodium palmitate would have at similar concentrations.

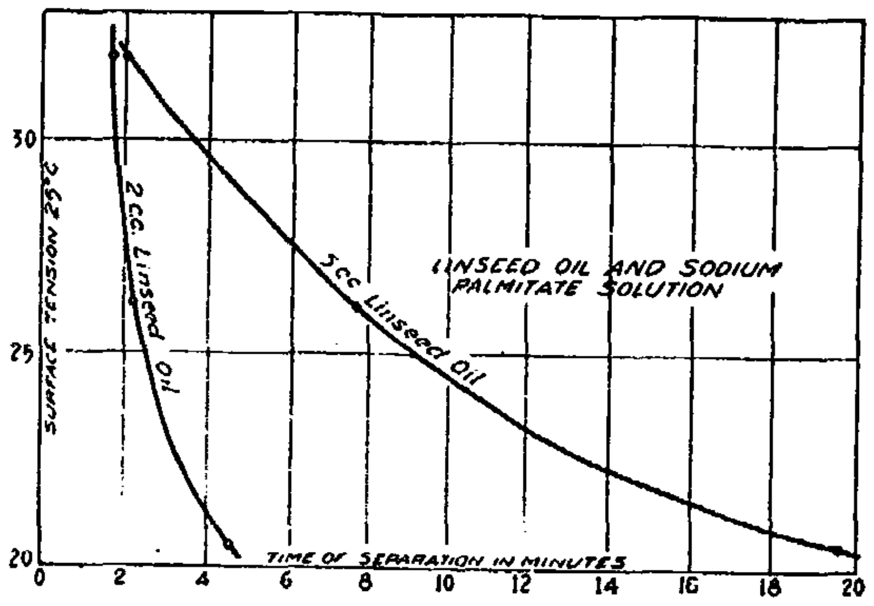

Fig. 4

Conclusions

1. The surface tensions of solutions of sodium stearate and sodium palmitate have been determined.

2. It has been shown that solutions of soap decrease in surface tension as they increase in concentration. This is in contrast to the change in surface tension which solutions of sodium hydroxide and many salts undergo with similar changes in concentration.

3. The relative emulsifying power of solutions of sodium palmitate and of sodium stearate for kerosene and linseed oil was determined by shaking by hand for five minutes and observing the time of noticeable separation. The relationship between the surface tension and the emulsifying power of the solutions studied, is shown to be that with increase of the concentration of the soap solution there is an increase of emulsifying power or vice versa, as the surface tension increases the emulsifying power decreases.

4. While this is true, it is also to be seen that the viscosity of a liquid has much effect upon the permanence of its emulsions. Emulsions containing 5 cc of kerosene to 10 cc of soap solution break down more rapidly than emulsions containing 2 cc of kerosene while the reverse is true of emulsions containing 2 cc and 5 cc, respectively, of linseed oil to 10 cc of soap solutions, the latter being the more stable.

5. The presence of glycerine does not affect the surface tension to any large extent. Glycerine should have no deleterious effect on the cleansing power of soap. A large amount of sodium carbonate, however, raises the surface tension and for this reason would not be desirable in cleansing soaps.

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ADSORPTION BY PRECIPITATES. III

BY HARRY B. WEISER AND EDMUND B. MIDDLETON

The Adsorption of Precipitating Ions by Hydrous Aluminum Oxide

In a recent communication[1] on adsorption by hydrous ferric oxide, a critical survey was given of the work of Whitney and Ober[2] on adsorption of cations by arsenic sulphide, of Freundlich[3] on adsorption by arsenic sulphide, and of Freundlich and Schucht[4] on adsorption by mercuric sulphide. Whitney and Ober conclude from their results that equivalent amounts of all precipitating ions are carried down by a precipitated colloid; and Freundlich concludes that equivalent amounts of all cations are adsorbed at their precipitation concentration; and further, that cations of different valence are equally adsorbed from equimolar solutions which would explain the fact that precipitation values which correspond in the first instance to equivalent amounts, are very different. From an analysis of their experimental data and the conditions under which they were obtained, it seemed to us that their results were scarcely accurate enough to justify their conclusions. Sources of error arise from the difficulties involved in the experimental methods; the relatively slight adsorption in the cases studied; and the failure to take into account the adsorption by the neutralized particles during the process of agglomeration and settling. From the results obtained by a study of the amounts of various cations adsorbed by precipitated hydrous ferric oxide, conclusions were reached that are at variance in certain respects to the conclusions reached by Whitney and Ober and by Freundlich. It was pointed out that the total amount of a given ion carried down by a precipitated colloid is determined by (*a*) the ad-

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[1] Weiser and Middleton: Jour. Phys. Chem., **24**, 30 (1920).

[2] Jour. Am. Chem. Soc., **23**, 842 (1901).

[3] Zeit. phys. Chem., **73**, 385 (1910).

[4] Ibid., **85**, 641 (1913).

sorption of the electrically charged particles during the process of neutralization and (*b*) the adsorption of the electrically neutral particles during the process of agglomeration and settling. Failure to take *b* into account has led to the erroneous conclusion that the amounts of all precipitating ions carried down by a precipitated colloid are equivalent. It was further pointed out that the adsorption of equivalent amounts of precipitating ions will neutralize a given amount of colloid providing the stabilizing effect of the ion having the same charge as the colloïd is maintained constant; but the amounts adsorbed by the neutralized particles will vary with the nature of the adsorbing medium, the nature of the adsorbed ion and the concentration of the ion in the solution. Accordingly the determination of adsorption at the precipitation concentration, as a rule, will not give comparable results on account of the variability of the latter and the consequent variability in the degree of saturation of the adsorbent by the adsorbed phase.

While the manuscript on adsorption by hydrous ferric oxide was in preparation, investigation on adsorption of anions by hydrous aluminum oxide were being carried out in this laboratory. Accordingly a survey of the results of Freundlich's pupils, Ishizaka[1] and Gann[2] on adsorption by aluminum oxide was reserved for this communication.

Ishizaka studied the relationship between the adsorption by alumina and coagulation of colloidal aluminum oxide. The colloidal alumina used for determining precipitation values was prepared by the hydrolysis of aluminum acetate according to Crum's method; and the alumina used for the adsorption experiments was "grown alumina" that is prepared by rubbing aluminum foil with mercury. The adsorption values were determined in the usual way, by shaking a quantity of aluminum oxide powder with a solution of a certain concentration and determining the amount adsorbed by the change in concentration of the solutions. Adsorption

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[1] Zeit. phys. Chem., **83**, 97 (1913).

[2] Kolloidchem. Beihefte, **8**, 63 (1916).

values were obtained at different concentrations and the adsorption isotherms plotted. On account of the transparency of gelatinous alumina, precipitation values were determined by determining the concentration of electrolyte which produced a given change in viscosity of the solution in a given time.[1] The results of the investigation can be given best by quoting a few paragraphs from the theoretical part of Ishizaka's paper written by Freundlich and Ishizaka.

"The investigation was undertaken in order to determine to what extent the theory of the relation between the precipitation and adsorption of colloids advanced by Freundlich applies. It has been explained already, that in order to compare different electrolytes, the precipitation value can be defined as that concentration which raises the viscosity of the colloid ten percent in thirty minutes. It must be emphasized particularly that this definition is arbitrary and that it would be more nearly right to derive it from the precipitation velocity constants which are dependent on the nature of the electrolyte, and to compare these values. However, since, as we shall see later, it is impossible to represent the precipitation velocity mathematically in a final way, one must be content with this preliminary definition.

"According to the observations of Schulze, Hardy, etc., the coagulation depends first on the nature of the oppositely charged ions; in the case of positive colloidal $Al(OH)_3$, on the nature of the anion. According to Freundlich's view, like valent ions which are most strongly adsorbed will precipitate most strongly since the adsorbed amount necessary to cause coagulation is obtained at a lower concentration in the solution. With like valent anions, adsorbability and precipitating action should parallel each other. Now if one compares the results on "grown alumina" given in Table I with the table of precipitation values, one sees that for univalent anions the parallelism actually exists to a marked extent. For example, one notes the strong adsorption of potassium salicylate and its low precipitation value and the small

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[1] Cf. Kawamura: Jour. Coll. Sci. Tokyo Imp. Univ., **25**, Art. 8 (1908).

adsorption of potassium sulphanilate and its large precipitation value. In order to explain the differences again found between one, two and three valent ions, Freundlich assumes that the amounts adsorbed during the coagulation are equivalent to each other, while the adsorption isotherms for the different ions coincide if the adsorption values are expressed in moles. The necessary result is that the precipitation values lie very far apart. Now Fig. 1 shows that the adsorption curves for the univalent anions (Cl, NO_3, CNS) coincide approximately, hence it follows that the precipitation values of these ions are approximately the same as shown in Table IX. However, the curves for potassium sulphate and potassium chromate do not coincide with the above-mentioned curves; but lie appreciably higher. This is not at variance with the observed great differences in the precipitation values between one and two valent anions, which differences are much greater if one compares equivalent adsorbed amounts. The variation is somewhat greater in this case since the adsorption calculated in moles is greater for divalent than for univalent ions. In the light of these observations, it is probably impossible to calculate the precipitation values on the basis of adsorption in so simple a manner as Freundlich has done. However, the curve for potassium ferrocyanide lies just above the curve for the divalent ions. This again corresponds more nearly to the expected behavior."

By examining the adsorption isotherms in which the adsorption values are expressed in moles, we find the order of adsorption of anions to be: salicylate > ferrocyanide > oxalate > chromate > tartrate > sulphate > chloride > nitrate > thiocyanate > sulphanilate, while the precipitation values as determined give the order: ferrocyanide > sulphate > oxalate > tartrate > chromate > salicylate > chloride > nitrate > thiocyanate > sulphanilate. If the adsorption is expressed in equivalents the only change in the order is that the univalent salicylate ion instead of leading the list comes just above sulphate. From this we see that although the most strongly adsorbed ion seems to precipitate in lowest concentration in the case of the univalent ions, there are marked variations from this rule in the case of the multivalent ions even when the adsorption values and precipitation values are compared qualitatively. As pointed out, the adsorption isotherms for certain univalent ions coincide approximately, indicating that equivalent amounts of certain ions are adsorbed in equimolar concentrations. However, the isotherms for the divalent ions are considerably above those for the univalent ions and moreover they do not coincide even approximately. These variations from the simple relationships developed by Freundlich were recognized by Freundlich and Ishizaka who attempt to explain them as follows:

"These observations contradict in certain respects the measurements of Freundlich on arsenic sulphide. There he found that different cations ($NH_4^{\cdot}$, $UO_2^{\cdot\cdot}$, $Ce^{\cdot\cdot\cdot}$ and $Al^{\cdot\cdot\cdot}$) were adsorbed approximately equally from equimolar solutions. The irregular behavior with alumina as adsorbent can have different causes. In the first place, the difference between the alumina powder and the particles of $Al(OH)_3$ in the colloidal state were doubtless very much greater than the differences between the arsenic sulphide powder and the particles of arsenic sulphide in the colloid; it is therefore altogether possible that simpler relations would obtain for the adsorption of different ions by the $Al(OH)_3$ of the colloid. Another explanation deserves consideration: In the adsorption by arsenic sulphide, the determinations are made in the region of saturation. From the recent work of Schmidt[1] and Marc[2] it is known that at higher concentration, there is a so-called saturation value of the adsorbed material which does not change appreciably with the concentration. In these investigations with alumina as Fig. 1 shows, the adsorption determinations are at the beginning of the adsorption curves, far from the saturation value. According to the latest work

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[1] Zeit. phys. Chem., 74, 689 (1910).

[2] Ibid., 75, 710 (1911).

of Marc,[1] very much simpler relations hold for the adsorption of different materials near the saturation value. This may be the reason that the relationships in the case of arsenic sulphide are simpler than in the case of alumina."

Ishizaka also determined the amount of oxalate and ferrocyanide ions adsorbed when colloidal alumina was precipitated by electrolytes. He found that the amounts adsorbed were not only not equivalent but varied with the concentration of the electrolyte. This observation is in direct contradiction to Freundlich's conclusion based on the experiments with arsenic sulphide, namely, that equivalent amounts of ions are carried down by the precipitated colloid. The explanation of this variation suggested by Freundlich and Ishizaka is that the adsorption values were determined for arsenic sulphide in the region of the precipitation value, whereas, the values for colloidal alumina were determined above the precipitation value. They conclude that "smaller concentrations should have been used in the determination of these adsorption values such as were used in the determination of precipitation values."

From the explanation of the so-called abnormalities observed by Ishizaka it would follow, that in order to get equimolar amounts adsorbed, equimolar solutions of relatively high concentrations must be used; and in order to get equivalent amounts adsorbed, the concentration must be the precipitation concentration. As pointed out in our recent paper, the meager data do not justify the conclusion that equivalent amounts of all ions are adsorbed from equimolar solutions. Moreover, it was pointed out that the amounts adsorbed at the precipitation value will be equivalent only in case the precipitation values are the same and the adsorption by the precipitated particles is negligible. Such uniformity of conditions seldom obtains; hence, although the adsorption of equivalent amounts of ions causes neutralization, the actual amounts of various ions carried down, in general, will not be equivalent.

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[1] Zeit. phys. Chem., 81, 641 (1913).

It seems to us very questionable whether the adsorption values for a given substance determined by shaking up a solid powder with the electrolyte are comparable with the precipitation values of a colloidal solution of the substance. Moreover, it seems unsafe to draw conclusions from adsorption data where the degree of adsorption is so small as Ishizaka found with grown alumina, 0.002 to 0.055 millimol per gram. In a more recent communication, Gann[1] determined a few adsorption values for alumina precipitated from the colloidal condition. The colloid prepared by Crum's method was precipitated by different electrolytes and the adsorption was calculated from the change in concentration of the electrolyte before and after precipitation. The precipitate was so gelatinous that it was found necessary to filter out the particles with an ultrafilter before making the final analysis. Such a gelatinous precipitate unquestionably carries down relatively enormous amounts of water. As previously pointed out,[2] this may introduce an appreciable error in the determination of adsorption values by the method described above. Adsorption values were determined for salicylate, picrate, oxalate, ferricyanide and ferrocyanide ions. Colorimetric methods were employed throughout except with oxalate ion, which was determined by titration with permanganate. The precipitation values of the electrolytes were taken as the concentration in solution which correspond to the same velocity constant. The velocity of coagulation was determined from the change in viscosity with the time. It was found that for every electrolyte there is only a narrow range of concentration in which the velocity can be measured, "For every electrolyte can be assigned a 'threshold value' below which it is not possible to follow the coagulation. For the sake of comparison it is better to designate it as the precipitation value: with univalent ions it is the concentration at which the constant K, has a definite numerical value—0.01

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[1] Kolloidchem. Beihefte, 8, 63 (1916).

[2] Weiser and Middleton: Loc. cit.

was chosen; with multivalent ions (and picrate ion) the mean concentration in the measurable region of concentrations can be taken as the precipitation value with sufficient accuracy."

For the purpose of testing Freundlich's theory that equivalent amounts of ions are adsorbed at the precipitation concentration, Freundlich and Gann compared the adsorption values for the five ions above mentioned. Unfortunately the data were such that direct comparison could not be made. "For salicylate and picrate ion, the precipitation values fall in the region of concentration at which adsorption was determined. For the other ions the precipitation value is lower but the adsorption measurements are so exact that extrapolation is quite unobjectionable. The results show that ferro- and ferricyanide are adsorbed completely at the precipitation concentration." Considering the error inherent in the determination of adsorption by a highly gelatinous precipitate using the indirect method and considering the objections to colorimetric methods of analysis, it is by no means certain "that extrapolation is quite unobjectionable." Moreover, the adsorption values were determined on one colloid and the precipitation values on another and correction had to be made for this. The results are given in Table I.

TABLE I

Ion	Precipitation value millimols per liter	Adsorption value at the precipitation value	
		In millimols	In milliequivalents
Salicylate	8.0	0.30	0.30
Picrate	4.0	0.18	0.18
Oxalate	0.36	0.18	0.36
Ferricyanide	0.10	0.09	0.27
Ferrocyanide	0.08	0.073	0.29

From the above results Freundlich and Gann conclude that "the amounts adsorbed calculated in equivalents agree remarkably well with the exception of the value for the picrate ion. The very different precipitation values are really concentrations which correspond to the adsorption of equivalent amounts. Reference has already been made to the difficulties with picrate ion; however, the latter is not off so much that the adsorbed amount falls outside the order of magnitude of adsorption in the other cases."

Even if we conclude that the sources of error in the above experiments compensate each other and that the adsorption values are correct, we find the agreement less satisfactory than it might appear at first sight: picrate ion is admittedly way off being 40 percent lower than the mean value for the other four ions; moreover, oxalate ion is 20 percent higher than this mean and ferricyanide is 15 percent lower than this mean. Such variations might be attributed to experimental errors but it is unsafe to do this since the corrected results might show greater rather than lesser variations.

From the above survey of the work that has been done on adsorption of anions by both powdered and colloidal alumina, it seems to us that nothing more definite can be said concerning the relationship between the precipitation values of ions and the actual amount carried down, than that there is a tendency for the ion with the lowest precipitation value to be carried down the most and vice versa. In order to determine to what extent our conclusions reached from a quantitative study of adsorption by hydrous ferric oxide were applicable to other cases, the following series of experiments were carried out with colloidal alumina.

EXPERIMENTAL

Precipitation Values of Colloidal Hydrous Aluminum Oxide

Preparation of the Colloidal Alumina.—Colloidal alumina was prepared by the method described in detail by Weiser.[1] Sufficient aluminum chloride to make 2 grams of Al_2O_3 was precipitated with a slight excess of sodium carbonate and was thoroughly washed by the aid of the centrifuge until the precipitate started to go into colloidal solu-

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[1] Jour. Phys. Chem., 24, 505 (1920).

tion. To the hydrous oxide was then added 100 cc of warm acetic acid containing one-third of the acid necessary to form normal aluminum acetate. The solution was kept at 50 degrees until all the oxide was taken up, after which it was filtered, diluted to 150 cc and boiled very vigorously for 36 to 48 hours, replacing the water as it evaporated. In this way was prepared an almost clear, odorless colloidal solution in which the acetic acid concentration was so low that it could not be detected by the taste. Since a quantity of colloid was necessary, a number of portions were prepared as nearly as possible in the same way and the several portions were mixed and diluted to a concentration of 1.150 grams per liter. The colloid was allowed to stand for three weeks before starting any experiments and it was found to be unchanged so far as could be determined qualitatively. Later quantitative experiments showed that the colloid was very stable, undergoing no appreciable change in a month's time. However, the work was so planned that the experiments were all carried out on the same colloid with as much dispatch as possible in order to minimize any errors that might arise from the colloid undergoing a slight change.

Determination of Precipitation Values.—The usual method of determining precipitation values consists in mixing varying amounts of electrolyte with a definite amount of colloid until such concentration is found that it will just cause coagulation, within a definite time. Complete coagulation is readily ascertained with a colored colloid like hydrous ferric oxide; but the problem is less simple with colloidal hydrous alumina on account of the transparency of the latter. To determine the critical concentration Kawamura[1] took advantage of the change in viscosity which the colloidal solution undergoes, on coagulation. This viscosity method was employed by Ishazaka and by Gann in the manner described earlier in this paper. By some preliminary experiments on the colloid prepared as above described, we found that it was entirely possible

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[1] Jour. Coll. Sci. Tokyo Imp. Univ., 25, Art. 8 (1908).

to determine accurately the concentration of electrolyte which just caused coagulation within a definite time, particularly in the case of those electrolytes that precipitated in low concentration. The method employed was as follows:

Since the precipitation value is influenced by the rate of addition of electrolyte, the method of stirring, the time of standing, etc., the experimental conditions must be maintained constant throughout. The mixing was accomplished in a very satisfactory way, making use of the mixing apparatus described in the paper on hydrous ferric oxide. Into the inner tube of this apparatus was measured a definite quantity of electrolyte of known strength which was subsequently diluted to 20 cc; and surrounding it was placed 20 cc of the colloidal solution. After stoppering, the apparatus was inverted with a quick jerk that mixed the contents rapidly and effectively. The contents of the apparatus were then poured into a tube 2.5 cm in diameter and 10 cm in length which was stoppered and allowed to stand twenty-four hours. The tube with contents was next placed in the centrifuge and centrifuged for ten minutes at 3000 r. p. m. If the concentration of electrolyte was below the precipitation value, no precipitate or only a very slight precipitate was thrown down; if at or above the precipitation value a voluminous precipitate was obtained that was readily distinguished. In order to determine whether precipitation was complete when near the critical concentration, a portion of the supernatant liquid after centrifuging was pipetted off; ammonia added; the solution allowed to stand for several hours and finally centrifuged. The presence of a very small amount of alumina was easily detected in this way. A series of observations in the immediate region of the precipitation value enabled us to determine the critical concentration to within 0.05 to 0.10 cc of $N/100$ solution in 40 cc with those electrolytes that precipitate in low concentration. The precipitation value of electrolytes that precipitate in high concentration were determined in the same way but the results were less accurate.

However, no difficulty whatsoever was found in getting the order of precipitation values.

Potassium salts were used throughout all the experiments in order to minimize the effect of the cation. It was necessary to use half-normal solutions of salts with univalent anions but $N/100$ solutions of other salts were employed. The $N/100$ solutions were made up from the standardized $N/50$ solutions used in the adsorption experiments subsequently described. A 2 cc Ostwald pipette was employed to measure the $N/100$ solutions. The results are recorded in Table II. In the first column is given the anions; in the second, the number of cubic centimeters in 20 cc that just failed to precipitate completely 20 cc of the colloid; in the third, the number of cubic centimeters in 20 cc that caused complete precipitation; in the fourth, the precipitation value expressed in milliequivalents per liter, calculated from the data in column three; in the fifth, the precipitation value expressed in millimoles per liter.

TABLE II

Precipitation Values of Potassium Salts

Salt	Electrolyte cc	Electrolyte cc	Precipitation value	
			Milliequivalents per liter	Millimoles per liter
Ferrocyanide	1.45 $N/100$	1.50 $N/100$	0.375	0.094
Thiosulphate	1.45 $N/100$	1.50 $N/100$	0.375	0.188
Ferricyanide	1.50 $N/100$	1.60 $N/100$	0.400	0.133
Citrate	1.70 $N/100$	1.75 $N/100$	0.438	0.146
Sulphate	2.10 $N/100$	2.15 $N/100$	0.538	0.269
Oxalate	2.75 $N/100$	2.80 $N/100$	0.700	0.350
Phosphate	4.10 $N/100$	4.15 $N/100$	1.038	0.346
Chromate	5.15 $N/100$	5.20 $N/100$	1.300	0.650
Dithionate	6.40 $N/100$	6.50 $N/100$	1.625	0.813
Dichromate	7.00 $N/100$	7.10 $N/100$	1.775	0.888
Chloride	11.00 $N/2$	11.50 $N/2$(?)	143.7(?)	143.7
Nitrate	12.00 $N/2$	12.50 $N/2$(?)	156.3(?)	156.3
Bromide	13.00 $N/2$	13.50 $N/2$(?)	168.7(?)	168.7
Iodide	17.00 $N/2$	17.50 $N/2$(?)	218.7(?)	218.7

There is a difference of opinion as to whether the precipitation value should be expressed in equivalents or in moles. Freundlich prefers to express it in terms of the number of ions in unit volume. However since the neutralization of a colloid stabilized by preferential adsorption of ions carrying charges of a given sign is accomplished by the adsorption of ions carrying an equal number of charges of opposite sign, it seems to us more logical to express the precipitation value in equivalents. If so expressed the order of ions beginning with the one with lowest precipitation value is as follows: ferrocyanide > thiosulphate > ferricyanide > citrate > sulphate > oxalate > phosphate > chromate > dithionate > dichromate > chloride > nitrate > bromide > iodide. For the ions that are common to each series, the order is the same as determined by Ishazaka and by Gann except that the latter investigators found that sulphate precipitates in lower concentration than citrate. Again the high precipitation values of univalent ions and the extremely low precipitation values of certain multivalent ions are evident. However, the valency law can scarcely be said to apply even approximately. Thus tetravalent ferrocyanide and divalent thiosulphate precipitate in the same concentration as nearly as could be determined; trivalent citrate precipitates in lower concentration than sulphate and oxalate while trivalent phosphate precipitates in higher concentration; moreover, the precipitation value of dichromate is five times that of thiosulphate, although both have the same valence. Comparing these results with those obtained with hydrous ferric oxide,[1] we find the order of ions to be the same except that potassium dichromate precipitates colloidal ferric oxide in much lower concentration relatively, than it does colloidal alumina. The similarity between the two cases might be expected, since the physical character of the two hydrous oxides is quite similar and since the method of preparation of the colloidal solutions is essentially the same.

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[1] Weiser and Middleton: Jour. Phys. Chem., **24**, 50 (1920).

In certain cases the ions arrange themselves in the same order, irrespective of whether the precipitation value is expressed in equivalents or in moles.[1] However, if the values for colloidal alumina are expressed in moles, thiosulphate falls below ferricyanide and citrate. This is more nearly in line with the valency rule; but it is of interest to note that the difference between the molar precipitation value of thiosulphate and the other divalent ions is much greater than the difference between trivalent citrate and divalent thiosulphate.

For the purpose of determining the accuracy of the above method of finding precipitation values, the precipitation experiments were repeated on another colloidal alumina containing 0.886 gram of alumina per liter. The results are given in Table III which is similar to Table II. It will be observed that the precipitation values are slightly less as we should expect with a weaker colloid; but the order of ions is the same as was found with the stronger colloid. From this it is evident that there is no difficulty in checking the precipitation values providing an arbitrary method of procedure is rigidly adhered to.

TABLE III

Precipitation Values of Potassium Salts

(Colloid: 0.886 g per l)

Salt	Electrolyte cc.	Electrolyte cc.	Precipitation value	
			Milli-equivalents per liter	Millimoles per liter
Ferrocyanide	1.10 *N*/100	1.15 *N*/100	0.288	0.072
Thiosulphate	1.10 *N*/100	1.15 *N*/100	0.288	0.144
Ferricyanide	1.15 *N*/100	1.20 *N*/100	0.300	0.100
Sulphate	1.75 *N*/100	1.80 *N*/100	0.450	0.225
Phosphate	3.00 *N*/100	3.10 *N*/100	0.775	0.258
Chromate	3.90 *N*/100	4.00 *N*/100	1.000	0.500
Dithionate	4.80 *N*/100	4.90 *N*/100	1.225	0.612
Dichromate	5.00 *N*/100	5.10 *N*/100	1.275	0.637

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[1] Weiser and Middleton: Loc. cit.

Adsorption Values of Hydrous Aluminum Oxide

The method of procedure followed in the determination of adsorption values of hydrous aluminum oxide was essentially the same as used in the experiments on hydrous ferric oxide.[1] As in the latter case the colloid was coagulated by the addition of a definite quantity of electrolyte and the adsorption found by determining the total amount of electrolyte remaining after washing the precipitate. This method of procedure is preferable to the usual indirect method in that it avoids the error introduced by a highly gelatinous precipitate like hydrous alumina, adsorbing solvent as well as solute. Since the precipitate must be washed it is evident that the method of analysis is applicable only to those cases where the precipitation is irreversible. Accordingly the adsorption of multivalent ions only was determined.[2]

As emphasized frequently, the determination of adsorption values at the precipitation concentration cannot give comparable values on account of the variability of the latter and the consequent variability in the adsorption by the precipitated colloid. Accordingly such amounts of electrolyte and colloid were used that four or five times as much electrolyte remained as was adsorbed. The procedure was as follows: In the outer compartment of the mixing apparatus previously described[3] was placed 150 cc of colloid containing 1.150 grams per liter and in the inner compartment was placed 50 cc of an $N/50$ solution of the electrolyte whose adsorption it was desired to measure. The two solutions were mixed rapidly and uniformly by inverting the apparatus and shaking, after which the contents were transferred quantitatively to a 250 cc wide-mouth bottle which was subsequently stoppered. After standing for exactly 24 hours the bottle was placed in the centrifuge and centrifuged for thirty minutes at 2000 r. p. m. The extremely gelatinous precipitate was matted so firmly in the bottom of the bottle by

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[1] Weiser and Middleton: Loc. cit.

[2] Cf. Weiser: Jour. Phys. Chem., 24, 505 (1920).

[3] Weiser and Middleton: Loc. cit.

this procedure that the solution could be poured into a beaker without disengaging any of the precipitate. The inside of the bottle was rinsed, after which a small amount of water was added and the bottle shaken by a rotary motion until the precipitate was completely broken up. After transferring the contents of the bottle to a special thick-walled tube of 60 cc capacity, the total volume of solution was made up to 50 cc. The solution was next centrifuged for twenty minutes at 3000 r. p. m., after which the supernatant liquid was added to the beaker and the tube rinsed carefully. Twenty cubic centimeters of water were now added to the tube which was subsequently stoppered and shaken very thoroughly until the precipitate was broken up. The total volume was made up to 50 cc; the contents shaken up; and the centrifuging carried out as before. The wash water was added to the remainder and the process repeated. This method of washing was comparatively rapid, considering the character of the precipitate; and was very effective. Only a trace of electrolyte was found in the third wash water. The supernatant liquid and washings were either evaporated and analyzed directly or were diluted to a definite volume and an aliquot part taken for analysis. The method of analysis was the same as that used in standardizing the original solution. The adsorption of the following ions was determined: chromate, dichromate, oxalate, ferricyanide, ferrocyanide, thiosulphate, sulphate, dithionate, phosphate. Potassium salts were used throughout since they were more readily obtainable than the acids. Since the accuracy of the analytical method is of particular importance, the method of analysis of each ion is described in some detail.

Adsorption of Chromate Ion

Method of Analysis.—The volumetric method of Seubert and Hinke,[1] which was found so satisfactory in the determination of dichromate,[2] was employed. Thirty cubic centimeters

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[1] Zeit. anorg. Chem., 14, 1147 (1902).

