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THE PHYSICAL PROPERTIES OF A NUMBER OF PURE ESTERS

1

BY J. HOWARD MATHEWS AND KATHARINE E. FAVILLE

In connection with an extended series of measurements of the heats of vaporization of organic liquids being made by one of us, an examination of the literature made it apparent that the data concerning the physical properties of many of these substances were very meagre; and since in many cases the discrepancies between the values obtained by different observers were of considerable magnitude it seemed desirable to make re-determinations of a number of these properties, particularly for a number of the esters, which we had reason to believe were in a very pure condition.

Schumann,[1] who measured the vapor pressures of twenty-eight esters, purified them by chemical treatment, and subjected them to fractional distillation. He measured the boiling points at pressures above and below 760 mm and obtained the values for the boiling points at 760 mm by interpolation. Of all the esters studied by him, only one had a constant boiling point (methyl formate); the rise in boiling point during distillation averaged 0.35°, in some cases going as high as 0.7°. Schiff,[2] in his work on the measurement of the molecular volumes of some of the esters, used samples of material whose boiling points changed as much as one degree. He attributed this inconstancy to a dissociation of the esters on standing and stated that esters of organic acids seldom have a constant boiling point. Young and Thomas[3] seem to have been more successful than has anyone else in the preparation of pure esters, as their preparations distilled within limits as narrow as 0.05°. Their method of purification, which is probably now the standard method for the purification of esters, consisted in treating them with concentrated solutions of potas-

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[1] Drude's Ann., 12, 40 (1881).

[2] Liebig's Ann., 220, 71 (1883).

[3] Jour. Chem. Soc., 63, 1191 (1893).

sium carbonate to neutralize any organic acid present, then washing to remove the salt formed and the small amounts of alcohol; shaking with solid potassium carbonate to remove a considerable amount of the water taken up by the ester; and, finally, distilling with phosphorus pentoxide to remove the last traces of water. The homologous esters, if present, were removed by fractional distillation.

The esters used by us were obtained in kilogram quantities from Kahlbaum, and were of the highest quality obtainable. They were purified by chemical treatment (about as outlined above) and were subjected to fractional distillation in a special apparatus so devised as to keep the liquid always boiling under a pressure of 760 mm. Our experience was not as happy as that of Young and Thomas, and we are inclined to agree with Schiff (and others) that the esters are continually undergoing change. This belief has been strengthened by our experience in redistilling some of our purified material several months after the first distillation. Wherever we have made such tests we have found that the boiling point had changed, though in some cases the change was not great. Although our fractionating device enabled us to secure material which distilled within a very narrow and exact range, we were forced in some cases to choose wider temperature limits than we desired in order to have enough material for all the measurements we contemplated, including the heat of vaporization work. In no case, however, were the limits wide enough so that the material included enough impurities to have any appreciable effect on the measurements made. During the distillation of the fractions chosen the rises in the boiling points, with the exceptions of isobutyl valerianate and ethyl butyrate, which were very impure to start with, was within the limits of 0.01 to 0.25° C, the average rise being 0.12°.

The distilling apparatus mentioned consists of a distilling flask (see figure) as designed by Richards and Barry[1] with the addition of a cistern at the bottom. By means of a coil of platinum wire contained in this cistern the liquid in the flask

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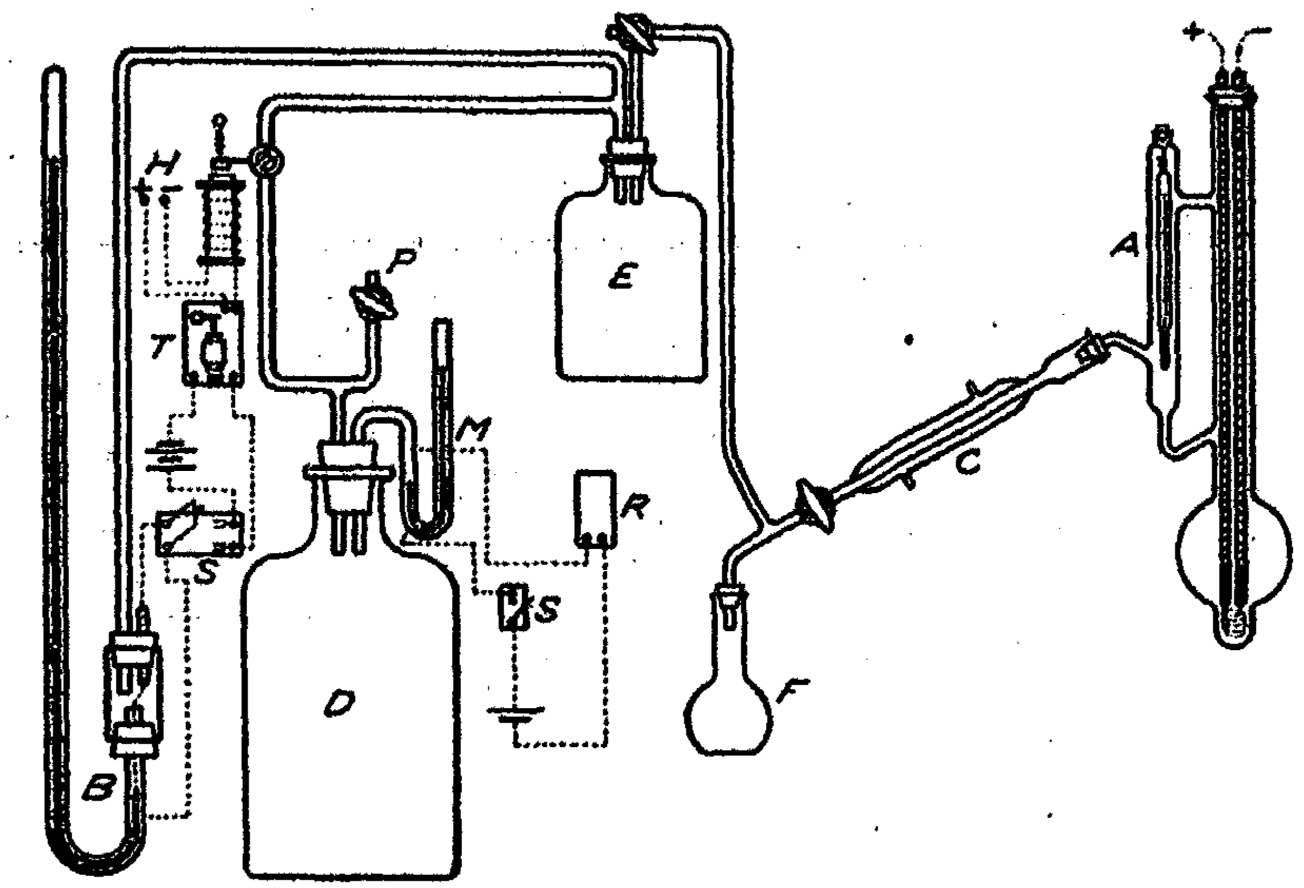
[1] Jour. Am. Chem. Soc., 36, 1787 (1914).

is heated electrically.[1] Stout copper wires pass down the glass tubes to the bottom where they are connected electrically with the platinum wire by means of a few drops of mercury, and are connected at the top with a source of current. By means of a side tube leading from the lower part of the condenser, the distilling apparatus is connected with a pressure regulating device, shown diagrammatically in the accompanying figure.



B is an ordinary syphon barometer. A platinum wire is sealed into the wall of the short arm a little below the top of the mercury column, and another extends down through the top of the tube to the surface of the mercury. A switch (S), a telegraph relay (T), and a source of current are all in circuit with the barometer, as shown. When current passes through the electromagnet (H) the valve in the tube leading from the bottle (E) to the bottle (D) is opened as the armature is pulled down. By means of compressed air run in at (P), the pressure in the bottle (D) is kept above 760 mm, the bottle serving merely as a pressure reservoir. The bottle (E) is

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[1] Cf. Richards and Mathews: Jour. Am. Chem. Soc., 30, 1282 (1908).

connected with the distilling apparatus, the barometer, and the bottle (D).

When the distillation is started, the apparatus is left under atmospheric pressure until drops begin to fall into the receiver (F), then the cock in bottle (E) and the two switches (S) are closed, and air under pressure is run into (D) at (P). The wire in the barometer tube leading down to the mercury column is so adjusted that as the pressure in the system falls below 760 mm, electrical connection will be established and the valve will be opened slightly by the magnet.[1] When the pressure rises to 760 mm the electrical connection is broken and air ceases to pass into the system. Thus the pressure is automatically kept at 760 mm, due allowance for the barometer corrections being made at the time of setting. The barometer must, obviously, be kept in a room of constant temperature. In our work the setting of the mercury column to the proper height was accomplished with the aid of a Societe Genevoise cathetometer. It is evident that if the pressure in (D) should fall below 760 mm this automatic device would not work. To guard against this possibility the manometer (M) is placed at the top of the bottle (D). Two platinum wires are sealed into the walls of the tube, one below the level of the mercury column and the other above. These wires are connected with the switch (S), the buzzer (R), and a source of current. When the pressure falls to a certain point (always above 760 mm) the buzzer sounds, and thus notifies the operator to run in more air at (P).

When it is necessary to change the receiver (F), the cock in (E) is closed, so that the distilling apparatus is shut off from the bottle (E). The cock in the delivery tube of the condenser is also closed. The flask (F) can then be removed and another be put in its place; the cocks are opened again in the same order, and distillation proceeds without having been affected by any change in pressure.

By means of this apparatus a very constant pressure can

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[1] The oxidation of the mercury surface by the sparking which takes place when the circuit is broken can easily be avoided by the use of a condenser.

be maintained, the change in level of the mercury being of the order of 0.01 mm.

The thermometers used in the distillation and in the other parts of the work had either been standardized by the Bureau of Standards or were compared with instruments so standardized.

The boiling points of the liquids studied are given in Table I, together with whatever values have been given by other investigators.

The sample of isobutyl valerianate was not as good as the other esters. It was very impure to start with, the original material as obtained from Kahlbaum boiling approximately from 130 to 170°. Attempts were made to purify it according to the method given by Wade[1] for the purification of ethyl acetate and similar esters. The procedure was, briefly, as follows:

1. The ester was distilled from a large quantity of water three times. Each distillation should remove considerable of the alcohol content.
2. The distillate was dried over solid potassium carbonate for two days, after which it was decanted off and distilled.
3. It was allowed to stand over phosphorus pentoxide for three days, poured off and distilled.
4. Finally it was fractionally distilled at 760 mm pressure. The product after purification boiled from 160 to 168.5°, most of it coming over between the limits 167–168.5, however. Measurements were made on this fraction. By repetition of the process the ester could undoubtedly have been obtained with a more constant boiling point, but the process was so wasteful of material that it was deemed best not to carry the purification further, as sufficient material for the measurements probably would not have remained. The values given for the constants for this ester are therefore not so certain as the values for the others.

Measurements of densities, viscosities, vapor pressures, specific inductive capacities, and indices of refraction were made. Each property will be taken up separately.

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[1] Jour. Chem. Soc., 87, II, 1656 (1905).

TABLE I—BOILING POINTS AT 760 MM

Substance	M. and F.	Thomas-Young[1]	Schumann[2]	Linnemann[3]	Timmermans[4]
Isoamyl formate	123.46–123.56°	—	—	—	—
Isobutyl formate	98.15– 98.25	—	97.9– 98.3°	—	—
Propyl acetate	101.57–101.77	101.55°	100.8–101.2	101.9°	—
Ethyl propionate	99.12– 99.22	99.0	97.3– 98.9	98.8	99.1°
Propyl propionate	121.0 –121.25	—	122.2–122.7	122.4	—
Ethyl butyrate	120.0 –120.5	—	119.9–120.4	121.1	—
Isobutyl valerianate	167.0 –168.5	—	168.7–169.1	—	—

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[1] Jour. Chem. Soc., 63, 1191 (1893).

[2] Drude's Ann., 12, 40 (1881).

[3] Liebig's Ann., 160, 195 (1871).

[4] Bull. Soc. belg., 24, 244 (1910).

Density Determinations

For the density determination an Ostwald-Sprengel pycnometer of about 50 cc capacity was used. Since it was desired to make the measurements at 20° a thermostat, electrically controlled and regulated, whose temperature did not vary from 20° by an amount greater than ±0.03°, was employed. A counterpoise, consisting of a second pycnometer of similar size and shape, was used in all weighings. The counterpoise was wet and dried in the same manner as the pycnometer proper, the usual precautions as to drying and weighing being observed. All weighings were duplicated by refilling the pycnometer and weighing a second time. The weighings were made with a set of Sartorius weights which had been standardized by the Bureau of Standards.

The humidity of the air in the balance room was always measured at the time of weighing, an Assmann's psychrometer being used for this purpose. The weights obtained were reduced to *vacuo*, the corrected values for the density of air being used. From these data the densities of the liquids were calculated, the density of water being taken as 0.9982 at 20°.

The values obtained for the densities of the esters are given in the table below (Table II), together with whatever

TABLE II

Substance	Density at 20°	Density as found by others	
Isoamyl formate	0.8773	0.8706	Richards and Stull[1]
Isobutyl formate	0.8832	0.8754	Richards and Stull[1]
		0.8818	Eisenlohr[2]
Propyl acetate	0.8869	0.8856	Brühl[3]
		0.8884	Young and Thomas[4]
Ethyl propionate	0.8904	0.8907	Richards and Stull[1]
		0.8901	Young and Thomas[4]
Propyl propionate	0.8809	—	
Ethyl butyrate	0.8784	0.8785	Richards and Stull[1]
Isobutyl valerianate	0.8544	—	

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[1] Jour. Am. Chem. Soc., 34, 971 (1912).

[2] Zeit. phys. Chem., 75, 585 (1910).

[3] Liebig's Ann., 200, 139 (1880).

[4] Jour. Chem. Soc., 63, 1191 (1893).

values have been given by other observers for the same temperature. Unfortunately the values found in the literature are usually for temperatures other than 20°. It will be noted that the values often differ considerably from those found by other observers.

Viscosity Measurements

The literature contains few data on the viscosities of the esters, although other classes of organic compounds have been quite generally studied. It therefore seemed worth while to make such measurements.

The method used was that described by Ostwald[1] and is so familiar that it needs no description. The viscosimeters used were of the closed type, to prevent evaporation and contamination with water vapor. Water was used as the standard substance of known viscosity as its viscosity has been most carefully measured, and as it is so easily purified. The absolute viscosity of water was taken to be 0.01007 dynes per sq. cm at 20°, this value being obtained through interpolation of the data given by Thorpe and Rodger.[2] During the measurements the temperatures of viscosimeter and liquid were maintained at 20° in the thermostat already mentioned. The time of outflow was recorded with a stop-watch capable of being read to 0.1 second.

Ten or twelve readings were taken on each substance, then a similar viscosimeter was used for a second series of readings. The readings were very constant, as is shown by the following readings taken with propyl acetate. With viscosimeter No. II the times of outflow were: 59.0, 59.0, 59.0, 59.0, 59.0, 59.0, 59.0, 59.0, 59.0, and 59.0 sec. For viscosimeter No. I the times of outflow were: 68.0, 69.0, 69.05, 69.0, 69.1, 68.9, 69.0, 69.1, 69.0 and 69.0 sec. The data and values for viscosity calculated therefrom appear in the following table (Table III).

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[1] "Physiko-Chemische Messungen," page 260.

[2] Phil. Trans., 185A, 397 (1894).

TABLE III—VISCOSITY DATA

Substance	Number of viscosimeter	Time of outflow for water	Time of outflow for liquids	Density at 20°	Specific viscosity at 20°	Viscosity in dynes per cm²
Ethyl propionate	I	105.5	63.95	0.8904	0.541	0.00545
Ethyl propionate	II	89.02	54.75	0.8904	0.548	0.00551
Propyl propionate	I	105.5	80.34	0.8809	0.672	0.00677
Propyl propionate	II	89.02	68.27	0.8809	0.676	0.00680
Isoamyl formate	I	105.5	95.0	0.8750	0.789	0.00794
Isoamyl formate	II	89.02	80.14	0.8750	0.789	0.00794
Isobutyl formate	I	105.5	75.7	0.8832	0.635	0.00640
Isobutyl formate	II	89.02	64.6	0.8832	0.642	0.00646
Isobutyl valerianate	I	105.5	137.85	0.8534	1.117	0.01120
Isobutyl valerianate	II	89.02	116.4	0.8534	1.118	0.01120
Ethyl butyrate	I	105.5	79.47	0.8784	0.663	0.00668[1]
Ethyl butyrate	II	89.02	67.5	0.8784	0.667	0.00671
Propyl acetate	I	105.5	69.0	0.8869	0.581	0.00585
Propyl acetate	II	89.02	59.0	0.8869	0.588	0.00592

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[1] One of us had previously found the value of 0.659 for the specific viscosity of ethyl butyrate at 20°, and 0.00664 for the absolute viscosity. No other data could be found which had been taken at 20°. (Mathews: Doctorate Dissertation. Harvard University, 1908.)

The work of Thorpe and Rodger has shown that the property of viscosity is both additive and constitutive; in a homologous series the numerical value for the increment CH_2 increasing as the series is ascended. As can be seen from the table, the value for the absolute viscosity increases in a homologous series of esters, and the effect of each additional CH_2 group decreases as the series is ascended. Thorpe and Rodger's work makes it evident that for the consideration of relationships between the viscosities of different substances, the viscosity constants of compounds should be compared at temperatures where the slopes of the viscosity-temperature curves for the different substances are the same. Since the data here reported were all taken at 20° no more definite comparisons can be made.

Vapor Pressure Measurements

The method used for the measurement of vapor pressures of the esters was that of Ramsay and Young.[1] This method is in common use, and needs no detailed description. It has the advantage over the static method that any volatile impurity contained in the substance whose vapor pressure is being measured will have a much smaller effect on the total vapor pressure. The vapors are continually passing over into the condenser and the fresh liquid is evaporating continually about as fast as it is supplied; while in the static method the vapors of a volatile impurity could cause equilibrium at a point where a large percentage of the total vapors might consist of the impurity. Furthermore, distillation can be produced at any desired temperature by merely varying the pressure under which the liquid evaporates. The pressures were read from a mercury manometer, and corrected at 0°. These values were then plotted as ordinates against the corresponding pressures as abscissae.

The values obtained experimentally are given in the tables below, as well as the values gotten by reading from the curves for every change of 5° in temperature. Wherever data have

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[1] Jour. Chem. Soc., 47, 42(1885).

been found giving vapor pressures of the esters as determined by other investigators these are also given for comparison.

Table IV—Isoamyl Formate

Experimental data		Values interpolated from curve	
Temp.	Pressure in mm Hg	Temp.	Pressure in mm Hg
122.50°	722.2	120.0°	679
115.45	587.3	115.0	602
110.05	497.8	110.0	493
105.30	426.4	105.0	422
100.75	366.4	100.0	360
94.40	295.2	95.0	307
90.55	257.8	90.0	258
84.20	213.2	85.0	217
79.94	179.2	80.0	180
75.01	143.9	75.0	147
74.87	143.8	70.0	121
69.50	116.7	65.0	98
65.39	97.7	60.0	79
59.64	77.5	55.0	63
54.90	61.7	50.0	49
49.98	49.0	—	—
47.98	44.6	—	—

Table V—Isobutyl Formate

Experimental Data

Temp.	Press. in mm Hg	Temp.	Press. in mm Hg
97.41°	737.6	73.75°	337.8
96.16	711.7	69.75	291.75
93.71	638.7	67.00	261.3
91.26	611.0	65.00	242.5
90.35	591.3	61.96	216.2
89.28	571.6	60.17	201.2
88.27	553.3	57.30	179.4
87.31	536.1	54.14	154.3
86.25	517.8	50.31	133.4
85.52	504.9	48.66	123.3
85.47	505.3	44.68	105.4
85.02	497.5	39.90	84.9
84.18	483.4	35.79	68.7
83.79	477.2	32.79	53.9
77.10	379.7	—	—

TABLE VI—ISOBUTYL FORMATE
Interpolated Values

Data read from the curve		From Schumann's data	
Temp.	Press. mm	Temp.	Press. mm
95.0°	687	95.0°	699
90.0	586	90.0	—
85.0	497	85.0	497
80.0	417	80.0	423
75.0	352	75.0	358
70.0	294	70.0	300
65.0	243	65.0	249
60.0	200	60.0	200
55.0	165	55.0	165
50.0	139	50.0	139
45.0	107	45.0	107
40.0	84	40.0	85
35.0	62	35.0	65

TABLE VII—ETHYL PROPIONATE
Experimental Data

Temp.	Press. in mm Hg	Temp.	Press. in mm Hg
98.33°	739.2	82.47°	441.0
97.12	709.9	80.77	414.1
96.21	690.2	77.86	373.1
95.35	670.7	74.76	332.4
94.59	656.0	70.56	284.9
93.54	634.1	66.16	238.0
92.77	618.8	65.66	232.7
91.67	597.0	61.75	204.7
90.48	574.1	57.38	173.6
89.57	556.8	55.51	157.9
88.66	540.7	54.76	152.3
87.84	526.2	50.63	127.3
86.96	515.7	51.02	129.5
86.20	498.1	48.78	117.1
85.39	486.6	44.66	97.6
84.28	467.9	39.85	78.8
83.56	457.0	36.06	65.8
—	—	33.80	58.8
—	—	32.17	54.4

TABLE VIII—ETHYL PROPIONATE
Interpolated Values

Temp.	Press. from curve mm	Young and Thomas mm	Schumann mm
35.0°	63		65
40.0	80	78	84
45.0	101		104
50.0	125	123	129
55.0	154		159
60.0	188	188	193
65.0	228		239
70.0	277	279	283
75.0	332		345
80.0	399	403	417
85.0	475		445
90.0	564	569	587
95.0	663		680
100.0	785	785	797

TABLE IX—PROPYL PROPIONATE

Experimental data		Interpolated values	
Temp.	Press. in mm Hg	Temp.	Press. from curve in mm Hg
121.5°	726.1	120.0°	703
115.1	599.4	115.0	597
109.8	504.6	110.0	509
104.4	423.9	105.0	398
100.3	369.8	100.0	367
95.3	310.1	95.0	310
90.5	265.9	90.0	263
84.4	215.7	85.0	218
84.0	211.4	80.0	180
79.7	176.3	75.0	147
74.8	146.6	70.0	122
70.7	123.3	65.0	98
65.4	104.4	60.0	78
60.7	82.3	55.0	63
55.7	63.7	50.0	49
49.8	49.8	—	—

TABLE X—ETHYL BUTYRATE

Experimental data		Interpolated values		
Temp.	Press. in mm Hg	Temp.	Press. from curve	Schumann
119.3°	722.2	120.0°	749	—
115.5	647.0	115.0	632	665
110.4	548.6	110.0	540	565
105.5	472.0	105.0	460	484
100.3	395.9	100.0	392	406
94.9	328.1	95.0	332	345
90.8	282.8	90.0	305	293
66.8	119.6	85.0	235	247
62.1	96.4	80.0	197	205
59.0	81.1	75.0	163	171
56.5	72.5	70.0	135	140
53.2	63.0	65.0	111	115
49.9	54.0	60.0	90	94
48.8	50.2	55.0	72	75
—	—	50.0	55	57

TABLE XI—ISOBUTYL VALERIANATE

Experimental data		Interpolated values		
Temp.	Press. in mm Hg	Temp.	Press. in mm Hg	Schumann's values
167.7°	734.2	170°	785	783
163.5	674.6	165	694	690
160.2	611.6	160	605	600
154.4	518.7	155	527	523
149.8	453.8	150	455	450
144.3	381.0	145	390	389
140.5	335.6	140	328	331
135.1	284.8	135	305	285
130.4	243.7	130	237	240
125.8	212.2	125	203	204
120.6	176.9	120	172	172
115.7	147.3	115	144	145
110.6	122.5	110	120	121
105.8	102.9	105	100	102
101.7	83.7	100	84	84
97.4	77.7	95	70	70
95.0	68.8	90	60	55
92.0	61.3	—	—	—

The values quoted from Schumann[1] were obtained by plotting his experimental data, and reading from the curves the values for the pressures corresponding to the desired temperatures.

The vapor pressures of propyl acetate were not measured as the sample was small and the full amount was needed for the heat of vaporization measurements.

From a comparison of the three sets of data, where such comparison is possible, it will be seen that the values obtained by us agree well with those found by Young and Thomas but do not, in general, agree with those obtained by Schumann.

Young and Thomas attempted to ascertain how far the generalizations of van der Waals regarding "corresponding" temperatures, pressures, and volumes are true for members of a group of closely allied compounds. They had previously found that these generalizations hold good for the four monohalogen derivatives of benzene, but when compounds of different chemical character were compared they found much greater deviations. They had found that these deviations were the greatest in the cases of the alcohols and acetic acid; so they considered it necessary to study the behavior of the esters formed from the alcohols and fatty acids.

The generalization which they made was that "if two substances are compared at pressures which are proportional to their critical pressures, their boiling points on the absolute scale will be proportional to their absolute critical temperatures, and their volumes, both as liquid and as saturated vapor, will be proportional to their critical volumes." We are here concerned with the first part of this generalization only, that regarding temperature and pressure.

Their calculations were carried out in the following manner: They took the pressures at the same fractions of the critical pressures that they had taken in the case of the benzene derivatives, using the ratios of the different pressures of fluorobenzene to its critical pressure as the pressure ratios at which to compare the boiling points of the esters. They first

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[1] Loc. cit.

calculated the vapor pressures of the different esters corresponding to the given ratios of their critical pressures. These different vapor pressures of the different esters were then "corresponding" pressures. The absolute boiling points of the esters at these "corresponding" pressures were found from the curves. Finally, the ratios of these absolute temperatures to the absolute critical temperatures of the esters were calculated. These final ratios for all the different esters of their "corresponding" temperatures to their critical temperatures should be constant for any given ratio of pressure to critical pressure, independent of the nature of the substances. But on examination they found a distinct, though not very great, deviation from constancy. They also found that these boiling point ratios in a homologous series rise slightly with increase in molecular weight, and that the values for isomers differ, the formates having the lowest and the acetates the highest values for the esters studied by them.

In order to examine in like manner the esters whose vapor pressures we had measured, it was necessary to take the values for the critical constants given by other observers. The only complete data found in the literature for the esters in question are given below.

Ester	t_k	p_k	Observer
Ethyl propionate	272.4	34.64	Nadejdine[1]
Ethyl propionate	272.9	33.16	Young[2]
Ethyl butyrate	292.8	30.24	Nadejdine
Isobutyl formate	278.2	38.29	Nadejdine

In the above table t_k is the critical temperature in degrees centigrade, and p_k is the critical pressure in atmospheres. Young and Thomas, in comparing the data obtained by them for the critical constants obtained by other observers, state that their results agree fairly well with those of Nadejdine in the cases of all the esters investigated. The results of

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[1] Rep. d. Phys., 23, 639 (1887).
[2] Dublin Proc., 12, 374 (1910).

Nadejdine are also confirmed by the later work of Young[1] for a number of substances. So, using the data of Nadejdine, calculations were made similar to those made by Young and Thomas. Table XII gives the pressures of the different esters corresponding to the stated fraction of their critical pressures. Table XIII gives the boiling points (absolute) which correspond to the vapor pressures given in Table XII. In Table XIV are tabulated the ratios of the temperatures in the preceding table to the critical temperatures of the esters.

TABLE XII—PRESSURES CORRESPONDING TO THE GIVEN FRACTIONS OF THE CRITICAL PRESSURE

Press. of fluorbenzene in mm Hg	Corresponding fraction of critical pressure of fluorbenzene	Ethyl propionate (Nadejdine's constant) mm	Ethyl propionate (Thomas and Young's constant) mm	Isobutyl formate (Nadejdine's constant) mm	Ethyl butyrate (Nadejdine's constant) mm
20	0.000590	15.53	14.87	17.17	13.56
50	0.001474	38.80	37.15	42.89	33.88
100	0.002949	77.64	74.32	85.82	67.77
200	0.005898	155.27	148.64	171.63	135.55
400	0.011800	310.65	297.38	343.38	271.19
760	0.022410	589.97	564.77	652.14	515.03

TABLE XIII—BOILING POINTS (ABSOLUTE) AT "CORRESPONDING PRESSURES"

Ratio of pressure to critical press.	Ethyl propionate (Nadejdine's constants)	Ethyl propionate (Young and Thomas' constants)	Isobutyl formate (Nadejdine's constants)	Ethyl butyrate (Nadejdine's constants)
0.000590	293.5°	292.0°	295.25°	307.5°
0.001474	301.0	300.5	303.0	315.75
0.002949	312.0	311.25	313.5	327.25
0.005898	328.25	325.75	329.0	343.0
0.011800	346.0	345.0	347.25	362.1
0.022410	364.5	363.0	366.25	381.5

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[1] Loc. cit.

TABLE XIV—RATIOS OF ABSOLUTE TEMPERATURES AT CORRESPONDING PRESSURES TO ABSOLUTE CRITICAL TEMPERATURES

Ratio of pressure to critical press.	Ethyl propionate (Nadejdine's constants)	Ethyl propionate (Young and Thomas' constants)	Isobutyl formate (Nadejdine's constants)	Ethyl butyrate (Nadejdine's constants)
0.000590	0.5379	0.5350	0.5356	0.5435
0.001474	0.5520	0.5504	0.5496	0.5581
0.002949	0.5721	0.5702	0.5688	0.5784
0.005898	0.6059	0.5966	0.5969	0.6062
0.011800	0.6345	0.6320	0.6299	0.6400
0.022410	0.6683	0.6650	0.6645	0.6744

Young and Thomas find that in those final ratios of the absolute temperature at corresponding pressures to absolute critical temperatures there is a distinct deviation from constancy. The *greatest* variations from the mean value of the constants for each of the six ratios as calculated from our data are: 1.02, 1.01, 0.79, 0.93 and 0.94 percent, respectively, whereas the values found by Young and Thomas for the ten esters studied by them show deviations of from 2 to 3 percent over the same range of temperature pressure ratios. The greater constancy of the boiling point ratios found by us seems to show that the vapor pressure measurements we have made are very nearly correct, and are probably more accurate than those which have been made by other observers.

Measurements of Specific Inductive Capacity

The specific inductive capacity of organic compounds has had very little attention, and the data available are meagre. Much of the data given by different investigators are not comparable as the measurements were made with waves of different lengths. It therefore seemed desirable to make measurements on these esters.

Drude's second method[1] for the measurement of dielectric constants was used. The method has now become a standard one and therefore need not be described, especially as Drude

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[1] Drude: Zeit. phys. Chem., 23, 282 (1897).

gives such a detailed description. While not as accurate as his first method, this second method has the advantages of requiring only a small amount of substance and of allowing the cell containing the substance to be kept closed during the experiment. Temperature control is also more difficult with the first method.

The apparatus was standardized by getting scale readings at 20° for mixtures of acetone and benzene whose specific inductive capacities are known. The scale readings were plotted against the known values for the dielectric constants of the mixtures, thus giving a calibration curve for the apparatus.