[2] Weiser and Middleton: Jour. Phys. Chem., 24, 57 (1920).

of an approximately $N/50$ solution of the salt was diluted to 65 cc in a 500-cc glass-stoppered Erlenmeyer flask. To this solution was added 10 cc of eight percent sulphuric acid; after which the flask was stoppered and allowed to stand for ten minutes. The liberated iodine was titrated in the usual way with starch as indicator. The results of the standardization are given in Table IV.

TABLE IV

Standardization of Potassium Chromate

Solution taken cc	Thiosulphate taken. 0.037084N cc	Normality of chromate ion	
			Average
30.00	24.13	0.019884	
30.00	24.15	0.019901	
30.00	24.14	0.019894	0.019893

Determination of Adsorption.—To 150 cc of the colloid containing 0.1725 gram of aluminum oxide were added 50.27 cc of the standard chromate solution which was equivalent to 50 cc of $N/50$ salt. The solution containing the unadsorbed salt was evaporated to a small volume, transferred to an Erlenmeyer flask and analyzed. The results of a series of four determinations of the adsorption value are given in Table V which is self-explanatory.

TABLE V

Adsorption of Chromate Ion

Thiosulphate taken 0.037084 N cc	$N/50$ potassium chromate cc			Adsorption value milliequivalents		
	Taken	Remaining	Adsorbed		Per gram of Al_2O_3	
						Average
34.34	50.00	42.45	7.55	0.1510	0.8754	
34.40	50.00	42.52	7.48	0.1496	0.8672	
34.40	50.00	42.52	7.48	0.1496	0.8672	
34.35	50.00	42.48	7.52	0.1504	0.8719	0.8704

Adsorption of Dichromate Ion

Method of Analysis.—The method of analysis for dichromate was identical with that used for chromate. The results of the standardization are given in Table VI.

TABLE VI

Standardization of Potassium Dichromate

Solution taken cc	Thiosulphate taken. 0.03708 *N* cc	Normality of dichromate ion	
			Average
25.00	40.45	0.020006	
25.00	40.50	0.020025	
25.00	40.50	0.020025	0.020019

Determination of Adsorption.—After precipitating the colloid and washing in the usual way, the solution and washings were evaporated to 200 cc diluted to 250 cc and 100 cc taken for analysis. The results of a series of experiments are given in Table VII.

TABLE VII

Adsorption of Dichromate Ion

Thiosulphate taken 0.03708 *N* cc			*N*/50 potassium dichromate cc			Adsorption value milliequivalents		
I	II	Average	Taken	Remaining	Adsorbed		Per gram Al_2O_3	
								Average
28.92	28.87	28.89	50.00	44.63	5.37	0.1074	0.6226	
28.69	28.67	28.68	50.00	44.31	5.69	0.1138	0.6596	
28.98	28.98	28.98	50.00	44.78	5.22	0.1044	0.6052	
28.85	28.85	28.85	50.00	44.58	5.42	0.1084	0.6282	0.6289

By comparing the adsorption value of dichromate ion with that of the other ions investigated, it will be noted that the former is comparatively low. This is in line with the observations made during the washing of the precipitate obtained with potassium dichromate. Even on the second washing the precipitate tended to go back into colloidal solution; and if the attempt was made to wash it a third time, a large portion was peptized. This reversibility of precipitation indicates that the adsorption is comparatively slight in accord with the analytical results above given. These results do not agree with the observations of Ishizaka[1] who found that the adsorption of dichromate ion by "grown alumina" was much greater than that of any other ion: "However, we are not dealing with a pure adsorption process in this case; but with a chemical process as well, since the usual yellow-red color of potassium dichromate is changed by the adsorbent into the yellowish color of potassium chromate. A drop of acid brings back the original color again which is a sure proof that potassium dichromate is changed by the alumina into potassium chromate. The solution after adsorption has almost the same conductivity as before the adsorption; indeed, it frequently increases after adsorption. . . . . Investigations have not yet been undertaken for the purpose of explaining this phenomenon."

As we observed no change in color of the dichromate solution after adsorption and as the adsorption value of dichromate ion was low, it was quite evident that there was a fundamental difference between our experiments and Ishizaka's. The difference was that Ishizaka determined adsorption by powdered alumina while our experiments were carried out with a colloidal alumina stabilized by preferential adsorption of hydrogen ion. In a dichromate solution there is equilibrium between the dichromate and chromate ion that may be represented as follows: $Cr_2O_7'' + H_2O \rightleftarrows 2H'' + 2CrO_4''$. Now if a substance is added to this solution which shows a strong preferential adsorption for hydrogen ion it will shift the equilibrium to the right and so increase the concentration of chromate ion at the expense of dichromate ion. This is exactly what Ishazaka did. Alumina shows a strong adsorption for hydrogen ion[2] and so brings about the

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[1] Loc. cit.

[2] Weiser: Jour. Phys. Chem., 24, 505 (1920).

decomposition in accord with the above equation. Our experiments, on the other hand, were quite different. The colloidal alumina exists in faintly acid solution and is stabilized by adsorbed hydrogen ion. Under such circumstances one would expect little if any decomposition which is in accord with the observed facts.

It is of interest that dichromate ion is adsorbed the least of all the divalent ions studied by both colloidal aluminum oxide and colloidal ferric oxide. The conditions of precipitation were similar except that dichromic acid instead of potassium dichromate was used for precipitating the ferric oxide colloid.

Adsorption of Oxalate Ion

Method of Analysis.—Oxalate ion was determined volumetrically by titration with permanganate. The permanganate solution was prepared several days before using and was standardized against a weighed sample of Kahlbaum's oxalic acid "for analysis." All titrations were carried out at the same temperature in the same volume and in the presence of the same amount of sulphuric acid. The data on the standardization of potassium oxalate are recorded in Table VIII.

Table VIII

Standardization of Potassium Oxalate

Potassium oxalate cc	Potassium permanganate (1 cc = 1.367 cc $N/50$ oxalic acid) cc	Normality of oxalate ion	
			Average
23.54	17.06	0.019810	
24.90	18.03	0.019801	
34.14	17.50	0.019824	0.019812

Determination of Adsorption.—The experiments were carried out in the usual way with the results recorded in the first four experiments in Table X.

Since it was important to know whether the colloid had undergone any appreciable change during the course of this investigation, a determination was made on adsorption of oxalate ion five weeks after the four determinations referred to above. The result recorded under experiment 5, Table X, shows that the colloid is very stable indeed. This is in accord with the observations of Ishizaka and of Gann referred to earlier in this paper. Since the adsorption experiments herein recorded were completed within a period of three weeks, any change in the colloid is negligible.

On account of the gelatinous character of the precipitated alumina, it seemed desirable, to allow the solution to stand for 24 hours before centrifuging and washing the precipitate. Moreover, the velocity of precipitation varies with the conditions of precipitation and the nature and concentration of the electrolyte.[1] Since the velocity of precipitation is quite rapid in the presence of excess oxalate ion it was desired to know whether the adsorption value would be approximately the same if the determination was made immediately after precipitation instead of waiting for 24 hours. Accordingly a determination was made following the usual procedure in all respects except that the centrifuging was started immediately after the addition of the electrolyte. The result given under experiment 6, Table IX, justifies the conclusion that in this instance the adsorption value is the same within

TABLE IX
Adsorption of Oxalate Ion

Exp. No.	Permanganate cc	N/50 oxalic acid cc			Adsorption value milliequivalents		
		Taken	Remaining	Adsorbed		Per gram Al_2O_3	
							Average
1	29.45	50.00	40.27	9.73	0.1946	1.1281	1.1420
2	29.23	50.00	39.96	10.04	0.2008	1.1640	
3	29.33	50.00	40.10	9.90	0.1980	1.1478	
4	29.45	50.00	40.27	9.73	0.1946	1.1281	
5	29.37	50.00	40.16	9.84	0.1968	1.1409	
6	29.43	50.00	40.25	9.75	0.1950	0.1304	

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[1] Ishizaka: Loc. cit.; Gann: Loc. cit.; Freundlich: Zeit. Kolloidchemie, 23, 163 (1918).

the limits of experimental error, whether the washing is carried out immediately or after 24 hours.

Adsorption of Ferrocyanide Ion

Method of Analysis.—The analysis of ferrocyanide was accomplished volumetrically by oxidation of ferrocyanide to ferricyanide by potassium permanganate. An *N*/50 solution of ferrocyanide was prepared by direct weighing of Kahlbaum's potassium ferrocyanide "for analysis." This solution was used to standardize the permanganate in accord with the directions given by Müller and Diefenthaler.[1] The difficulty with the method is that the end-point is not well defined particularly in dilute solutions on account of the green color of potassium ferricyanide. We found it altogether impossible to determine the end-point with the necessary degree of accuracy in the ordinary way. The method finally adopted was to titrate the solution in a colorimeter similar in all respects to that used by Weiser and Sherrick[2] in a previous investigation. A solution of potassium ferricyanide of suitable concentration was used for comparison in following the titration. At the end-point the color changed from the yellowish green which is characteristic of ferricyanide to yellowish red. This change was so readily detected with the colorimeter that the titrations were entirely satisfactory as shown by the data in Table X.

TABLE X

Standardization of Permanganate against Ferrocyanide

Ferrocyanide *N*/50 cc	Permanganate cc	Cc of ferrocyanide equivalent to 1 cc of permanganate	
			Average
31.75	32.70	0.9709	
29.95	30.75	0.9740	
32.15	33.05	0.9728	
31.20	32.05	0.9734	
28.15	28.85	0.9757	0.9733

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[1] Zeit. anorg. Chem., 67, 418 (1910).

[2] Jour. Phys. Chem., 23, 205 (1919).

Determination of Adsorption.—A series of experiments on adsorption of ferrocyanide ion were carried out in the usual way with the results given in Table XI.

TABLE XI
Adsorption of Ferrocyanide Ion (*a*)

Permanganate required cc	*N*/50 ferrocyanide cc			Adsorption value milliequivalents	
	Taken	Remaining	Adsorbed		Per gram Al_2O_3
32.40	50.00	36.39	13.61	0.2722	1.5780
32.51	50.00	36.51	13.49	0.2698	1.5640
29.88	50.00	33.56	16.44	0.3288	1.9060
28.00	50.00	31.45	18.55	0.3710	2.1507

The results recorded in the above table are unsatisfactory to say the least. The cause of the wide variation in the results was the instability of the ferrocyanide in faintly acid solution. The solutions which were colorless at first became distinctly green on standing over night even when precaution was taken to exclude the air. To eliminate this source of error a series of experiments were carried out in which the solutions were analyzed as soon as possible after precipitation instead of being allowed to stand 24 hours. Since the precipitation velocity in the presence of excess ferrocyanide ion is very rapid, this variation in the method of procedure is

TABLE XII
Adsorption of Ferrocyanide Ion (*b*)

Permanganate required cc	*N*/50 Ferrocyanide			Adsorption value milliequivalents		
	Taken	Remaining	Adsorbed		Per gram Al_2O_3	
						Average
39.80	50.00	38.72	11.28	0.2256	1.3072	
40.10	50.00	39.03	10.97	0.2194	1.2719	
40.05	50.00	38.98	11.02	0.2204	1.2777	
40.15	50.00	39.08	10.92	0.2184	1.2661	1.2807

permissible, as shown from the experiments with oxalate ion described in the preceding section. The results obtained by the modified procedure are quite satisfactory as shown in Table XII.

Adsorption of Ferricyanide Ion

Method of Analysis.—Ferricyanide was analyzed iodometrically by the method of Müller and Diefenthaler.[1] To the neutral solution of ferricyanide contained in a glass-stoppered Erlenmeyer flask was added potassium iodide and zinc sulphate. The ferricyanide was reduced with the liberation of iodine and ferrocyanide ion was removed from solution as zinc ferrocyanide as fast as formed. The liberated iodine was titrated with thiosulphate. The method was quite satisfactory, as shown in Table XIII.

TABLE XIII
Standardization of Potassium Ferricyanide

Ferricyanide taken cc	Thiosulphate used 0.017879 N cc	Normality of ferricyanide ion	
			Average
40 00	17 60	0 023588	
40.00	17.64	0.023642	
40.00	17.60	0.023588	
40.00	17.62	0.023615	0.023608

TABLE XIV
Adsorption of Ferricyanide Ion

Thiosulphate required 0.017879 N cc	$N/50$ ferricyanide cc			Adsorption value milliequivalents		
	Taken	Remaining	Adsorbed		Per gram Al_2O_3	
						Average
14.74	50.00	39.51	10.49	0.2098	1.2162	
14.74	50.00	39.51	10.49	0.2098	1.2162	
14.80	50.00	39.67	10.33	0.2066	1.1977	
14.71	50.00	39.43	10.57	0.2114	1.2255	1.2139

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[1] Loc. cit.; cf. Mohr: Liebig's Ann., 105, 60 (1858).

Determination of Adsorption.—The analysis of the solution after precipitation and washing was carried out as described above with the results that are tabulated in Table XIV.

Adsorption of Thiosulphate Ion

Method of Analysis.—An approximately $N/50$ solution of thiosulphate was prepared from Kahlbaum's reagent "for analysis." This was standardized iodometrically in the usual way. The results are given in Table XV.

TABLE XV
Standardization of Thiosulphate

Thiosulphate used cc	Iodine solution required 1 cc = 0.0028874 g I cc	Normality of thiosulphate ion	
			Average
30.00	11.45	0.017366	
33.97	12.95	0.017346	
36.60	13.93	0.017317	
38.00	14.48	0.017337	0.017341

Determination of Adsorption.—The results of the experiments on adsorption of thiosulphate ion are recorded in Table XVI.

TABLE XVI
Adsorption of Thiosulphate Ion

Iodine cc	$N/50$ thiosulphate cc			Adsorption value milliequivalents		
	Taken	Remaining	Adsorbed		Per gram Al_2O_3	
						Average
18.82	50.00	42.82	7.18	0.1436	0.8325	
18.90	50.00	43.00	7.00	0.1400	0.8116	
18.92	50.00	43.04	6.96	0.1392	0.8070	
18.85	50.00	42.88	7.12	0.1424	0.8255	0.8191

Adsorption of Sulphate Ion

Method of Analysis.—An approximately $N/50$ solution of potassium sulphate was analyzed by the usual gravimetric method. The precipitation was effected by a definite excess of barium chloride added drop by drop to the boiling sulphate solution containing 0.2 cc of concentrated hydrochloric acid. The solution with precipitate (225 cubic centimeters) was digested four hours at approximately 100 degrees before filtration. The results are given in Table XVII.

Table XVII

Standardization of Potassium Sulphate

Potassium sulphate taken cc	Barium sulphate found g	Normality of sulphate ion	
			Average
50.00	0.1173	0.020099	
50.00	0.1171	0.020064	
50.00	0.1172	0.020082	
50.00	0.1170	0.020048	0.020073

Determination of adsorption.—Since a gravimetric method of analysis was employed, it was necessary to use particular care in washing the precipitate to avoid introducing any particles of alumina in the wash water. The solution was evaporated so that the precipitation of barium sulphate could be carried out in the same volume used in the standardization. The adsorption value is recorded in Table XVIII.

Table XVIII

Adsorption of Sulphate Ion

$BaSO_4$ found g	*N*/50 potassium sulphate cc			Adsorption value milliequivalents		
	Taken	Remaining	Adsorbed		Per gram Al_2O_3	
						Average
0.0966	50.00	41.38	8.62	0.1724	0.9994	
0.0970	50.00	41.55	8.45	0.1690	0.9797	
0.0963	50.00	41.21	8.79	0.1758	1.0191	
0.0968	50.00	41.47	8.53	0.1706	0.9890	0.9968

Adsorption of Dithionate Ion

Method of Analysis.—Barium dithionate was first prepared and purified by recrystallization. A solution of the potassium salt was prepared by mixing exactly equivalent solution of barium dithionate and potassium sulphate; and filtering off the precipitated barium sulphate. For analysis 50 cc portions of an approximately $N/50$ solution of the dithionate were placed in an Erlenmeyer flask and heated to boiling on an electric hot-plate. Without stopping the boiling, 10 cc of concentrated hydrochloric acid were added and the solution taken to dryness. By this procedure the dithionate was converted into sulphate with the loss of sulphur dioxide. Oxidation of the latter was avoided since air was excluded by the rapid boiling of the solution in a flask. The residue of sulphate was dissolved in water and analyzed by exactly the same procedure described in the preceding section. The results follow.

TABLE XIX
Standardization of Potassium Dithionate

Potassium dithionate taken cc	Barium sulphate found g	Normality of dithionate ion	
			Average
50.00	0.1119	0.019174	
50.00	0.1128	0.019328	
50.00	0.1127	0.019311	
50.00	0.1126	0.019294	0.019276

Determination of Adsorption.—The supernatant liquid after precipitation and the washings were placed in an Erlenmeyer flask and taken to dryness in the presence of hydrochloric acid as in the analysis of the original dithionate solution. The residue of sulphate was analyzed and the adsorption value of dithionate ion calculated. See Table XX.

Adsorption of Phosphate Ion

Method of Analysis.—An approximately $N/50$ solution of disodium hydrogen phosphate was prepared and analyzed

Table XX

Adsorption of Dithionate Ion

$BaSO_4$ found g	$N/50$ potassium dithionate cc			Adsorption value milliequivalents		
	Taken	Remaining	Adsorbed		Per gram Al_2O_3	
						Average
0.1037	50.00	44.41	5.49	0.1098	0.6365	
0.1030	50.00	44.12	5.88	0.1176	0.6817	
0.1031	50.00	44.17	5.83	0.1166	0.6759	
0.1042	50.00	44.64	5.46	0.1092	0.6330	0.6568

volumetrically by the modified Pemberton method.[1] Forty cubic centimeters of solution contained in a glass-stoppered Erlenmeyer flask were placed in a bath at 40 degrees; and to the solution were added 15 cc of concentrated ammonium nitrate solution and 35 cc of ammonium molybdate solution containing 100 grams per liter. After standing 30 minutes at 40 degrees the flask was shaken vigorously for 5 minutes and returned to the water bath for thirty minutes more before filtering and washing the precipitate as described by Pemberton. Following this uniform procedure very satisfactory results were obtained.

Table XXI

Standardization of Disodium Phosphate

Na_2HPO_4 taken cc	$N/10$ base required to dissolve phosphomolybdate cc			Normality of phosphate ion	
	Base	Acid	Difference		Average
40.00	72.29	7.46	64.83	0.021141	
40.00	72.17	6.52	65.65	0.021296	
40.00	72.03	7.06	64.97	0.021186	
40.00	72.31	7.38	64.93	0.021172	0.021198

Determination of Adsorption.—The solution after precipitation and washing was evaporated to 40 cc before pre-

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[1] Sutton: "Volumetric Analysis."

cipitating the phosphate as described above. The results are given in Table XXII.

TABLE XXII
Adsorption of Phosphate Ion

N/10 base required to dissolve phosphomolybdate cc			*N*/50 phosphate cc			Adsorption value milliequivalents		
Base	Acid	Difference	Taken	Remaining	Adsorbed		Per gram Al_2O_3	
								Average
52.84	8.09	44.75	50.00	29.18	20.82	0.4164	2.4138	
52.62	8.03	44.59	50.00	29.08	20.92	0.4184	2.4255	
52.76	8.06	44.70	50.00	29.15	20.85	0.4170	2.4173	
52.51	8.31	44.20	50.00	28.87	21.13	0.4226	2.4498	2.4266

Discussion of Results

The results of the experiments above described have been summarized in Table XXIII. For the purpose of comparison, the precipitation values and adsorption values are expressed both in equivalents and in moles.

TABLE XXIII

Anion	Precipitation value		Adsorption value per gram Al_2O_3	
	Milliequivalents per liter	Millimoles per liter	Milliequivalent anions	Milligram anions
Ferrocyanide	0.375	0.094	1.2807	0.3202
Thiosulphate	0.375	0.188	0.8191	0.4096
Ferricyanide	0.400	0.133	1.2139	0.4046
Sulphate	0.538	0.269	0.9968	0.4984
Oxalate	0.700	0.350	1.1420	0.5710
Phosphate	1.038	0.346	2.4266	0.8088
Chromate	1.300	0.650	0.8704	0.4352
Dithionate	1.625	0.813	0.6568	0.3284
Dichromate	1.775	0.888	0.6289	0.3185

From the table it will be noted that all the ions are relatively strongly adsorbed by the hydrous oxide. Indeed the adsorption values for hydrous alumina are approximately one-third larger than they were for hydrous ferric oxide. The results confirm the conclusion reached from the investigations on hydrous ferric oxide, namely, that the amounts of various ions carried down by a precipitated colloid are not even approximately equivalent. Thus the adsorption value of ferrocyanide is more than twice that of dichromate; and of phosphate is almost four times that of dichromate. It will be recalled that Gann studied the adsorption of ferrocyanide, ferricyanide and oxalate ions by hydrous alumina and from his results Freundlich and Gann concluded that the amounts adsorbed at the precipitation value were equivalent. This choice of ions was particularly happy since they are adsorbed to about the same extent as shown in the above table. Indeed, our adsorption values for these particular ions approach equivalence much more closely than Gann's, although the former were not determined at the precipitation concentration, for the reasons given earlier in this paper.

Freundlich's assumption that the same amounts of all ions are adsorbed from equimolar solutions would seem to be disproven by the results of this investigation. Considering the ions of the same valence which were adsorbed from equimolar solutions, we find that thiosulphate is adsorbed approximately 25 percent more than dichromate; while chromate, sulphate and oxalate are adsorbed, respectively, 35, 60 and 80 percent more than dichromate. As before explained, if the adsorption ceased with the neutralization of the charge on the particles, then the amounts adsorbed would be equivalent, other conditions remaining the same; but adsorption does not stop with the neutralization of the charge since the finely divided electrically neutral particles act as an adsorbent. Accordingly the actual amounts carried down, in general, will not be equivalent but will vary with the specific adsorbability of the ions as shown by the results above recorded.

If the assumption is made that the most readily adsorbed ion precipitates in lowest concentration and vice-versa, then the order of adsorption of the ions deduced from the precipitation values expressed in equivalents, is:

ferrocyanide, thiosulphate > ferricyanide > sulphate > oxalate
phosphate > chromate > dithionate > dichromate.

If the adsorption value is expressed in moles, thiosulphate and ferricyanide would change places in the above series. From the adsorption values expressed in milliequivalents we get the following order of ions:

phosphate > ferrocyanide > ferricyanide > oxalate > sulphate >
chromate > thiosulphate > dithionate > dichromate.

Although there is a tendency for the most strongly adsorbed ions to precipitate in lowest concentration it is evident from the above series that the order of adsorption of ions deduced from precipitation values may show marked variations from the order determined by direct analysis. This result confirms the result obtained with hydrous ferric oxide. On account of the magnitude of the adsorption values, the accuracy of the analytical methods employed in their determination, and the care exercised to maintain uniform conditions, it would seem that the adsorption values are quite accurate. Moreover, there is no doubt as to what is meant by the adsorption value. Since the order deduced from precipitation values is not the same as the order found by analysis, it would seem either that the precipitation values were not determined with sufficient accuracy or that the factors which determine the precipitation value were not all taken into account. It will be recalled from the historical survey at the beginning of this paper that the precipitation value has been variously defined by different investigators. In its most usual sense it is regarded as the concentration of electrolyte that will cause complete coagulation of a colloid within a definite time. The actual concentration necessary is determined by the valency of the precipitating ion; the degree of ionization of the electrolyte; the tendency of the electrolyte to hydrolyze; the mobility of the precipitating ion, which frequently decreases with increasing dilution because of increased hydration; the stabilizing influence of the ion having the same charge as the colloid; the velocity of coagulation; and the method of procedure followed in the addition of the electrolyte. It is quite evident, therefore, that the precipitation concentration of an electrolyte may not be determined exclusively by the specific adsorbability and the valence of the precipitating ion. Accordingly, the order of adsorption deduced from precipitation values may be incorrect; and so may be quite different from the order determined by direct analysis, particularly if the precipitation values are low and comparatively close together. This latter fact must not be overlooked. Where there is a wide difference in the precipitation values of different electrolytes, it is probable that the valence and the specific adsorbability of the precipitating ions are the outstanding factors; but where the precipitation values are relatively very close together such as the values for the multivalent ions considered in this investigation, it is probably incorrect to assume that the precipitation concentration is determined exclusively by the specific adsorbability of the precipitating ion.

From the results described in the last two papers on "Adsorption by Precipitates," it has been shown that in general, the amounts of various ions carried down by a precipitated colloid are not equivalent and that the precipitation values of electrolytes are not determined exclusively by the adsorbability of the precipitating ions. Experiments are planned for the immediate future which will attempt to establish quantitatively the relationship between the precipitation values of electrolytes and the adsorption of the precipitating ions by choosing such conditions that influences other than the specific adsorbability of the precipitating ions are reduced to a minimum.

Summary

The results of this investigation may be summarized briefly as follows:

(1) An investigation has been made of the precipitation of colloidal alumina by electrolytes and of the adsorption of the

precipitating ions by the hydrous oxide. The results of this investigation confirm the results of similar experiments on hydrous ferric oxide.

(2) The precipitation concentrations of a number of electrolytes for colloidal hydrous aluminum oxide have been determined. If the assumption is made that the most readily adsorbed ion precipitates in lowest concentration and vice-versa, the order of adsorption of anions deduced from the precipitation values expressed in equivalents, is: ferrocyanide > thiosulphate > ferricyanide > citrate > sulphate > oxalate > phosphate > chromate > dithionate > dichromate > chloride > nitrate > bromide > iodide. If the precipitation value is expressed in moles ferricyanide and thiosulphate exchange places in the above series.

(3) The adsorption of a number of precipitating ions by hydrous alumina oxide has been determined by direct analysis and a detailed account of the methods of analysis has been given. The determinations were confined to the multivalent ions since the adsorption of univalent ions was so slight that the precipitate was readily peptized by washing, owing to removal of the precipitating agent.

(4) The amounts of the various anions carried down by the precipitated colloid are not even approximately equivalent. Although the adsorption of equivalent amounts will neutralize a definite quantity of colloid, the actual amounts carried down by the precipitate, in general, will not be equivalent, since the amounts adsorbed by the neutralized particles will vary with the adsorbability of the ions. The order of adsorption beginning with the ion most readily adsorbed is: phosphate > ferrocyanide > ferricyanide > oxalate > sulphate > chromate > thiosulphate > dithionate > dichromate.

(5) The order of ions deduced from the precipitation values of electrolytes is not the same as the order found by direct analysis. The reason is that the precipitation values of electrolytes are not determined exclusively by the valence and adsorbability of the precipitating ions.

(6) Ishizaka found that potassium dichromate was con-

verted into chromate in the presence of powdered alumina. The explanation of this phenomenon is as follows: The equilibrium in solution between dichromate ion and chromate ion may be represented by the equation, $Cr_2O_7'' + H_2O \rightleftarrows 2\,H + 2\,CrO_4''$. Alumina shows such a strong preferential adsorption for hydrogen ion that the presence of the oxide in a finely divided condition shifts the equilibrium to the right with the formation of chromate ion at the expense of dichromate. Colloidal alumina stabilized by preferential adsorption of hydrogen ion, has a comparatively slight effect on the equilibrium.

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THE CHEMICAL POTENTIAL OF PHENOL IN SOLUTIONS CONTAINING SALTS; AND THE TOXICITY OF THESE SOLUTIONS TOWARDS ANTHRAX AND STAPHYLOCOCCUS

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The experiments here recorded were carried out under the supervision of Prof. W. Lash Miller in the chemical laboratory of the University of Toronto during the winter of 1909–1910, in order to supply further evidence as to the connection between the toxicity of phenol solutions containing salts and the chemical potential of the phenol in them, and in the hope of finding an explanation of the results obtained by Lemon[1] with 0.6 percent phenol solutions.

Determination of Chemically Equivalent Solutions, Using Kerosene as Immiscible Solvent

Lemon's experiments had shown that in the case of sodium chloride phenol and anthrax spores, the toxicity of a solution containing both phenol and salt is the same as that of a solution containing phenol alone, if the concentrations of the two solutions are so chosen that both are in equilibrium with the same solution of phenol in toluene; or, in shorter form, that a given solution of phenol is isotoxic with its "chemically equivalent" solution of phenol and salt. His experiments with 0.6 percent phenol and staphylococcus, however, gave irregular results, and in nearly every case the "equivalent" was found to be very much less toxic than the pure phenol solution.

Before extending the experiments to include other salts, it seemed necessary to clear up this discrepancy; and in the first place a redetermination of the chemical equivalents was undertaken. After unsuccessful attempts to measure the partial pressure of the phenol by drawing air through the solutions and then through a solution of potassium hydrate (the amount passing over in 24 hours was too small for analysis)

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[1] Jour. Phys. Chem., 24, 570 (1920).

the equilibrium between phenol solutions and kerosene was studied. The use of this hydrocarbon instead of toluene offers the advantage, that in the equilibrium experiments a much smaller proportion of the phenol goes into the upper layer; with dilute solutions the ratio is about ker. : water : : 1 : 4.5, as against tol. : water : : 2 : 1 and when the concentration of the phenol is increased the ratio remains almost constant, instead of greatly increasing as with toluene. The results of equilibrium experiments with kerosene, when plotted, thus give nearly straight lines, which is convenient for interpolation; and because of the relatively small concentration of the phenol in the hydrocarbon, there is not so much danger of the water content of the upper layer, and therefore the solubility of phenol in it, being affected by addition of salt.