Great care was taken to obtain pure benzene and pure acetone. The benzene was prepared by the method suggested by Richards and Shipley[1] and the acetone by the method of Limpricht.[2] The benzene had a constant freezing point, and the acetone distilled between the temperature limits 56.87–56.88 at 760 mm pressure.

In order to control the temperature of the liquid while its specific inductive capacity was being measured, the cell was surrounded by a bath of water maintained at constant temperature. The "zero" of the apparatus was checked up each time it was used by taking the reading when a piece of copper wire was inserted in place of the cell. Several portions of each ester were measured, about twelve readings being made on each sample, and the average of all of these readings was considered to be the true setting. The values obtained are given below in Table XV, together with the values obtained by others who have used the same method.

Drude used the esters as they were obtained from Kahlbaum, without purification of any sort. Furthermore, he had no means of temperature control, or if he did have the fact is not stated, the measurements being made at different temperatures, probably the prevailing temperature of the

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[1] Jour. Am. Chem. Soc., 36, 1825 (1914).

[2] Liebig's Ann., 93, 238 (1855).

laboratory. These facts, especially the first, probably account for the differences between the values found by him and by us.

TABLE XV

Values found by M. and F.		Values obtained by others		
Substance	Spec. ind. cap. at 20°	Spec. ind. cap.	Temp. of meas.	Observer
Isobutyl formate	5.93	6.41	19.0°	Drude
Isoamyl formate	4.98	—	—	—
Propyl acetate	8.10	5.65	19.0	Drude
Ethyl propionate	5.75	5.68	18.5	Drude
Propyl propionate	4.66	—	—	—
Ethyl butyrate	5.91	5.12	18.0	Drude
Isobutyl valerianate	8.21	—	—	—

The property of specific inductive capacity is largely dependent on constitution; compounds of similar character and constitution having values which are of about the same magnitude. As can be seen from the few cases tabulated, the value decreases with ascent in a homologous series. However no definite relationship between this and other physical properties seems to have been found as yet.

Measurement of Refractive Indices

The literature contains but little data on the refractive indices of the esters, especially those of higher molecular weight.

A Pulfrich refractometer was used, and the measurements were made at 20° with sodium light. Several readings were taken on a sample of material, then a fresh portion was placed in the cell and a second series of readings was taken. This procedure was followed in the case of each ester, to be certain that no change was taking place in the material in the cell. The values found are given in Table XVI, together with whatever values have been found by other observers.

TABLE XVI

Substance	Refractive index 20°. $\mu\mu$ = 589	$n^{20°}$	Observer
Isobutyl formate	1.38568	—	—
Isoamyl formate	1.39772	—	—
Propyl acetate	1.38422	1.38438	Brühl[1]
Ethyl propionate	1.28414	1.38385	Eisenlohr[2]
Propyl propionate	1.39325	—	—
Ethyl butyrate	1.40002	1.39599	Landolt[3]
Isobutyl valerianate	1.40569	—	—

Laboratory of Physical Chemistry
University of Wisconsin
June, 1917

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[1] Liebig's Ann., 200, 139 (1880).

[2] Zeit. phys. Chem., 75, 585 (1910).

[3] Pogg. Ann., 122, 545 (1864).

CONTACT CATALYSIS. IV

BY WILDER D. BANCROFT

False Equilibria

We have seen that the poisoning of a catalytic agent is due to marked adsorption, which cuts down the adsorption of the reacting substances. We have also seen that the presence of sulphur trioxide tends to decrease the rate of reaction of sulphur dioxide and oxygen. We can now imagine a hypothetical case in which one of the reaction products is adsorbed so strongly that it acts as a poison. In that case we shall get entirely different results depending on the amount of catalytic agent present. If there is a large excess of catalytic agent the reaction will run to an end or to true equilibrium before the catalytic agent is entirely poisoned. If, on the other hand, there is only a small amount of catalytic agent, it will be poisoned very early in the course of the reaction and we shall have an apparent equilibrium reached from only one side which will vary with the amount of catalytic agent. For any given amount of catalytic agent we shall get an apparently definite end-point; but the value of the end-point will vary with the amount of catalytic agent taken. At least one case of this sort has been recognized definitely. Neilson[1] has studied the splitting of salicin and of amygdalin by platinum black. "It is found that the amount of splitting of salicin in a given time reached a maximum, and then with increasing time the amount of splitting was not proportional to the time, being materially less in the last twenty-four hours than it was in the preceding. This is due, no doubt, to the effect of the products of the splitting—especially the saligenin. It is more probably due, however, to the salicylic acid produced by the oxidation of saligenin to salicylic acid by the platinum. It is well known that salicylic acid has a marked retarding action on enzymes as shown by Kastle and Loeven-

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[1] Am. Jour. Physiology, 15, 148 (1906).

hart[1] in its action on lipase; and by Neilson[2] in its action on platinum black in the hydrolysis of ethyl butyrate.

"The experiments with amygdalin and platinum black were carried out in the same way as those with salicin. It was anticipated, however, that the amount of splitting by the action of platinum black on the amygdalin would be small, as it is well known from Bredig's work on the catalysis of hydrogen peroxide by colloidal platinum,[3] and from Neilson's work[4] on the hydrolysis of ethyl butyrate by platinum black, that hydrocyanic acid has a marked retarding action on the catalytic action of platinum. One of the splitting products of amygdalin is hydrocyanic acid; and according to the above experiments one would expect the action of platinum black on amygdalin to be retarded, if not stopped entirely. Such, indeed, was found to be the case, as the first experiment with tightly corked flasks was entirely negative. It occurred to me that by leaving the flasks uncorked the hydrocyanic acid would volatilize and the action would then proceed. This is in keeping with the well-known fact that removing one of the products of a chemical reaction allows the action to go on to completion. By leaving the flasks uncorked it was found by a qualitative test that platinum splits up the amygdalin. It was further seen that the action did not go on to completion, as the amount of sugar produced was small."

A much more interesting case, which has not previously been recognized as coming under this head, is that of false equilibria. Duhem[5] thought that it might be possible to have a reaction run a short way and then reach an apparent equilibrium which would not be the same as that apparently reached by the reverse reaction. These apparent but irreversible equilibria he called false equilibria for the obvious reason that they were not true equilibria. Roozeboom[6] has suggested

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[1] Am. Chem. Jour., 24, 491 (1900).

[2] Am. Jour. Physiology, 10, 197 (1903).

[3] Bredig: "Anorganische Fermente," 68 (1900).

[4] Neilson: Am. Jour. Physiology, 10, 197 (1903).

[5] Traité élementaire de Mécanique chimique, 1, 201 (1897).

[6] Zeit. phys. Chem., 28, 293 (1899).

calling them unilateral equilibria because the apparent equilibrium can only be reached from one side, while I once suggested calling them bilateral equilibria[1] because different apparent equilibria were reached from the two sides. The question of nomenclature has been unimportant because most people have considered that false equilibria were merely the result of experimental error. Since false equilibria, as defined by Duhem, are generally believed to be non-existent, it will be profitable to see exactly what Duhem's theory was before trying to decide how much of it should be revised today.

"The law of the displacement of the equilibrium with the temperature, which is the fundamental law of chemical mechanics, remained unknown for a very long time. It was hard to discover because it was contradicted by an enormous number of special cases; because it is an incomplete law; and because the classical thermodynamics, from which it follows logically, is itself an incomplete science and not in accord with an immense number of experimental facts. Let us examine some of the contradictions between the law of the displacement of the equilibrium with the temperature and the definitely established facts of chemistry. Gaseous water forms from oxygen and hydrogen with a considerable evolution of heat. Suppose now we consider a chemical system containing the elements of water. If we heat it either at constant volume or at constant pressure, we ought, according to the law of the displacement of the equilibrium, to observe the following phenomena. At low temperatures most of the gas should be present as water vapor and the amount of water vapor in the system should decrease as the temperature rises. These predictions are confirmed satisfactorily by experiments at high temperatures; but they do not hold at all at low temperatures. Below a dull red heat a system consisting of a mixture of water vapor, hydrogen, and oxygen remains in equilibrium no matter what its composition, even though it consists of perfectly dry hydrogen and oxygen, for

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[1] Bancroft: Jour. Phys. Chem., 5, 182 (1901).

it is only at a temperature of the dull red that these gases begin to react.

"Carbon dioxide and sulphur dioxide also form with a marked evolution of heat. When oxygen is heated at constant volume in presence of carbon or sulphur, the amount of carbon dioxide or sulphur dioxide should be very large at low temperatures and should decrease continuously with rising temperature. As a matter of fact oxygen can be kept indefinitely in contact with carbon or sulphur at low temperatures without reacting with these substances. It is only at a red heat that the reaction takes place. At higher temperatures these systems follow the law for the displacement of the equilibrium with the temperature, as was shown by H. Ste. Claire Deville.

"It would be possible to cite an infinite number of exothermal compounds which do not conform to the law of the displacement of the equilibrium with the temperature. Similar exceptions are to be found among endothermal compounds. Silver oxide is formed from silver and oxygen with absorption of heat. Consequently, at constant pressure, a system consisting of silver oxide, silver, and oxygen, should contain less oxygen and more silver oxide, the higher the temperature. This is true to the extent that oxygen does not attack silver at low temperatures and that silver oxide is formed at very high temperatures, as was shown by Proust, by H. Ste. Claire Deville and Debray, and by MM. Troost and Hautefeuille. On the other hand silver oxide does not decompose below 100° as the theory requires.

"Hyper-ruthenic acid behaves in a similar manner. It is formed from oxygen and ruthenium dioxide with absorption of heat. At high temperatures oxygen reacts direct with ruthenium dioxide, just as it should; but the theory proves at fault at lower temperatures, because it is only above 107° that liquid hyper-ruthenic acid decomposes into ruthenium dioxide and oxygen; at lower temperatures it is perfectly stable. There are many other instances.

"All the exceptions which we have cited and all those which we might have cited have one characteristic in common. When the classical thermodynamics, as hitherto developed, predicts that a system will be in equilibrium under certain conditions, it will be in equilibrium under those conditions; but it may happen that it is also practically in equilibrium under conditions when it ought not to be in equilibrium according to the theories as outlined. This general rule may be formulated in the following way: Whenever the classical thermodynamics predicts that it is impossible for a system to change from one state to another, that change cannot be realized experimentally; but when the classical thermodynamics predicts that a system will necessarily change from one state to another, the predicted change does not always occur. This generalization has been stated very clearly by J. Moutier.[1]

"We will give the name of false equilibria to those equilibria which can be realized experimentally although thermodynamic theory, as hitherto developed, calls them impossible; we will give the name of true equilibria to those equilibria which are in conformity with thermodynamic theory. Since experiment shows that both are always realizable, we will now develop and complete the thermodynamical theories so as to take account of the false equilibria as well as of the true equilibria.

"It is easy to see which of the hypotheses, on which our present thermodynamical theory rests, is the one which excludes the possibility of the phenomena of false equilibria. We have recognized that a system defined by variables, which we have arbitrarily called normal, is kept in equilibrium by external influences A,B,...L, defined without ambiguity as functions of the temperature T and of the normal variables $\alpha,\beta, \ldots \lambda$ by the equations of equilibrium

$$\begin{aligned} A &= f_\alpha(\alpha,\beta,\ldots\lambda,T), \\ B &= f_\beta(\alpha,\beta,\ldots\lambda,T), \\ &\ldots\ldots\ldots\ldots\ldots\ldots \\ L &= f_\lambda(\alpha,\beta,\ldots\lambda,T). \end{aligned}$$

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[1] Bull. Soc. philomathique, Jan. 10 (1881); Encyclopédie chimique de Frémy, Introduction, 2 (1881).

These equations can be solved for $\alpha,\beta\ldots$, giving

$$\alpha = h_A(A,B,..L,T),$$
$$\beta = h_B(A,B,..L,T),$$
$$\cdots\cdots\cdots\cdots$$
$$L = h_L(A,B,...L,T).$$

The functions h_A, $h_B,\ldots h_L$ may have a limited or an unlimited number of values for each set of values of A,B,...L,T; but if they have an unlimited number of values, these values are not continuous. If then we determine a set of values of the variables $\alpha,\beta\ldots\lambda$, which will define a state of equilibrium of the system at the temperature T and under the external influences A,B,...L, we may find for this set of values, either a single solution, or several solutions or an infinite number of solutions; but, in this last case, these infinite sets of values for $\alpha,\beta,\ldots\lambda$ will not correspond to a continuous series of states of the system.

"This conclusion does not hold for systems which show the phenomenon of false equilibrium. Take, for instance, a system containing hydrogen, oxygen, and water vapor at 200° under constant atmospheric pressure. Whatever the percentage of water vapor and whatever the percentage of hydrogen and oxygen, the system is in equilibrium. At the same temperature of 200° and at the same atmospheric pressure, we may have an infinite number of states of equilibrium and these form a continuous series. All the cases of false equilibria behave similarly. Since the phenomena of false equilibrium do not conform to one of the fundamental hypotheses of the classical thermodynamics, it is not surprising that the conclusions to be drawn from thermodynamical theory do not enable us to predict the phenomena of false equilibrium.

"The false equilibria which one meets in chemical mechanics have analogies among purely mechanical equilibria. Take, for instance, a body which slides on an inclined plane. According to the theorems of the classical dynamics, this body cannot be in equilibrium under the action of gravity. As a matter of fact, with a given body and a given inclined plane there will be equilibrium when the slope is less than a certain value. We can account for this contradiction by saying that there is friction between the body and the inclined plane, and that the classical dynamics takes no account of friction. If we analyze this or any other case of equilibrium due to friction, we can deduce the following generalization. Whenever the mechanics which ignores friction predicts that a given system is in a state of equilibrium, that system will be in equilibrium; but it may happen that the system will be in equilibrium under conditions not foreseen by the mechanics which ignores viscosity. This generalization brings out strikingly the analogy between mechanical equilibria due to friction and the chemical false equilibria. The analogy is even closer because the mechanics which ignores friction may be considered as a special case of the classical thermodynamics.....

"It has been held[1] that the equations of the mechanics which ignores friction are entirely general; but we should apply them to abstract bodies, perfectly rigid and perfectly polished, whereas actual bodies are more or less plastic and more or less rough. This gives rise to disagreements between the predictions of mechanics and the facts; but these discrepancies will disappear if we take account of the plasticity and roughness of actual bodies instead of applying the equations of mechanics to idealized substances with which we are not experimenting. If we introduce into the equations of statics and dynamics a new term in order to account for the effects of friction, it is not because we considered the original equations as inadequate or imperfect; but is merely to handle in mass by this fictitious term the varied and complex phenomena which give rise to friction and which cannot be handled in detail.

"This view is well founded to a certain extent. An important part of the phenomena of friction is due to the roughness and plasticity of the substances in contact. As evidence of this we find that the friction decreases as we work with harder and more highly polished bodies; but it does not follow

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[1] Appel: Traité de Mécanique rationelle, 1, 271.

necessarily that all the phenomena of friction can be ascribed in the last analysis to slight irregularities of the surfaces in contact.

"A view similar to that which has just been outlined in regard to friction has been put forward by J. W. Gibbs[1] in regard to chemical false equilibria. In discussing chemical equilibria he considers the systems as composed of one or more phases, each homogeneous throughout, and the different phases having no effect one on another. Actual systems are more complicated because the phases of which they are composed vary in composition at the bounding surfaces and because the different elementary masses exercise, one on another, influences which are very powerful but which are noticeable only at very short ranges. These forces account for the phenomena of capillarity and they should also account for the phenomena of false equilibrium which are not covered when the principles of the classical thermodynamics are applied to idealized forms of natural systems.

"There is unquestionably a great deal of truth in what Gibbs says. Capillary phenomena do account for a certain number of the phenomena of false equilibrium. They show, for instance, why a bubble of vapor cannot form in the midst of a homogeneous liquid, while the liquid can evaporate whereever there is a bubble of gas or vapor. It also accounts for retarded boiling, and for boiling starting when a bubble of gas is introduced. It also accounts for a large number of phenomena, such as: the supersaturation of solutions of gases which ceases when a gas bubble is introduced; the suspended decomposition of certain endothermal compounds like liquid nitrous acid and hydrogen peroxide, where decomposition takes place on introducing gas bubbles or porous substances which contain air; and also the retarded condensation of supersaturated water vapor where condensation takes place when drops of water or particles of dust are present.

"Analogous to these phenomena are also: the supercooled liquids which solidify when a small crystal is added;

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[1] Trans. Conn. Acad., 3, 129, 416.

supersaturated salt solutions which crystallize on addition of the solid salt or of an isomorphous salt; and also the delayed changes of certain crystalline modifications into others, such as the change at ordinary temperature of monoclinic sulphur into rhombic sulphur, a change which takes place on contact with a particle of rhombic sulphur. It is also to capillary action that one must attribute the properties of certain hygroscopic substances and the many phenomena due to porous substances.

"Many of the false equilibria are thus apparent false equilibria. If the experimental data do not conform to the predictions of the classical thermodynamics, it is not that the fundamental laws of this science are inexact or incomplete but merely that the substances which we use experimentally have not the idealized properties which we ascribe to them. Is this, however, the whole explanation? Can all the phenomena attributed to viscosity or classed under the heading of false equilibria be accounted for by the classical equations of mechanics and thermodynamics by taking into account some hitherto unnoticed complications in the systems studied experimentally? When put in this form the question cannot be answered. One can always claim that the mechanical and chemical false equilibria can be accounted for in accordance with the equations of the classical mechanics and thermodynamics assuming that the unknown complications will be discovered later. It seems to me, therefore, that the question should be put in a different form. Do the equations of the classical mechanics and thermodynamics depend solely on certain hypotheses? When the equations break down, may we not ascribe the failure to the equations themselves, instead of postulating that the trouble is due to the inadequacy of the concepts by which we have represented the actual substances, and to which we have applied these equations? In other words does the deduction of these equations rest upon certain hypotheses such that we could throw them overboard and replace them by other hypotheses from which we could deduce more satisfactory thermodynamics and mechanics, which would take account of false equilibria and friction?

"When the question is put in this form, there is no doubt about the answer. The deduction of the equations of the classical thermodynamics and of the mechanics of substances devoid of friction, which is a special branch, rests upon at least one entirely arbitrary hypothesis, which is as follows: When the state of the system is given, the external forces, which keep it in equilibrium in this state, are determined without ambiguity by the so-called equations of equilibrium of the system. As has been already shown, we are not forced to accept this hypothesis. If we reject it and if we deny the existence of the equations of equilibrium, we can without contradiction introduce into the equations of the classical mechanics and thermodynamics a term which will take account of the false equilibria and of the phenomena of friction."

After nineteen pages of mathematical discussions which I omit, Duhem[1] proceeds as follows: "Either at constant pressure or at constant volume, the two lines which limit the regions of false equilibrium are, at low temperatures, very far from the line corresponding to the true equilibria. As the temperature rises they come nearer the latter line and approach it asymptotically as the temperature increases indefinitely. Thus the field of false equilibria is very large at low temperatures, contracting as the temperature rises, until at high temperatures it is an exceedingly thin strip, all points in which are extremely close to the line corresponding to true equilibrium. At low temperature one may obtain states of equilibrium which differ widely from those predicted by the classical thermodynamics. At high temperatures, on the other hand, no equilibrium can be obtained which differs appreciably from the equilibria predicted by the classical theory. Chemical mechanics, therefore, gives rise to more simple laws at high temperatures than at low ones. In order to discover the relation between chemical mechanics and thermodynamics, it was necessary to know the chemistry of high temperatures, a point which the genius of H. Ste. Claire Deville recognized. If people had confined themselves to the study of reactions

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[1] Traité élémentaire de Mécanique chimique, 1, 227 (1897).

at low temperatures, the results would have been complicated by the terms due to friction and thermochemistry would not have discovered the fundamental laws of chemical mechanics. We may also note that dynamics came into its own from the day when the physicists, and especially Galileo, dared to ignore friction and to formulate the laws of dynamics such as the law of inertia. It is true that the dynamics thus created is incomplete; but it prepared the way for the more complete dynamics which takes account of friction."

Working in Duhem's laboratory, Pélabon studied the reaction between selenium and hydrogen with special reference to the theory of false equilibrium. He found that above 320° the equilibrium was strictly reversible but that at lower temperatures different end-points were obtained for the formation and the decomposition of hydrogen selenide. At 170° the gas phase contained about 28 percent H_2Se when starting with hydrogen selenide and zero percent when starting from hydrogen and selenium. At 270° the corresponding values were about 16 and 4.9, while at 300° they were 17 and 12.5, respectively. Similar results were obtained by Pélabon[1] for hydrogen sulphide. These results have been called in question by Bodenstein.[2] "Hélier and Gautier[3] reported on the slow reaction between hydrogen and oxygen, and between carbon monoxide and oxygen in a heated porcelain tube. The reaction only went to a definite end-point dependent on the temperature although neither water nor carbon dioxide dissociated at all at these temperatures. Pélabon[4] obtained similar results in a study of the formation of hydrogen sulphide from hydrogen and sulphur, and also when he studied the reaction of selenium with hydrogen,[5] the reaction in this latter case

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[1] Mém. Sci. phys. Bordeaux, [5] 3, 257; Comptes rendus, 135, 35, 686 (1897).

[2] Zeit. phys. Chem., 29, 155, 315 (1899).

[3] Comptes rendus, 122, 566 (1896); Hélier: Ann. chim. phys., [7] 10, 521; 11, 78 (1897).

[4] Comptes rendus, 124, 686 (1897).

[5] Pélabon: Ibid., 121, 401 (1895); 124, 360 (1897); Zeit. phys. Chem., 26, 657 (1898).

giving rise to a reversible equilibrium above 320° whereas at lower temperatures both the formation and the decomposition were very limited in amount.

"The common characteristic of all these investigations is that the reaction under investigation comes to a halt before the reacting substance is used up and before the reaction is balanced by the reverse reaction. The states thus obtained bear a superficial resemblance to the equilibria which are accounted for by thermodynamics and the mass law and they have consequently been called 'false'[1] or 'apparent'[2] equilibria. These false equilibria have interested the physical chemists very much. While Ostwald[3] has outlined the three investigations in rather non-committal reviews in the *Zeitschrift für physikalische Chemie*, van't Hoff[4] has accepted the results of the French investigators completely and has shown the relation between them and the observations which he himself had made with his students on the slow oxidation of phosphorus and phosphine. There certainly is some resemblance between the two sets of experiments.

"That these investigations attracted a great deal of attention is not surprising. Reactions, which come to a halt before being balanced by the reverse reaction, would constitute an entirely new class of phenomena and if Duhem's attempt at a thermodynamic treatment of the case should have even a fraction of the success which followed the application of the mechanical theory of heat to true equilibria, this would constitute an enormous advance for physical chemistry or for all the natural sciences. After studying the experimental data in these papers, it seems to me that a somewhat sceptical observer would feel that the experiments were not sufficient to establish definitely a law of such fundamental importance and especially one which contradicts everything we have known before. Pélabon's experiments are quite insufficient to prove

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[1] Duhem: Traité élémentaire de Mécanique chimique, 1, 203 (1897).

[2] Van't Hoff: "Vorlesungen," 1, 206.

[3] Zeit. phys. Chem., 19, 499 (1896); 24, 382 (1897).

[4] "Lectures on Theoretical Physical Chemistry," 1, 211, 236 (1898).

that the false equilibria are really final states in the formation and decomposition of hydrogen sulphide because with increasing time the data given as equilibrium data show a slight but recognizable drift, while in the experiments on hydrogen sulphide the author gives the data for the so-called equilibria without any proof at all that they represent equilibria.[1] Hélier has treated this fundamental question more thoroughly for he has followed the gradual attainment of the false equilibrium in a complete series and thus has established conclusively its existence under his conditions. On the other hand there are many points in his paper both in regard to the arrangement of the experiment and to the data, which are open to criticism and which make it very possible that serious errors may have occurred.

"For these reasons it seemed to me desirable to obtain more and, especially, more carefully determined data. If the new experiments confirmed the results of the earlier work, it was to be expected that a more careful study of the gradual approach to equilibrium might give some clue to the puzzle, just as the study of the reverse reaction was necessary to the complete understanding of the dynamic nature of the true equilibria. On the other hand, if the new experiments did not confirm the actual occurrence of false equilibria, there was no longer any discrepancy between the results and the law that all reactions come to a halt only at the absolute zero. Further, this would eliminate a group of phenomena which can only with difficulty be fitted into the theories of physical chemistry. In either case it seemed to me that the experiments referred to showed that the reactions in question were admirably suited for the study of gas reactions taking place regularly, and that alone would have induced me to study these reactions more closely. This conclusion has turned out to be right. With these things in mind I have studied the three reactions—the formation of hydrogen sulphide, hydrogen selenide, and water."

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[1] [This statement was shown by Duhem to be wrong and was later withdrawn by Bodenstein.]

In a later paper on the formation and decomposition of hydrogen sulphide, Bodenstein[1] says: "The formation of hydrogen sulphide from hydrogen and an excess of sulphur proceeds until the hydrogen is completely used up, the reaction running with a smoothness such as is rare in gas reactions, especially in those involving heterogeneous equilibria. The figures[2] given by Pélabon for the limits of formation of hydrogen sulphide are, therefore, nothing more than arbitrarily selected points from a reaction that is still going on. The theoretical speculations of Duhem in regard to false equilibria have, therefore, no experimental basis."

Naturally this brought a reply from Duhem.[3] "We now come to the discrepancy between the results of Bodenstein and Pélabon. Pélabon found that hydrogen sulphide is formed when hydrogen gas is heated with liquid sulphur in a closed vessel below 350°. According to Pélabon this reaction is a limited one and according to Bodenstein it runs to an end. To what can this discrepancy be due since it is quite certain that Pélabon's data represent end states in spite of Bodenstein's contention to the contrary? At any given temperature the reaction between hydrogen and sulphur is a limited one; but the actual limit depends on the mass of the sulphur, increasing with it, so that the reaction can be practically complete if the mass of the sulphur is sufficiently large. To illustrate this I give a few data from the article cited by Bodenstein. At 280° with a tube holding about 7 cc the end value x in percentages is 33.56, 60.4 or 90.3 for masses of sulphur equal to 0.02, 0.1, or 1.0 g, respectively. This effect is due to the marked adsorption of hydrogen sulphide by liquid sulphur, which was studied carefully by Pélabon, and especially in the paper[4] which Bodenstein did not cite. Pélabon has compared this absorption with the absorption of hydrogen

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[1] Zeit. phys. Chem., 29, 321 (1899).

[2] When considered as reaction velocity measurements, these data agree approximately with those I have obtained.

[3] Zeit. phys. Chem., 29, 711 (1899).

[4] Pélabon: Comptes rendus, 24, 35 (1897).

selenide by liquid selenium, a phenomenon which he discovered and studied. Because Ditte overlooked this absorption, he made a number of errors in his experiments on the formation and dissociation of hydrogen selenide, errors which were corrected by Pélabon.

"Bodenstein appears not to have thought or cared about this absorption of hydrogen sulphide by liquid sulphur. How much sulphur did he have in his tubes? No weights are given. He tells only that the sulphur was introduced in coarse lumps; that he always added enough so that the vapor should be saturated; that he, however, avoided too large an excess because that introduced complications; and that the liquid sulphur was distributed in fine drops all over the walls of the tube before the experiment began. All that one can make out of these statements is that he doubtless used much larger masses of sulphur than were used in Pélabon's experiments which he attacks. Pélabon added 0.02 g sulphur to a tube of about 7 cc content. Since Bodenstein used a tube of 30 cc content, he should have used less than 0.1 g sulphur to make his results comparable with those of Pélabon. Since Bodenstein did not weigh the sulphur he has wasted his time over a lot of useless experiments."

In a paper on the formation of hydrogen selenide which appeared before this criticism of Duhem but probably after the latter was written, Bodenstein[1] finds that liquid selenium increases the rate of formation and of dissociation of hydrogen selenide. By using an excess of selenium he succeeded in obtaining reversible equilibria at temperatures below 320° and he, therefore, concludes that Pélabon's data are wrong. This conclusion does not hold if the equilibrium varies with the amount of selenium present as Duhem believes. In a third paper, Bodenstein[2] tried in vain to repeat Hélier's work on false equilibria with hydrogen and oxygen. Since the reaction was shown to take place solely at the walls of the con-

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[1] Zeit. phys. Chem., 29, 429 (1899).

[2] Ibid., 29, 665 (1899).

taining vessel, it is possible that the discrepancy is due to differences in the materials of the porcelain tubes.

In a reply to Duhem, Bodenstein[1] points out that to form ten percent hydrogen selenide at 250° without any catalytic agent would probably require about seven months and that Pélabon did not carry on his experiments long enough to make sure that equilibrium was reached. He also states that he weighed the sulphur in his experiments, though he did not give the weights. For tubes holding 22 cc he used 0.15 g sulphur and for tubes holding 70 cc 0.37 g sulphur. Bodenstein's account of his experimental work is good and the data of Hélier and of Pélabon have never been confirmed either by themselves or by anybody either in Duhem's laboratory or elsewhere. Consequently it is not surprising that people have considered the theory of false equilibria as effectively disproved.

While the experiments of Hélier and of Pélabon may have been faulty, it does not follow necessarily from Bodenstein's work that they were. Bodenstein has throughout made the tacit assumption that the mass of the catalytic agent has no effect on the equilibrium and he has not considered the possibility of the catalytic agent being poisoned. On the other hand, if hydrogen selenide is adsorbed strongly by liquid selenium or hydrogen sulphide by liquid sulphur, the catalytic agent would be poisoned to a greater or lesser extent depending on the amount of catalytic agent present.[2] With more selenium or sulphur the reaction would go farther, just as Duhem says, and reversible equilibrium would be obtained in case sufficient catalytic agent were present. There is no doubt that Bodenstein used more sulphur and more selenium than Pélabon did and it is therefore possible, though not proved, that the discrepancy between Pélabon's results and those of Bodenstein, is due to the differences in the amount of sulphur and selenium taken by the two investigators.

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[1] Zeit. phys. Chem., 30, 567 (1899).

[2] [Bodenstein claims that sulphur has no catalytic action; but this is probably wrong.]

To make the argument complete, it should be shown that liquid sulphur adsorbs hydrogen sulphide strongly or liquid selenium hydrogen selenide. Pélabon[1] has observed some surprising results with liquid sulphur and hydrogen sulphide. At 170° liquid sulphur takes up a small amount of hydrogen sulphide and at 440° it takes up more. This hydrogen sulphide is apparently not given off again until the sulphur solidifies. Even if the sulphur is allowed to cool in a vacuum the hydrogen sulphide is not evolved until the sulphur solidifies. We are dealing here with relatively large masses of gas because Pélabon states that eight grams of sulphur took up 2.56 cc hydrogen sulphide at 440°. As Pélabon himself points out, this is not a true solution of hydrogen sulphide. While one would like to see the matter studied more carefully, it seems probable that liquid sulphur adsorbs a certain amount of hydrogen sulphide so strongly that the vapor pressure of the latter is very small. If solid sulphur does not show this adsorption, that would account for the gas being evolved when the sulphur solidified. I do not know at all why the apparent adsorption should increase so with the temperature. One is, of course, tempted to connect it with the variation in the relative amounts of the different modifications of liquid sulphur; but in that case the hydrogen sulphide should be given off on cooling or it should be possible, by suitable manipulation, to make the sulphur take up a great deal more hydrogen sulphide at 170°. It is quite possible that this is the case because Pélabon had no theory to guide him in this matter. In connection with this it is interesting to note that Smith and Holmes[2] found that hydrogen sulphide changes the amount of amorphous sulphur in the melt.