The determinations were carried out as follows: Merck's cryst. phenol was distilled three times, rejecting the first and last portions, and collecting the part boiling at 181–182° C; 49.97 g of the last distillate, collected in a weighing glass, was dissolved in water and made up to one liter. Measured amounts of this original 5 percent solution, and weighed amounts of Merck's sodium chloride, were made up to 50 cc in a volumetric flask for the equilibrium experiments. In each of the latter 50 cc of the aqueous solution and 30 cc purified kerosene were placed in a tall narrow-necked glass-stoppered bottle (capacity about 90 cc) and stood in a thermostat at 33° C; after the temperature of the bath had been attained, the bottles were well shaken for 30 seconds and allowed to settle, this shaking was repeated three or four times. Suitable amounts of the two layers were then pipetted out for analysis, using a bulb tube for the lower layer.[1] In the aqueous layer the phenol was determined by the method of Lloyd;[2] the phenol in the upper layer was extracted five times by shaking in a separating funnel with normal potassium hydrate, the washings were united and acidified, and the phenol determined by the same method. All the kerosene

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[1] Jour. Phys. Chem., 24, 570 (1920).

[2] Jour. Am. Chem. Soc., 27, 16 (1905).

used in this work had been purified by shaking repeatedly with a 25 percent solution of potassium hydrate, until the washings gave no titre with the hypobromite solution used in the determination of phenol.

The following are the results obtained:

No salt; aqueous (obs.)	6.66	4.36	3.74	2.92	1.954	0.787% phenol
Kerosene layer (obs.)	1.63	1.03	0.835	0.643	0.427	0.176% phenol
Kerosene layer (calc.)	1.48	0.97	0.831	0.649	0.434	0.175% phenol
Ratio (obs.)	4.08	4.23	4.48	4.54	4.58	4.56 Aq/Ker

2% NaCl; aqueous	1.337	0.934 % phenol
Kerosene	0.319	0.224 % phenol
Ratio	4.19	4.18 Aq/Ker

5% NaCl; aqueous	4.184	2.65	2.240	1.794 % phenol
Kerosene	1.530	0.847	0.680	0.537 % phenol
Ratio	2.74	3.13	3.30	3.36 Aq/Ker

10% NaCl; aqueous	3.593	2.41	2.069	1.54 % phenol
Kerosene	2.336	1.159	0.953	0.687 % phenol
Ratio	1.54	2.08	2.17	2.24 Aq/Ker

15% NaCl;			20% NaCl;	
aqueous	2.523	1.344 % phenol	aqueous	1.539 % phenol
Kerosene	1.722	0.870 % phenol	Kerosene	1.754 % phenol
Ratio	1.47	1.54 Aq/Ker	Ratio	0.88 Aq/Ker

The ratio "(weight phenol in 100 cc aqueous layer)/(weight phenol in 100 cc kerosene layer)" increases with decrease in the concentration of the phenol; but for solutions without salt, containing less than 4 percent phenol, the results are expressible within the experimental error by a linear formula, setting the ratio constant at 4.50. The concentrations of phenol in kerosene so calculated are given after "Kerosene layer (calc.)" above.

For solutions containing salt which are in equilibrium with solutions in kerosene containing 0.22 percent phenol or less, that is which are chemically equivalent to a one percent solution of phenol in water or to more dilute solutions, the ratio has been assumed to be constant with the values given after "ratio" in the following table; dividing these ratios by 0.46 gives the "factor" by which the concentration of phenol in the saltless solution must be multiplied in order to obtain the chemically equivalent concentration of phenol in solutions containing from 2.0 percent to 20 percent sodium chloride.

Sodium chloride, %	0	2	5	10	15	20
Ratio	4.6	4.2	3.3	2.2	1.5	0.9
Factor	1.00	0.91	0.72	0.48	0.33	0.20

Calculated in this manner, the phenol solutions used by Lemon in his experiments with staphylococcus, viz.: 0.80, 0.70 and 0.60 percent phenol in water, are equivalent to solutions containing 2.0 percent salt and 0.73, 0.64 and 0.55 percent phenol, respectively; as calculated from Prof. Lash Miller's experiments with toluene, the equivalent solutions should contain 2.0 percent salt and 0.72, 0.63 and 0.54 percent phenol. The results of my experiments with kerosene, therefore, confirm those obtained with toluene; and the unexpected outcome of Dr. Lemon's work with staphylococcus cannot be accounted for by errors in the determination of the equivalents.

The Toxicity of 1.0% Phenol, and Other Solutions towards Staphylococcus at 0° C

In his experiments with anthrax spores, Lemon found good agreement between the toxicities of the phenol solutions and those of their chemical equivalents; in his experiments with staphylococcus the discrepancy seemed to increase with the dilution of the solutions. To test this, I undertook a couple of experiments with concentrations of phenol higher than those used by Lemon with staphylococcus, and worked at 0° C in order to bring the rate within measurable limit, a preliminary experiment having shown that while 0.8 percent phenol kills all the cocci in 15 minutes at 33° C, about 5000 colonies developed when the poison was allowed to act at zero. The solutions compared were not in every case exactly equivalent, as the experiments were made before the method of calculation described above had been adopted.

Staph. in poison	2	6	10	14	18 minutes
0.9% phenol	1400	311	240	93	45 colonies
0.44% ph. + 10% NaCl	2800	600	87	67	— colonies

As calculated above, the equivalent of 0.9 percent phenol is 0.43 percent phenol + 10 percent NaCl.

Staph. in poison	4	6	9	12	15 minutes
1.0% phenol	197	70	34	41	0 colonies
0.5% ph. + 10% NaCl	152	36	—	9	1 colonies

As calculated above, the equivalent of 1.0 percent phenol is 0.48 percent phenol + 10 percent NaCl.

Staph. in poison	3.5	6.5	9.5	12.5	15.5 minutes
0.835% ph. + 2.0% NaCl	2200	342	150	18	23 colonies
0.44% ph. + 10% NaCl	3600	1000	790	483	219 colonies

Both these solutions are chemically equivalent to 0.92 percent phenol.

These results serve to confirm the conclusion that discrepancies of the magnitude of those observed by Lemon occur only with the most dilute solutions.

The Toxicity of Distilled Water and of 0.2% NaCl towards Staphylococcus

As the discrepancies and irregularities observed by Lemon cannot be accounted for by error in the composition of the equivalent solutions, and as they were greatest when the solutions were most dilute, it seemed probable that they might be due to plasmolysis of the cocci occasioned by the low osmotic pressure of the 0.6 percent phenol solution (about 1.75 atmos.) as compared with that of its equivalent (0.54 percent ph. + 2.0 percent NaCl, osm. press. about 18 atmos.). Experiments in which distilled water was used as the "poisonous liquid" were accordingly carried out, following closely the procedure described by Lemon; they showed that, like 0.6 percent phenol, distilled water is a more powerful poison

Staph. in poison	1	2	120	125 minutes
Dist. water, room temp.	inf.	inf.	2	1 colonies

than Lemon found 0.54 percent ph. + 2.0 percent NaCl to be. Another series showed that 0.2 percent NaCl solution, which has about the same osmotic pressure as 0.6 percent phenol, caused death at a rate comparable to that usually found by Lemon with the 0.6 percent phenol solution.

Staph. in poison	1	5	15	20	90 minutes
Dist. water	5000	—	38	—	1 colonies
0.2% NaCl	—	2800	—	1760	—

On repeating the experiments with another culture of staphylococcus, very different results were obtained:

Staph. in poison	15	50 minutes
Dist. water	373	343 colonies
0.2% NaCl	—	298 colonies

This shows how great a difference there may be in the resistance of different cultures towards water and towards a dilute salt solution; it serves to explain Lemon's observation that his Culture No 15 lived for two hours in 0.60 percent phenol, nearly as long as in the chemical equivalent.

Adaptation of Staphylococcus to Distilled Water

A colony, grown on agar, was removed with the usual precautions, shaken up with distilled water, and let stand 50 minutes at room temperature, after which a loopful was used to infect 10 cc neutral agar at 45° C, and a plate was poured in the usual way. A colony from this (first) plate was treated with distilled water for two hours, and a second plate poured. A colony from the second plate was treated with distilled water for three hours, and a third plate poured. Over 8,000 colonies grew on this third plate.

The culture so obtained, while much more resistant to water than the original culture, was much less resistant to phenol; and 2.0 percent sodium chloride solution, in which the original culture grew unharmed, killed the new completely within a quarter of an hour.

Staph. in poison for 15 min. at room temp.

Dist. water	234 colonies;	0.1% phenol	182 colonies;
0.2% phenol	27 colonies;	0.4%, 0.6%, 0.8% ph., 0 col.	
2.0% NaCl	0 colonies;		

The irregular results observed by Lemon with dilute solutions must therefore be ascribed to the variability of the cultures employed by him in respect to their resistance to solutions of low osmotic pressure. Most of his cultures, like my own prepared in a similar way, were just able to stand an osmotic pressure of two atmospheres (that of 0.7 percent phenol), but were measurably injured by 1.75 atmos. (0.6 percent phenol, or 0.2 percent NaCl); while his culture No. 15 was more resistant, and his No. 16 was less.

Chemical Equivalents of Eleven Phenol-Salt Solutions Used by Paul and Krönig

On page 446 of their paper "Ueber das Verhalten der Bakterien zu chemischen Reagentien," Paul and Krönig[1] record the number of anthrax spores left alive after immersion for 24 hours 10 minutes in 4 percent phenol solutions containing various salts at the constant concentration of one formula weight per liter.

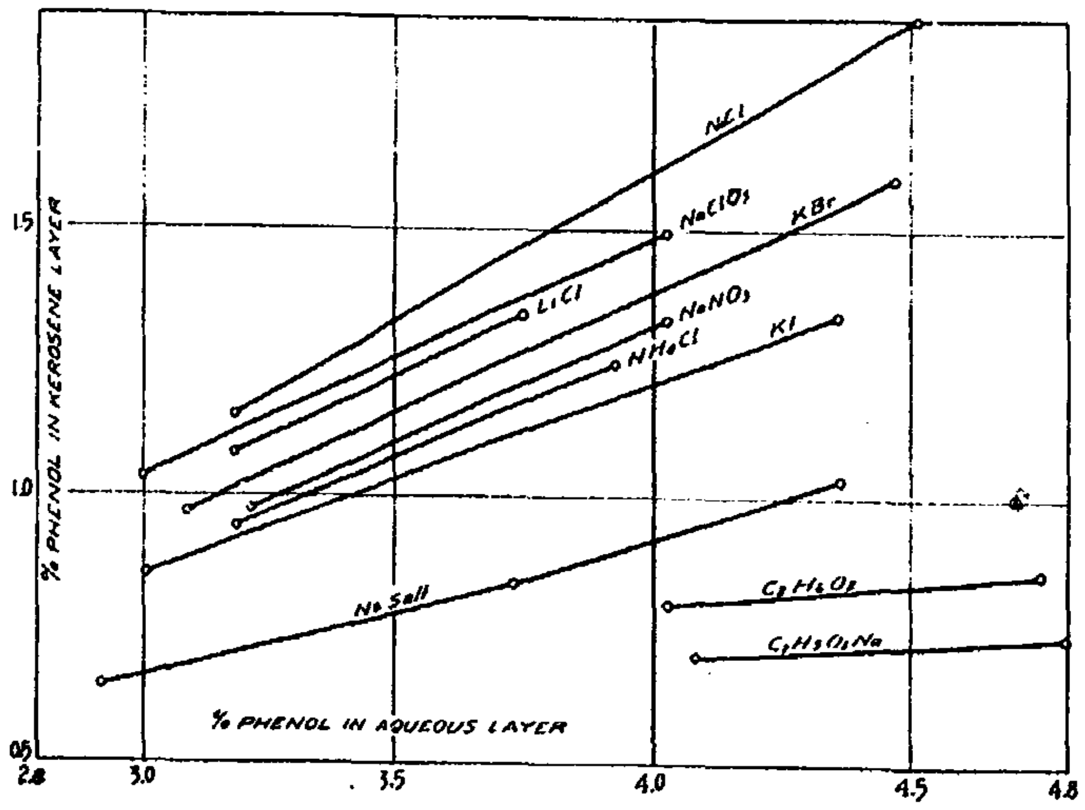

Fig. 1

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[1] Zeit. phys. Chem., 21, 414 (1896).

In order to determine the chemical equivalents of these solutions, I made up with each salt two different solutions, each of them normal with respect to the salt, but one containing more and the other less than four grams of phenol per hundred cubic centimeters; these were shaken with the purified kerosene, and the two layers analyzed as described above. The results are given in columns 2–5 of the following table, and in Fig. 1, and from them by linear interpolation the chemical equivalents of the 4 percent solutions were calculated; these are given in column 6 of the table, while column 7 gives the number of colonies left alive in the experiments of Paul and Krönig.

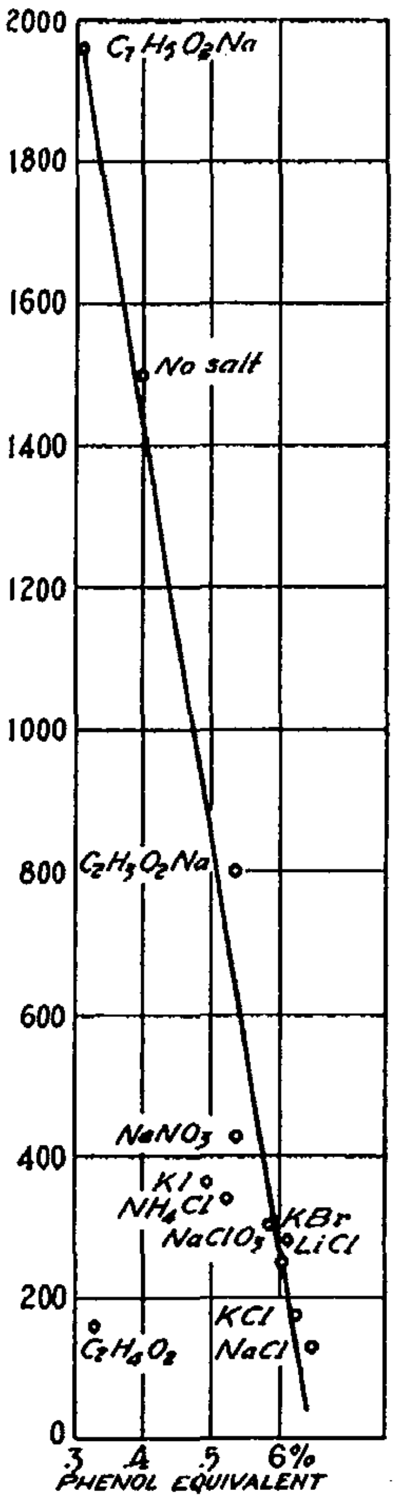

Fig. 2

In the table the solutions are arranged in the order of the concentrations of their equivalent phenol solutions, so that if the toxicity depended only on the chemical potential of the phenol, the first would be the least toxic and the last the most.

The accompanying cut, Fig. 2, in which the ordinates give the number of colonies and the abscissas the chemical equivalents of the poison used, shows that in general the toxicity depends on the chemical potential of the phenol; solutions containing acetic acid, potassium iodide, or ammonium chloride, however, proved to be much more toxic than would have been expected from the chemical work. It is likely enough that potassium iodide itself would act as a poison; the behavior of ammonium chloride is more unexpected. As to acetic acid, it is well known that slight varia-

	Aq.	Ker.	Aq.	Ker.	Equiv.	Col.
Sod. benzoate	4.076	0.696	5.87	0.774	3.1	1963
Acetic acid	4.292	0.795	4.752	0.863	3.3	160
No salt	—	—	—	—	4.0	1505
Pot. iodide	3.05	0.854	4.36	1.34	5.0	368
Am. chloride	3.196	0.948	3.934	1.25	5.3	336
Sod. nitrate	3.216	0.976	4.036	1.334	5.4	422
Sod. acetate	3.06	0.925	5.72	2.08	5.4	804
Pot. bromide	3.088	0.972	4.48	1.06	5.8	295
Lith. chloride	3.190	1.077	3.76	1.34	6.1	253
Sod. chlorate	2.99	1.03	4.03	1.49	6.15	280
Pot. chloride	2.94	1.01	3.89	1.44	6.25	174
Sod. chloride	3.19	1.15	4.54	1.92	6.5	131

tions in the acidity or alkalinity of a culture medium affect the growth; but Paul and Krönig's experiments (their table 24, p. 438) show that normal acetic acid by itself is not toxic to anthrax. Experiments of my own show that addition of acetic acid to phenol increases the toxicity of the solution to staphylococcus; a further study of this case seems called for.

Staph. in poison, 0° C	3	6	9	12	15	minutes
1.0% phenol	331	111	81	0	6	colonies
1.0% ph. + 3.0% acetic	8	0	0	0	0	colonies

The acid solution was chemically equivalent to 0.9 percent phenol.

Summary

Determination of the chemical equivalents of phenol-NaCl solutions, using kerosene as immiscible solvent, confirm and extend the results obtained with toluene.

The abnormal results obtained by Lemon in his experiments with 0.60 percent phenol, are due to plasmolysis of the cocci.

The increase, or decrease, in toxicity caused by adding ten different salts to 4 percent phenol solution, is primarily due to the change in the chemical potential of the phenol.

The increased toxicity caused by adding acetic acid needs further study.

The University of Toronto
June, 1920

NEW BOOKS

Les Colloides. *By J. Duclaux. 18 × 12 cm; pp. vii + 288. Paris: Gauthier-Villars et Cie, 1920.*—This subject is treated under the following heads: general methods of making colloidal solutions; general properties of colloidal solutions; optical properties and filtration; constitution of colloidal particles; colloids and the ionic theory; adsorption; colloids and adsorption; physical properties in living organisms; technique of the study of colloids. The author starts with Graham's view that colloids and crystalloids are opposing terms. He is also a believer in the chemical theory of colloids and considers that the ferric chloride which may be present in colloidal ferric oxide is part of a compound and is not merely a stabilizer. He assumes the existence of a cation and of an insoluble anion consisting of ferric oxide with varying amounts of chlorine attached. In other words he looks upon all colloids in something the same way that McBain looks upon soaps.

Under methods of preparation Duclaux lists metathetical reactions, hydrolysis, and electrical disintegration, which is hardly an exhaustive classification and at that he does not mention Svedberg's method with the oscillatory discharge. There is no reference to peptization in this chapter. Under general properties the author takes up: color; viscosity; rigidity; taste; irreversibility; freezing; adhesion; coagulation; formation of jellies; molecular weight. Under coagulation the precipitation of albumin on boiling is given as the simplest case, which is unfortunate because we are not very certain why albumin coagulates under these circumstances. The simplest case is the coagulation of an electrically stabilized sol by an electrolyte and that is not discussed as such, because the author's theory does not recognize the stabilization of sols by adsorbed ions.

The author does not make use of the Brownian movements to account for colloidal suspensions not settling; but contents himself with showing that the rate of settling is negligible with particles which are small enough, p. 51. While this is perfectly true, it does not meet the case in which the particles are a good deal coarser than his minimum and yet do stay suspended apparently indefinitely. He goes out of his way to make trouble for himself, p. 52, by explaining why it is impossible to clarify a colloidal solution by centrifuging, whereas many of them, which are stable under ordinary conditions, do precipitate when centrifuged. Under ultra-filtration reference is made to Martin, Malfitano, Borrel, Roux and Salimbeni; but Bechhold's name is not mentioned although he has studied the subject more systematically than anybody else. There is no reference to him even in the bibliography at the end of the book.

On p. 113 the author calls the colloidal ion in a sol the granule, while the granule and the true ions form a micelle. The micelle is therefore the ionized colloid. Under electrical stress the granule moves to one pole and the true ions of the micelle to the other. The optical heterogeneity of the sols depends on the size of the granule, p. 117. By going at the subject in this way, the author is really connecting the colloidal solutions with the true solutions instead of with the coarse suspensions. The reviewer believes that this is a mistake; and Duclaux's book is certainly not a striking proof of the advisability of his point of view. Everything is vague and while the author says that he explains everything, it is a little difficult to get anything definite out of the book.

Dyeing is cited as a case of adsorption, p. 138; but there is no reference to the effect of acids, alkalies, and salts. On p. 197 the author points out that in many cases colloidal membranes do not act like sieves; and he accounts for this by saying that, under certain conditions, the pores open and let things through while under other conditions they close and prevent the passage of substances which went through under other circumstances. There is no attempt made to show what the conditions are which make the pores open or close, and it seems not to have occurred to the author that his hypothesis will not account for selective filtration of a mixed solution unless he assumes that it is always the smaller substance which passes through. As a matter of fact it is quite impossible to account for the behavior of semipermeable membranes by any hypothesis involving sieves. On p. 229 under coagulation of salts, Duclaux states that it is quite impossible to tell whether the precipitation is due to the sodium ion or the chlorine ion. This seems unnecessary because it is a simple matter to determine whether the so-called granule is charged positively or negatively. Adsorption of the ion with the same charge would increase the stabilization and not cause precipitation; but Duclaux cannot admit this, because he does not believe that sols are stabilized by ions.

Occasionally the author is extremely definite. He is perfectly clear, p. 160, that the color of the so-called starch-iodide is not due to the formation of any definite compound and he also emphasizes the fact that we do not know why iodine should be blue.

The paragraph in regard to cobra venom, p. 173, was entirely new to the reviewer. "M. Delezenne finds a considerable quantity of zinc in snake poisons, the amount being greater the more active the poison. The dried cobra venom contains 5–6 parts per thousand of zinc, which is about fifteen percent of the mineral matter in the poison. The zinc evidently comes from the bodies of animals on which the serpent has fed. In the tissues of these animals the amount of zinc averages about 0.2 part per thousand, or only one-thirtieth of the concentration in the venom. [One-twelfth seems to be better arithmetic.] The animals on which the serpents feed are mostly herbivorous and the zinc content of plants is usually less than 0.1 part per thousand, or less than half of that in animals. The plants themselves get their nourishment from the soil which normally contains very little zinc and there must be many places where the zinc content is less than 0.1 part per thousand (250 grams per cubic meter). The relatively large amount of zinc in the cobra venom is, therefore, the result of a triple or quadruple concentration: in the plants, in the animals, in the cobra, and finally in the venom. This concentrating is specific because iron, which is certainly more abundant than zinc in most soils, does not concentrate in the venom."

The cumulative effect of very small doses is well brought out by the experience of the English ship Triumph in 1810, p. 172. A lot of mercury in the hold escaped from the containers and inside of three weeks two hundred men on board suffered from mercury poisoning while all the animals died.

Wilder D. Bancroft

The Book of the Damned. *By Charles Fort. 21 × 14 cm; pp. 298. New York: Boni and Liveright, 1919. Price, $1.90.*—It is perfectly true that scientific men, as a rule, reject and then forget facts which do not fit the theories of the moment, and it is also true that things which have been rejected at one time may be honored later when a new theory has come to the front. The author's book gives an account of phenomena which are now damned; but which he believes will some day be important facts in a broader science. He shows that many things have appeared to fall from the sky under conditions which make it seem impossible to him that they have been carried up in the air temporarily by a whirlwind somewhere else. The discovery of Chinese seals scattered in Ireland, p. 152, is difficult to explain on the ground of fraud. Many things have been found throughout the world which are either prehistoric or came from some other world. The pigmy flints, p. 160, and coffins, p. 162, the vitrified forts, p. 165, the cup marks, p. 204, the luminous wheels of the Persian Gulf, p. 258, and the mysterious tracks in Devonshire and elsewhere, p. 293, are phenomena which seem mysterious.

In order to account for the alleged phenomena, the author postulates that portions of the sky are gelatinous, p. 47, and that somewhere above the earth's surface there is a region in which gravity is not operative, a super-sargasso sea, pp. 87, 241. Substances raised from the earth's surface to this region are held there until shaken down by storms. He believes also that near the earth, p. 154, there are round worlds, spindle-shaped worlds, worlds shaped like a wheel, worlds shaped like titanic pruning hooks, worlds linked together by filaments, tremendous worlds, and tiny worlds. In the past, inhabitants of many of the other worlds are assumed to have come here, p. 157. To account for the pygmy relics, it is assumed that the tiny inhabitants of the hypothetical Elvera came here on hunting excursions in hordes as dense as bats, p. 161. The vitrified forts are accounted for by the assumption of electric blasts from another hypothetical world, Azuria, which was wrathy because the inhabitants of this world would not turn blue, p. 165. "The vast blue bulk of Azuria appeared in the sky. Clouds turned green. The sun was formless and purple in the vibrations of wrath that were emanating from Azuria. The whitish, or yellowish, or brownish peoples of Scotland, Ireland, Brittany, and Bohemia fled to hill tops and built forts. In a real existence, hill tops, or earliest accessibility to an aerial enemy would be the last choice in refugees. But here, in quasi-existence, if we are accustomed to run to hill tops in times of danger, we run to them just the same, even with danger closest to hill tops. Very common in quasi-existence: attempt to escape by running closer to the pursuing. They built forts, or already had forts, on hill tops. Something poured electricity upon them. The stones of these forts exist to this day, vitrified, or melted, or turned to glass."

In order to account for the fall of icicles, the author assumes, p. 181, the existence of a vast field of aerial ice a few miles above the earth. It is inert to earth's gravitational force; but if it sags, the lower portion may become affected to such an extent that the water dripping from it falls as icicles.

The author believes that Elvera, Azuria and other worlds have crossed the field of telescopic vision but have not been seen because it would be improper to see them, p. 184.

The phenomena reported almost exclusively from the Persian Gulf are quite normal if we assume, p. 262, the presence in the sky of vast wheel-like constructions which are "especially adapted to roll through a gelatinous medium from planet to planet. Sometimes they enter this earth's atmosphere because of miscalculations or because of stresses of various kinds. They are likely to explode and therefore have to submerge in the sea. They stay in the sea a while, revolving with relative leisureliness until relieved, and then emerge sometimes close to vessels. Seamen tell of what they see; but their reports are interred in scientific morgues. I should say that the general route of these constructions is along latitudes not far from the latitudes of the Persian Gulf."

The style of the book is almost incredibly bad. *Wilder D. Bancroft*

A History of Chemistry. *By F. J. Moore. 21 × 15 cm; pp. xiv + 292. New York: McGraw-Hill Book Company, Inc., 1918. Price: $2.50.*—In the preface the author says: "The value of the historical method for studying every department of human thought is now so universally recognized that it requires no emphasis, but to the younger student of chemistry it may be not superfluous to point out that, by observing the errors and misunderstandings of the past, we learn to avoid errors in our own thinking; by acquaintance with the way in which great men have solved problems, we are assisted in solving problems of our own; by observing the different aspects presented by the same facts in the light of successive theories, we acquire an insight obtainable in no other way into the nature, limitations and proper function of all theories. Finally, as we study how man's knowledge of nature has broadened and deepened with the years, we acquire a better understanding of the trend of thought in our own times, and of the exact bearing of each new discovery upon the old but ever recurring problems of the science. At no period has the development of chemistry been more rapid or more interesting than it is to-day, and the author indulges the hope that even this brief sketch of its history may assist the reader to follow that development with a fuller appreciation of its significance."

The chapters are entitled: chemistry among the ancients; chemistry in the Middle Ages; chemistry in the Renaissance; Boyle and his contemporaries; the later phlogistians; Lavoisier; the law of definite proportions; the early history of galvanic electricity; Humphry Davy; Berzelius, the organizer of the science; dualism in organic chemistry; the reaction against Berzelius; Gerhardt and the chemical reformation; the transition from the type theory to the valence theory; the periodic law; Bunsen Berthelot and Pasteur; organic chemistry since 1860; inorganic chemistry since 1860; the rise of physical chemistry; radio-activity and its influence upon atomic theory.

The bulk of the book deals with the period since 1790. It is therefore rather more interesting to the average chemist than the corresponding book by Campbell Brown, which made a specialty of the really early history of chemistry. On p. 237 it is probable that most people will get the impression that Gibbs' paper on heterogeneous equilibrium was devoted practically exclusively to the phase rule. It is quite certain from the remarks on the flowing electrode, p. 250, that the author believes that we have a method for measuring true single potential differences. *Wilder D. Bancroft*

THE CATALYTIC DECOMPOSITION OF HYDROGEN PEROXIDE BY SODIUM IODIDE IN MIXED SOLVENTS[1]

BY VAN L. BOHNSON

1. Historical

It is well known that the velocity of a chemical reaction is influenced by the composition of the medium in which it takes place. The first case on record was noted by Berthelot and Péan de St. Gilles,[2] who reported the velocity of esterification to be less in ether than in benzene. The literature records a large number of experiments which illustrate an effect of the solvent, a few of the results of which are summarized in Table I. The figures represent the relative velocity constants of the several reactions in the different solvents, and are quoted from a more comprehensive table given by Patterson and Montgomerie.[3] The reactions represented in the summary are:

(I) The reaction between triethylamine and ethyl iodide.[4]

(II) The transformation of a triazole derivative into a diazoanilid ester.[5]

(III) The inversion of menthone.[6]

(IV) The transformation of anissynaldoxime into anisantialdoxime.[7]

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[1] Part of a thesis submitted to the Graduate School of the University of Wisconsin in partial fulfilment of the requirements for the degree of Doctor of Philosophy.

[2] Berthelot and Péan de St. Gilles: Ann. Chim. Phys., (3) **66,** 62 (1862).

[3] Patterson and Montgomerie: Jour. Chem. Soc., **101,** 26 (1912).

[4] Menschutkin: Zeit. phys. Chem., **6,** 41 (1890); see also Ibid., **1,** 611 (1887).

[5] Dimroth: Liebig's Ann., **335,** 1; **338,** 143; **373,** 336; **377,** 127; **399,** 91.

[6] Tubandt: Liebig's Ann., **339,** 41; **354,** 259; **377,** 284.

[7] von Halban: Zeit. phys. Chem., **67,** 129 (1909).

TABLE I

Solvent	I	II	III	IV	V
Water	—	0.0043	—	—	8.26
Methyl Alcohol	286.6	1.0	1.0	1.0	2.07
Ethyl Alcohol	203.3	1.92	2.6	1.0	1.86
n-Propyl Alcohol	—	—	3.38	1.8	1.69
Isobutyl Alcohol	143.3	—	4.64	—	0.96

With these solvents in mind, it is interesting to note that the action of sodium hydroxide on alkyl bromides is slower in methyl alcohol than in *n*-propyl, but fastest in ethyl alcohol, while the velocity of decomposition of iodoform[1] in sunlight increases according to the solvent in the following order: methyl alcohol, ethyl alcohol, propyl alcohol.