Duhem has used the term "false equilibrium" to signify any mixture of hydrogen, oxygen and water vapor, for instance, which was not in reversible equilibrium. At other times he has limited it to cases where a partial reaction has taken place without the reaction running to an equilibrium. It is in the

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[1] Comptes rendus, 124, 35 (1897).

[2] Zeit. phys. Chem., 42, 469 (1903).

latter sense that I shall use the term hereafter. While the phenomena of false equilibria must appear in all cases where the reaction velocity is negligible in the absence of a catalytic agent and when the catalytic agent is poisoned sufficiently by one or more of the reaction products, we cannot claim as Duhem did that the apparent end-point depends solely on the temperature. It depends on the temperature and on the relative mass of the catalytic agent which is a very different thing. From this point of view the false equilibria do not present any theoretical difficulties. Whether hydrogen and oxygen really react with immeasurable slowness at ordinary temperatures in the absence of a catalytic agent is of great importance theoretically; but fortunately it does not need to be discussed now because we are undoubtedly dealing with catalytic agents whenever we have to consider false equilibria. If one wishes to apply a special name to these phenomena we can say that false equilibria are the results of autotoxic catalysis.

Since enzymes are poisoned by many substances in something the same way that colloidal platinum is, it seems worth while to see whether autotoxic catalysis would account for some of the peculiarities in enzyme action which have puzzled people. If autotoxic catalysis occurs, we should expect that the presence of the reaction products would cut down the reaction velocity even though the reverse reactions were negligible. If the poisoning action of the reaction products is sufficient, we should get false equilibria if we started with small amounts of the enzymes and the reaction would run to an end if we took larger amounts of the enzymes. Both these phenomena have been observed.

Tammann[1] points out that it seems to be rather a general thing that the reaction products cut down the action of unorganized ferments. "It has been said that unorganized ferments lose their activity as a result of their action in causing hydrolysis of substances. The proof for this statement is not forthcoming. As will be shown, it is not probable that

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[1] Zeit. phys. Chem., 18, 426 (1895).

a ferment is weakened as a result of its action. It is a fact that while it is acting it does lose some of its activity; but it is very probable that this decrease in activity is independent of the action itself. The following experiments do not answer the question whether the retarding action of the reaction products is due to an acceleration of the rate of decomposition of the ferment or to a partial conversion of the ferment into an inactive or less active modification. Cases are known[1] in which the reactions, such as that of emulsion or amygdalin or salicin at low temperatures, come apparently to a halt after some time or proceed at a scarcely noticeable rate even though there are considerable amounts of amygdalin or salicin still present. In such cases the reaction can be carried further either by removing the decomposition products or by raising the temperature. The effect produced by removing the reaction products is an argument in favor of the view that the catalytic action of the ferment has been decreased and against the assumption of an increase in the rate of decomposition of the ferment."

Kastle and Loevenhart[2] studied the action of lipase on ethyl butyrate. They found that the rate of decomposition varied but slightly with the concentration of the ester, which is not unreasonable if the rate of diffusion of the reaction products out of the lipase phase is the important factor.[3] They also found that the reaction was incomplete unless relatively large amounts of the enzyme were employed. I do not quite understand their reasoning in regard to this. "Whether with lipase of different origin or with varying amounts of the same enzyme the limits reached in all cases would be the same is a matter which can only be settled by further investigation. The fact that the hydrolysis is not complete under ordinary circumstances is in keeping with the more or less regular falling off in the velocity of the reaction described in the above, and is probably to be explained by the fact that the hydrolysis

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[1] Tammann: Zeit. phys. Chem., 16, 285 (1892).

[2] Am. Chem. Jour., 24, 491 (1900).

[3] Cf. Nelson and Vosburgh: Jour. Am. Chem. Soc., 39, 790 (1917).

of an ethereal salt [ester] by lipase is a reversible process, and that the enzyme, as a catalytic agent, is concerned chiefly in bringing about a condition of chemical equilibrium between the ethereal salt and the water and the product of the hydrolysis. Acids also have been found to greatly inhibit activity of the enzyme, so that the great falling off in the rate of the hydrolysis is doubtless, to some extent at least, assignable to this cause."

There seems to be a tacit assumption that the equilibrium concentration depends on the amount of the catalytic agent, which is not true as regards the ordinary theory. The authors seem also to make a curious distinction between butyric acid as an acid and butyric acid as a reaction product of ethyl butyrate.

Kastle and Loevenhart do not feel certain that the reaction products always retard the reaction. "In spite of the vast amount of work which has been done upon the enzymes, we possess at present no unifying conception as to the manner of their action. For the solution of this problem, we must probably look to the study of the kinetics of enzyme action, and one of the first questions to present itself in this connection is, are the enzymes reversible in their action? If so, then an accumulation of the products of their action should have an increasingly inhibiting effect on the further progress of the change, until finally equilibrium would be established between the initial substance and the products of the change.

"O'Sullivan and Tompson,[1] in their exhaustive study of the action of invertase on cane sugar, could not observe any inhibiting effect from the presence of the products of the change. On the other hand Sheridan Lea[2] found the digestion of starch by salivary diastase to be more rapid and much more complete when the products of digestion were removed by dialysis than when the digestion was performed under identical conditions but without this precaution. He obtained similar results in his investigation of tryptic digestion. As

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[1] Jour. Chem. Soc., 57, 926 (1890).

[2] Jour. Physiology, 11, 226 (1890).

to the effect of peptone on peptic digestion, the views are somewhat contradictory. Kühne[1] states that peptone has a retarding effect on peptic digestion, while the opinion of Chittenden and Ely[2] contradicts this."

Kastle and Loevenhart are wrong in postulating that a retarding of the reaction by the presence of the reaction products necessarily connotes reversibility. It may be due to the toxic action of the reacting products of the catalytic agent. We can formulate the effect due to the reaction products more clearly now. When the action of the catalytic agent is merely due to the increased concentration of the reacting substances at the surface of the catalytic agent, the reaction products need not necessarily have any effect on the reaction velocity in the case of a practically irreversible reaction. If the increased reaction velocity is due in part or entirely to the fact that the catalytic agent adsorbs one or more of the reaction products more strongly than the reacting substances, the presence of the reaction products will necessarily affect the reaction velocity, though the change in the reaction velocity, being due to a specific adsorption, may be very small in some cases and very large in others.

Since writing these four papers my attention has been called to two papers by Bodenstein and Fink[3] in which are set forth clearly some of the points which have been emphasized in this series. The only explanation that I can offer for overlooking these important papers, which are really due to Fink, is that when I read them I did not know enough to appreciate their real value.

The general conclusions of this paper are:

1. If one of the reaction products is adsorbed sufficiently strongly by a catalytic agent, it will poison that catalytic agent.

2. If a catalytic agent is poisoned sufficiently the reaction will come practically to a halt.

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[1] "Lehrbuch physiol. Chemie," 39 (1866).

[2] Jour. Physiology, 3, 327.

[3] Zeit. phys. Chem., 60, 1, 46 (1907).

3. When a reaction is brought to a standstill because the catalytic agent is poisoned by one of the reaction products, the apparent equilibrium will depend on the relative amount of the catalytic agent.

4. A system in which there was a constant amount of catalytic agent would present the phenomena of Duhem's false equilibria if the catalytic agent were poisoned sufficiently by one of the reaction products.

5. Melted selenium acts as a catalytic agent for the reaction between hydrogen and selenium; it is apparently poisoned by hydrogen selenide.

6. Melted sulphur probably acts as a catalytic agent for the reaction between hydrogen and sulphur, though this is disputed by Bodenstein; it is apparently poisoned by hydrogen sulphide.

7. It is possible, though not proved, that the discrepancy between Pélabon's and Bodenstein's results with hydrogen sulphide and hydrogen selenide is due to Bodenstein having used relatively more sulphur and more selenium than Pélabon did, just as was claimed by Duhem.

8. With varying amounts of catalytic agent to be poisoned, one may get all possible false equilibria between the limit of no reaction and the limit of reversible equilibrium.

9. The theory of false equilibrium as outlined in this paper is in harmony with all our thermodynamical relations.

10. The phenomena of false equilibria are to be observed in enzyme reactions.

11. An enzyme reaction often will not run to an end unless a large excess of enzyme be present.

12. In many cases the presence of the reaction products cuts down the reaction velocity in enzyme reactions even though the reaction is practically irreversible.

Cornell University

THE VELOCITY OF SAPONIFICATION OF CERTAIN ESTERS BY TENTH-NORMAL POTASSIUM HYDROXIDE IN DIFFERENT SOLVENTS AT 25° C[1]

BY ERNEST ANDERSON AND H. B. PIERCE[2]

Purpose of the Investigation.—This investigation was undertaken for two purposes; first, to determine whether or not the ratio of the velocities of saponification of any ester A in the four solvents used is the same as the ratio of any other ester B; second, to determine whether or not the velocities of saponification of the esters of any two alcohols with the same acid always have the same ratio irrespective of what the acid may be, and conversely whether or not the esters of any two acids with the same alcohol always have the same ratio irrespective of what the alcohol may be.

It is evident that if these two questions could be answered in the affirmative the whole problem of determining velocities of saponification would be rendered extremely simple. For instance, if the ratio of the velocities of saponification in the different solvents were known it would be possible to calculate the velocity of saponification of an ester in any of the solvents after determining experimentally its velocity of saponification in one solvent. Furthermore, by tabulating the acids along a vertical column and the alcohols along a horizontal column and determining the velocity of saponification of all the esters of one alcohol with the various acids and all the esters of one acid with the various alcohols, it would be easy to calculate by simple proportion the velocity of saponification of any ester in the table. As an illustration consider the following table which gives the velocity of saponification of certain esters by 1/10 normal potassium hydroxide at 25° C in a solution of 90 percent methyl alcohol.

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[1] Contribution from the Massachusetts Agricultural College.

[2] The authors wish to thank Mr. C. Wies and Mr. O. M. O'Neil for assistance in some of the experimental work.

	Methyl	Ethyl	*n*-Propyl
HI	—	0.0_435	—
Formic	—	0.145	—
Acetic	0.0_3442	0.0_3447	0.0_345
Benzoic	0.0_466	—	—

One might readily assume that the saponification constants belonging in the blanks were: methyl iodide and *n*-propyl iodide 0.0_435; methyl formate 0.145; ethyl benzoate 0.0_466.

Previous Work.—A review of the literature makes it almost certain that the second of these questions must be answered in the negative and that the first probably will be only approximately true. The immense amount of work that has been done on the subject of steric hindrance, on the velocity of esterification, and velocity of hydrolysis of esters, makes it extremely probable that the ratio of the velocities of saponification of the esters of two alcohols with an acid or two acids with an alcohol may vary a great deal depending on the acid and the alcohol.

The velocity of saponification of ethyl acetate seems to have been measured accurately first by Warder.[1] Soon after came a series of accurate and comprehensive measurements by Reicher,[2] on the relative effects of the various bases and of the alcohol radical. At about the same time Ostwald[3] studied the velocity of saponification of esters by sodium hydroxide. The effect of neutral salts on the velocity of saponification was studied by Arrhenius,[4] by Spohr,[5] by Kellogg[6] and by Armstrong and Watson.[7] Conrad and Brückner,[8] Hjelt,[9] and Sudborough and Feilmann[10] made measurements on the

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[1] Ber. deutsch. chem. Ges., 14, 1361 (1871).
[2] Liebig's Ann., 228, 251 (1885).
[3] Jour. prakt. Chem., 35, 112 (1887).
[4] Zeit. phys. Chem., 1, 110 (1887).
[5] Ibid., 2, 194 (1888).
[6] Jour. Am. Chem. Soc., 31, 403, 886 (1909).
[7] Proc. Roy. Soc., 79, 564 (1907).
[8] Zeit. phys. Chem., 7, 290 (1891).
[9] Ber. deutsch. chem. Ges., 29, 110 (1896); 31, 1844 (1898).
[10] Proc. Chem. Soc., 13, 241 (1897).

velocity of saponification of polybasic acids and especially on the relation between the saponification constant and the strength of the acid. Goldschmidt[1] made measurements on the saponification of acetoacetic ester. Findlay and Turner,[2] Findlay and Hickmans,[3] and Dean[4] studied the effect of hydroxyl and alkyloxyl groups. Williams and Subdorough[5] compared the saponification of esters of saturated and unsaturated acids. Meyer and Kellas[6] and recently McCombie and Scarborough[7] studied the saponification of derivatives of ethyl benzoate. Bischoff and Hedenström[8] and McCombie and Scarborough[9] have made exhaustive examinations of the velocities of saponification of aryl and benzyl esters of dibasic fatty acids as well as of the phenyl and substituted phenyl esters of monobasic acids. Brussoff[10] studied the velocity of reaction of alcoholic potassium hydroxide on various alkyl iodides. Korschum[11] has determined the velocity of saponification of a large number of pyrrole derivatives.

The influences of the solvent on the velocity reactions is extremely great as has been shown by many investigators. Furthermore one reaction may be hastened by one solvent and retarded by another solvent while a second reaction may be affected just the reverse by the two solvents. Menschutkin[12] has done some comprehensive work on the influence of the solvents. Patterson and Montgomerie[13] have brought together much of the data of earlier investigators. Reference should also be made to the monograph by Protze.[14] More

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[1] Ber. deutsch. chem. Ges., 32, 3396 (1899); 33, 1150 (1900).

[2] Jour. Chem. Soc., 87, 747 (1905).

[3] Ibid., 95, 1004 (1909).

[4] Am. Jour. Sci., 35, 605 (1915).

[5] Jour. Chem. Soc., 101, 412 (1912).

[6] Zeit. phys. Chem., 24, 221 (1897).

[7] Jour. Chem. Soc., 107, 156 (1915).

[8] Ber. deutsch. chem. Ges., 35, 4094 (1902).

[9] Jour. Chem. Soc., 105, 1304 (1914).

[10] Zeit. phys. Chem., 34, 129 (1900).

[11] Bull. Soc. chim. Paris, 19, 164, 221 (1916).

[12] Zeit. phys. Chem., 6, 41 (1890); 34, 157 (1900).

[13] Jour. Chem. Soc., 101, 26 (1912).

[14] "Ueber den Einfluss des Losungsmittels auf die Reactionsgeschwindigkeit" (Berlin, 1912).

work has been done on the influence of the solvent on the velocity of esterification and on the hydrolysis of esters[1] than on the velocity of saponification. However, Findlay and Turner,[2] and Findlay and Hickmans[3] have compared the velocity of saponification of esters in water, and in alcohol containing varying amounts of water. Anderson and Brown[4] compared the velocity of saponification of fats and oils in three alcohols.