It is frequently pointed out that there is a parallelism between reaction velocity and the dissociating power (i. e., according to Nernst, the dielectric constant) of the medium. While this seems to be roughly true, for example, in reactions I and V, above, it obviously does not hold for II, III and IV, as may be seen by reference to the constants in Table II. Again, the conversion of ammonium cyanate into urea takes place with a velocity thirty times as great in 90% alcohol as in water,[2] although the dissociating power of the latter is several times that of the former. The velocity of saponification of an ester with sodium or potassium hydroxide, moreover, is greatest in the medium of lowest dissociating power, and vice versa.[3]

Spring[4] has suggested that the reason for the slower decomposition of hydrogen peroxide in ether and alcohol solution may be due to the lowering of the surface tension of the solution.

Glycerine has been suggested in pharmacy as a preservative for hydrogen peroxide solutions, and it has been assumed

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[1] Comanducci and Meduri: Gazz. chim. ital., 48 I, 238 (1918).

[2] Walker and Kay: Jour. Chem. Soc., 71, 489 (1897).

[3] Cajola and Cappellini: Gazz. chim. ital., 30 I, 233 (1900).

[4] Spring: Zeit. anorg. Chem., 10, 161 (1895).

TABLE II

Solvent	Dielectric constant	Viscosity	Surface tension
Water	81.1 at 18°(*a*)	0.00891 at 25°[1]	70.6 at 30°(*g*)
Methyl Alcohol	31.2 at 20°(*b*)	0.005564 at 25°[1]	23.02 at 20°(*g*)
Ethyl Alcohol	25.8 at 20°(*b*)	0.01114 at 25°[1]	20.20 at 40°(*g*)
n-Propyl Alcohol	22.2 at 20°(*b*)	0.01962 at 25°[1]	23.82 at 16.4(*g*)
Isobutyl Alcohol	20.0 at 20°(*b*)	0.04034 at 20°(*e*)	22.72 at 16°(*g*)
Amyl Alcohol	16.0 at 20°(*b*)	0.03923 at 23.7(*f*)	23.72 at 16.4(*g*)
Pyridine	12.4 at 20°(*c*)	0.00885 at 25°[3]	38.4 at 17°(*g*)
Glycerol	39.1 at 20°(*d*)	6.33 at 25°[4]	64.53 at 18°(*h*)

Selected from Landolt and Börnstein. Observers: (*a*) Turner; (*b*) Abegg and Seitz; (*c*) Schlundt; (*d*) Drude; (*e*) Gartenmeister; (*f*) Thorpe and Rodger; (*g*) Ramsay and Shields; (*h*) Domke.

that this may be due to the viscosity of the solution.[1] Several investigators have adopted this point of view and brought forward evidence that the viscosity of the medium may be a factor in slowing down a reaction. Buchböck,[5] for example, investigated the rate of hydrolysis of carbonyl sulphide in various neutral salt solutions, and pointed out that the greater the viscosity of the solutions, the greater the retarding effect. He later repeated the work,[6] revising his results according to van't Hoff's theory (discussed below) and concluded that the velocity of decomposition of thiocarbonic acid is inversely proportional to the viscosity of the solution.

According to Raschig,[7] monochloramin reacts in ammoniacal solutions as follows: either

$$(1)\quad 3NH_2Cl + 2NH_3 = N_2 + 3NH_4Cl$$

or

$$(2)\quad NH_2Cl + NH_3 = NH_2.NH_2.HCl$$

only traces of hydrazine being formed.

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[1] Dunstan: Jour. Chem. Soc., **85**, 817; **87**, 12 (1905).
[2] Hartley: Thomas and Appleby: Ibid., **93**, 544 (1908).
[3] Jones and Schmidt: Am. Chem. Jour., **42**, 37.
[4] Böhm and Leyden: D. R. P. 185,597.
[5] Buchböck: Zeit. phys. Chem., **23**, 123 (1897).
[6] Buchböck: Zeit. phys. Chem., **34**, 229 (1900).
[7] Raschig: Verh. Ges. Naturforscher, 2 I, 120 (1907); Eng. P. 139 (1908).

Upon the addition of substances which increase the viscosity of the solution, such as glycerin, starch, dextrin, albumen, casein, and glue, the yield of hydrazine can be increased to 50–80% of the theoretical. Acetone, which lowers the viscosity, increases the velocity of reaction (1). It has been assumed that this effect is related to the evolution of a gas in one of the reactions.

The evidence in favor of a viscosity hypothesis is balanced, however, by equally important evidence to the contrary. Arrhenius[1] found the velocity of inversion of cane sugar to be accelerated by the addition of salts which both raise and lower the viscosity of the solution; Euler[2] pointed out the influence of neutral salts in the hydrolysis of ethyl acetate to be the reverse of that assumed by Buchböck and Reformatsky[3] found the velocity of hydrolysis of methyl acetate was not influenced in the slightest by the addition of sufficient quantities of gelatine or agar agar to make the solution jell at a temperature 10° below the working temperature.

Van't Hoff[4] pointed out that the solvent exerts a twofold influence; it may act not only as a true catalyst, accelerating both the direct and the reverse reaction to the same extent, but it may have the further effect of shifting the final equilibrium. This second effect is eliminated from the velocity constant by expressing concentrations of reacting substances in terms of the solubility in the different solvents. In this manner a constant should be obtained which is the same no matter what solvent is used, provided no influences are at work other than those considered in the development of the theory. Dimroth's[5] results confirm this theory, while those of von Halban[6] seem to argue against it. Bugarszky,[7] studying the reaction between ethyl alcohol and bromine,

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[1] Arrhenius: Zeit. phys. Chem., **2**, 284 (1888); **28**, 317 (1899).

[2] Euler: Zeit. phys. Chem., **36**, 641 (1901).

[3] Reformatsky: Zeit. phys. Chem., **7**, 34 (1891).

[4] Van't Hoff: Lectures (English ed.), I, 221.

[5] Dimroth: Loc. cit.

[6] von Halban: Loc. cit.

[7] Bugarszky: Zeit. phys. Chem., **71**, 705 (1910).

obtains by this method nearly identical constants for the solvents carbon tetrachloride and carbon disulphide, but a greatly increased value for benzyl bromide, and concludes, therefore, that the latter takes part in the reaction.

Comparatively little exhaustive work has been done on velocity of reaction in mixed solvents. Hemptinne and Bekaert[1] measured the velocity of the reaction between triethylamine and ethyl bromide in half-and-half mixtures of various solvents. Euler[2] points out that they obtained a maximum deviation from the mixture line in those cases which show the greatest deviation of the dielectric constant. Cohen[3] studied the velocity of inversion of cane sugar in several water-alcohol mixtures, and Patterson and Forsyth[4] the reaction between iodic and sulphurous acids in aqueous mixtures of methyl alcohol and of acetone. Millar[5] and Braune[6] studied the decomposition of diazoacetic ester in alcohol-water mixtures, finding a minimum velocity at about 11% water. The products of this reaction are different with alcohol than with water, both substances taking part in the reaction.

This paper presents the results of a study of the velocity of decomposition of hydrogen peroxide as influenced by the medium in which it takes place; the reaction differs from most of the reactions heretofore studied in that one of the products is a gas. The solvents used were mixtures of water with varying concentrations of one of the following: methyl, ethyl, *n*-propyl, isobutyl and amyl alcohols, glycerine, and pyridine.

Experimental

For determining the velocity of decomposition of hydrogen peroxide, the gasometric method was used. It has been shown by Walton[7] to be fully as accurate as the titrimetric method,

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[1] Hemptinne and Bekaert: Zeit. phys. Chem., **28**, 225 (1899).

[2] Euler: Loc. cit.

[3] Cohen: Zeit. phys. Chem., **28**, 145 (1899).

[4] Patterson and Forsyth: Jour. Chem. Soc., **101**, 40 (1912).

[5] Millar: Zeit. phys. Chem., **85**, 129 (1913).

[6] Braune: Ibid., **85**, 170 (1913).

[7] Walton: Ibid., **47**, 185 (1904).

and can be used in cases where catalyst or solvent would be oxidized by the permanganate used in the latter method.

Apparatus.—The apparatus was essentially that described by Walton, constructed in quadruplicate to permit four determinations at one time. Reaction flasks of special design were supported by a shaking device in a thermostat, and connected by means of capillary tubing with the tops of jacketed burettes in which the evolved oxygen was collected. The catalyst, held in a glass capsule, was supported in the neck of the reaction flask in such a way that it could be dropped into the reaction mixture at any desired instant. Thorough stirring was insured by placing glass beads in the bottom of the flask.

The evolved gas was collected and measured over water, and a leveling tube connected with the bottom of each burette made possible the rapid adjustment of the water levels. Water from the thermostat was pumped through the burette jackets, thus obviating a variable temperature correction. All experiments were performed at 25° C.

Method.—A measured volume (25 cc) of hydrogen peroxide solution in the solvent mixture to be investigated was pipetted into the reaction flask, which previously had been thoroughly cleaned, steamed, and dried. Exactly 1 cc of the catalyst solution was then placed in the glass capsule, which was supported in the neck of the reaction flask. The temperature in thermostat and burette jackets being constant, and the burettes and leveling tubes having been filled with water, the flask was placed in the thermostat and connected with a gas burette. An initial reading of volume was made, the catalyst dropped into the reaction mixture, and the shaker started. After waiting until from 5 to 8 cc of gas had been evolved, in order to be sure of a regular evolution of gas, volume readings were taken at measured intervals until about three-fourths or seven-eighths of the hydrogen peroxide had been decomposed. A final reading was taken when there was no appreciable change in volume after a half-hour interval. Table III shows a typical data and result sheet. Complete data for the duplicates are omitted.

TABLE III

Sodium Iodide Catalysis of Hydrogen Peroxide in Water

1. NaI = 0.02053 mols per liter

Bar. = 738 mm Temp. = 25° C a = 36.28

t (Minutes)	Observed volume (cc)	Milligrams of dry O_2	x	a-x	0.4343K
0	4.00	4.90	—	—	—
5	8.05	9.87	4.97	31.31	0.01279
9	10.90	13.36	8.46	27.82	0.01281
17	15.75	19.30	14.40	21.88	0.01292
27	20.40	25.00	20.10	16.18	0.01298
38	24.00	29.42	24.52	11.76	0.01287
60	28.65	35.12	30.22	6.06	0.01295
79	30.83	37.79	32.89	3.39	0.01302
Final reading 3 hrs. later	33.60	41.18	36.28	—	—
1 cc O_2 over water at 738 mm and 25° C = 1.2257 mg				Average	0.01290
				Duplicates,	0.01285 0.01286
				Mean,	0.01287
K_s = 0.4343 K × 10^4 = 128.7					

Calculations.—Walton[1] has shown that the sodium iodide catalysis of hydrogen peroxide in aqueous solution is a monomolecular reaction. The velocity constant can, therefore, be calculated from the well known expression

$$0.4343 \text{ K} = \frac{1}{t} \log \frac{a}{a - x}$$

where x represents the amount of substance decomposed (i. e., the amount of oxygen evolved) in the time t, and a represents the concentration of hydrogen peroxide at t = 0; a may, therefore, be represented by the total amount of oxygen evolved *after* the time selected as the starting point (t = 0).

As the table shows, the weight of dry oxygen in milligrams was calculated for each reading, in order that the velocity constants obtained may be independent of the barometer pressure. Incase the barometer varied before the ob-

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[1] Walton: Loc. cit.

taining of the final reading, appropriate correction was made.

In order to conserve space, the remaining results of this research have been condensed to the form shown in Table IV, where K_s represents $0.4343\ K \times 10^1$.

TABLE IV

Sodium Iodide Catalysis of Hydrogen Peroxide in Water

2. NaI = 0.1026 mols per liter

t	x	K_s
a =	46.85	
3	16.70	638
5	24.29	635
7	30.11	638
9	34.51	643
13	40.51	622
		635
		Duplicate, 605
		Mean, 620

Materials.—In all cases the purest materials obtainable were used. The water was distilled from a large copper still, over permanganate, and the middle portion of the distillate was used. The hydrogen peroxide was Merck's "Perhydrol," sometimes from glass bottles, sometimes from paraffin containers. Samples from two such sources gave constants which checked within the limits of error, and checked as well against a constant obtained from a sample of the middle portion of a lot distilled in vacuo. A measured amount of perhydrol (generally about 1.5 cc) was diluted to 100 cc with the solvent to be used. 25 cc of such a solution usually gave a total oxygen evolution of about 40 to 45 cc or approximately 50 to 55 mg. The initial concentration was, therefore, approximately 0.12 to 0.15 mols per liter.

The sodium iodide had been recrystallized several times and completely dried in an air bath. Standard catalyst solutions were made up by weighing out the dry salt and making up the solution to a known volume. The concentration of catalyst in the reaction flask is expressed in mols per liter.

The alcohols used as solvents were distilled, dried with anhydrous copper sulphate, and redistilled, and in some cases further dried with sodium and again redistilled. The glycerine used was Merck's, sp. gr. 1.26, British Pharmacopoeia. Samples of pyridine from two sources were used, one which had been prepared by the writer for a previous research, and one prepared by Professor Koenig in this laboratory. Both samples had been dried repeatedly over potassium hydroxide and re-

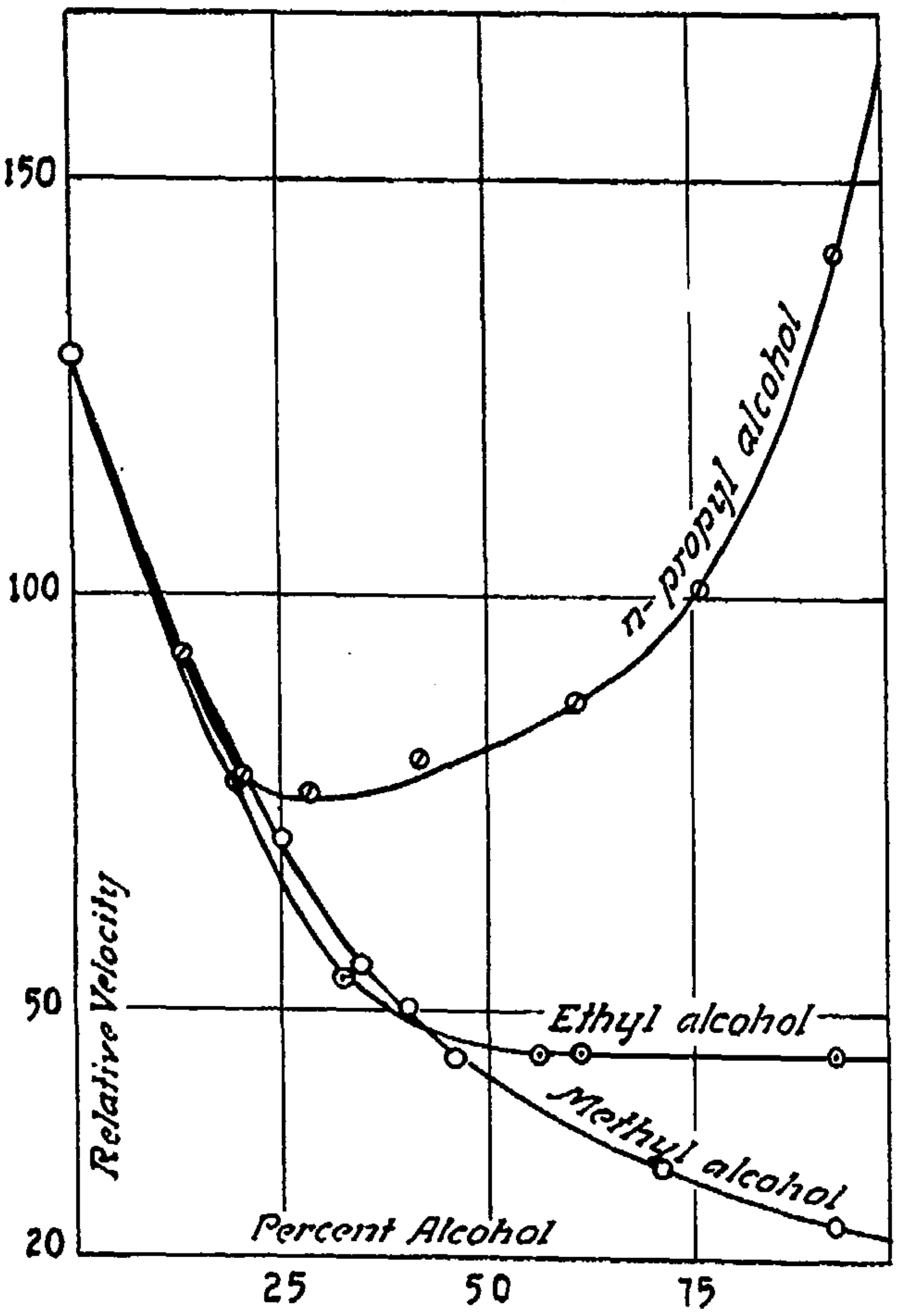

Fig. 1

distilled, and gave velocity constants that checked each other well within the limit of error. All the solvents used were made up by mixing known volumes of the components; the composition of the mixture in the reaction flask was then calculated in percentage of alcohol by weight, in which all the results are expressed.

3. Results

Velocity of Reaction in Water-Alcohol Mixtures.—Tables V, VI, VII and VIII give the results of experiments using as solvents binary mixtures of water with methyl alcohol, ethyl alcohol, and *n*-propyl alcohol. The results are graphically shown in Fig. 1.

TABLE V

Catalysis in Mixtures of Methyl Alcohol with Water

NaI = 0.02053 mols per liter

C = % Alcohol by weight

t	x	K_s	t	x	K_s	t	x	K_s
1. C = 24.0%			2. C = 34.5%			3. C = 46.0%		
a =	50.02		a =	37.62		a =	51.10	
15	10.78	70.1	11	4.91	55.2	11	5.44	44.4
23	15.54	70.3	23	9.53	55.2	23	10.67	44.2
34	21.14	70.2	36	13.79	55.1	39	16.83	44.5
47	26.59	70.1	53	18.48	55.3	59	23.12	44.3
64	32.23	70.2	73	22.60	54.7	83	29.28	44.5
87	37.75	70.2			55.1	107	34.08	44.6
		70.2	Duplicate,		56.1	128	37.50	44.9
Duplicate,		71.6	Mean,		55.6			44.5
Mean,		70.9				Duplicate,		44.1
						Mean,		44.3
4. C = 70.8%			5. C = 93.5%					
a =	47.46		a =	49.40				
9	2.97	31.2	10	2.83	25.6			
23	7.24	31.3	22	5.88	25.0			
45	13.10	31.2	41	10.32	24.8			
64	17.64	31.5	60	14.24	26.3			
94	23.65	31.9	91	19.92	24.6			
117	27.47	32.1	114	23.53	24.6			
		31.5			25.1			
Duplicate,		31.2	Duplicate,		24.4			
Mean,		31.3	Mean,		24.7			

Table VI

Catalysis in Mixtures of Ethyl Alcohol with Water

NaI = 0.02053 mols per liter
C = % alcohol by weight

t	x	K_s	t	x	K_s	t	x	K_s
1. C =	19.3%		2. C =	32.6%		3. C =	40.0%	
a =	49.80		a =	48.16		a =	52.90	
6	4.97	76.1	16	8.75	54.3	7	4.11	50.2
14	10.88	76.5	27	13.87	54.6	15	8.51	50.8
34	22.4	76.3	43	20.21	54.9	26	13.61	49.7
47	28.12	76.8	60	25.73	55.2	36	18.01	50.2
65	34.22	77.6	92	33.45	55.9	53	24.26	50.3
81	38.31	78.6	126	38.72	56.1	74	30.56	50.6
		76.9			55.2			50.4
Duplicate,		78.5	Duplicate,		52.8	Duplicate,		50.2
Mean,		77.7	Mean,		54.0	Mean,		50.3
4. C =	56.1%		5. C =	61.0%		6. C =	93.4%	
a =	47.22		a =	39.95		a =	48.69	
17	7.51	44.2	12	4.72	45.5	6	2.91	44.6
27	11.36	44.3	28	10.10	45.1	17	7.79	44.5
43	16.83	44.5	50	16.22	45.4	29	12.48	44.4
60	21.63	44.3	74	21.53	45.5	51	19.77	44.4
92	28.87	44.6				81	27.45	44.5
126	34.35	44.8			45.4			
		44.5						44.5
Duplicate,		45.3				Duplicates,		44.2
Mean,		44.9						46.5
								45.6
						Mean,		45.2

TABLE VII

Catalysis in Mixtures of *n*-Propyl Alcohol with Water

NaI = 0.02053 mols per liter
C = % alcohol by weight

t	x	K_s	t	x	K_s	t	x	K_s
1. C = 13.0%			2. C = 19.8%			3. C = 28.3%		
a =	48.76		a =	48.22		a =	47.22	
6	5.95	94.2	4	3.37	78.7	6	4.86	78.6
11	10.27	93.4	12	9.4	78.5	12	9.08	77.3
18	15.63	93.2	20	14.6	78.3	20	14.11	77.1
25	20.23	93.1	30	20.15	78.3	30	19.51	77.2
34	25.29	93.4	40	24.76	78.2	59	30.74	77.5
43	29.42	93.4	58	31.34	78.6	81	36.20	78.
56	34.26	94.						
					78.4			77.6
		93.5	Duplicate,		77.8	Duplicate,		75.9
			Mean,		78.1	Mean,		76.7
4. C = 41.8%			5. C = 61.0%			6. C = 76.5%		
a =	48.07		a =	47.18		a =	43.55	
5	4.30	81.4	4	3.64	87.2	4	3.91	102.1
11	8.87	80.5	12	10.18	88.0	10	8.99	100.4
23	16.65	80.3	20	15.61	87.2	17	14.12	100.1
28	19.38	80.4	30	21.41	87.5	29	21.20	99.6
37	23.80	80.2	40	25.98	86.9	51	30.09	100.0
48	28.29	80.3	58	32.63	88.1			
63	33.16	80.7						100.4
71	35.30	81.1			87.5	Duplicate,		101.9
			Duplicate,		88.0	Mean,		101.1
		80.6	Mean,		87.7			
Duplicate,		80.2						
Mean,		80.4						
			7. C = 93.9%					
			a =	47.77				
			5	7.23	142.5			
			9	12.18	142.			
			15	18.48	141.6			
			23	25.14	141.1			
			28	28.52	140.9			
			35	32.38	140.6			
			47	37.35	140.7			
					141.3			
			Duplicate,		142.2			
			Mean,		141.7			

TABLE VIII—SUMMARY

Catalysis in Water-Alcohol Mixtures

C = % alcohol by weight

Methyl alcohol		Ethyl alcohol		*n*-Propyl alcohol	
C	K_s	*C*	K_s	*C*	K_s
0	128.7	0	128.7	0	128.7
24.0	70.9	19.3	77.7	13.0	93.5
34.5	55.6	32.6	54.0	19.8	78.1
46.0	44.3	40.0	50.3	28.3	76.7
70.8	31.3	56.1	44.9	41.8	80.4
93.5	24.7	61.0	45.4	61.0	87.7
		93.4	45.2	76.5	101.1
				93.9	141.7

In Tables IX and X are given the results of experiments using as solvents a few aqueous mixtures of isobutyl and amyl alcohols, which are only partially miscible with water. In no case were oxidation products of the alcohols detectable after the completion of the reaction.

TABLE IX

Catalysis in Isobutyl Alcohol

NaI = 0.02053 mols per liter

C = % alcohol by weight

t	*x*	K_s	*t*	*x*	K_s
1. C =	1.9%		2. C =	93.4%	
a =	44.56		*a* =	40.33	
5	5.76	120	2	6.77	399
13	13.46	121	5	14.89	400
23	21.05	120	7	19.20	401
37	28.50	120	11	25.66	399
49	32.96	118	16	31.14	399
		120			399
	Duplicate,	121		Duplicate,	395
	Mean,	120.5		Mean,	397

TABLE X

Catalysis in Amyl Alcohol

NaI = 0.02053 mols per liter
93.5% alcohol

t	x	K_s
a =	32.70	
5	15.28	547
10	23.35	544
14	27.17	551
		547
Duplicate,		528
Mean,		537

Velocity of the Reaction in Glycerol-Water Mixtures.—The results of experiments using glycerol-water mixtures as solvents are given in Table XI, and represented graphically in Fig. 2.

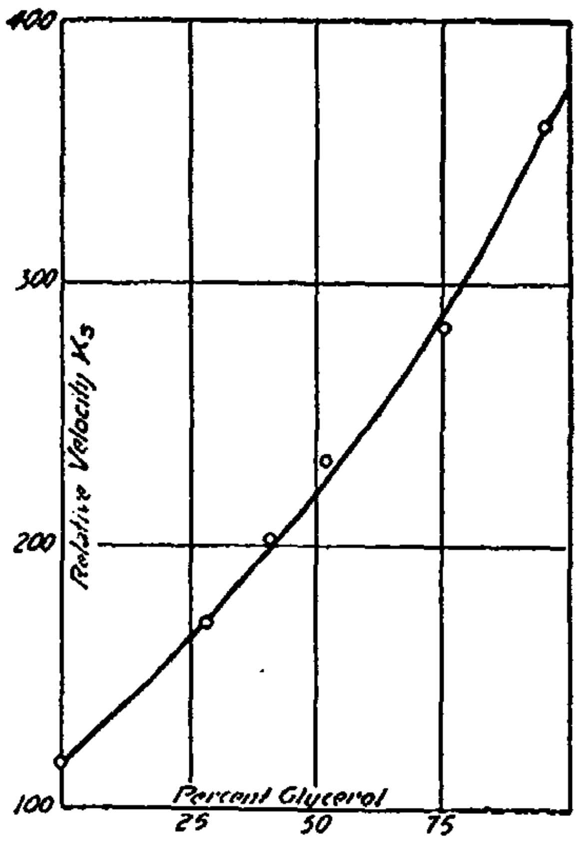

Fig. 2

TABLE XI

Catalysis in Mixtures of Glycerol with Water
NaI = 0.02053 mols per liter
C = % glycerol by weight

t	x	K_s	t	x	K_s	t	x	K_s
1. C =	13.9%		2. C =	28.2%		3. C =	41.3%	
a =	46.56		a =	48.18		a =	41.31	
3	4.83	158	5	8.73	174	3	5.30	199
7	10.35	156	9	14.47	172	7	11.44	201
13	17.29	155	19	25.25	170	13	18.78	202
20	23.91	156	28	31.97	169	19	24.43	204
31	31.44	157			—	28	30.48	208
		—			171			—
		156						203
4. C =	51.8%		5. C =	75.6%		6. C =	95.7%	
a =	45.53		a =	51.26		a =	29.04	
3	6.86	236	5	14.50	288	3	6.57	371
7	14.40	236	10	24.72	285	7	12.81	361
13	23.17	237	14	30.55	281	11	17.02	348
17	27.51	237	19	35.88	276			—
24	33.31	238			—			360
34	38.49	238			283			
		—						
		237						
	Duplicate,	227						
	Mean,	232						

SUMMARY

C	K_s
0	128.7
13.9	156
28.2	171
41.3	203
51.8	232
75.6	283
95.7	360

Velocity of the Reaction in Pyridine-Water Mixtures.—The concentration of catalyst used in the previous experiments (0.02053 mols NaI per liter) was found to accelerate the reaction in a concentrated pyridine solution to a comparatively small extent, as shown in Expt. 9, Table XII. A catalyst of five times that concentration was, therefore, used in determining the effect of pyridine upon the reaction. The results of these experiments are given in Table XII and graphically represented by Fig. 3.

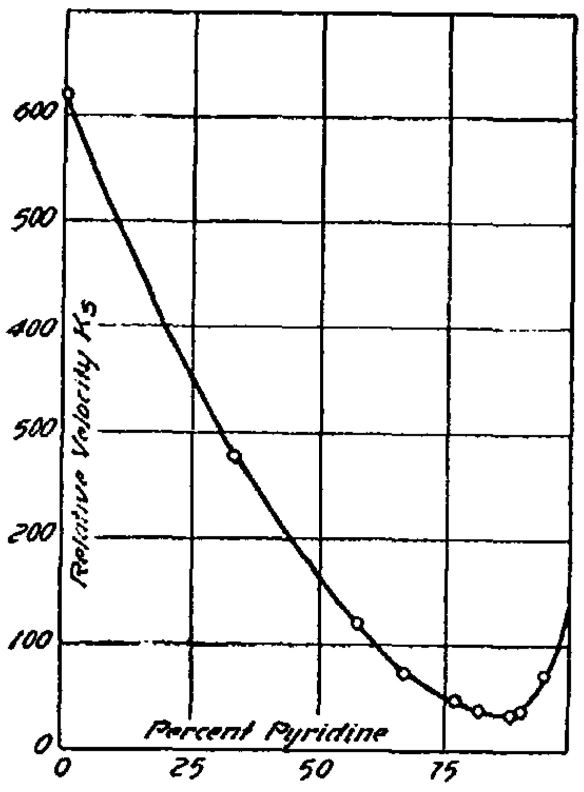

Fig. 3

TABLE XIIa

Summary: Catalysis in Water-Pyridine Mixtures

C	K_s
0	620
33.5	278
57.3	120
67.1	72
76.8	48
81.7	39.3
88.5	35
90.2	38.6
94.7	71.2

TABLE XII

Catalysis in Water-Pyridine Mixtures

NaI = 0.1026 mols per liter
C = % pyridine by weight

t	x	K_s	t	x	K_s	t	x	K_s
1. C = 33.5%			2. C = 57.3%			3. C = 67.1%		
a =	25.83		a =	42.56		a =	46.90	
4	5.71	271	5	5.56	122	8	5.86	72.4
9	11.22	271	10	10.39	122	20	13.18	71.6
17	17.25	281	15	14.63	122	33	19.57	71.1
			23	20.24	122	51	26.40	70.5
		274	36	27.20	123	73	32.22	69.1
Duplicate,		282						
Mean,		278			122			70.9
			Duplicate,		117	Duplicate,		73.2
			Mean,		120	Mean,		72.0
4. C = 76.8%			5. C = 81.7%			6. C = 88.5%		
a =	45.56		a =	46.75		a =	48.34	
11	5.21	48.0	14	5.67	40.1	15	5.39	34.2
24	10.46	47.2	33	12.33	40.3	30	10.24	34.5
39	15.81	47.5	51	17.67	40.4	62	18.76	34.4
57	21.21	47.7	73	23.18	40.7	83	23.31	34.4
85	27.77	48.0	102	28.93	41.1	108	27.89	34.6
111	32.31	47.4						
					40.5			34.4
		47.6	Duplicate,		38.1	Duplicate,		35.7
Duplicate,		48.5	Mean,		39.3	Mean,		35.0
Mean,		48.0						
7. C = 90.2%			8. C = 94.7%			9. NaI = 0.02053 mols/liter		
a =	47.25		a =	38.75		a =	47.13	
14	5.57	38.9	7	4.16	70.5	25	1.71	6.4
30	11.15	38.9	17	9.26	69.8	49	3.39	6.6
51	17.28	38.8	30	14.88	70.1	90	6.04	6.6
77	23.41	38.6	42	19.05	70.0	120	7.61	6.4
100	27.75	38.4	63	24.88	72.4	151	9.41	5.7
127	31.83	38.3	84	29.13	72.0			
		38.7			70.8			6.3
Duplicate,		38.3	Duplicate,		71.6	Duplicate,		7.1
		38.9	Mean,		71.2	Mean,		6.7
Mean,		38.6						

4. Discussion of Results

By extrapolation, the following constants ($K_s = K \times 10^4$) are obtained for the velocity of the reaction in the pure solvents, using in each the same concentration of sodium iodide as catalyst.