Preparation of Reagents and Method of Procedure

The solvents used were water, methyl alcohol, 90 percent by weight; ethyl alcohol, 90 percent by weight, and isoamyl alcohol, density 0.8166 at 20°/15°. The three alcohols were purified by dissolving 1 g $AgNO_3$ in 5 cc water and adding to 2 liters of each of the following: 95 percent commercial methyl alcohol (Columbian spirit), 95 percent commercial ethyl alcohol, and commercial isoamyl alcohol. After standing 24 hours with occasional shaking 20 g commercial NaOH, dissolved in a small volume of water, were added to each of the alcohols and again allowed to stand 24 hours. The solutions were then filtered to remove most of the precipitate and the alcohols distilled, care being taken to leave considerable alcohol in the distillation flask. The methyl and ethyl alcohols were then diluted with water respectively to the densities, 0.8235 at 15°/4° and 0.8240 at 15°/15°, these corresponding to 90 percent by weight. When necessary, the amyl alcohol was diluted with water to density 0.8166 at 20°/15°. If amyl alcohol has more water than this in it, water will separate when sufficient KOH is added to make a 2/10 normal solution.

Next sufficient KOH was dissolved in each of the alcohols to make the solution slightly more than 2/10 normal. The

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[1] Cf. Lapworth: Jour. Chem. Soc., **93**, 2163, 2187 (1908); Goldschmidt and Udby: Zeit. phys. Chem., **60**, 728 (1907); Goldschmidt: Zeit. Electrochemie, **15**, 4 (1909); Sudborough and Turner: Jour. Chem. Soc., **101**, 237 (1912); Kolhatkar: Ibid., **107**, 921 (1915).

[2] Jour. Chem. Soc., **87**, 747 (1905).

[3] Ibid., **95**, 1004 (1909).

[4] Jour. Phys. Chem., **20**, 195 (1916).

solutions were allowed to stand until the slight amounts of K_2CO_3 had settled out and then filtered rapidly. The solutions were then titrated with 1/10 normal HCl using phenolphthalein; diluted to 2/10 normal and again accurately standardized. Large amounts of the alcohols were purified at first and sufficient alcoholic KOH prepared at once to last throughout the investigation.

A carbonate free water solution of KOH was prepared by adding carefully to a water solution of KOH, small amounts of $Ba(OH)_2$ solution until all carbonates had been precipitated and minute traces of $Ba(OH)_2$ were in solution. The solution was then allowed to settle, filtered from $BaCO_3$, standardized with 1/10 normal HCl and diluted with CO_2 free water until 2/10 normal.

The esters used, except ethyl propionate, ethyl butyrate and methyl salicylate, were prepared according to the directions given in Beilstein's Handbook; and were purified until they had the correct boiling point. The three esters mentioned were obtained from Eimer and Amend. The first two were further purified until they had the correct boiling point, but methyl salicylate was used just as it came and was synthetic oil of wintergreen. In a few cases the esters evidently still contained some of the corresponding alcohol with them since they required less than the theoretical amount of alkali.

The exact procedure followed in the investigation is given below. A volume of ester slightly less than would be saponified by 200 cc of 1/10 normal KOH was placed in a 100 cc volumetric flask and made up to the mark with the desired solvent which had already been brought to the temperature of the thermostat. This solution was then poured into a 400 cc flask and set in the thermostat. The volumetric flask was washed, dried, and filled to the mark with 100 cc of the corresponding 2/10 normal KOH solution. After the two solutions had reached constant temperature they were mixed. By this procedure the ester was in every case being saponified by 1/10 normal KOH. At suitable intervals, which depended on the velocity of the particular reaction, 10 cc of the reaction mixture were withdrawn and run into 10 cc of 1/10 normal HCl, the time being accurately noted. The excess HCl was then titrated with 1/10 normal $Ba(OH)_2$ using phenolphthalein as indicator. In the case of some esters it was necessary to titrate in 25 cc of CO_2 free ethyl alcohol so that the resulting solution would be clear. Wherever amyl alcohol was the solvent it was necessary to titrate in ethyl alcohol. Furthermore because of the viscosity of amyl alcohol it was found best to wash the 10 cc pipette each time with ethyl alcohol. The burette measured 10 cc and was graduated directly to 0.02 cc and could be read to 0.002 cc.

TABLE I

Saponification Constants of Certain Esters by 1/10 Normal Potassium Hydroxide in Different Solvents

Ester	Solvent			
	Water	Methyl Alcohol	Ethyl Alcohol	Amyl Alcohol
Ethyl bromide	—	$0.0_{4}19$	$0.0_{4}43$	$0.0_{4}22$(?)
n-Propyl bromide	—	$0.0_{4}10$	$0.0_{4}17$	$0.0_{4}19$(?)
i-Butyl bromide	—	$0.0_{5}77$	$0.0_{4}12$	$0.0_{4}15$(?)
i-Amyl bromide	—	$0.0_{5}40$	$0.0_{5}6$	$0.0_{4}16$(?)
Methyl iodide	—	$0.0_{3}19$	$0.0_{3}72$	$0.0_{3}32$
Ethyl iodide	—	$0.0_{4}37$	$0.0_{4}70$	$0.0_{4}33$
n-Propyl iodide	—	$0.0_{4}11$	$0.0_{4}29$	$0.0_{4}24$(?)
i-Butyl iodide	—	$0.0_{5}8$(?)	$0.0_{4}24$	$0.0_{4}37$(?)
i-Amyl iodide	—	$0.0_{5}7$(?)	$0.0_{4}13$	$0.0_{4}20$(?)
Methyl formate	—	0.155	—	—
Ethyl formate	—	0.145	—	—
Methyl acetate	0.1136	$0.0_{3}442$	$0.0_{2}315$	$0.0_{2}65$
Ethyl acetate	0.0639	$0.0_{3}447$	$0.0_{2}302$	$0.0_{2}69$
n-Propyl acetate	0.0435	$0.0_{3}45$	$0.0_{2}298$	$0.0_{2}72$
i-Butyl acetate	—	$0.0_{3}45$	$0.0_{2}272$	$0.0_{2}82$
i-Amyl acetate	—	$0.0_{3}44$	$0.0_{2}297$	$0.0_{2}69$
Benzyl acetate	—	$0.0_{3}45$	$0.0_{2}305$	$0.0_{2}69$
Phenyl acetate	—	$0.0_{4}49$	$0.0_{4}40$(?)	$0.0_{4}36$(?)
Ethyl propionate	—	$0.0_{3}285$	$0.0_{2}155$	$0.0_{2}4$
Ethyl butyrate (*n*)	—	$0.0_{3}17$	$0.0_{3}84$	$0.0_{2}23$
Methyl benzoate	—	$0.0_{4}66$	$0.0_{3}36$(?)	$0.0_{2}10$(?)
Ethyl benzoate	—	$0.0_{4}66$	$0.0_{3}32$	$0.0_{3}17$
Methyl salicylate	—	—	$0.0_{4}30$(?)	$0.0_{4}10$

In the case of all the rapid reactions the time was taken with a stop-watch reading to fractions of a second. Duplicate determinations were run on each ester and where these did not check, other determinations were made.

Results Obtained

The above table gives in a compact form the constants obtained for 23 esters in the four solvents used. On account of the slight solubility of most of these esters in water, only three were examined in that solvent. The formates are saponified with extreme rapidity and could be determined in only the slowest solvent, methyl alcohol. Similarly some of the esters were saponified so slowly that they were examined in only the fastest solvents, amyl and ethyl alcohol. The constants given in this table are in most cases the average of several determinations.

Conclusions from the Table

It was found very difficult to get a satisfactory constant in the case of some of the reactions, especially where they were very slow. In general ethyl alcohol gives the most satisfactory constants and amyl alcohol the least satisfactory. Those constants after which questions have been placed are only approximations, and should be redetermined. However, they probably are very near the correct value. In most of these questionable cases our results give no constant but decreasing values as will be seen by reference to the determinations at the close of the paper. It is possible that the effect of the salt formed during the reaction[1] may be greater in the amyl alcohol which has less water present than in the ethyl alcohol. Ostwald[2] and many later investigators have shown that the salt formed during the reaction does not affect the velocity of saponification by a strong base, but decreases very much the velocity of saponification by weak bases. The ionization of potassium hydroxide in the amyl alcohol used may be so small

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[1] Arrhenius: Zeit. phys. Chem., 1, 101 (1887); 2, 284 (1888).

[2] Jour. prakt. Chem., 35, 112 (1887).

that the salt formed may affect very much the velocity constant.

It is evident from the following table that the ratios of the constants of one ester in any two of the solvents may be quite different from those of another ester in the same two solvents. It is not possible, therefore, to calculate with any degree of exactness the velocity of saponification of an ester in one of these solvents from the known velocity in a second solvent and the ratio of the velocities of a second ester in the two solvents unless the two esters are very closely related. Findlay and Hickmans[1] have investigated this point. Their ratios for eight esters in the two solvents, water and 30 percent ethyl alcohol, vary from 1.4 to 2.4, and they assume that the ratio is not the same for different esters.

TABLE 2

Ester	Ratio of constants in solvents		
	K_{H_2O}/K_{CH_3OH}	$K_{C_2H_5OH}/K_{CH_3OH}$	$K_{C_5H_{11}OH}/K_{C_2H_5OH}$
Ethyl bromide	—	2.3	—
n-Propyl bromide	—	1.7	—
i-Butyl bromide	—	1.5	—
i-Amyl bromide	—	1.5	—
Methyl iodide	—	3.8	0.44
Ethyl iodide	—	1.9	0.47
n-Propyl iodide	—	2.6	—
Methyl acetate	257	7.1	2.1
Ethyl acetate	143	7.0	2.2
n-Propyl acetate	97	6.6	2.4
i-Butyl acetate	—	6.0	3.0
i-Amyl acetate	—	6.7	2.3
Benzyl acetate	—	6.8	2.2
Ethyl propionate	—	5.4	2.6
Ethyl butyrate	—	5.0	2.7
Ethyl benzoate	—	5.0	0.6

An examination of Table I will show that variation in the alcohol radical of the ester affects the velocity of the reaction

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[1] Jour. Chem. Soc., 95, 1004 (1909).

very differently, depending on the acid radical with which they are combined. Thus while all the acetates, except phenyl, have practically the same constant in any alcohol, the iodides and bromides have decreasing constants as the alcohol radical increases in mass. Methyl iodide is saponified more than ten times as fast as ethyl iodide. This has long been known from investigations on the influence of various factors, reference to which was given earlier in the article.

Experimental Data and Calculations

As already described, in carrying out a determination, the ester dissolved in the solvent is mixed with the alkali dissolved in the solvent. At intervals, the volume of 1/10 normal alkali remaining in 10 cc of the mixture is determined as follows:

Ten cc of the mixture are run into 10 cc of 1/10 normal HCl. The excess acid is then titrated with 1/10 normal $Ba(OH)_2$. The difference between the volume of 1/10 normal HCl used and 1/10 normal $Ba(OH)_2$ used gives the volume of 1/10 normal alkali present in 10 cc of the mixture. This value is given in the second column of the experimental tables.

The second order reaction formula used in the calculations is

$$K = \frac{2.3025}{T_e t} \log \frac{T_t(T_o - T_e)}{T_o(T_t - T_e)}.$$

K = velocity constant.

T_o = volume of 1/10 normal alkali present in 10 cc of the mixture at first titration.

T_e = volume of 1/10 normal alkali present in 10 cc of the mixture at the end of the reaction.

T_t = volume of 1/10 normal alkali present in 10 cc of the mixture at time t.

t = time in minutes after the first titration.

In the experimental data T_o is the first value and T_e the last value under the second column.

In all cases the concentration of the ester was slightly less than 1/10 normal while the alkali was very close to that value at the beginning. The exact strengths of the various solutions are given below. No corrections for strengths of solutions were applied to any of the volumes.

HCl = 0.994 1/10 normal.
$Ba(OH)_2$ = 0.988 1/10 normal.
Amyl alcoholic KOH = 0.965 1/10 normal.
Ethyl alcoholic KOH = 1.001 1/10 normal.
Methyl alcoholic KOH = 1.00 1/10 normal.
Water solution of KOH = 0.998 1/10 normal.

These were the strengths after equal volumes of alkali and ester had been mixed.

In Water Solution

Methyl Acetate 1.4 cc			Ethyl Acetate 1.6 cc		
t	T_t	K	t	T_t	K
0	5.975		0	7.25	
1.45	3.805	0.1105	2.67	4.495	0.06595
2.15	3.295	0.1147	3.60	4.110	0.06594
2.97	2.930	0.1148	4.43	3.870	0.06534
3.85	2.680	0.1132	5.33	3.680	0.06434
4.60	2.505	0.1176	6.30	3.510	0.06431
5.31	2.405	0.1125	7.31	3.385	0.06348
6.15	2.300	0.1119	8.30	3.315	0.06075
E	1.860		9.30	3.210	0.06227
			10.35	3.130	0.06317
			E	2.830	

In Water Solution | In Methyl Alcohol Solution

n-Propyl Acetate 2 cc			Ethyl Bromide 1.3 cc		
t	T_t	K	t	T_t	K
0	6.480		0	9.932	
3.45	3.775	0.04649	56	9.859	0.0_41846
4.25	3.515	0.04594	98	9.848	0.0_41281
5.11	3.295	0.04488	149	9.812	0.0_41240
5.97	3.145	0.04296	259	9.634	0.0_41740
6.80	3.010	0.04181	400	9.462	0.0_41846
7.70	2.880	0.04177	513	9.288	0.0_42001
8.63	2.750	0.04055	1118	8.534	0.0_42227
E	1.500		1359	8.329	0.0_42509
			1593	8.032	0.0_42768
			E	3.117	

In Methyl Alcohol Solution

***n*-Propyl Bromide 1.5 cc**			***i*-Butyl Bromide 2 cc**		
t	T_t	K	t	T_t	K
0	9.942		0	9.823	
59.6	9.894	0.0_41294	34	9.814	0.0_67559
97.7	9.872	0.0_41214	123	9.788	0.0_66963
258.6	9.812	0.0_58492	234	9.759	0.0_66406
400.9	9.742	0.0_58584	376	9.686	0.0_68656
490.3	9.682	0.0_59198	465	9.676	0.0_67459
1118.0	9.298	0.0_41046	1314	9.355	0.0_68833
1239.0	9.178	0.0_41135	1509	9.317	0.0_68373
1593.0	9.120	0.0_59612	E	5.376	
E	3.880				

***i*-Amyl Bromide 1.6 cc**			**Methyl Iodide 1.2 cc**		
t	T_t	K	t	T_t	K
0	9.952		0	9.658	
237.9	9.924	0.0_63296	40.5	9.102	0.0_31807
379.6	9.898	0.0_63935	172.5	7.704	0.0_31813
1098.0	9.757	0.0_64897	271.3	6.858	0.0_31919
1319.0	9.722	0.0_64840	321.8	6.508	0.0_31892
1574.0	9.642	0.0_65551	375.5	6.212	0.0_31874
E	6.165		414.5	5.994	0.0_31878
			457.5	5.796	0.0_31862
			E	1.384	

Ethyl Iodide 1.4 cc			***n*-Propyl Iodide 1.8 cc**		
t	T_t	K	t	T_t	K
0	9.816		0	9.902	
217	9.274	0.0_43503	92	9.820	0.0_41096
268	9.138	0.0_43567	123	9.816	0.0_41193
312	9.044	0.0_43516	183	9.752	0.0_41257
367	8.933	0.0_43522	243	9.712	0.0_41094
460	8.748	0.0_43551	303	9.668	0.0_41089
505	8.638	0.0_43549	363	9.590	0.0_41212
E	2.120		E	2.512	

i-Butyl Iodide 2 cc			*i*-Amyl Iodide 2.5 cc		
t	T_t	K	t	T_t	K
0	9.176		0	9.858	
212	9.116	$0.0_{5}5141$	215	9.765	$0.0_{6}8450$
272	9.105	$0.0_{5}4758$	275	9.742	$0.0_{6}9084$
332	9.050	$0.0_{5}7183$	335	9.738	$0.0_{6}7729$
411	8.978	$0.0_{6}9471$	396	9.700	$0.0_{6}8602$
472	8.938	$0.0_{6}9959$	E	5.070	
E	3.380				