Water	128.7
Methyl Alcohol	23
Ethyl Alcohol	45
n-Propyl Alcohol	164
Isobutyl Alcohol	above 397
Amyl Alcohol	above 537
Glycerol	376
Pyridine	7

Pyridine, the solvent having the lowest dielectric constant, appears to exert the greatest retarding effect on the reaction, while the latter is accelerated most in amyl alcohol, the dielectric constant of which is but little greater than that of pyridine. If the alcohols alone are considered, the velocity of reaction decreases as the dielectric constant of the solvent increases, a result entirely at variance with the usual assumptions. Hence there appears to be no direct relation between the velocity of this reaction and the dielectric constant of the pure solvent.

Drude[1] has shown that the dielectric constant of mixtures of water and methyl alcohol varies directly with the concentration of the alcohol. We have found no such direct proportionality in aqueous alcohol mixtures between the reaction velocity and the concentration of the alcohol. It is obvious, therefore, that if there is a relation between the dielectric constant of a medium and the velocity of a reaction in that medium, it is in most cases entirely offset by some other effect.

Again, of all the solvents used, pyridine has the lowest viscosity, and in it the reaction goes slowest, while it is much faster in the medium having the greatest viscosity, pure glycerol. Considering the alcohols (with the exception of

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[1] Drude: Zeit. phys. Chem., 23, 267 (1897).

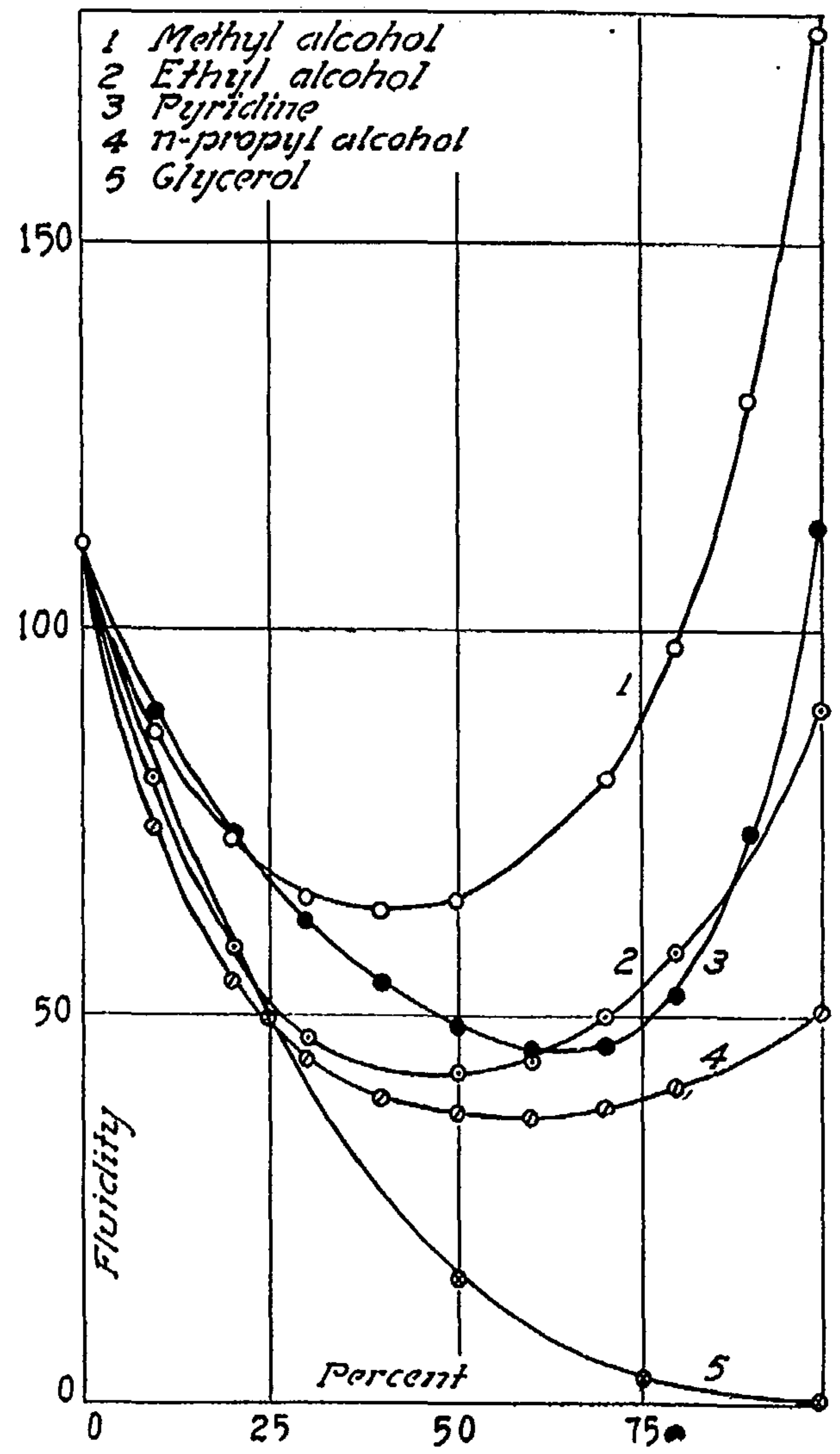
1 Methyl alcohol
2 Ethyl alcohol
3 Pyridine
4 n-propyl alcohol
5 Glycerol
150
100
50
0
Fluidity
Percent
0
25
50
75
1
2
3
4
5

Fig. 4

amyl alcohol) as a group, the greater the viscosity, the greater is the velocity constant. This result is contrary to expectations, if the viscosity of the medium is the major influence on the velocity of the reaction, and we must, therefore, conclude, as in the case of the dielectric constant, that whatever relation there may be between the viscosity of the solvent and the velocity of a reaction is quite overbalanced by another and greater influence.

Such an influence might be due in the case of pyridine, for example, to the formation of an addition compound of the pyridine with the hydrogen peroxide, since the former is well known to be basic while the latter has been shown to have weak acidic properties.[1]

In Table XIV are given the viscosities and fluidities of aqueous mixtures of all the solvents used. The fluidities are shown graphically in Fig. 4.

TABLE XIV

Viscosities and Fluidities at 25°[2]

%	Methyl alcohol		Ethyl alcohol		*n*-Propyl alcohol		Pyridine		Glycerol	
	η	ϕ	η	ϕ	η	ϕ	η	ϕ	η	ϕ
0	0.0089	111.1	0.0089	111.1	0.0089	111.1	0.0089	111.1	0.0089	111.1
10	0.0115	86.9	0.0124	80.7	0.0134	74.6	0.0112	89.2		
20	0.0137	72.9	0.0170	58.8	0.0183	54.6	0.0135	74.1		
25									0.0200	50.0
30	0.0153	65.3	0.0213	46.9	0.0224	44.6	0.0160	62.5		
40	0.0157	63.7	0.0234	42.7	0.0253	39.5	0.0184	54.4		
50	0.0153	65.3	0.0234	42.7	0.0266	37.6	0.0204	49.0	0.0615	16.3
60	0.0139	71.9	0.0224	44.6	0.0270	37.0	0.0219	45.7		
70	0.0123	81.3	0.0199	50.2	0.0259	38.6	0.0217	46.1		
75									0.3203	3.1
80	0.0102	98.0	0.0174	57.5	0.0244	41.0	0.0189	52.9		
90	0.0077	129.7	0.0143	69.9	0.0222	45.0	0.0135	74.1		
100	0.0056	178.5	0.0111	90.1	0.0196	51.0	0.0088	113.6	6.330	0.16

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[1] Calvert: Zeit. phys. Chem., **38**, 513 (1901).

[2] The data in this table were obtained by interpolating the results of: Dunstan: Jour. Chem. Soc., **85**, 817 (1904); **87**, 12 (1905) (alcohols); Hartley, Thomas and Appleby: Jour. Chem. Soc., **93**, 544 (1908) (pyridine); Jones and Schmidt: Am. Chem. Jour., **42**, 37 (1909) (glycerol).

It will be noted by comparing these curves with Figs. 1 to 3 that in no case is the solution of minimum fluidity the one in which there is a corresponding minimum in the reaction velocity. It has been suggested by Dr. Bancroft[1] that the reaction velocity in the mixture may be a resultant of the velocities of two different reactions, one in each of the solvents, with the effect due to viscosity superimposed upon them.

In order to further investigate the possible effect of the viscosity of the medium, the reaction velocity was determined in a gelatine solution of marked viscosity (of such a concentration that it solidified at a temperature only a few degrees below that of the thermostat. The results obtained are given in Table XIII.

TABLE XIII
Catalysis in Gelatine Solution
NaI = 0.02053 mols per liter
K_s for water = 128.7

t	x	K_s
a =	44.01	
5	4.53	94.3
13	10.79	94.0
22	16.71	94.2
34	22.99	94.4
62	32.65	94.5
		94.3

The velocity in this glycerine solution is shown to be about 28% slower than in water with the same concentration of catalyst. This result indicates that the viscosity of the medium does exert an effect upon the decomposition of hydrogen peroxide, in spite of the fact that it exerts no effect on the hydrolysis of methyl acetate.[2] The two reactions differ, however, in that one of the products of the former is a gas, and in such a case it is to be expected that the influence of viscosity would be greater. In the case of solvents other than

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[1] In a personal letter to Professor Walton.

[2] Reformatsky: Loc. cit.

gelatine solution, it is apparent that the effect of viscosity is masked by one of greater influence.

An inspection of the surface tension data in Table II will reveal that there is no important relation between that property of the solvent and the velocity constant, the values of surface tensions of the alcohols being quite similar, while the velocity constants in the several alcohols differ widely. Some measurements were made of the surface tensions of the various pyridine solutions used in these experiments, after the hydrogen peroxide was completely decomposed. The apparatus used was of the torsion wire type which records the force necessary to detach a platinum ring from the surface of the solution. The results follow:

Percent pyridine	33.5	57.3	67.1	76.8	81.7	88.5	90.2	94.7
Dial reading	55	53	52	50	49	48	47	47

The slight difference in the surface tension of concentrated and dilute pyridine solutions, and the absence of a maximum or minimum, make it clear that the relation between surface tension of the solvent and reaction velocity is negligible.

Walton[1] has shown that the velocity of decomposition of hydrogen peroxide by sodium iodide in water solution is directly proportional to the concentration of the iodide ion. It is, therefore, of interest to consider the conductivity of sodium iodide in such aqueous mixtures as are used in these experiments. The following values were obtained by Jones and his co-workers.

TABLE XV

NaI = 0.0312 mols per liter

Percent alcohol	Molecular Conductivity	
	Methyl alcohol[2]	Ethyl alcohol[3]
0	106	106
25	70.6	49
50	57.2	35.5
75	56.5	30.7
100	72.0	26.8

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[1] Walton: Loc. cit.

[2] Jones: Carnegie Institution Publication No. 80, 47.

[3] Wightman, Davis, Holmes and Jones: Jour. Chim. phys., 12, 385 (1914).

These values are shown graphically in Fig. 5. It will be noted at once that the conductivities of sodium iodide in water mixtures of these alcohols are not in accord with an assumption that the velocities of reaction in the same solvents are due entirely to the concentration of iodide ion.

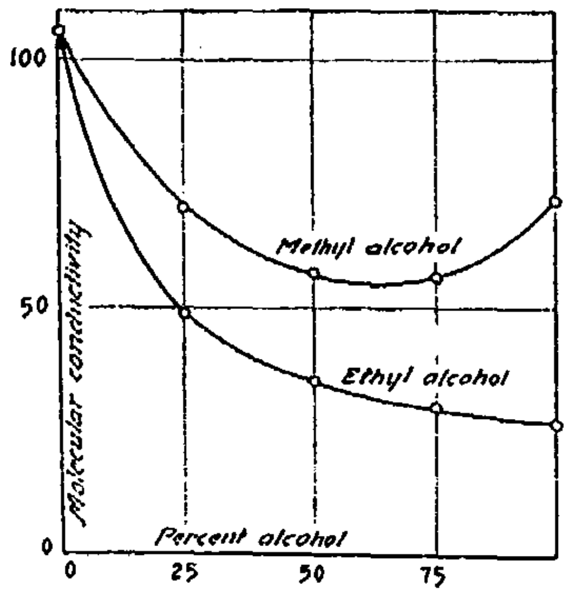

Fig. 5

The van't Hoff theory heretofore mentioned is obviously not applicable to homogeneous systems of mixed solvents such as the one studied, the solubility of the catalyst or hydrogen peroxide in the separate solvents not being a factor. The final equilibrium is the same in all of these experiments, complete decomposition of the hydrogen peroxide being attained.

The foregoing considerations must lead to the conclusion that there is no outstanding relation between the velocity of decomposition of hydrogen peroxide as influenced by sodium iodide and the dielectric constant, viscosity, or surface tension of the solvent. Whatever influence these properties may have, if any, must be counterbalanced by other effects.

It is noticeable that in the case of the alcohols, the reaction proceeds fastest in the solvent of highest molecular weight. It is known that alcohols of higher molecular weight are less associated than their lower homologues and it is possible that this property is a deciding factor in influencing the velocity of the reaction.

In general, it may be said that the solvent exerts a specific effect on the velocity of a reaction taking place in it, this effect being probably the resultant of several effects, among others those due to association of the solvent, its viscosity, its surface tension, the dissociation of the catalyst, and by no means least, a chemical reaction between solvent and dissolved substance.

The author desires to take this opportunity for expressing his appreciation to Professor J. H. Walton, at whose suggestion this research was undertaken, and under whose direction it was carried out, for his kindly interest and guidance during its progress.

5. Summary

1. The velocity of the catalytic decomposition of hydrogen peroxide by sodium iodide has been measured in different aqueous mixtures of methyl, ethyl, normal propyl, isobutyl and amyl alcohols, glycerol, and pyridine. The solvents apparently do not undergo oxidation; the decomposition of the hydrogen peroxide is complete.

2. The relative velocity of reaction in the pure solvents may be expressed by the following constants: methyl alcohol, 23; ethyl alcohol, 45; *n*-propyl alcohol, 164; isobutyl alcohol, 397; amyl alcohol, 537; glycerol, 376; pyridine, 7; water, 128.7; gelatine solution (of marked viscosity), 94.3. There is apparently no relation between the velocity of the reaction and the dielectric constant, viscosity, or surface tension of the pure solvent.

3. Curves for the reaction velocity in aqueous mixtures in some cases exhibit minima, but these do not correspond with the minima in the fluidity curves. No relation has been found to hold between the reaction velocity and any physical property of the mixed solvent.

4. It appears that the solvent exerts a specific effect on the velocity of a reaction, this effect being probably the resultant of a number of other effects due to association of the solvent, its viscosity and surface tension, the dissociation of the catalyst, and a possible reaction between solvent and dissolved substances.

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COAGULATION OF COLLOIDAL SOLUTIONS BY ELECTROLYTES: INFLUENCE OF CONCENTRATION OF SOL

BY E. F. BURTON AND MISS E. BISHOP

I. Introduction

The phenomenon of the coagulation of colloidal solutions by the addition of various electrolytes has occasioned more work probably than any other phase of colloidal study. As a result of early experiments by Schulze,[1] Linder and Picton,[2] and others and later work by Freundlich[3] and his co-workers, accepted qualitative laws have been laid down.

(1) The coagulation seems to depend only upon the ion in the electrolytic solution which bears a charge opposite in sign to that borne by the colloidal particles.

(2) The activity of any such ion in any electrolytic solution depends very greatly on the valency of the ion.

The efficiency of any electrolytic ion is expressed by a quantity called the coagulative power which is defined as follows: To a given volume of colloidal solution is added a quantity of electrolyte just sufficient to produce coagulation of the particles; if the molecular concentration of the electrolyte in the total volume of the mixture is c (now usually expressed in millimols per litre), then $1/c$ is called the coagulative power of the given electrolyte on the given sample of colloid.

It has been known for many years that this coagulation is an electrical phenomenon and it is well established that in coagulation the particles of the sol are wholly or partially discharged. One would naturally expect that the coagulating power of an ion would depend upon its valency, i. e., upon its electrical charge and at first sight one might conclude that the coagulating powers of uni-, di-, and trivalent ions might be in the ratio of 1 : 2 : 3. The experimental results referred to above pointed, however, to a complex relation between the coagulative powers of these ions. Averages of powers of uni-, di- and trivalent ions gave ratios of the order 1 : 30 : 1000.

Attempts have been made to see if such experimental numbers are given by any reasonable theories. Such theories have been suggested by Whetham[4] and Robertson[5] which lead to the expression 1 : x : x^2 as the above ratios, where x is a constant; an entirely different theory suggested by Freundlich[3] arrives at the ratios 1^n : 2^n : 3^n, where n is a constant. For certain values of x and n these two formulae may be made to approximate to the experimental ratios 1 : 30 : 1000.

In spite of the support given to such formulae by experimental results, this law of the dependence of coagulating power on valency, which has been called the Schulze-Linder-Picton law, has been very seriously questioned. (See Bancroft,[6] etc.) A very impartial summary of the present experimental evidence has been recently given by Wo. Ostwald.[7] In the following table taken from the latter paper are collected the coagulating powers with regard to arsenious sulphide sol of various electrolytes with uni-, di- and trivalent cations, the active coagulating ions since the particles of arsenious sulphide are negatively charged.

As is quite apparent from this table, the coagulating power of univalent (or divalent or trivalent) ions cannot be said to be the same. However, leaving out the single inorganic salt thallium sulphate and the complex organic salts quoted from Freundlich, there is a distinct break between the univalent and the divalent powers. The same can hardly be said for the transition between divalent ions and trivalent ions. There is this to be said, however, comparing the results for these two classes of ions given by Linder and Picton, the values of C for the trivalent ions are all quite below the value for the divalent ions.

Ostwald[8] and others are inclinded to throw over the Schulze-Linder-Picton law entirely. In making this sweeping condemnation of the former view these authors seem to have lost sight of one other variable, namely, the concentration of the colloidal solution on which coagulation experiments have been done.

TABLE I
Coagulation of Arsenious Sulphide
C = millimols per litre necessary to cause coagulation
Univalent ions

Electrolyte	Schulze[1] *C*	Linder and Picton[2] *C*	Freundlich *C*
Acetic acid	14900	—	—
$^1/_3$ H_3PO_4	ca. 1290	—	—
$^1/_2$ Oxalic acid	ca. 373	—	—
$^1/_2$ H_2SO_3	ca 257	—	—
$^1/_3$ K_3 citrate	—	—	240
K acetate	—	—	110
$^1/_2$ Li_2SO_4	—	124.4	—
$LiNO_3$	—	109.0	—
LiCl	185.4	—	58.4
$^1/_4$ $K_4Fe(CN)_6$	181.2	—	—
Na acetate	154.3	—	—
$^1/_2$ K_2SO_4	151.0	123.1	65.6
$^1/_2$ K_2 oxalate	131.2	—	—
KNO_3	117.6	104.7	50.0
$^1/_2$ Na_2SO_4	109.0	137.4	—
KI	107.3	102.2	—
NaI	—	117.0	—
$^1/_2$ K_2 tartrate	104.3	—	—
$^1/_3$ $K_3Fe(CN)_6$	100.5	—	—
$NaNO_3$	100.4	110.8	—
KCl	97.9	(97.9)	49.5
$KClO_3$	92.7	—	—
NH_4NO_3	90.5	73.9	—
NH_4I	—	73.9	—
NH_4Br	—	73.9	—
NH_4Cl	90.3	62.9	42.3
KBr	81.5	101.0	—
NaBr	—	109.0	—
NaCl	80.6	103.5	51.0
$^1/_2$ $(NH_4)_2SO_4$	80.4	95.8	—
$^1/_2$ H_2SO_4	80.0	92.4	30.1
HNO_3	57.5	57.5	—
HCl	49.4	58.7	30.8
HI	—	57.5	—
HBr	—	56.0	—
Guanidinnitrate	—	—	16.4
$^1/_2$ Tl_2SO_4	8.36	1.60	—
Strychninnitrate	—	—	8.0
Anilinchloride	—	—	2.52
p-Chloranilinchloride	—	—	1.08
Morphinchloride	—	—	0.425
Neufuchsine	—	—	0.114

TABLE II

Divalent ions

Electrolyte	Schulze[1] C	Linder and Picton[2] C	Freundlich C
$MgSO_4$	3.16	2.10	0.810
$Fe(NH_4)_2(SO_4)_2$	3.03	—	—
$MnSO_4$	2.31	2.02	—
$FeSO_4$	2.77	2.02	—
$CoSO_4$	—	1.96	—
$ZnSO_4$	1.86	1.68	—
$NiSO_4$	1.88	1.65	—
$CaSO_4$	2.64	1.60	—
$NiCl_2$	—	1.52	—
$FeCl_2$	—	1.42	—
$Co(NO_3)_2$	—	1.37	—
$ZnCl_2$	—	1.34	0.685
$CaCl_2$	2.06	1.31	0.649
$Ca(HCO_3)_2$	1.95	—	—
$CaBr_2$	—	1.31	—
$MgBr_2$	—	1.31	—
$CoCl_2$	—	1.29	—
$Sr(NO_3)_2$	—	1.29	—
$Ca(NO_3)_2$	—	1.29	—
$SrCl_2$	—	1.23	0.635
$Cu(NO_3)_2$	—	1.23	—
$BaCl_2$	1.68	1.18	0.691
$MgCl_2$	1.05	1.14	0.717
$Ba(NO_3)_2$	1.84	1.14	0.687
$CdCl_2$	—	1.01	—
$UO_2(NO_3)_2$	—	—	0.642
$CdBr_2$	—	0.964	—
$CdSO_4$	—	0.924	—
$CuSO_4$	—	0.911	—
$Cd(NO_3)_2$	—	0.899	—
$HgCl_2$	—	0.322	—
$PbCl_2$	—	0.225	—

TABLE III

Trivalent ions

Electrolyte	Schulze[1] C	Linder and Picton[2] C	Freundlich C
$^1/_2$ $Fe_2(SO_4)_3$	—	0.216	—
$^1/_2$ $Cr_2(SO_4)_3$	—	0.154	—
$CrCl_3$	0.316	—	—
$FeCl_3$	0.123	0.136	—
$^1/_2$ $Di_2(SO_4)_3$	—	0.080	—
$^1/_2$ $Al_2(SO_4)_3$	0.112	0.074	—
$^1/_2$ $La_2(SO_4)_3$	—	0.074	—
$^1/_2$ $Ce_2(SO_4)_3$	—	0.074	0.092
$AlCl_3$	0.090	0.062	0.093
$Al(NO_3)_3$	—	—	0.095
$NH_4Fe(SO_4)_2$	—	0.102	—
$KCr(SO_4)_2$	0.141	0.092	—
$KAl(SO_4)_2$	0.077	0.040	—
$KFe(SO_4)_2$	0.063	—	—
$NH_4Al(SO_4)_2$	—	0.040	—

Results given below suggest that the definition given above for the coagulating power of an electrolyte with regard to a chosen colloidal solution, say arsenious sulphide, has no meaning as stated, because the power varies widely with the concentration of the disperse phase of the sol itself.

II. Experimental Work

The extremely small concentration of the trivalent ions is so remarkable that the problem of finding how the coagulative power of a given electrolyte depends on the concentration of the colloid suggested itself. The results given by these experiments show quite remarkable differences in the action of uni-, di- and trivalent ions as the concentration of the colloidal solution is altered.

Three examples of aqueous colloidal solutions were used,

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[1] Schulze does not give these numbers but in the table C has been calculated from Schulze's results.

[2] Linder and Picton merely give relative results taking aluminium chloride as unity. Ostwald recalculates Linder and Picton's results by making the values of C for potassium chloride the same in the first two columns.

viz., gum mastic sol, Bredig copper sol and arsenious sulphide sol.

(1) The gum mastic sol was prepared by adding 25 cc of a strong alcoholic solution of gum mastic to one litre of distilled water. The conductivity of this stock mastic solution was 3×10^{-4} at 20° C.

(2) Bredig copper sol: this was made in the ordinary way by arcing between pure copper terminals held below the surface of distilled water. The conductivity of this solution was about 8×10^{-4} at 20° C and the concentration of the stock solution varied from 0.32 to 0.36 gram of copper per litre.

(3) Arsenious sulphide sol: prepared in the ordinary way by bubbling hydrogen sulphide gas through a solution of white arsenic. The sol was freed from excess of hydrogen sulphide by bubbling air through it. The conductivity was about 1×10^{-1} at 20° C and the concentration of the stock solution varied from 2.13 to 2.8 grams per litre for different samples.

The method of procedure was the same in each case. Preliminary experiments on a sample of given concentration fixed the amount of a given electrolyte necessary to produce coagulation. Then into each of five test-tubes were placed 30 cc of the given sample of sol and different numbers of drops of the electrolytic solution of known strength near the proper coagulating amount, were added to the different tubes, additional drops of purest distilled water being added in each case so as to bring the final volume up to the same for each test-tube. This was done for each concentration of the colloidal solution and after repeated trials the smallest amount of electrolyte which would cause the colloid to settle even after a considerable interval of time, and leave the liquid clear above, was determined. All of the solutions were treated in the same way as far as possible; each was shaken slightly after the electrolyte was added and the water used for dilution for a set of concentrations was of the same conductivity. The weak solutions as a rule took longer to settle so all of the solutions were allowed to stand some days before final examination.

TABLE IV

Gum Mastic Colloidal Solution

Coagulating concentration of electrolyte in millimols per litre

Electrolyte	Sol sample	Conductivity of original sol. 20°C	Percentage concentration in terms of original sol sample									
			100	50	33.3	25	16.6	10	6.6	5	3.3	2.5
Aluminium sulphate	I	2.88×10^{-5}	.043	.030	.024	.021	.015	.012	.009	.006	—	—
	II	3.79×10^{-5}	.036	.024	—	.015	.012	.009	—	.006	.006	.003
	III	3.10×10^{-5}	.061	.043	—	.030	—	.012	—	.009	—	—

TABLE V

Gum Mastic Colloidal Solution

Coagulating concentration of electrolyte in millimols per litre

Electrolyte	Percentage concentration in terms of original sol sample							
	100	50	25	16.6	10	6.6	5	2.5
Potassium chloride	205.2	243.0	297.7	464.7	631.6	—	—	—
Calcium chloride	11.53	—	(33%) 13.48	14.43	—	14.43	—	14.43
Aluminium sulphate	0.061	0.043	0.030	—	0.012	—	0.009	—

Electrical conductivity of original sol = 3.10×10^{-5} at 20° C.

In the cases of gum mastic and arsenious sulphide, we are dealing with negatively charged particles and consequently the metal ions in an electrolyte are the powerful coagulating ions. Series of experiments were carried out with solutions of the salts, potassium chloride, calcium chloride, and aluminium sulphate as examples of uni-, di- and trivalent metallic ions. In Table IV results using aluminium sulphate with three different samples of mastic solution are recorded; in Table V are given the results for the three above-named salts on the same stock solution of mastic. All of these results are illustrated graphically in Figs. 1 and 2.

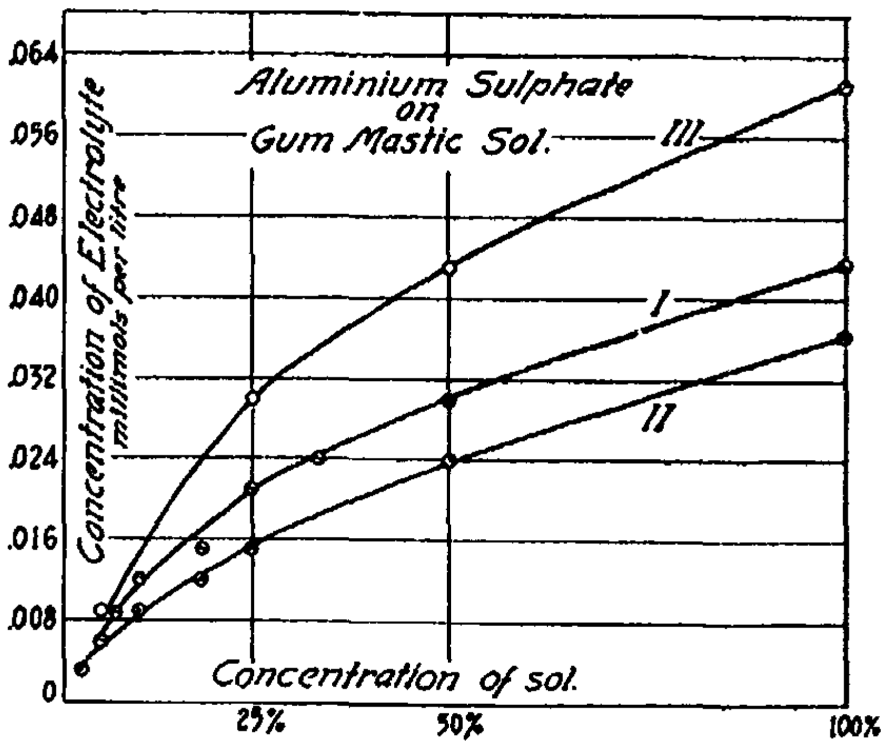

Fig. 1

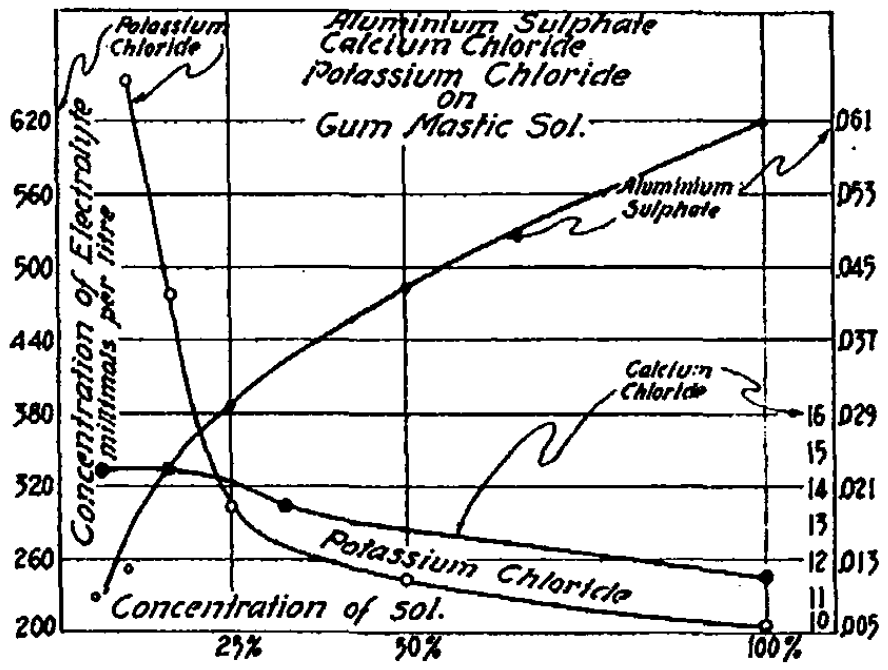

Fig. 2.

These results are, of course, not quoted from single experiments but are typical of numbers which can easily be duplicated. In Fig. 1 and Table IV we have an example of the nature of the agreement found in various experiments with the same colloidal solution but different samples.

In each curve, Figs. 1 to 4, the concentration of the disperse phase of the colloidal solution is plotted along the abscissa in percentages of the original concentration, which corresponds to the point at the extreme right; the ordinates give the concentration of the coagulating salt calculated in millimols per litre of the sample actually under observation.

In the first place, a glance at Table V shows the great variation in the concentration necessary to produce coagulation as one goes from univalent to divalent and trivalent ions; we get here numbers such as might be suggested by the Schulze-Linder-Picton law with proper values of x inserted.

However, when one compares how the concentration of the coagulating salt varies with the concentration of the particles in the colloidal solution, one is struck with the diverse nature of this variation. In every case, when dealing with a trivalent coagulating ion, the concentration of the coagulating ion varies almost directly as the concentration of the colloidal particles. Absolutely contrary to the variation with trivalent ions is that given by univalent ions; as the concentration of the colloidal particles is decreased, the number of electrolytic ions necessary per cc to produce coagulation actually increases—an increase which becomes very rapid as the concentration of the colloid is decreased further and further.

Intermediate between the univalent and trivalent ions are the divalent ions. In this case the necessary calcium ion concentration at first slightly increases as the concentration of the colloidal sol is decreased and then becomes constant for further decrease in colloidal concentration. Whereas the variation in electrolytic concentration in the case of univalent ions is from 205.2 to 631.6 and in the case of trivalent from 0.061 to 0.009, while the corresponding variation of the divalent concentration is from 11.5 to 14.4, we may probably be justified in treating the concentration of the divalent ion as sensibly constant.

The striking conclusion from these results is that manifestly if we are to select any numbers by which to test such a law as the Schulze-Linder-Picton law, it is of the utmost importance to take the concentration into account. From Table V we see at once that the ratios given between the coagulating powers (C_1, C_2, C_3) of the various ions at maximum and one-tenth maximum concentration of the colloid are, respectively, given by

$$\frac{1}{C_1} : \frac{1}{C_2} : \frac{1}{C_3} = 205.2 : 11.5 : 0.06 \text{ and } 631.6 : 14.4 : 0.012$$

from which we deduce that

$$C_1 : C_2 : C_3 = 1 : 17.4 : 3333 \text{ and } 1 : 44 : 52000.$$

TABLE VI

Arsenious Sulphide Colloidal Solution

Coagulating concentration of electrolyte in millimols per litre

Electrolyte	Percentage concentration in terms of original sol : 2.8 grms. per litre					
	100	50	25	16.6	6.6	2.5
Potassium chloride	59.3	67.8	76.3	80.5	89.0	106.0
Zinc sulphate	0.591	0.738	0.738	0.738	0.738	0.886
Aluminium sulphate	0.017	0.014	0.012	0.012	0.012	0.012

Electrical conductivity of original sol = 8.45×10^{-5} at 20° C.

In Table VI, similar results are recorded for the colloidal solution arsenious sulphide; the table gives comparable results for potassium chloride, zinc sulphate and aluminium sulphate on one and the same sample of arsenious sulphide. Fig. 3 illustrates the results of this table and shows exactly the same characteristics as the mastic curves.

In the case of colloidal copper since the particles are positively charged, the powerful ions are the acid radicle ions;

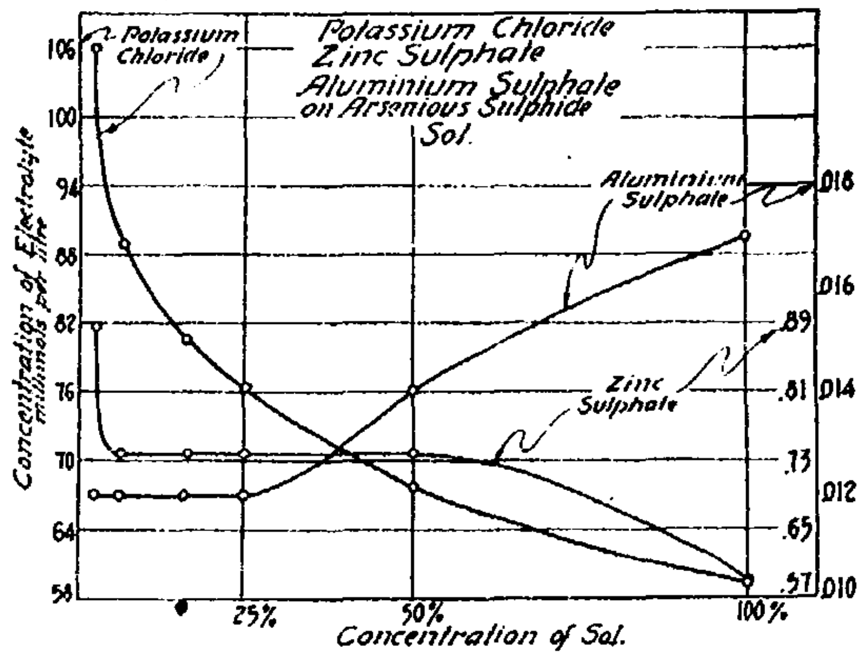

Fig. 3

as sources of typical uni-, di- and trivalent ions solutions of potassium chloride, potassium sulphate and potassium phosphate were used. The results are given in Table VII; the

TABLE VII

Copper Colloidal Solution

Coagulating concentration of electrolyte in millimols per litre

Electrolyte	Percentage concentration in terms of original sol : 0.32 grms. per litre					
	100	50	33.3	16.6	10	5
Potassium chloride	1.83	2.14	2.14	2.29	2.75	3.21
Potassium sulphate	0.041	0.041	0.041	0.041	0.041	0.044
Potassium phosphate	0.044	0.020	0.017	0.011	0.006	0.005

Electrical conductivity of original sol = 7.52×10^{-6} at 20° C.

table gives comparable effects of the three named salts on one and the same sample of copper colloidal solution. Fig. 4 illustrates the results of this table, and here again we have results for the action of uni-, di- and trivalent negative ions similar to results of the positive ions, a circumstance

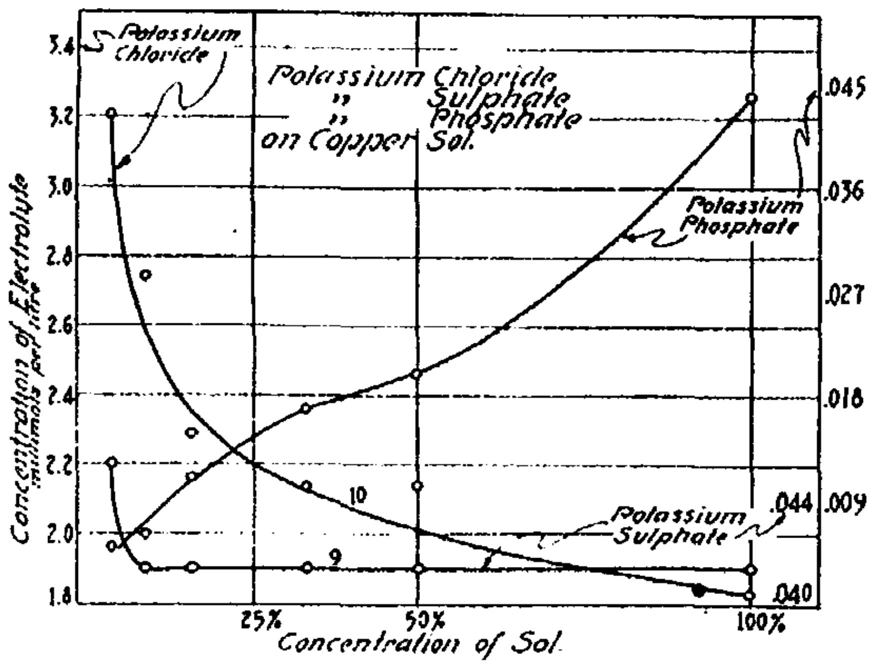

Fig. 4

which points to some far-reaching, underlying reason for this curious relation between coagulating power of ions and the concentration of the colloidal solution.

III. Conclusions

As a conclusion to these experiments we may say that the coagulative power of any given ion varies with the concentration of the disperse phase of the colloidal solution according to the following laws:

I. For univalent ions the concentration of ion necessary to produce coagulation increases with decreasing concentration of the colloid—this increase being very rapid with low concentrations of the colloid.

II. For divalent ions the concentration of ion necessary to produce coagulation is almost constant and independent of the concentration of the colloid.

III. For trivalent ions the concentration of ion necessary to produce coagulation varies almost directly with the concentration of the colloid.

As has been shown formerly in the work of Neisser and

Friedemann,[8] Bechhold,[9] Buxton and his co-workers,[10] and Burton,[11] on such solutions as mastic, platinum, gold and silver, there exist what have been called coagulation zones. That is, if one adds to various samples of the colloidal solution gradually increasing amounts of an electrolyte containing a coagulating trivalent ion, coagulation is produced when a certain concentration of this ion is reached and then for larger concentrations coagulation does not take place so readily. It is found, in this latter region, that the charge on the particle has been changed, as though the particle had adsorbed an overdose of the coagulating ion and had thereby been stabilized. Larger and larger concentrations of the electrolyte again causes rapid coagulation.

However, in the above experiments we can hardly be encountering this phenomenon because in all cases the coagulation observed was that which first appears, i. e., coagulation by a minimum quantity of electrolyte.

By contrasting the action of univalent and trivalent ions as the colloidal solution is diluted one is driven to the conclusion that we are dealing with two widely differing phenomena. That is, the essential mechanism by which univalent ions cause coagulation must be quite different from that by which trivalent ions produce this result. Or, from another point of view, there are possibly several elements entering into the process of coagulation. One set of these elements is particularly accentuated when one deals with univalent ions, another set is predominant in the use of trivalent ions. For example, on account of the very large amount of electrolyte added for the univalent ion compared with the amount added for the trivalent ion, the electrical conductivity in the former case is very considerably higher than in the latter case. Now if electrical conductivity is for any reason a potent factor in causing coagulation—a circumstance that may very well be—the influence of this factor might easily dominate the action with univalent ions but be of quite secondary importance in the case of trivalent ions. Combined with such an effect, there might be an influence of valency quite in the way that Whetham pictures it (or of adsorption as Freundlich pictures it) which might be the dominant feature with the trivalent ion but of secondary importance with the univalent ion.

That some such combination of effects is working is suggested by the relative action of the divalent ions as the colloidal solution is diluted. The averages of the ordinates of two of the curves in Figs. 2, 3 and 4, respectively, would give curves not unlike the third curve in each of these figures. In any of these cases by altering the potency which we assign to the trivalent ion effect in relation to the univalent ion effect, we could actually reproduce the divalent curves.

Such considerations would justify one in enunciating the following principles of coagulation:

I. There are, at least, two properties of the system made up of the colloidal solution plus electrolyte which have influence in determining the coagulating power of any ion.

II. These two influences are such that they tend to counteract one another to a certain extent.

III. These influences are such that one of them dominates the action of univalent ions, while the other dominates the action of trivalent ions. In the action of divalent ions, the two influences seem to be somewhat equalized.

There are many possibilities to suggest for these influences. In addition to electrical conductivity and valency cited above, we must remember that in all this work the influence of the ion bearing the same charge as the colloidal particle has almost always been ignored. This has often been commented on (see Bancroft,[6] Ostwald[7]). It does seem unscientific to ignore completely this ion charged similarly to the colloidal particle; one would suspect that it would oppose the action of the other ion. Now in dealing with the coagulating power of a univalent ion one always has present in the solution in equimolar concentration another ion of equal or greater valency, while in testing a trivalent ion, there is present in equimolar concentration another ion which is always of less valency than the ion tested. A proper appreciation of the concomitant action of these other ions charged similarly to the colloidal particle may throw a flood of light on the whole process of coagulation by electrolytes. In particular, this other ion may have a peptizing effect, or its presence in solution may exert a definite effect on the adsorption of ions by the colloidal particle. An exhaustive series of experiments with a carefully selected list of electrolytes, introducing as many combinations of valency as possible, would undoubtedly be of use provided a colloid of constant concentration were used throughout.

[1] Hans Schulze: Jour. prakt. Chem., **25,** 431 (1882); **27,** 320 (1883); **32,** 390 (1884).

[2] Linder and Picton: Jour. Chem. Soc., **67,** 63 (1895).

[3] H. Freundlich: Kapillarchemie, **1909;** Zeit. phys. Chem., **73,** 385 (1910); **79,** 168 (1912); **80,** 564 (1912); **85,** 641 (1913); **86,** 458 (1914); later papers in Kolloidchem. Beihefte, **1915** and **1916.** Ishizaka: Zeit. phys. Chem., **83,** 97 (1913).

[4] Whetham: Phil. Mag., (5) **48,** 474 (1899); "Theory of Solution," 396 (1902).

[5] Robertson: "Physical Chemistry of Proteins," 114 (1918).

[6] Bancroft: Second Report on Colloid Chemistry, Brit. Ass. Adv. Sci., 2 (1919); Jour. Phys. Chem., **19,** et seq.

[7] Wo. Ostwald: Zeit. Kolloidchemie, **26,** 28, 69 (1920).

[8] Neisser and Friedemann: Münch. med. Wochenschr., *11* (1903).

[9] Bechhold: Zeit. phys. Chem., **48,** 385 (1904).

[10] Buxton and co-workers: Zeit. phys. Chem., **57,** 47, 64, 76 (1907); **60,** 469, 489 (1908); Jour. Med. Research (Boston), **20,** 113, 311 (1909).

[11] Burton: Phil. Mag., (6) **12,** 476 (1906); "Physical Properties of Colloidal Solutions," 151 (1916).

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THE EFFECT OF ADSORBED GASES ON THE SURFACE TENSION OF WATER

BY SHANTI SWARUPA BHATNAGAR

The experiments of Stöckle and Meyer[1] on the surface tension of mercury in the atmosphere of various gases and in vacuum indicate that the adsorbed gases have a definite effect on the value of the surface tension.

Freundlich[2] is of the opinion that the differences between the static and the dynamic determinations of the surface tension of mercury are due to the adsorption of gases by mercury. In a thorough review of the problem, Bancroft[3] emphasizes the part played by adsorbed gases on the value of surface tension. These observations are, however, applicable only to the surface tension of mercury, as there are probably no data in literature as to the way in which the surface tension of water is affected by adsorbed gases.

The values of the surface tension of water obtained in vacuum in presence of the vapor of the liquid only, leave much to be desired. The liquid contains a lot of adsorbed gases, while the capillary tubes or the spherical disks employed for the determination of the surface tension have large quantities of adsorbed gases sticking hard to their surfaces. It was in order to obtain a value of the surface tension free from these effects that the following investigation was undertaken. Later, when the apparatus for determining T free from these effects had been designed, a few experiments were performed to see how the adsorption of various gases affected the value of T for water.

Selection of Method

Out of the numerous methods for determining surface tension, there is only one which can be conveniently tried in vacuum and that is the classic "capillary tube" method.

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[1] Freundlich: Kapillarchemie, 86 (1909).

[2] Kapillarchemie, 85 (1909).

[3] Theory of Emulsification, Part VIII. Jour. Phys. Chem., 20, 1 (1916).

This method is, however, subject to defects of inaccuracy and lack of sensitiveness, and although it is possible to minimize these defects by using a number of capillary tubes, i. e., by trying the "capillary multiplier method," it is very difficult, if not impossible, to remove adsorbed gases from the surface of such delicate and difficult-to-handle stuff. The dangers of destroying the uniformity of the bore of the capillary, and of producing distortion in the tube on strong heating, are numerous. Besides, the error due to the presence of adsorbed gases in the body of the glass will be greater in the capillary method than in the disk method, for, proportionate to the amount of water in contact a larger area of glass-surface is exposed to the liquid in the "capillary multiplier" method than in the disk method. The analytical problem of evaluating surface tension by the disk method, i. e., from a knowledge of the forces required to detach a circular disk from the surface of a liquid had been solved approximately by Laplace and Poisson, and advocated as an experimental method by Gay-Lussac,[1] Buys-Ballot,[2] Merian,[3] and Hagen.[1] Ferguson[5] has found that the solution of Laplace is faulty for disks of radii less than 7 or 8 cm. Ferguson, on analyzing the problem, gets

$$P = 2Ag\rho\left(a - \frac{a^2}{3r} - \frac{a^3\sqrt{2}}{3r^2}\right)$$

where P is the pull required to detach the disk, A its area, *g* the gravity constant, and ρ the density of the liquid and the *r* the radius of the disk.

This result is in agreement with that of Laplace's if the term in r^2 be suppressed. Whether such a suppression is legitimate or not depends upon the relative values of *r* and *a*. The effect of this third term in the equation, as pointed out by Ferguson, is appreciable, and can be negligible only when

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[1] Quoted by Laplace, op. cit., 54.

[2] Pogg. Ann., **71**, 177 (1847).

[3] Ibid., **73**, 485 (1848).

[4] Ibid., **77**, 449 (1849).

[5] Phil. Mag., (6) **25**, 507 (1913).

the disk has a radius of more than 7 or 8 cm. Ferguson has discussed at length the disadvantages, both practical and theoretical, arising from using a flat disk,[1] and he has suggested an ingenious method to minimize these defects by substituting for the disk, a segment of a sphere partly immersed in the liquid, so that the liquid touches the sphere round a small circle. The analysis of the forces acting on the sphere in contact with the liquid brings out the equation

$$M = 4\pi\rho a^2 \left\{ R - \frac{\sqrt{aR}}{3} - \frac{a}{3} \right\}$$

where m = weight required to detach the circular disk from the surface of water.

R = Radius of the sphere.

ρ = Density of the liquid.

Finding m, we can easily obtain the value of a^2 from the equation

$$a^2 = \frac{T}{g\rho}$$

where T is the surface tension and g the gravity constant. Thus we can evaluate T from a knowledge of m.

Use is made of this mathematical analysis by Ferguson in experiments described here, and a modification of Ferguson's apparatus suitable for the requirements of this investigation has been employed to find the value of the surface tension.

Description of the Apparatus and Experimental Work

The one obvious inconvenience in Ferguson's method was the balance. In order to avoid a big balance, a suitable spring was selected and used as a Jolly's balance, which easily gives accurate values to four significant figures. Now it is not possible to use a large sphere of radius from 7 to 8 cm. with a fine sensitive spring without risking elastic fatigue of the spring.[2] The next thing, therefore, was to find a suita-

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[1] Loc. cit.

[2] The spring used did not suffer from fatigue of elasticity for weights ranging up to 28 gms. The total pull in gms. has never exceeded 22 gms. in these experiments.

ble substitute for the sphere. A flat disk could not be a fit substitute for this sphere for reasons pointed out by Ferguson[1] in his paper on "The Solid Sphere in Contact with Liquid." A segment of a quartz sphere was therefore obtained from one of the best opticians here, and carefully tested for any irregularities of surface. It was found that the surface of curvature was quite regular.

In the centre of the spherical disk was cemented a millimeter quartz scale, after the disk had been carefully cleaned with alternate washings of HNO_3, KOH, alcohol, and boiling distilled water. The hook at the free end of the scale was then connected to the spring which hung freely in the glass tube C (Fig. 1), provided in the centre of a tightly-fitted brass cover B on a stout cylindrical jar of glass A. The brass cover was further perforated for admitting a tin condenser T and for passing any gases through the delivery tube D, and for connecting the whole apparatus to the air pump and manometer at *a*. A blank experiment was performed with the disk

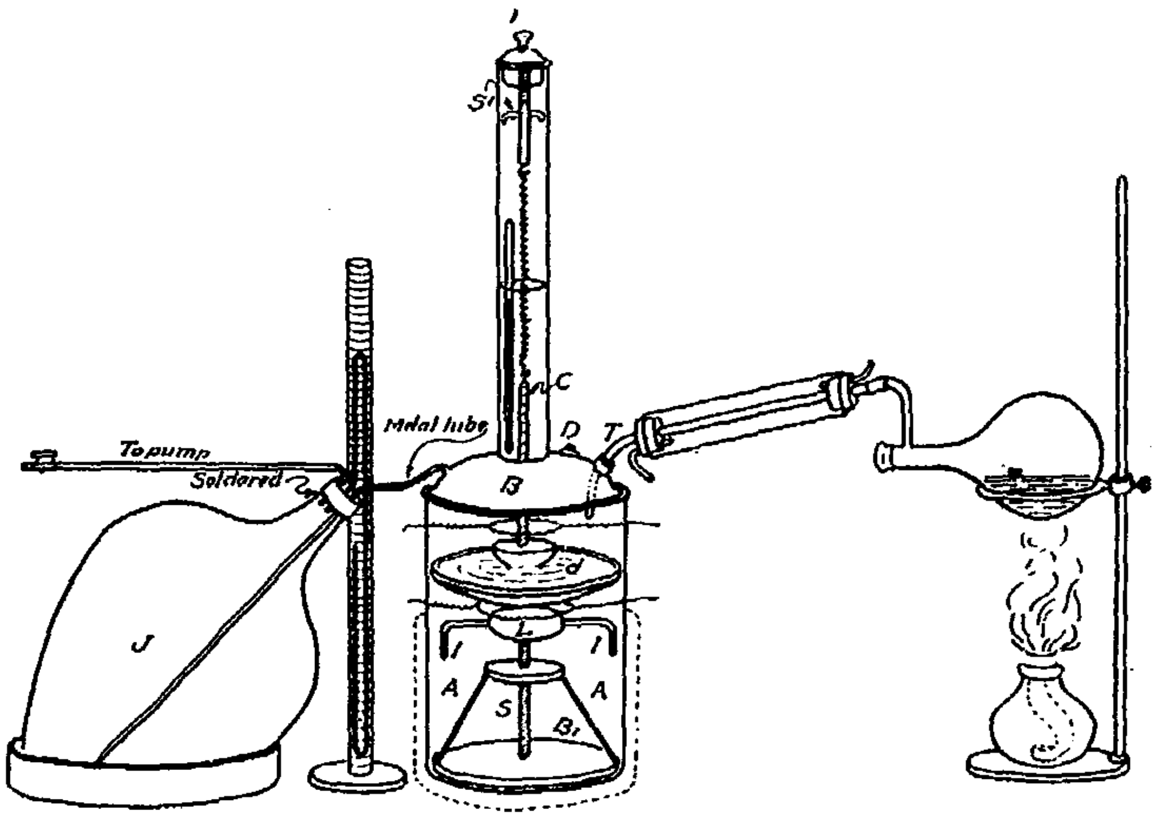

Fig. 1

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[1] Loc. cit.

in order to find out the approximate length to which the vessel containing water had to be lowered to detach the disk from the surface of the liquid. This helped in choosing the length and size of the screw S, which passed through the centre of a fine brass support B′ and was attached at one end to a lever L of the form shown in the diagram. The end pieces of the lever were of iron so that the screw could be raised or lowered at will by means of an electromagnet from outside the jar. The nickel-plated dish was cemented to the brass lever L and the perfect hemisphere attached to the spring balance hung in the centre of the disk as shown in the diagram. The tin condenser T was attached to the still as shown in the diagram. The latter consisted of an inverted distilling flask, the end of whose delivery tube was thinned down in the form of a jet and slipped into the tin condenser. The whole apparatus was arranged as shown in Fig. 1, which is self-explanatory. The opening at D was closed by means of a solder when readings in vacuum were taken. The brass cover, B, was made air-tight by means of a preparation of rosin and beeswax in equal quantities. Very careful experiments were made to calibrate the screw in order to calculate lengths in terms of the turning of the screw. A celluloid scale divided in 344 mm was pasted round the jar to find out the actual length if the screw moved even to a fraction of a complete round. The method employed for calculating length correct to four significant figures to which the disk was lowered in order to detach the disk from the surface of water and for converting the pull in terms of the weight, is given later. The methods for finding out the radius of curvature of the spherical disk are also described later.

In order to take readings for evaluating the surface tension in vacuum the apparatus was exhausted by a good Toepler's pump, and all the precautions described later were observed. The manometer readings were 0.006 mm. When the adsorbed gases from the sphere had been removed as much as possible by heating the sphere in a coil of resistance wire by electric current, the water was then distilled through the tin condenser by applying a very low flame to the inverted distilling flask. The condensed water was allowed to trickle in the nickel dish till it was very nearly full. The distilling was then stopped and the water was allowed to stand till it acquired the constant temperature of the thermostat. The sphere was next brought in position by adjusting the screw head S′ by an electro-magnet and the disk was gradually raised by means of the electro-magnet till the water surface just touched the apex of the sphere. This was easily noticed by a sudden swing of the spring scale downwards. Next the position of the pointer attached to the lever was noticed. The screw was then lowered by means of the electro-magnet, and the number of rounds being noted all the while till the disk was detached from the liquid surface. The number of rounds and the fractions calculated by noting the position of the pointer on the scale when the disk was just detached gave the measure of the pull in centimeters. This was repeated several times and consistent readings were obtained. For obtaining a number of consistent readings one precaution is necessary. When the first reading has been taken the disk attaches a drop of water with it which should be removed by allowing the disk to stand for some time in vacuum and letting the drop evaporate by a further vigorous motion of the air pump and by drying it further in the heated coils. For working this apparatus in the atmosphere the tube at D was opened to allow in a known quantity of the required gases from a reservoir with suitable arrangements for the drying and purification of the gases in question. The precautions observed in each case are treated under separate headings. For repeating the observation, the whole series of precautions had to be taken over again, and the quantity of gases admitted was always kept equal. No results were obtained to find the change of T with change in time. The next step was to convert the value of pull exerted in terms of weight. This was done by very carefully adding weights to the disk till they produced an equally long lowering of the spherical disk. A travelling microscope was used to see that the lowering produced by the addition of weights was exactly identical to that produced by the pull due to surface tension. The weight thus obtained gave us the *m* of the equation.

The experiments were tried in vacuum and in an atmosphere of air, carbon dioxide, hydrogen, carbon monoxide, and nitrogen, and the special precautions in individual cases are described under the experimental data of these individual cases. The following are the general precautions which have been taken throughout the work.

PRECAUTIONS

I. The Purification of Water From Absorbed Gases and Other Impurities

In order to see that the water contained no absorbed gases the following precautions were taken:

(*a*) The water was distilled in vacuum.

(*b*) A fresh sample of such distilled water was used in different experiments. After making a set of observations under one condition the water was siphoned off through the opening at D and a fresh sample distilled over again for immediate use in the next set of observations so that the water left little to be desired regarding freedom from absorbed gases.

In order to remove the possibilities of dissolved and volatile impurities from the water, the following precautions were taken:

(*a*) A sample of laboratory distilled water was redistilled through a Liebig's condenser, and the water examined for possible impurities of silicates and ammonia. The presence of both the impurities was noticed.

(*b*) In order to free the distilled water completely from volatile nitrogenous organic compounds it was necessary to redistil it after adding solutions of potassium permanganate and caustic potash. The examination of the water so distilled showed it to be perfectly free from ammonia, and gave no coloration with Nessler's solution.

(*c*) The presence of silicates though very slight, must be due to the glass condenser which was used in the blank experiment. This was replaced later by a tin condenser. A sample of the tin of which the condenser was made was analyzed and found to be free from lead, arsenic, and zinc. On redistilling water through this new condenser the silicates also disappeared.