Methyl Formate 1.2 cc			Ethyl Formate 1.4 cc		
t	T_t	K	t	T_t	K
0	4.183		0	5.115	
1.68	2.378	0.1508	0.79	3.738	0.1498
2.58	1.958	0.1562	1.66	3.008	0.1512
3.43	1.720	0.1559	2.42	2.686	0.1444
4.38	1.575	0.1474	3.26	2.432	0.1428
5.38	1.397	0.1554	4.02	2.278	0.1404
6.28	1.302	0.1555	4.88	2.138	0.1409
7.28	1.252	0.1469	5.73	2.034	0.1421
8.13	1.160	0.1581	E	1.690	
9.37	1.116	0.1515			
E	0.850				

Methyl Acetate 1.4 cc			Ethyl Acetate 1.8 cc		
t	T_t	K	t	T_t	K
0	8.734		0	8.618	
35.25	7.738	$0.0_{3}4479$	31.5	7.812	$0.0_{3}4494$
69.00	6.980	$0.0_{3}4576$	64.5	7.088	$0.0_{3}4581$
104.80	6.338	$0.0_{3}4483$	94.5	6.518	$0.0_{3}4669$
123.50	6.028	$0.0_{3}4553$	124.5	6.078	$0.0_{3}4648$
245.00	4.682	$0.0_{3}4478$	181.5	5.394	$0.0_{3}4613$
299.50	4.220	$0.0_{3}4576$	211.5	5.146	$0.0_{3}4502$
390.30	3.746	$0.0_{3}4420$	242.0	4.858	$0.0_{3}4537$
451.00	3.438	$0.0_{3}4457$	280.5	4.586	$0.0_{3}4492$
481.50	3.298	$0.0_{3}4487$	301.5	4.444	$0.0_{3}4485$
E	0.598		332.0	4.264	$0.0_{3}4457$
			361.7	4.052	$0.0_{3}4556$
			421.5	3.768	$0.0_{3}4528$
			474.0	3.534	$0.0_{3}4563$
			E	1.122	

n-Propyl Acetate 2 cc

t	T_t	K
0	8.244	
100.0	6.788	0.0_34361
114.0	6.612	0.0_34471
239.3	5.592	0.0_34414
290.5	5.280	0.0_34449
396.8	4.816	0.0_34396
449.5	4.622	0.0_34419
475.0	4.518	0.0_34487
E	3.000	

i-Butyl Acetate 2.4 cc

t	T_t	K
0	8.202	
147.8	5.406	0.0_34534
168.0	5.144	0.0_34553
198.0	4.872	0.0_34420
255.3	4.346	0.0_34479
287.0	4.088	0.0_34560
325.8	3.822	0.0_34550
342.3	3.744	0.0_34515
E	0.292	

i-Amyl Acetate 2.5 cc

t	T_t	K
0	9.944	
128.0	7.208	0.0_34402
150.5	6.912	0.0_34396
171.5	6.628	0.0_34451
202.3	6.308	0.0_34411
258.5	5.798	0.0_34432
291.5	5.528	0.0_34488
314.0	5.352	0.0_34541
330.0	5.254	0.0_34618
347.0	5.156	0.0_34528
E	2.696	

Benzyl Acetate 2.8 cc

t	T_t	K
0	9.766	
33.5	8.666	0.0_34477
53.0	8.078	0.0_34594
68.5	7.656	0.0_34651
108.5	6.816	0.0_34571
138.5	6.292	0.0_34590
163.0	5.942	0.0_34555
209.0	5.364	0.0_34560
223.3	5.200	0.0_34541
236.8	5.096	0.0_34518
256.8	4.896	0.0_34532
E	0.766	

Phenyl Acetate 2.5 cc

t	T_t	K
0	8.552	
66.0	8.392	0.0_44938
397.3	7.682	0.0_44921
451.0	7.578	0.0_44940
478.5	7.534	0.0_44896
E	2.615	

Ethyl Propionate 2 cc

t	T_t	K
0	9.805	
162.2	7.040	0.0_32826
195.5	6.640	0.0_32850
241.5	6.172	0.0_32861
262.5	5.990	0.0_32860
294.0	5.730	0.0_32869
335.0	5.435	0.0_32860
363.0	5.242	0.0_32867
458.0	4.720	0.0_32845
E	1.000	

Ethyl Butyrate 2.4 cc			Methyl Benzoate 2.3 cc		
t	T_t	K	t	T_t	K
0	9.764		0	9.712	
221	7.362	0.0_31743	172.0	8.904	0.0_46425
272	6.996	0.0_31732	226.0	8.590	0.0_46965
317	6.672	0.0_31730	267.5	8.488	0.0_46510
374	6.356	0.0_31712	375.0	8.032	0.0_46787
424	6.074	0.0_31718	415.0	7.874	0.0_46901
467	5.850	0.0_31730	459.0	7.716	0.0_46436
511	5.634	0.0_31737	E	1.375	
E	1.100				

Ethyl Benzoate 2.8 cc

t	T_t	K
0	9.600	—
220.0	8.534	0.0_46203
270.0	8.298	0.0_46443
323.0	8.062	0.0_46548
379.0	7.814	0.0_46847
430.5	7.676	0.0_46577
473.0	7.488	0.0_46779
518.0	7.326	0.0_46782
E	0.675	

In Ethyl Alcohol Solution

Ethyl Bromide 1.3 cc			*n*-Propyl Bromide 1.5 cc		
t	T_t	K	t	T_t	K
0	9.820		0	9.818	
118	9.462	0.0_44354	57	9.752	0.0_41772
183	9.275	0.0_44367	117	9.682	0.0_41850
271	9.052	0.0_44284	183	9.617	0.0_41696
370	8.800	0.0_44320	272	9.534	0.0_41645
563	8.352	0.0_44343	371	9.416	0.0_41751
1463	6.900	0.0_44201	1861	8.250	0.0_41614
1982	6.200	0.0_44417	2996	7.650	0.0_41534
2984	5.398	0.0_44314	3469	7.400	0.0_41543
3469	5.060	0.0_44382	E	3.190	
E	2.420				

i-Butyl Bromide 2 cc

t	T_t	K
0	9.720	
185	9.590	0.0_41410
273	9.545	0.0_41293
371	9.480	0.0_41324
448	9.410	0.0_41428
1471	9.000	0.0_41078
1862	8.750	0.0_41198
2998	8.390	0.0_41090
3350	8.190	0.0_41165
E	4.500	

i-Amyl Iodide 2 cc

t	T_t	K
0	9.870	
119	9.830	0.0_56522
372	9.750	0.0_56120
446	9.708	0.0_55530
1475	9.445	0.0_55751
1984	9.240	0.0_56545
2999	9.040	0.0_55883
3469	8.918	0.0_55951
E	4.450	

Methyl Iodide 1 cc

t	T_t	K
0	9.638	
36.72	8.058	0.0_37164
52.77	7.562	0.0_37063
67.43	7.176	0.0_36879
98.50	6.468	0.0_36960
150.20	5.602	0.0_36960
190.00	5.130	0.0_36876
219.60	4.822	0.0_36895
276.90	4.354	0.0_36885
335.40	3.958	0.0_37114
371.20	3.780	0.0_37000
E	1.995	

Ethyl Iodide 1.2 cc

t	T_t	K
0	9.692	
52.5	9.438	0.0_47158
221.0	8.758	0.0_46844
288.0	8.502	0.0_46939
344.0	8.280	0.0_47114
421.0	8.042	0.0_47011
542.0	7.692	0.0_47001
E	2.512	

n-Propyl Iodide 2 cc

t	T_t	K
0	9.818	
269	9.120	0.0_43192
1205	7.575	0.0_42847
1542	7.108	0.0_42869
1868	6.730	0.0_42864
2640	5.955	0.0_42907
3070	5.565	0.0_42956
4231	4.798	0.0_42993
E	1.020	

i-Butyl Iodide 1.8 cc

t	T_t	K
0	9.190	
262	8.770	0.0_42755
1202	7.790	0.0_42319
1535	7.450	0.0_42393
1811	7.160	0.0_42482
2631	6.615	0.0_42400
3073	6.350	0.0_42424
4226	5.770	0.0_42381
E	2.520	

i-Amyl Iodide 2.4 cc		
t	T_t	K
0	9.779	
261	9.560	$0.0_{4}1942$
1201	9.180	$0.0_{4}1221$
1534	9.018	$0.0_{4}1258$
1861	8.825	$0.0_{4}1348$
2632	8.595	$0.0_{4}1238$
3090	8.500	$0.0_{4}1161$
4225	8.050	$0.0_{4}1371$
E	5.180	

Methyl Acetate 1.4 cc		
t	T_t	K
0	9.398	$0.0_{2}3235$
5.94	8.282	$0.0_{2}3145$
8.99	7.864	$0.0_{2}3200$
12.83	7.352	$0.0_{2}3186$
15.72	7.036	$0.0_{2}3160$
18.78	6.738	$0.0_{2}3116$
22.20	6.462	$0.0_{2}3161$
24.92	6.212	$0.0_{2}3142$
28.12	5.992	$0.0_{2}3125$
31.07	5.804	$0.0_{2}3133$
38.42	5.380	$0.0_{2}3109$
41.62	5.236	$0\ 0_{2}3094$
44.73	5.102	$0.0_{2}3168$
51.55	4.852	
E	2.307	

Ethyl Acetate 1.6 cc		
t	T_t	K
0	9.042	$0.0_{2}2962$
6.43	8.118	$0.0_{2}2953$
8.23	7.696	$0.0_{2}3045$
10.91	7.332	$0.0_{2}2990$
13.72	7.000	$0.0_{2}3019$
16.73	6.712	$0.0_{3}3012$
19.35	6.464	$0.0_{2}3084$
22.68	6.138	$0.0_{2}3077$
26.28	5.864	$0.0_{2}3094$
29.32	5.642	$0.0_{2}3059$
32.55	5.462	$0.0_{2}3087$
35.77	5.258	$0.0_{2}3060$
41.82	4.962	$0.0_{2}3026$
50.37	4.614	$0.0_{2}3038$
58.76	4.268	
E	1.837	

n-Propyl Acetate 2 cc		
t	T_t	K
0	8.878	
6.06	7.788	$0.0_{2}3102$
12.17	7.054	$0.0_{2}3096$
15.02	6.718	$0.0_{2}2904$
18.28	6.398	$0.0_{2}2891$
21.50	6.054	$0.0_{2}2994$
24.45	5.822	$0.0_{2}2966$
27.38	5.582	$0.0_{2}2936$
30.70	5.376	$0.0_{2}2970$
33.80	5.188	$0.0_{2}2964$
44.06	4.628	$0.0_{2}2990$
66.02	3.824	$0.0_{2}2997$
92.63	3.236	$0.0_{2}2949$
E	1.298	

i-Butyl Acetate 2.4 cc			*i*-Amyl Acetate 2.5 cc		
t	T_t	K	t	T_t	K
0	7.856		0	9.660	
4.08	7.318	0.0_22703	3.04	9.056	0.0_22874
13.18	6.256	0.0_22632	6.23	8.542	0.0_22802
16.50	5.926	0.0_22641	13.17	7.538	0.0_22912
19.70	5.616	0.0_22721	16.85	7.110	0.0_22928
22.53	5.378	0.0_22660	19.88	6.804	0.0_22933
26.03	5.102	0.0_22781	23.22	6.482	0.0_22960
29.28	4.874	0.0_22715	26.17	6.238	0.0_22974
32.37	4.688	0.0_22680	29.83	5.976	0.0_22955
36.17	4.460	0.0_22715	33.43	5.728	0.0_22969
45.45	3.992	0.0_22810	36.68	5.564	0.0_22925
65.00	3.254	0.0_22856	40.52	5.320	0.0_22956
E	0.146		44.00	5.142	0.0_22980
			47.23	4.978	0.0_23004
			51.07	4.806	0.0_23009
			E	2.030	

Benzyl Acetate 2.8 cc			Phenyl Acetate 2.5 cc		
t	T_t	K	t	T_t	K
0	9.278		0	8.718	
6.05	7.892	0.0_23251	995	6.712	0.0_44425
9.53	7.266	0.0_23277	1154	6.588	0.0_44134
12.48	6.872	0.0_23152	1273	6.516	0.0_43942
15.80	6.440	0.0_23185	1493	6.282	0.0_43873
19.12	6.062	0.0_23147	1610	6.092	0.0_44007
22.63	5.748	0.0_23068	1785	5.888	0.0_44075
25.65	5.478	0.0_23066	E	1.684	
28.47	5.276	0.0_23048			
31.43	5.056	0.0_23038			
34.42	4.842	0.0_23041			
40.75	4.472	0.0_23039			
53.53	3.886	0.0_23004			
E	0.398				

Ethyl Propionate 2 cc			Ethyl Butyrate 2.3 cc		
t	T_t	K	*t*	T_t	K
0	9.776		0	9.680	
13.80	8.248	0.0_21541	127.0	5.932	0.0_38389
17.23	7.970	0.0_21536	148.0	5.642	0.0_38352
21.03	7.652	0.0_21547	180.5	5.250	0.0_38370
24.40	7.398	0.0_21560	215.7	4.921	0.0_38330
27.72	7.160	0.0_21535	261.2	4.575	0.0_38337
31.08	6.944	0.0_21581	294.2	4.403	0.0_38370
35.53	6.686	0.0_21570	342.5	4.112	0.0_38420
38.87	6.538	0.0_21536	E	2.820	
42.88	6.328	0.0_21543			
46.48	6.138	0.0_21561			
50.22	5.998	0.0_21547			
57.20	5.668	0.0_21565			
E	1.288				

Methyl Benzoate 2.3 cc			Ethyl Benzoate 2.8 cc		
t	T_t	K	*t*	T_t	K
0	9.668		0	9.620	
91.0	7.478	0.0_33764	57.0	8.218	0.0_33236
108.5	7.196	0.0_33793	75.0	7.876	0.0_33237
141.0	6.724	0.0_33684	96.0	7.466	0.0_33325
163.5	6.478	0.0_33550	117.0	7.148	0.0_33267
186.0	6.156	0.0_33667	136.0	6.876	0.0_33241
209.0	5.984	0.0_33519	160.3	6.520	0.0_33257
222.0	5.868	0.0_33499	190.5	6.192	0.0_33234
234.0	5.758	0.0_33516	217.5	5.876	0.0_33248
254.5	5.604	0.0_33502	244.5	5.606	0.0_33292
E	1.002		271.3	5.382	0.0_33268
			297.0	5.172	0.0_33254
			E	0.512	

In Amyl Alcohol Solution

Methyl Salicylate 2.5 cc			Ethyl Bromide 1.2 cc		
t	T_t	K	t	T_t	K
0	9.492		0	9.382	
273	8.970	$0.0_{4}2246$	258	8.878	$0.0_{4}2633$
1208	7.172	$0.0_{4}2822$	1056	7.812	$0.0_{4}2377$
1547	6.722	$0.0_{4}2805$	1173	7.640	$0.0_{4}2430$
1871	6.190	$0.0_{4}3002$	1334	7.515	$0.0_{4}2319$
2638	5.215	$0.0_{4}3275$	1427	7.420	$0.0_{4}2314$
3081	4.755	$0.0_{4}3406$	1623	7.360	$0.0_{4}2116$
E	0		2533	6.643	$0.0_{4}2064$
			3042	6.315	$0.0_{4}2023$
			E	1.220	