II. Selection of the Dish

The dish *d*, in which water is distilled in order to contain as little of occluded gases as possible, should have the following qualifications:

(*a*) It should be smoothed on the lathe in order to remove all points and angularities for the gases are more readily adsorbed at points than at a smooth surface.

(*b*) It should be made of a tough poreless metal.

(*c*) It should be made of a substance which is not acted upon by water and the gases (air, carbon dioxide, etc.) under the conditions of the experiment.

In these experiments a very carefully lathed and smooth nickel-plated nickel dish was employed, which was carefully cleaned for impurities such as grease, dust, etc., and finally carefully dried by heating by an electric current in vacuum.

III. The Cleaning of the Spherical Disk

The edges of the spherical disk had been very finely rounded by an expert optician. The disk was then carefully cleaned by alternate washings of nitric acid, caustic potash and alcohol, and was further boiled for 15 minutes in distilled water. The adsorbed gases were removed by heating it in a coil of resistance wire in high vacuum. This heating was continued for several hours.

IV. Other Precautions

In order to remove moisture from the apparatus a big bottle, J, full of concentrated sulphuric acid and several bottles of calcium chloride and other dehydrating agents, were included through (*a*) near the pump.

V. Temperature Control

The temperature was kept constant in a thermostat.

CALCULATIONS

Calibration of the Screw

The screw S was calibrated according to the following methods:

The outer jar, A, with the brass stand B and the screw and the lever L in position were arranged as shown in the diagram (2). The nickel dish was cemented to the lever L and the stand on which the jar A was placed was levelled by moving the bottom screws of the stand. Water was then put in the dish and a light float (Fig. 2) made by blowing a thin flat bulb at the end of a fine capillary tube was used as an index. The cross-wires of the telescope of a cathetometer were fixed on the mark M on the float, and the position of the two marks on the end pieces of the lever were also noticed. The electro-magnet was then brought into play, and the distance through which the mark M moved when a number of complete half-rotations of the screw took place was measured by the cathetometer. The following table gives the results obtained:

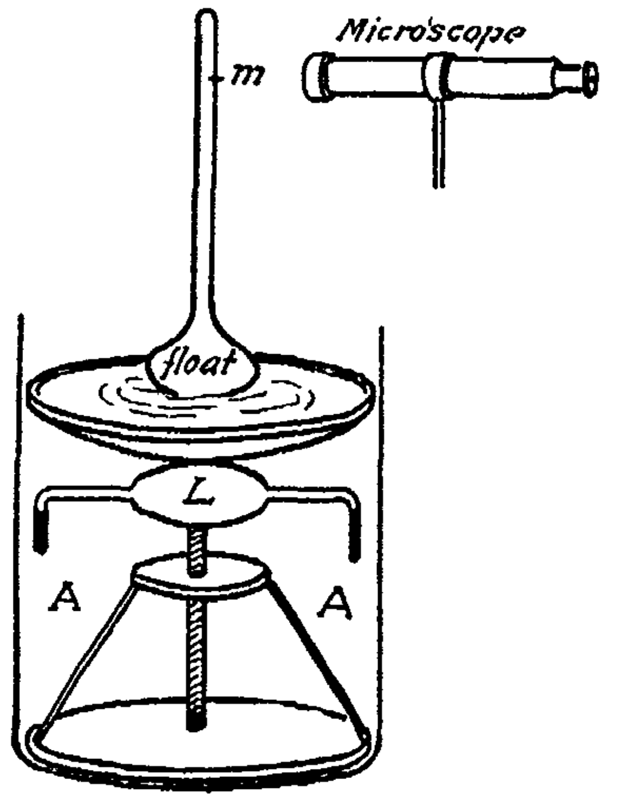

Fig. 2

Position of the mark M	Nos. of the ½-turn of the screw	Position of the mark M after the turning of the screw	Difference	Value in cm of the lowering produced by one comp. rotation
16.8515	2	16.725	0.1265	0.1265
16.725	2	16.600	0.125	0.125
16.6	4	16.345	0.255	0.1265
16.35	4	16.104	0.246	0.123
16.104	6	15.729	0.375	0.125
				Mean 0.125

Thus by noting the complete rotation of the screw it is possible to find the lowering of the level of the water accurately to four significant figures. If, however, the screw, instead of making a complete rotation, stands somewhere say at one-fourth of a complete rotation, the problem becomes a little difficult. In order to find out the value of the lowering of the screw in cm for even a part of fraction of a complete rotation, a thin celluloid scale was pasted round the jar A and the circumference was divided into 344 equal parts so that the movement of the pointer of the screw to any part of the scale indicative of the slightest movement of the screw could be calculated, one part being equal to $\frac{0.125}{344} = 0.0036$ cm, so that this afforded a very good and easy method of finding out the pull in terms of length by the simple counting of the complete rotation and part rotations of the screw. The pull was checked frequently by a cathetometer and gave concordant results.

Measurement of the Radius of Curvature

The measurement of the radius of curvature presented some difficulties. The sphereometers which were available did not fit the spherical disk. They were always a little too big for it. Consequently the following three methods were employed:

I. The convex surface of the spherical disk was silvered in the laboratory, and the radius of curvature measured according to the following method:

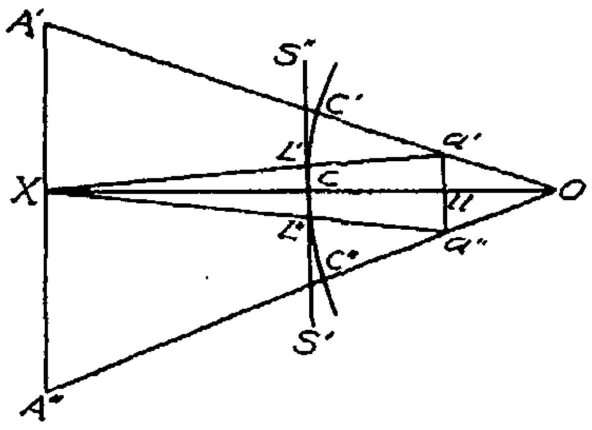

Fig. 3

Let O (Fig. 3) be the center of the reflecting surface, and OC the axis.

Suppose two objects, A', A'', placed at equal distances on each side of OC, and at the distance O from O.

Images of these two points will be formed by reflection at points a', a'', on the axes OA′, OA″, such that (calling the points where the axes OA, OA′ cut the spherical surface C′, C″.

$$\frac{1}{A'C'} - \frac{1}{a'c'} = -\frac{2}{OC}$$

or

$$\frac{1}{A'C'} = \frac{1}{a'c'} - \frac{2}{OC}$$

and

$$\frac{1}{A''C''} = \frac{1}{a''c''} - \frac{2}{OC}$$

Now the points being very distant, and therefore C′A′ very nearly equal to CX, we may assume that the straight line $a'a''$ cuts the axis OCX at a point u.

$$\frac{1}{CX} = \frac{1}{Cu} - \frac{2}{OC} \qquad (1)$$

and for the size of the image, we have

$$\frac{a'a''}{A'A''} = \frac{Ou}{OX} \qquad (2)$$

Hence, if CX = A, OC = r, A′A″ = L, Cu = x, and $a'a''$ = λ, we get from (1)

$$\frac{1}{A} = \frac{1}{x} - \frac{2}{r} \qquad (3)$$

Hence,

$$\frac{1}{A} + \frac{1}{r} = \frac{1}{x} - \frac{1}{r}$$

$$\therefore \frac{r + A}{A} = \frac{r - x}{x}$$

and therefore

$$\frac{x}{A} = \frac{r - x}{r + A}$$

and

$$\frac{\lambda}{L} = \frac{r - x}{r + x} \quad \therefore \frac{\lambda}{L} = \frac{x}{A}$$

From these two equations

$$x = \frac{Ar}{2A + r}\text{ and } \lambda = \frac{r}{2A + r}$$

Place a finely divided scale S″S′ immediately in front of the reflecting surface (but not so as to prevent all light falling on it; i. e., place it horizontally to cover nearly half the reflecting surface), and observe the images a', a'', and the scale S″S′ by means of a telescope so that its object-glass shall be as nearly as possible in the middle of the line AA′. The length L′L″ intercepted by the scale in this experiment was very carefully measured by means of a travelling microscope, and the points A′A″ were lighted by means of a single-filament electric lamp. Let the object-glass be at X, let L′L″ $= l$. Then joining Xa', Xa'', we get[1]

$$\frac{l}{\lambda} = \frac{\mathrm{XL}'}{\mathrm{X}a'} = \frac{\mathrm{A}}{\mathrm{A} + x}$$

$$\therefore l = \frac{\mathrm{A}}{\mathrm{A} + x} \times \frac{\mathrm{L}r}{2\mathrm{A} + r'}$$

or

$$1 = \frac{\mathrm{A}}{\mathrm{A} + \dfrac{\mathrm{Ar}}{2\mathrm{A} + r}} \times \frac{\mathrm{L}r}{2\mathrm{A} + r} = \frac{\mathrm{L}r}{2(\mathrm{A} + r)}$$

or

$$r = \frac{2\mathrm{A}l}{\mathrm{L} - 2l}$$

To make use of this method to find the radius of the curvature of the surface, place the surface opposite to, but at some distance from, a window. Then place horizontally a straight bar of wood, about half a meter in length between the surface and the window, fixing it with its ends equidistant from the surface, and at such a height that its reflection in the surface is visible to the eye placed just below the bar, and appears to cross the middle part of the surface. Fix a telescope under the centre of the bar with its object-glass in the same vertical plane as the bar, and focus it so as to see the image reflected in the surface.

It is best that the whole of the bar should be seen reflected in the surface. To accomplish this two well-defined patches of light from two single-filament lamps, the reflected images of which can be seen clearly, are allowed to fall through two points in the bar.

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[1] Cf. Practical Physics by Glazebrook and Shaw.

Now place against the reflecting surface a finely graduated scale, arranging it so that one edge of the image of the reflecting filament mark is seen against the divided edge of the scale. This distance between the two images is measured by means of a travelling microscope. This gives us the length l of the above formula. Measuring the length of the bar or the distance between the two sources of light gives us L; and measuring with a tape the distance between the reflecting surface in the center of the object-glass of the telescope, gives A. The following are the data:

Distance between the two points in the travelling microscope:

0.516 0.516 0.516 Mean, 0.616 cm.

Distance between the two filament lamps, 83.75 cm.

Distance between the reflecting surface and the object-glass 401.485 cm.

Substituting these values we get R.

$$= \frac{2Al}{L - 2 - l} = \frac{2 \times 0.516 \times 401.485}{83.75 - 1.032} = \frac{1.032 \times 401.485}{82.718}$$

$$= \frac{414.3}{82.718} = 5.007 \text{ cm.}$$

II. Sphereoscopic Method

In principle this method is essentially identical with the sphereometric method. The only difference is that there the rotation of a needle indicates the radius of the curvature so that if the rotation of the needle produced by a known curvature is noted, the curvature of any other surface can be calculated from the readings of the rotation produced in the sphereoscope. The best way to accomplish this is to get a number of readings by known movements by the legs of the sphereoscope, and to obtain a curve from these readings. The following readings were taken by adjusting the instrument against a fine screw gauge. A large number of readings were taken to obtain a good curve. The R can be read directly from the curve which can be obtained from the equation for the spherometer by plotting the following readings of the instrument:

Readings on the instruments	Repetition	Readings on the instruments	Repetition
—14.80	—14.72	2.43	3.37
—13.35	—13.28	4.00	3.82
—11.85	—11.82	5.40	5.30
—10.42	—10.42	6.85	6.80
— 9.00	— 8.98	8.30	8.22
— 7.67	— 7.68	9.63	9.65
— 6.28	— 6.30	11.58	11.20
— 4.80	— 4.88	12.82	12.68
— 3.33	— 3.50	14.20	14.20
— 1.92	— 1.93	15.75	15.58
— 0.45	— 0.00	17.23	17.18
1.00	0.90	18.93	19.02

III. The lens was further tested by the Professor in charge of the Opthalmic Department of the local Medical College, and the value of R obtained by the ophthalmometer was exactly 5.007 cm.

EXPERIMENTAL DATA AND CALCULATION OF T THEREFROM

The following observations were taken at 15° C:

IN VACUUM[1]

No. of observations	No. of complete half turns of the screw	No. of part turns of the screw	Final value of the pull in cm	Value of pull in terms of mass
1	32	143		
2	32	142.8		
3	32	140.8		
4	32	140.5		
5	32	144.5		4.1411
6	32	143.[illegible]		
7	32	140.8		
8	32	140.3		
Mean	32	141.8	2.066	4.1411

Now substituting the value of m and R and π and ρ in the equation

$$m = 4\pi\rho a^2 \left\{ R - \frac{\sqrt{aR}}{3} - \frac{a}{3} \right\}$$

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[1] Adsorbed gases removed at 0.006 mm.

We get

$$4.1411 = 4 \times \frac{22}{7} \times 0.999\, a^2 \left\{ 5.007 - \frac{\sqrt{a \times 5.007}}{3} - \frac{a}{3} \right\}$$

Solving this equation by Hornel's method of approximation, we get $a^2 = 0.0735$.
Now

$$a^2 = \frac{T}{g\rho}$$

where g is the gravity constant.

$$\therefore\ T = 0.0735 \times 0.999 \times 979.7$$
$$= 71.30 \text{ dynes.}$$

Special Precautions

The same as given above.

IN CARBON MONOXIDE

No. of observations	No. of complete half turns of the screw	No. of part turns of the screw	Final value of the pull in cm	Value of pull in terms of mass
1	32	323		
2	32	322		
3	32	329.7		
4	32	322.6		
5	32	323.8		
6	32	321.8		
7	32	321.8		
Mean	32	324.01	2.1301	4.237

Now substituting the value of m and R and π and ρ in the equation

$$m = 4\pi\rho a^2 \left\{ R - \sqrt{\frac{aR}{3}} - \frac{a}{3} \right\}$$

we get

$$4.237 = 4 \times \frac{22}{7} \times 0.999 \times a^2 \left\{ 5.007 - \sqrt{\frac{5.007 \times a}{3}} - \frac{a}{3} \right\}$$

Solving this equation by Hornel's method of approximation, we get $a^2 = 0.07527$.

Now

$$a_2 = \frac{T}{g\rho}$$

where a^2 is the gravity constant.

$$\therefore T = 0.999 \times 979.7 \times 0.07527$$
$$= 73.00 \text{ dynes.}$$

Special Precautions

1. The gas was prepared by the action of concentrated sulphuric acid on formic acid.

2. The gas before being stored in the reservoir passed through two wash-bottles—one containing water and the other caustic potash.

3. The gas from the reservoir was connected to the apparatus through a spiral tube in order to arrest particles of water which may splash off with the gas.

In Nitrogen

No. of observations	No. of complete half turns of the screw	No. of part turns of the screw	Final value of the pull in cm	Value of pull in terms of mass
1	32	323		
2	32	322		
3	32	329.7		
4	32	322.6		
5	32	323.8		
6	32	321.8		
7	32	321.8		
Mean	32	324.0	2.13	7.237

Now substituting the value of m and R and π and ρ in the equation

$$m = 4\pi\rho a^2 \left\{ R - \sqrt{\frac{aR}{3}} - \frac{a}{3} \right\}$$

we get

$$4.237 = 4 \times \frac{22}{7} \times 0.999 \times a^2 \left\{ 5.007 - \sqrt{\frac{a \times 5.007}{3}} - \frac{a}{3} \right\}$$

Solving this equation by Hornel's method of approximation, we get $a^2 = 0.07527$.

Now

$$a^2 = \frac{T}{g\rho}$$

when g is the gravity constant.

$$\therefore T = 0.7527 \times 979.7 \times 0.999 = \underline{\underline{73.00}} \text{ dynes.}$$

Special Precautions

1. The gas was prepared by heating ammonium nitrite in a strong round-bottom flask.

2. The gas as it issued out from the flask through the delivery tube passed through two wash-bottles, before being finally stored up in the gas reservoir for use in the instrument for determining surface tension.

IN HYDROGEN

No. of observations	No. of complete half turns of the screw	No. of part turns of the screw	Final value of the pull in cm	Value of pull in terms of mass
1	32	152		
2	32	150.8		
3	32	150.4		
4	32	150.4		
5	32	150.2		
Mean	32	150.7	2.07	4.227

Now substituting the value of m and R and in the equation

$$m = 4\pi\rho a^2 \left\{ R - \sqrt{\frac{aR}{3}} - \frac{a}{3} \right\}$$

we get

$$4.227 = 4 \times \frac{22}{7} \times 0.999 \times a^2 \left\{ R - \sqrt{\frac{aR}{3}} - \frac{a}{3} \right\}$$

Solving this equation by Hornel's method of approximation we get $a^2 = 0.0751$.

Now

$$a^2 = \frac{T}{g\rho}$$

when g is the gravity constant.

$$\therefore T = 0.999 \times 979.7 \times 0.0751 = \underline{72.83} \text{ dynes.}$$

Special Precautions

1. The gas was prepared by the action of dilute sulphuric acid on zinc.

2. The gas before entry into the apparatus passed through

a wash-bottle containing water, in order to dissolve all soluble impurities.

3. The wash-bottle through which the gas bubbled was connected by means of a fine spiral tube in order to arrest the water which may splash off with the gas.

4. The precautions described for carbon monoxide were also all observed with hydrogen.

EXPERIMENTAL DATA AND CALCULATION OF T THEREFROM

The following observations were taken at 15° C.

IN AIR

No. of observations	No. of complete half turns of the screw	No. of part turns of the screw	Final value of the pull in cm	Value of pull in terms of mass
1	32	322		
2	32	329		
3	32	322.6		
4	32	320.8		
5	32	322.4		
Mean	32	324	2.133 cm.	4.242 cm.

Now substituting the value of m and R and π and ρ in the equation

$$m = 4\pi\rho a^2 \left\{ R - \sqrt{\frac{aR}{3}} - \frac{a}{3} \right\}$$

we get

$$4.242 = 4 \times \frac{22}{7} \times 0.999 \times a^2 \left\{ 5.007 - \sqrt{\frac{a \times 5.017}{3}} - \frac{a}{3} \right\}$$

Solving this equation by Hornel's method of approximation we get $a^2 = 0.07535$.

Now

$$a^2 = \frac{T}{g\rho}$$

where g is the gravity constant.

$$\therefore T = 0.999 \times 979.7 \times 0.07538 = \underline{\underline{73.1}} \text{ dynes.}$$

Special Precautions

The same as given above.

In CO_2

No. of observations	No. of complete half turns of the screw	No. of part turns of the screw	Final value of the pull in cm	Value of pull in terms of mass
1	32	152		
2	32	150.8		
3	32	151.0		
4	32	150.4		4.228
5	32	151.0		
6	32	150.8		
7	32	152.8		
Mean	32	151.2	2.08	4.228

Now substituting the value of m and R and π and ρ in the equation

$$m = 4\pi\rho a^2 \left\{ R - \sqrt{\frac{aR}{3}} - \frac{a}{3} \right\}$$

We get

$$4.228 = 4\pi \times 0.999\, a^2 \left\{ R - \sqrt{\frac{aR}{3}} - \frac{a}{3} \right\}$$

Solving this equation by Hornel's method of approximation we get $a^2 = 0.07512$.

Now

$$a^2 = \frac{T}{g\rho}$$

where g is the gravity constant.

$$\therefore\ T = 0.999 \times 979.7 \times 0.07512 = 72.85 \text{ dynes.}$$

Special Precautions

The same as given above. The gas was prepared by the action of dilute sulphuric acid on pure sodium carbonate.

Summary and Discussion of Results

Atmosphere	Value of T at 15° C.
Vacuum	71.3
Hydrogen	72.83
Nitrogen	73.00
Carbon Monoxide	73.00
Carbon Dioxide	72.85
Air	73.1

1. The values of the surface tension for water obtained in various gases and in vacuum are shown in the table above.

It is interesting to note that the increase in value of T for water in gases is proportional to the rise in their densities, in all cases excepting for carbon dioxide. A conspicuous lowering of T in case of CO_2 may be explained on the solubility of the gas in water. Stöckle and Meyer's data on the value of T for mercury show a similar discrepancy with CO_2. In general, their results also indicate a rise in the value of T for a corresponding increase in the density of the gaseous atmosphere.

It has been endeavored throughout to exclude adsorbed gases as far as possible. It is intended to get still better results by using a Langmuir pump, by heating the disk to a still greater temperature, and by substituting for the brass lid a glass lid which can be sealed and made perfectly air-tight.

2. A slight modification has been proposed in the optical method of determining radius of curvature of curved surfaces by making use of single filament lamps and travelling microscopes for greater accuracy.

3. Results with substances like olive oil which have practically zero vapor pressure are reserved for a later contribution. It appears that when all gases are excluded from the apparatus, the pull in case of olive oil is much greater than when gases are present. This tends to show that perhaps the pull indicates the interfacial tension between quartz and oil. It is premature to draw a conclusion from this slender and solitary observation. An instrument is under construction in which a pull greater than those observed in the present investigation can be measured, and it is intended to obtain results in high vacuum, with all adsorbed gases removed as far as possible, with olive oil and other such materials having practically zero vapor pressure.

The author takes this opportunity of thanking Professor J. M. Benade for his help in constructing the apparatus and for the benefit of his expert advice in high vacuum experiments.

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THE TOXICITY OF MERCURIC CHLORIDE, AND ITS SOLUBILITY IN AQUEOUS ALCOHOL

BY J. STANLEY LAIRD

Among the solutions whose toxicity towards anthrax spores was studied by Paul and Krönig, was included a series containing one-sixteenth formula-weight $HgCl_2$ per litre (about 1.75 g. per 100 cc) of aqueous alcohol of various concentrations. They found a pronounced maximum of toxicity in the solution containing about 25% alcohol by weight.

For lack of a suitable immiscible solvent it seemed impossible to determine the chemical potential of the mercuric chloride in these solutions by the method employed with the phenol-salt solutions, and the problem was attacked from another angle.

The boiling points of solutions of mercuric chloride in water (from 4% to 20% $HgCl_2$) and in absolute alcohol (from 3% to 28% $HgCl_2$) have been determined by Beckmann.[1] In the aqueous solutions the "molecular weight" varied from 283 to 319, in the alcoholic solutions from 264 to 271. Thus for concentrations up to 5% or 6% mercuric chloride the amount of work necessary to double the concentrations of solutions containing a fixed amount of the salt is the same, within 7 or 8 percent, whether the solvent be water or alcohol. If it be assumed that the same holds true for solutions containing both water and alcohol—this seems a reasonable enough assumption, though there is no evidence available either way—then one of two things must follow: either (*a*) the toxicity of the aqueous-alcoholic solutions must depend on something other than the chemical potential of the mercuric chloride they contain, or (*b*) the solubility of mercuric chloride in aqueous alcohol of various strengths must show a minimum[2] in the neighborhood of 25% alcohol.

To decide this, I made up solutions containing from 10%

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[1] Beckmann: Zeit. phys. Chem., 6, 453, 460 (1890).

[2] Lash Miller: Jour. Phys. Chem., 1, 636 (1897).

to 51% by weight of alcohol, added powdered mercuric chloride in excess, and stirred at 18° C (the temperature of P. and K.'s experiments) until equilibrium was attained; 5 cc portions were then removed by a pipette, and their content of mercuric chloride determined by precipitation with hydrogen sulphide. The following are the results:

Ethyl alcohol	0	5	10	15	20	25	30	40	50	51	%
$HgCl_2$ in 100 cc	6.24	—	5.63	5.43	5.15	5.08	5.86	7.58	—	11.3	g
Colonies[1]	113	383	199	184	86	70	287	335	1824	—	

There is a pronounced minimum of solubility in 24% alcohol, corresponding closely to the maximum toxicity observed by Paul and Krönig.

The University of Toronto
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[1] Paul and Krönig: Zeit. phys. Chem., 21, 448 (1896).

THE TOXICITY TOWARDS STAPHYLOCOCCUS OF DILUTE PHENOL SOLUTIONS CONTAINING SODIUM BENZOATE

BY KENNETH E. BURGESS

The irregularities observed by Lemon[1] in his experiments on *staphylococcus* with low concentrations of phenol were referred by Laird[2] to plasmolysis of the cocci due to the low osmotic pressure of the solutions employed; if this explanation be the right one, addition of any indifferent substance in suitable concentration ought to remove the abnormality. At the suggestion of Prof. Lash Miller I put this conclusion to the test, in the winter of 1913–4.

Sodium benzoate was chosen, as that salt had less effect on the toxicity of phenol towards anthrax than any other of the dozen salts studied by Paul and Krönig; and as, according to Laird, two atmospheres is the lowest osmotic pressure that is at all safe, a twentieth-normal solution was employed. Blank experiments showed that decinormal sodium benzoate was better for the cocci; but unless a number of equilibrium determinations were to be made, it was obviously better to keep down the concentration of the salt.

Time	0	20	35	40	45	50	55	60	Minutes
N/30 sod. ben.	3000	1500	1500	—	100	—	55	—	colonies
N/20 sod. ben.	3000	2500	—	2500	—	1500	—	1000	colonies
N/10 sod. ben.	2000	1500	1500	—	—	1500	—	900	colonies
N/12 NaCl	3000	3000	3000	—	2500	2500	—	—	colonies

The determinations were made with a 24-hour culture of *staphylococcus pyogenes aureus*, following the technique used by Lemon; but much time and labor was saved by adding methylene-blue to a drop of the liquid and examining it under the microscope before pouring a plate. A high magnifying power was needed for these small objects (oil immersion,

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[1] Jour. Phys. Chem., 24, 570 (1920).

[2] Ibid., 24, 664 (1920).

1000 to 2000 diam.) and there were usually only about a dozen cells in the field, so no attempt was made to institute a quantitative comparison of the results obtained by the two methods; as my object in using the dye was merely to get a hint when to stop, no record has been kept of these observations. The results of one of the preliminary trials of the method, however, have been preserved; in this experiment the number of colonies on the plates was larger than is convenient, and evidently no great pains were taken in counting them, but it may serve as an illustration of the use of the stain in connection with plating work. Two fields were examined under the microscope; the poison was 0.4% phenol.

Time	0	10	20	30	40	40	50	60	70	80	90	Minutes
In field (1)	—	8	8	16	14	16	20	10	20	8	8	cells
of wh. stained	—	0	1	4	3	2	5	5	13	7	8	cells
In field (2)	—	10	10	20	15	18	22	12	25	9	9	cells
of wh. stained	—	1	0	5	4	3	6	6	14	8	9	cells
On plate	—	500	500	400	500	300	500	500	100	60	0	colonies

The results in each of the following tables were obtained with cocci from the same suspension; two plates were poured at each interval, the readings are separated by a comma. In each table the least toxic solution is put first: "Ph 0.1" means 0.1 g phenol per 100 cc; "B" that the solution was twentieth-normal with respect to sodium benzoate.

An experiment in which 1.25% phenol was used, with and without sodium benzoate, gave thickly sown plates immediately after poison and yeast had been brought together, but three minutes later all the cocci were dead.

Time	0	15	25	Minutes
Ph 1.0 B	600, 600	10, 12	0, 0	colonies
Ph 1.0	600, 650	5, 6	0, 0	colonies

Time	0	15	30	45	60	75	Minutes
Ph 0.75 B	250, 240	275, 200	90, 80	40, 45	1, 0	0, 0	colonies
Ph 0.75	300, 310	130, 135	20, 18	2, 1	0, 0	—	colonies

Time	0	15	25	35	45	55	60	Minutes
Water	50, 55	30,35	25,25	25, 28	8, 6	6, 7	0, 0	colonies
Ph 0.25; B	135, 130	50,40	40, 40	30, 25	10, 9	0, 0	—	colonies
Ph 0.25	80, 90	25, 25	6, 7	1, 0	0, 0	—	—	colonies

Time	0	15	30	40	50	60	Minutes
Ph 0; B	210, 200	195, 190	190, 190	165, 155	160, 160	150, 140	colonies
Ph 0.20; B	210, 200	120, 125	125, 120	120, 115	115, 115	115, 110	colonies
Water	220, 200	155, 150	145, 140	95, 85	45, 50	35, 40	colonies
Ph 0.20	200, 215	175, 165	—	75, 70	60, 60	6, 5	colonies

As was to be expected from the results with anthrax, and from Laird's distribution experiments, this low concentration of sodium benzoate has hardly any effect on the toxicity of 1.0% phenol; its increasing efficiency as a life preserver in the more dilute solutions is in full accord with the explanation put forward by Laird.

In the final set, the toxicity of 0.1, 0.3 and 0.5% phenol in presence of *N*/20 sodium benzoate was compared; all abnormality has disappeared, 0.1% phenol has practically no effect and increase in the concentration of the phenol hastens death.

Time	0	15	20	45	55	Minutes
Ph 0; B	350, 400	—	100, 125	5, 3	0, 0	colonies
Ph 0.10; B	750, 800	—	350, 400	5, 6	0, 0	colonies
Ph 0.20; B	250, 300	—	50, 60	0, 0	—	colonies
Ph 0.50; B	350, 400	0, 0	—	—	—	colonies

Summary

Determinations of the rate at which staphylococcus is poisoned by dilute solutions of phenol with and without addition of sodium benzoate, confirm the conclusion that the abnormalities observed by Lemon were due to plasmolysis.

Addition of methylene-blue and examination under the microscope before pouring the plates saves much time and prevents disappointment in work of this kind.

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THE ACTION OF METHYLENE-BLUE AND CERTAIN OTHER DYES ON LIVING AND DEAD YEAST

BY CHAS. G. FRASER

In the experiments of Scheurlen,[1] Beckmann,[2] Paul and Krönig,[3] Lemon,[4] and Laird,[5] the number of cells remaining alive after immersion for a measured time in a poisonous liquid was determined by mixing a known volume of the cell suspension with melted agar jelly, pouring on a petri dish, incubating, and counting the number of colonies that appeared. This procedure involves a wait of three or four days after the completion of the poisoning experiment before its result is known.

Other criteria of death have been employed in similar investigations. Bokorny[6] for instance, who compared the toxicities of some 50 different chemicals towards infusoria, algae, etc., relied on the mobility of the test objects or of their cilia, etc., or on the persistance of protoplasmic streaming in the cells as signs of life; Kahlenberg and True[7] and Heald[8] relied on the cessation of growth of the rootlets used as test-objects and on their general appearance (flabbiness) as evidence of death; Galeotti,[9] used this last characteristic in his experiments on the poisoning of iris petals. According to Moll,[10] the fact that plasmolysis occurs only with living cells has been employed to distinguish living from dead cells by Lange[11] and by Strecke.[12]

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[1] Arch. exp. Path. Pharm., 37, 74 (1895).

[2] Centralbl. Bakteriologie, 20, Abt. 1, 577 (1896).

[3] Zeit. phys. Chem., 21, 414 (1896).

[4] Jour. Phys. Chem., 24, 570 (1920).

[5] Ibid., 24, 664 (1920).

[6] Pflüger's Archiv Physiol., 110, 174 (1905); 111, 341 (1906).

[7] Bot. Gazette, 22, 81 (1896).

[8] Ibid., 22, 125 (1896).

[9] Zeit. wiss. Mikroskopie, 11, 172 (1894).

[10] Progressus rei botanicae, 2, 297 (1908).

[11] Flora, 1891, 52; see Moll: loc. cit.

[12] Inaug. Diss. Amsterdam (1904); see Moll: loc. cit.

With the possible exception of the last mentioned, none of these seems adapted to the case of yeast. There seemed more to hope from the use of dyes. According to Klöcker,[1] "The distinguishing of dead cells from living ones has been assiduously carried on in most brewery laboratories since the microscope came into general use. But the value of the indications given by the reagents employed for this purpose has been very much overestimated. The question seems to deserve proper investigation. According to Wehmer, a half percent methylene-blue solution will stain the dead cells indigo blue, while the living cells remain colorless." Mosso[2] has published a paper with the title "Anwendung des Methylgrün zür Erkennung der chemischen Reaktion und des Todes der Zellen;" on reading it, however, it appears that methylgreen acted as a poison towards the cells studied (leucocytes, ciliated epithelia, etc.) and that by the time enough to color them anyway deeply had been absorbed, they died. Similar observations were made by Bokorny; in discussing experiments with infusoria in 0.01% Victoria-blue,[3] for instance, he says, "one can see quite distinctly that the body of the infusorian becomes colored while it is still alive (recognized by its movements) and that death occurs only when the coloration has reached a certain intensity." The name "vital dyes" has been given to a group of substances, thionine derivatives prominent among them,[4] which have the power of staining the nerves of certain animals while they are still alive. Ehrlich, to whom this discovery is due, was of opinion that the staining could occur only during the lifetime of the tissue affected; subsequent experiments, however, have shown that this conclusion was too broad; indeed, Galeotti[5] who besides .contributing work of his own on salamanders and on iris petals has provided a most convenient summary of

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[1] Fermentation Organisms, tr. by Allan and Millar, Longmans-Green (1903).

[2] Pflüger's Arch. Physiol., 113, 397 (1888).

[3] Ibid., 110, 178 (1905).

[4] Biol. Centralbl., 6, 221 (1897).

[5] Zeit. wiss. Mikroskopie, 11, 172 (1894).

his predecessors' work, comes to the exactly opposite conclusion, viz., that only cells whose vitality has been impaired are capable of taking on the stain.

The Action of a Number of Dyes on Yeast Cells

To be of use for the purpose in hand, a dye must be able to distinguish sharply between living and dead yeast cells, more particularly when death has been brought about by the action of phenol; it must have no toxic action of its own on the yeast, at least in the time necessary for the test, and at the concentration used; if in addition it should stain quickly, so much the better.

A number of the dyes commonly used in microscopic work were tested from this point of view, including Grübler's methylene-blue, fuchsin, Congo-red, erythrosin, and safranin (water soluble); Merck's methylene-blue, gentian violet, and methyl-green, and Kahlbaum's methylene-blue 6 B extra. For most of these I am indebted to the kindness of Prof. Thomson, of the department of Botany and of Prof. Piersol, of the department of Biology. Aqueous solutions of each were made containing 0.5 g per 100 cc (gentian violet 0.4 g); these were suitably diluted and added in turn to a suspension of yeast cells. To test their action on living yeast, a suspension was made from 0.6 g Fleischmann's yeast cake and 100 cc distilled water; the reactions of this suspension towards dyes remained unaltered for twenty-four hours at room temperature. The action on dead cells was tested with a portion of this suspension which had been heated to boiling and cooled again ("boiled yeast"); and a third suspension ("mixed yeast"), made by mixing equal volumes of "live" and "boiled," was used to compare the colors in the same microscopic field. A magnification of 430 diameters was employed; the fraction given as stained is a rough estimate only; the percentage of dye is the number of grams dye per 100 cc of the liquid containing dye and yeast.

Congo-red: (*living*) 0.25%, 1 min. 0 std.; 60 min. 1 or 2 cells std.; (*boiled*) 0.25%, all light orange after standing an hour; (*mixed*) 0.25%, 1 min. 0 std.; 60 min. about half.

Eosin: (*living*) 0.25%, none stained in an hour; (*boiled*) 0.25% 1 min. all stained, not so dark as erythrosin; 0.05%, stained pink slowly; (*mixed*) distinction poor.

Erythrosin: (*living*) 0.25% none stained in 100 min.; (*boiled*) 0.25% all stained pink in 1 min., dark red in about 3 min.; (*mixed*) 0.25% half std., sharp distinction after 3 min.

Fuchsin: (*living*) 0.25% 1 min. nearly all std.; 0.05% 1 min. one-fifth std. 13 min. nearly all std.; 0.005% 100 min. none std.; (*mixed*) 0.05%, 2 min. 5% std.; 15 min. less than half std.; 60 min. about half faintly stained.

Gentian-violet: (*living*) 0.20%, 0.02%, 1 min. all std. deep violet; 0.002% 60 min. 0 std.; (*boiled*) 0.002%, all stain slowly; (*mixed*) 0.002%, 3 min. about half std. light purple.

**Methylene-blue 6B extra:* (*living*) 0.05%, 1 min. 0 std., 45 min. about one quarter of the cells dark blue; 0.01% 60 min. 0 std.; (*boiled*) 0.005% 1 min. all std. distinctly; (*mixed*) 0.005% 1 min. half std., good distinction.

Methyl-green: (*living*) 0.25%, 1 min. few std., 15 min. nearly all std.; 0.05%, 60 min. 0 std.; (*mixed*) 0.05%, half std., good distinction.

Neutral-red: (*living*) 0.01%, 1 min. three-quarters std.; 0.002%, 10 min. 0 std., 75 min. about half faintly std. (*boiled*) 0.02% 1 min. all pink-violet; 0.002% 1 min. 0 std., 100 min. all faint orange.

Safranin: (*living*) 0.25%, 0.05%, 1 min. all std.; 0.005% 1 min. 0 std., 20 min. one-quarter std., 45 min. half std.; (*mixed*) 0.005% 1 min. half std. a dirty pink.

Phenol (about one percent) was then added to a portion of the yeast suspension, and left at room temperature for three hours, which is longer than is necessary to kill all the cells. This "phenolized yeast" was then mixed with an equal volume of the various dye solutions, giving a solution containing one-half percent of phenol, and a dye concentration chosen in the light of the preceding results.

Eosin: 0.05%, 1 min. all std. faintly; 80 min. much darker.

Erythrosin: 0.25% needs a minute to stain; color as deep as with methylene-blue 0.01%.

Fuchsin: 0.005% very light stain; 0.01% not as dark as with methylene-blue 0.01%.

Gentian-violet: 0.002% stain light, comes slowly; 0.004% not so dark as with methylene-blue 0.01%.

Methylene-blue 6B extra: 0.005% needs a minute to stain light blue; 0.01% much darker and quicker stain.

Methyl-green: 0.05% stained about as dark as methylene-blue 0.01%.

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*The other brands of methylene blue were somewhat more toxic.

Neutral-red: 0.002% none stained; 0.01% all stained as in the absence of phenol.

Safranin: 0.005% all stained light orange-pink.

From these results it appears that gentian-violet, neutral-red and safranin have too much action on living yeast to be convenient indicators; Congo-red on the other hand has too little action on the dead cells; fuchsin, neutral-red and safranin are too faint; while eosin, erythrosin, methyl-green and methylene-blue 6 B extra would serve.

The question whether the presence of these dyes in small amounts would prevent reproduction of the yeast in culture media was then taken up, and for this purpose a "malt" solution was prepared by dissolving 30 g of malt extract (a brown sticky stuff) in water, making up to 200 cc, boiling and filtering. To 4 cc of this "malt" was added 0.5 cc or 1.0 cc of the solution of a dye, and 2 cc of yeast suspension; the mixtures were left in test tubes plugged with cotton wool in an incubator at 25° C. The concentration of dye in the mixture was in each case less than would completely stain unboiled yeast, viz., Congo-red 0.04%, eosin 0.04%, erythrosin 0.04%, fuchsin 0.014%, gentian-violet 0.006%, methylene-blue 0.07%, neutral-red 0.003%, safranin 0.014%. After a dozen hours the occurrence of fermentation could be recognized in every case, by a stream of small bubbles rising through the tube; and in every case reproduction of the yeast was taking place, under the microscope an increase in the number of cells could be observed, and numerous double cells and chains of three and four were to be seen.

This result made it easy in certain cases to answer the next question, viz., when a dye has acted on yeast long enough to stain most of the cells, have those remaining unstained lost their power of reproduction? Mixtures were made up of the same composition as before, but instead of mixing in the order: malt, dye, yeast, the yeast was added directly to the dye, which was thus present in concentration two or three times greater than in the former instance; and before putting in the malt, the mixture was let stand until most of the cells were stained. Even when only a few percent of the cells remained colorless, fermentation and reproduction took place after adding the malt; this was not quite what was expected, as in a number of cases where wort-agar had been seeded with a mixture of stained and unstained cells, the number of colonies formed was much less than corresponded to the number of unstained cells. When the dye had acted for a long time, and no unstained cells could be found under the microscope, no fermentation took place after adding the malt.

Methyl-green seemed to behave quite differently from the other dyes, though not enough time was spent on the matter to make sure that the results obtained with it could not be duplicated with others. When 0.25 cc or less, of 0.50% methyl-green solution was added to 4 cc malt, and then 2 cc yeast suspension was put in, fermentation took place in from 7 to 30 hours; but if 0.5 cc or 1.0 cc of the dye were used, no fermentation was observed, no increase in the number of cells, and no chains of cells. Examined under the microscope, the cells were turgid, but after some days in the solution they became granular; they remained unstained by the methyl-green, and were not stained when methylene-blue was added to a concentration of 0.005%. When the dye-malt-yeast mixture was heated to 100° C, the cells promptly stained green; the same when phenol was added; thus the dye had evidently not lost its staining power by mixing with the malt.

An hour after adding 2 cc yeast suspension (count 150) to the solution made from 1.0 cc methyl-green 0.50% and 4 cc malt, 0.25 cc of the mixture was pipetted into 4 cc sterile malt and put away at 25° C; similar tubes were prepared after 2, 4, 17 and 29 hours; neither fermentation nor reproduction took place in these tubes in 5 days, although the concentration of the dye was much less than that at which yeast grows readily. When some more of the original yeast (kept in water in the meantime) was put in, fermentation took place about as quickly in a parallel experiment with malt; this shows that the cell, not the medium, was at fault.

Two percent agar-agar was dissolved in malt, and a drop of the original malt-dye-yeast mixture added 7 hours after it had been made up; a second plate was seeded from the same solution 98 hours after it had been made up. Yeast colonies grew plentifully on both plates; where the dye had acted 7 hours about 20 to 25% of the cells grew, after 98 hours about one percent.

This work with methyl-green is being continued; it is only mentioned here because of the evidence it affords that yeast cells may be alive, unstainable, and capable of reproduction in some media, and yet incapable of reproduction in other media in which normal yeast cells grow readily. In case of contradiction arising between the evidence of stain and plates this should be borne in mind.

Of the four dyes named on page 745 as suitable for indicators, erythrosin gives better distinction than eosin, while the behavior of methyl-green in hindering reproduction in the culture medium makes it for some work less safe than methylene-blue; the choice thus lies between erythrosin and methylene-blue.

For use with the camera, blue is not the best, as it requires a long exposure during which the light and heat may increase the number of cells stained. With a Wratten screen B (green), or with an "isolar" screen, using 4 mm objective, no ocular, 100 watt tungsten lamp, and Ilford rapid plates, about thirty seconds exposure were needed to give a good negative.

For direct observation with the microscope, however, blue is much less fatiguing to the eyes than red; I, therefore, decided to adopt methylene-blue in my further work, and studied its behavior with a number of reagents apt to be used in quantitative toxicological work with yeast. In the presence of carbinol 20%, alcohol 20%, or acetone 20%, and methylene-blue 0.005%, boiled cells stain green. With M. B. 0.005% and acetic acid 0.05% they also stain green, in shade about as dark as the blue obtained in the absence of the acid; with 0.15% acetic acid the stain is a very faint green, addition of ammonia restores the blue. No great pains need be taken to avoid excess of ammonia, immersion in normal ammonia for a quarter of an hour does not cause living cells to stain. Mercuric chloride 0.1% gives a purplish precipitate and the cells do not stain. Sodium chloride 12% gives a purplish precipitate, and under the microscope long hair-like crystals (Pelet-Jolivet[1] found that the amount of methylene-blue absorbed by wool is influenced by the addition of sodium sulphate, and Ross[2] that the action of the same dye on leucocytes is interfered with by neutral salts). If silver nitrate, 0.12%, be added to an equal volume of the yeast suspension, boiled a moment to kill the cells, ("silver-yeast") and then an equal volume of 0.03% methylene-blue be added, the cells are barely stained a greenish tint; if the concentration of the silver be decreased or that of the dye be increased, the cells stain bluer. With this silver-yeast, neutral-red behaves much as methylene-blue; eosin stains the cells but forms a pink film visible under the microscope; erythrosin, gentian-violet, and methyl-green act as with ordinary boiled cells.

My thanks are due to Prof. W. Lash Miller under whose direction this work was carried out.

Summary

The behavior of nine dyes with living yeast and with yeast killed by boiling or by the action of phenol, was studied with the object of finding a convenient criterion of death in quantitative toxicological investigations with microbes. Erythrosin and methylene-blue 6 B extra proved the best.

In a solution of extract of malt to which methyl-green has been added, yeast cells may lose their power of reproduction without becoming stained.

The University of Toronto
July 1920

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[1] Arch. Sci. phys. nat. Genève, (4) 27, 27; from Chem. Centr., 1909, I, 879.

[2] Jour. Physiol., 37, 327; Chem. Centralbl., 1908, II, 1693.

NEW BOOKS

Modern Pulp and Paper Making. *By G. S. Witham, Sr. 23 × 16 cm; pp. 600. New York: The Chemical Catalog Company, 1920. Price: $6.00.*—In the preface the author says: "During thirty-seven years of experience in the pulp and paper industry the author has frequently and repeatedly felt the need of a practical work on the manufacture of pulp and paper, as carried on in America, that would not be so abstruse and technical as to be beyond the grasp of the average papermaker, and which at the same time would not merely skim the surface of the various sub-divisions of the art.

"In the present volume an attempt has been made to describe the equipment and processes actually used in pulp and paper plants on this continent today, giving such practical information as would be of help to men working around these plants from day to day. It is hoped that the present volume will be useful to practical papermakers and, at the same time, that it may possibly be of service to technical men not intimately in touch with the pulp and paper industry and desiring to know the salient facts about it."

The titles of the chapters are: processes by which pulp is produced; materials from which pulp is produced; varieties of paper; the saw mill; the wood room; the sulphite mill; the acid plant; the soda process; the sulphate process; the ground wood mill; bleaching; the beater room; the machine room; the finishing room; general design of pulp and paper plants; the power plant; testing of paper and paper materials; paper defects, their cause and cure; personnel; useful data and tables.

On the first page the author says: "Wood is, at the present time, the raw material most used in the paper pulp industry; consequently, the manufacture of wood pulp possesses the greatest interest from a technical and industrial point of view. The processes by which rags and other materials are converted into pulp will be fully dealt with in a later chapter. Wood is converted into pulp suitable for the manufacture of paper by two distinct classes of methods. The first class includes the mechanical methods which produce mechanical wood pulp or ground wood. The second class includes the various chemical methods, which produce chemical pulp or cellulose. This class comprises such methods as the sulphite, soda, sulphate, and Kraft processes." It is interesting to note, p. 177, that the sulphate process for making pulp is really a sulphide process.

On p. 5 we read that vegetable substances have come to be of the greatest importance for the manufacture of paper and that the commercial value of any one vegetable substance depends on the quantity of cellulose that the fibers contain, the quality of this cellulose, and the facility with which the cellulose can be extracted from the fibers. The author states that whatever the form in which cellulose occurs it is chemically the same. The organic chemists might perhaps take issue with that.

Under varieties of paper the author distinguishes: book paper, writing paper, wrapping paper, tissue and cigarette paper, bag paper, parchment paper, news print, filter paper, hangings, roofing and building paper.

"A good cigarette paper should be absolutely neutral in flavor and aroma while the cigarette is burning. A very few vegetable fibers possess these properties, the selection of material is most important in making this kind of paper. Pure flax, or linen fiber, hemp fiber and ramie, are usually used. Rice straw was formerly extensively used for making cigarette paper, but this stock does not possess strength to satisfy the requirements of modern cigarette making machinery. Chemical wood pulp is only used for the cheapest grades of cigarette papers. It is deficient in tensile strength unless it is too thick. Straw papers usually contain silicic acid, which is undesirable in cigarette papers, as it confers disagreeable burning properties to the paper. Excessive use of cotton fiber gives the lamp-wick odor found in some of the cheaper grades of cigarette paper.

"Porosity is necessary to admit air for the proper combustion of the paper. Cigarette papers are being made somewhat thicker today than formerly on account of the necessity for strength in paper to be used on cigarette machines and the manufacture of paper of the proper thickness and strength with sufficient porosity is quite a problem. Opaqueness is also necessary in order to give a good appearance to the finished cigarette. If the paper is not sufficiently opaque, the tobacco will show through the paper giving the cigarette a grayish or mottled appearance when packed which is undesirable from the cigarette manufacturers' point of view. Securing the necessary opaqueness without making the paper too thick is one of the nice points in the manufacture of this variety of paper."

Under bleaching, p. 202, we read: "Wood pulp, regardless of the process by which it is made, requires to be bleached if it is to be used in any of the finer varieties of light colored paper. Rag pulp, straw pulp and pulp made from esparto, jute, etc., and most of the other miscellaneous materials from which paper of any kind is made, require bleaching in order to enhance the value of the product. The bleaching of rag stock is a comparatively simple matter owing to the comparative freedom of such stock from colored impurities which have to be eliminated by the bleaching agent. It should be borne in mind that most rag stock of the better grade is made from material which has already been submitted to bleaching in the processes of textile manufacturing, and any coloring matter which may be present is in the form of dyes which have been added by the textile manufacturer or finisher, and which are relatively easy to remove when compared with the coloring materials embodied in wood pulp which are an integral part of the fiber itself.

"Wood pulp, no matter how carefully made, and whether produced by the sulphite or soda process, always has associated with the cellulose a portion of the lignin or incrusting matter ordinarily present in the raw fiber and this lignin carries with it certain colored bodies of highly complex chemical composition. These colored impurities cannot be removed by any amount of washing or mechanical treatment. They are united in a chemical manner with the fiber or cellulose and a chemical process is necessary for their removal. In addition to the colored materials that are ordinarily present in the fiber, other dark colored substances are produced during the process of digesting the pulp by the chemical action of the acid or alkaline liquids on the various complex substances contained in natural wood.

"Wood pulps and pulps made from esparto, straw, jute, etc., require a much more drastic bleaching than rag pulp, resulting in a much larger consumption of the chemical used for bleaching purposes and a much greater proportional loss in weight through the bleaching process."

While the beater is used to cut the fibers to a given length, this is not its only function—or its most important one, p.226. "No less vital than the cutting of the fibers to a certain length is the separating of the bundles of fibers (which will exist to a certain extent in even the best grades of sulphite and kraft pulps) and to brush or stroke the fibers into greater flexibility.

"The tiny fibers are stroked out by the blunt knives of the beater, in somewhat the same manner that a hairbrush strokes out human hair, and, moreover, the fibers are caused to curl at the ends. Upon the ability of these fibers to curl and connect with each other, when allowed to "bond" (by removal of the surrounding liquid) depends the strength and toughness of the resulting paper. If these fibers are not drawn out to the correct degree, they will not grasp and entwine with each other in the manner which we denote by the term "felting." It will readily be appreciated that not only must the fibers be "brushed out" and made flexible, but—in order to obtain a sheet which will have strength and thickness—the fibers must be kept long in the beater. This applies with particular emphasis to papers of light basis-of-weight, of which a great deal is expected—as, for example, fine writings, ledger and bond paper and 28 and 30-pound kraft wrapping and bag papers."

The size, alum, water-glass, starch, and color are all added in the beater room. The author distinguishes only four kinds of dyes, p. 255: basic dyes, acid dyes, direct dyes, and vat dyes, the last of which are used but little in the paper industry. The acid dyes require alum to set them; but the basic dyes apparently dye paper direct. When dyeing textiles, basic dyes are not supposed to dye cotton without a mordant. The difference with paper is either because paper is not washed after it is finished or because the size acts as a mordant; but the author does not discuss this. In regard to pigments, p.254, he says that: "Pigments color the stock by becoming enmeshed with the fibers in the beater. The size and alum helps the fibers to retain the pigments, which adhere in small particles to the surface of the fiber. Pigments do not penetrate the substance of the fiber as do dyestuffs. There is probably no chemical action between the cellulose of the fiber and the pigment, whereas in the use of dyestuffs the combination seems to be more chemical than mechanical."

The machine ordinarily used for making paper is the Fourdrinier machine, which consists essentially, p.282, "of a device for allowing carefully screened pulp of constant consistency to flow onto a horizontal wire screen, made in the form of an endless belt and travelling constantly away from the point where the pulp flows on it. The water in the pulp drains through the wire, this drainage being assisted by suction boxes applied under the wire at certain points. At the end of the wire farthest from the point where the pulp flows on it, is a pair of rolls between which the film of fibers from the wire passes. At this point the film of fibers still contains much moisture, so it is passed through other felt-covered rolls, which press more water out of it. Next it passes through a long series of steam-heated iron cylinders, always supported by a layer of felt which travels with the paper, and these cylinders drive out all the remaining water except a small percentage always present even in paper commonly considered quite dry. Finally the paper passes through polished calendar rolls to give it a "finish" and onto reels where it is wound up."

The book is intended to be essentially a practical treatise and consequently there is no discussion of theory anywhere, and this is carried to such a point that the author does not even say, as most people do, that one function of the beater is to hydrate the stock. The author has done the work that he has planned in an excellent way, and the book will be of great value to everybody. The publishers call attention to the fact that this is the first book to be written dealing with the pulp and paper industry as carried in America. This is important, because the pulp and paper industry has developed in America along quite different lines from the industry in the European countries, and to a much greater extent. Mr. Witham's book is therefore in a sense a pioneer one.

Wilder D. Bancroft

A History of Chemistry. *By J. Campbell Brown. Second edition. 23 × 15 cm; pp. xxx + 544. Philadelphia: P. Blakiston's Son and Co., 1920. Price: $6.00.*—The book is divided into two parts: ancient history and modern history. In the first part the subheads are: the early workers; the early writers; the Greek physicians and philosophers; the Roman, Alexandrian, and Byzantine schools; the Orientals; the pseudo-Geber; the technical traditions; the alchemical treatises of the Middle Ages; alchemists of the twelfth and thirteenth centuries; the alchemists of the fourteenth century; the protest of Paracelsus; the later mediaeval alchemists; the philosophy of the alchemists; the aims and methods of the alchemists; the symbolism of the alchemists; the philosopher's stone.

In the second part the subdivisions are: the iatrochemists; the phlogistonists; the anti-phlogistonists; the quantitative period; the rise of electrochemistry; the chemistry of the early nineteenth century; the rise of organic chemistry; the chemistry of the later nineteenth century; the chemistry of the carbon compounds; physiological chemistry; agricultural chemistry; the doctrines of atomicity and valency; the doctrine of isomerism; the doctrines of chemical affinity and kinetics; the doctrine of acids, bases and salts—electrochemistry; the chemical elements.

On p. 71 the author expresses the belief that "the origin of chemistry was not due to the Arabs, and that they did little to extend or improve chemical knowledge. What they did know they derived partly from Hellenic culture through Syriac sources, and partly from the temple laboratories of Egypt. Much of their knowledge they did not understand, and they involved it in a mystical confusion, which for centuries hindered the progress of the science. It is not to the Arabs that the real credit is due, but to the clear thinkers and observers of Western Europe."

On p. 110 we read: "Paracelsus did little by actual discovery to advance either science or medicine. His great work was effecting a breach with tradition, and setting physicians and alchemists free from the bondage in which they were held by convention. He borrowed his medical treatment from others—barber-surgeons, old women and quacks—and his fearless nature made him employ the powerful and dangerous medicines prepared from mercury, opium, and antimony more boldly than any before him had ventured to do. . . . The great debt which chemistry owes to Paracelsus is the influence he exerted in discarding the ideas of the ancients, and even of the more modern alchemists, and in teaching that the object of chemistry was not to make gold but to ameliorate disease.

The art of making drugs was one of the original branches of alchemy, but for many centuries this had been obscured by endeavors to effect the transmutation of metals. Paracelsus reinstated it in its prominent position. He used preparations not only of antimony, but of mercury, lead, iron, blue vitriol, and (for external use) arsenic. He said that the most energetic poisons might become precious medicines, and endeavored to concentrate in essences, extracts, and mixtures the active principles of various drugs."

The author is not enthusiastic about Basil Valentine, p. 196. "We have devoted a considerable space to Basil Valentine, on account of the reputation which he enjoyed in the Middle Ages, a reputation second only to that of Paracelsus. But in truth his works do not merit the deference they received, and as the knowledge imputed to him is almost certainly not his, but belongs to a far later period, it is needless to enter into a more lengthened exposition of his views. The best advice which can be given to the student of chemical history is to receive with caution all that is said about Basil Valentine in text-books and histories."

If Ehrlich were still alive, he might be interested in a paragraph about Lemery, p. 212: "Lemery was no empty theorist, but aimed at the exposition of facts by means of experiments. Yet one of his theoretical conceptions was very odd, and shows how far astray a capable man may wander, when he deserts observed facts for philosophical speculations. He thought that chemical combinations between two substances, such as an acid and a base, might be accounted for by supposing that the particles of the one substance were sharp, and those of the other porous, and that combination was effected by the *fitting of the points into the holes!*"

The author's remarks on the Daltonian theory are distinctly interesting, p. 333, even if one does not agree with them. "Of course it is founded upon an impossible assumption. Matter, however minutely divided, must conceivably be capable of further division. Our reason cannot conceive anything which, if it existed at all, could not be split in half. But this does not affect the value of the theory as a convenient working hypothesis, and so chemists suppose that the proportions in which bodies combine with each other depend on the weights of the ultimate atoms of which they are respectively composed, and are identical with them."

The volume will prove valuable as a reference book. It seems a pity that the modern incandescent lamp should have been overlooked, in the second edition, p. 522. "Tungsten is of commercial importance, being used for the production of steel, and for fire-proofing fabrics." *Wilder D. Bancroft*

The Chemists' Year Book. *Edited by F. W. Atack. Volumes I and II. Fifth edition. 15 × 10 cm; Vol. I, pp. 422; Vol. II, pp. 713. New York: Longmans, Green and Co., 1920. Price: $7.00.*—In the first volume the general heads are: atomic weights; qualitative analysis; reagents; volumetric analysis; gas analysis; ultimate analysis of organic substances; electrochemical analysis; spectrum analysis; general properties of inorganic substances; general properties of organic compounds; useful memoranda; five-figure logarithms. In the second volume the general heads are: thermal constants; viscosity; refractive indices; cryoscopic constants; densities; solubilities; vapor pressures; crystallography; properties of minerals; water analysis; fuels and illuminants; analysis of silicates; acid and alkali manufacture; oils and fats; paints and pigments; agricultural chemistry; carbohydrates; beer and spirits; tannin materials; fibers; coal tar products; physiological chemistry; india rubber; tobacco; photography.

The pages on electrochemical analysis and on photography show how much can be presented in a small space. Since tannin is miscible practically in all proportions with water, it should at least be called very soluble, p. 354. If cobaltous compounds are to be listed as cobalt compounds, p. 162, they should be put before cobaltic compounds. The editor has certainly got together a marvellous amount of information and the fact that the book has been revised every year seems to show that there is a distinct demand for it.

Wilder D. Bancroft

Chemical French. *By Maurice L. Dolt. Second edition. 22 × 15 cm; pp. vi + 413. Easton: The Chemical Publishing Co., 1920. Price: $4.00.*— The first edition was reviewed in *1918* (**22**, 460). The book has been so successful that a new edition has now appeared. The author has corrected many of the errors in the first edition, which is an almost unprecedented thing for any author to do. In the new edition there has been added a selection from Le Chatelier. The book was a good one originally and is better now.

Wilder D. Bancroft

ERRATA

The following corrections are to be made:

Page 225, line 21, Fig. 4 instead of Fig. 2.
Page 226, line 8, Fig. 2 instead of Fig. 4.
Page 229, line 2, $\sqrt{2}$ instead of $^1/_2$.
Page 270, line 17, insert missing half of bracket.
Page 414, Fig 8, delete $^1/_3$ size. The cut is approximately full size; but the exact dimensions may depend on the method or on the observer's methods and preferences.

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