In Amyl Alcohol Solution

n-Propyl Bromide 1.5 cc			*i*-Butyl Bromide 2 cc		
t	T_t	K	t	T_t	K
0	9.370		0	9.657	
133	9.125	$0.0_{4}3019$	999	8.868	$0.0_{4}1658$
232	8.995	$0.0_{4}2693$	1107	8.823	$0.0_{4}1593$
934	8.412	$0.0_{4}1845$	1276	8.705	$0.0_{4}1602$
1054	8.313	$0.0_{4}1829$	1371	8.670	$0.0_{4}1561$
1222	8.145	$0.0_{4}1986$	1562	8.655	$0.0_{4}1395$
1304	8.180	$0.0_{4}1811$	2476	8.270	$0.0_{4}1302$
1500	8.130	$0.0_{4}1547$	2981	8.100	$0.0_{4}1251$
2410	7.760	$0.0_{4}1326$	E	4.100	
2920	7.510	$0.0_{4}1314$			
E	2.580				

i-Amyl Bromide 2 cc			Methyl Iodide 1 cc		
t	T_t	K	t	T_t	K
0	9.305		0	9.618	
72	9.225	$0.0_4 2367$	23.77	9.098	$0.0_3 3245$
176	9.127	$0.0_4 2259$	91.20	7.938	$0.0_3 3122$
238	9.078	$0.0_4 2191$	126.90	7.476	$0.0_3 3101$
335	9.010	$0.0_4 2034$	151.10	7.148	$0.0_3 3167$
1037	8.698	$0.0_4 1434$	177.50	6.838	$0.0_3 3201$
1152	8.650	$0.0_4 1403$	242.50	6.312	$0.0_3 3068$
1324	8.525	$0.0_4 1509$	288.50	5.736	$0.0_3 3416$
1410	8.550	$0.0_4 1348$	E	2.030	
2515	8.260	$0.0_4 1103$			
3021	8.080	$0.0_4 1114$			
E	4.460				

Ethyl Iodide 1.4 cc			*n*-Propyl Iodide 2 cc		
t	T_t	K	t	T_t	K
0	9.520		0	9.46	
262	8.750	$0.0_4 3786$	88	9.24	$0.0_4 3355$
347	8.565	$0.0_4 3676$	165	9.07	$0.0_4 3310$
426	8.370	$0.0_4 3659$	216	8.93	$0.0_4 3485$
1113	7.300	$0.0_4 3120$	302	8.88	$0.0_4 2737$
1380	6.960	$0.0_4 3054$	385	8.75	$0.0_4 2683$
1698	6.580	$0.0_4 3002$	1068	8.15	$0.0_4 1935$
2955	5.400	$0.0_4 2997$	1334	7.94	$0.0_4 1848$
E	0.650		1654	7.66	$0.0_4 1839$
			2606	7.07	$0.0_4 2668$
			2910	6.88	$0.0_4 1693$
			E	1.56	

i-Butyl Iodide 1.8 cc			*i*-Amyl Iodide 2.4 cc		
t	T_t	K	*t*	T_t	K
0	9.335		0	9.62	
196	8.740	0.0_45186	28	9.44	0.0_46422
247	8.680	0.0_44552	60	9.42	0.0_47173
333	8.590	0.0_43917	117	9.29	0.0_46114
423	8.520	0.0_43402	192	9.15	0.0_45448
1103	7.890	0.0_42545	242	9.06	0.0_46588
1365	7.760	0.0_42878	331	9.04	0.0_43977
1687	7.520	0.0_43506	415	8.96	0.0_43655
E	2.560		1099	8.68	0.0_42063
			1362	8.62	0.0_41795
			1686	8.44	0.0_41766
			2637	8.28	0.0_41457
			2942	8.21	0.0_41264
			E	4.60	

Methyl Acetate 1.4 cc			Ethyl Acetate 1.6 cc		
t	T_t	K	*t*	T_t	K
0	8.598		0	8.734	
	5.424	0.0_26668	2.08	7.944	0.0_27096
11.66			8.08	6.336	0.0_27278
16.50	4.724	0.0_26705	12.92	5.576	0.0_27039
17.66	4.596	0.0_26686	17.83	4.996	0.0_26936
24.75	3.984	0.0_26440	22.80	4.546	0.0_26898
29.61	3.612	0.0_26510	31.02	4.012	0.0_26787
32.67	3.480	0.0_26333	38.07	3.696	0.0_26662
39.05	3.192	0.0_26198	49.15	3.318	0.0_26561
47.83	2.888	0.0_26022	E	1.934	
E	0.887				

n-Propyl Acetate 2 cc			*i*-Butyl Acetate 2.4 cc		
t	T_t	K	*t*	T_t	K
0	7.916		0	7.298	
6.40	5.992	0.0_27266	6.11	5.374	0.0_28030
7.57	5.724	0.0_27379	7.10	5.112	0.0_28252
11.17	5.100	0.0_27333	8.15	4.902	0.0_28221
12.40	4.904	0.0_27379	11.18	4.398	0.0_28083
17.52	4.302	0.0_27317	12.37	4.176	0.0_28290
22.53	3.842	0.0_27224	20.73	3.248	0.0_28243
27.26	3.516	0.0_27176	25.13	2.922	0.0_28166
32.17	3.236	0.0_27111	36.17	2.316	0.0_28151
39.13	2.904	0.0_27131	41.15	2.102	0.0_28233
43.68	2.718	0.0_27191	48.03	1.878	0.0_28233
E	0.911		58.91	1.596	0.0_28307
			E	0	

i-Amyl Acetate 2.5 cc			Benzyl Acetate 2.8 cc		
t	T_t	K	*t*	T_t	K
0	8.956		0	8.458	
4.39	7.334	0.0_27127	1.52	7.660	0.0_26887
13.50	5.422	0.0_27251	3.00	7.098	0.0_26977
16.37	5.073	0.0_26727	7.15	5.888	0.0_27318
21.93	4.518	0.0_27042	8.81	5.536	0.0_27127
25.13	4.262	0.0_27017	13.00	4.766	0.0_27046
27.83	4.098	0.0_26904	14.45	4.578	0.0_27068
30.84	3.918	0.0_26850	20.47	3.880	0.0_26902
33.87	3.738	0.0_26908	26.27	3.378	0.0_26774
36.97	3.586	0.0_26913	31.73	3.036	0.0_26761
40.34	3.478	0.0_26751	37.46	2.736	0.0_26705
43.55	3.376	0.0_26649	43.00	2.482	0.0_26814
E	1.715		55.52	2.042	0.0_26832
			E	0.088	

Phenyl Acetate 2.5 cc			Ethyl Propionate 2 cc		
t	T_t	K	*t*	T_t	K
0	8.266		0	9.264	
197	7.818	0.0_44225	5.83	7.628	0.0_24485
995	6.596	0.0_33851	9.10	7.004	0.0_24324
1154	6.502	0.0_33550	10.30	6.778	0.0_24366
1274	6.486	0.0_33266	13.30	6.362	0.0_24226
1492	6.274	0.0_33253	18.60	5.758	0.0_24087
1612	6.162	0.0_33203	24.30	5.248	0.0_23953
1781	6.008	0.0_33237	30.70	4.782	0.0_23877
2451	5.696	0.0_42851	38.20	4.326	0.0_23845
E	1.466		46.55	3.958	0.0_23748
			53.65	3.696	0.0_23699
			E	0.942	

Ethyl Butyrate 2.4 cc			Methyl Benzoate 2.3 cc		
t	T_t	K	*t*	T_t	K
0	9.398		0	9.234	
6.77	8.138	0.0_22595	5.87	8.520	0.0_21569
11.00	7.608	0.0_22478	12.57	8.058	0.0_21293
14.25	7.258	0.0_22424	16.97	7.838	0.0_21181
19.03	6.806	0.0_22356	23.23	7.500	0.0_21142
25.30	6.336	0.0_22240	35.40	6.954	0.0_21055
30.97	5.952	0.0_22201	47.48	6.502	0.0_21014
38.65	5.516	0.0_22179	67.41	5.886	0.0_39642
43.30	5.234	0.0_22197	81.65	5.500	0.0_39620
49.27	5.004	0.0_22140	127.30	4.608	0.0_39149
E	0.760		E	0.425	

Ethyl Benzoate 2.4 cc			Methyl Salicylate 2.4 cc		
t	T_t	K	t	T_t	K
0	9.130		0	9.278	
15.5	8.090	0.0_31894	257	9.090	0.0_41408
24.0	7.640	0.0_31867	347	8.972	0.0_41517
33.8	7.160	0.0_31871	1057	8.425	0.0_41245
45.5	6.770	0.0_31766	1177	8.350	0.0_41201
53.0	6.515	0.0_31735	1337	8.150	0.0_41304
62.5	6.050	0.0_31891	1429	8.146	0.0_41197
76.2	5.820	0.0_31734	1624	8.050	0.0_41174
90.0	5.490	0.0_31717	2534	7.500	0.0_41171
115.0	4.980	0.0_31693	3045	7.190	0.0_41166
131.5	4.720	0.0_31669	E	0.700	
152.0	4.410	0.0_31663			
184.5	4.087	0.0_31588			
231.0	3.560	0.0_31629			
E	0.580				

SOME STUDIES OF SOAP SOLUTIONS. II

BY VICTOR LENHER AND GEORGE M. BISHOP

It has been shown[1] that the same amount of soap will not necessarily be sufficient to emulsify the same quantity of different kinds of oils. In the previous experiments, where quantitative emulsifications were made, the temperature was controlled for the most part to 25°. The results herewith reported have been obtained by studying the emulsifying action of soap solutions on certain of the more common oils and water at 100°.

Conditions of Experiments.—The total volume of mixture was always 100 cc, the difference between the amount of oil and soap solution added being made up with distilled water. The emulsions were stirred five minutes, and if at the end of another five minutes neither constituent had separated, the emulsion was considered satisfactory. At first sight, these conditions may seem rather arbitrary, but actually they are fairly standard. Practically all laundry washing is done in boiling water, and the suds or emulsions when once formed are usually washed away within five minutes, thus obviating the necessity for an emulsion remaining permanent for a longer time. Furthermore, most of the emulsions break within the first two or three minutes, or else they remain permanent for hours. The same type of stirring apparatus was used in these experiments as we have heretofore[2] used.

Materials Used.—The sodium oleate used was prepared from very pure sodium hydroxide and very pure oleic acid. The oils used were high grade commercial oils.

Procedure.—Ten cc of the oil were measured into the glass jar. All measurements of oils were made with pipettes. Three cc of $N/10$ sodium oleate solution and 87 cc of water were added to the oil. The total volume of oil, soap and water was 100 cc in all cases. The water bath around the jar was brought

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[1] Lenher and Buell: Jour. Ind. Eng. Chem., 8, 701 (1916).

[2] Ibid., 8, 701 (1916).

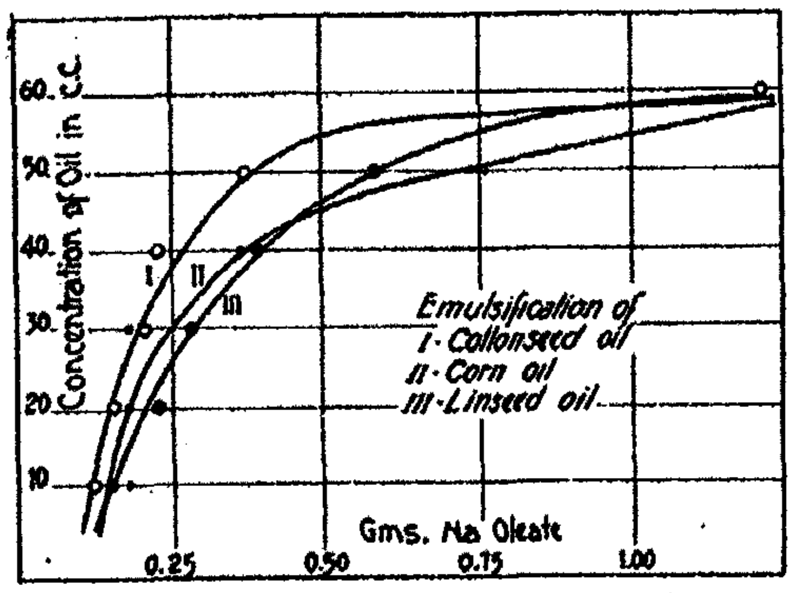

Fig. 1

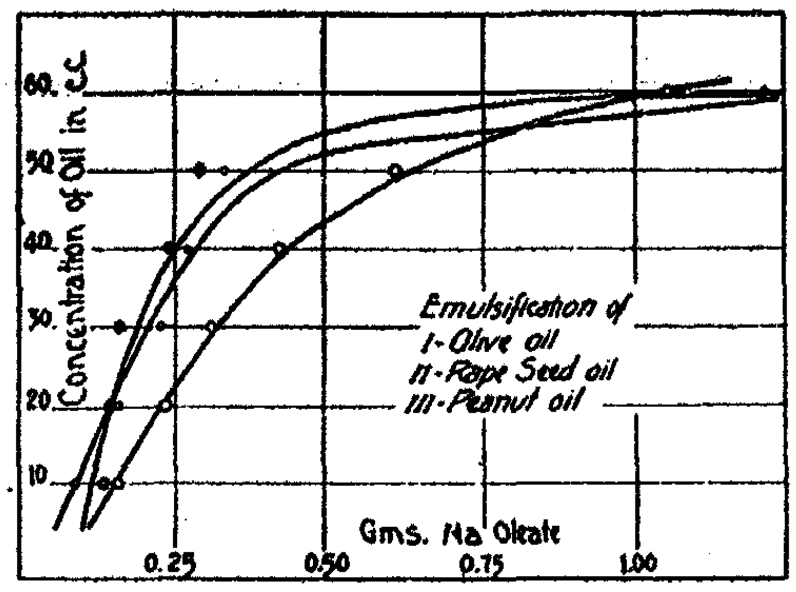

Fig. 2

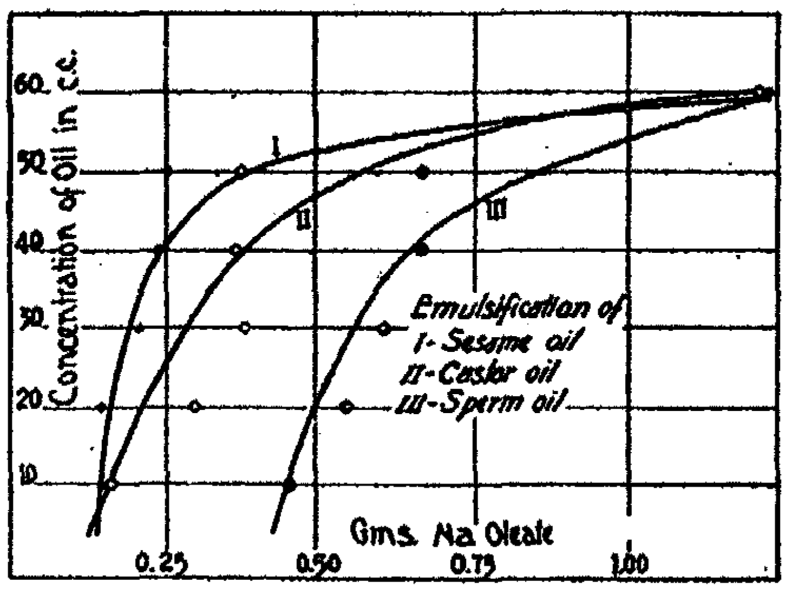

Fig. 3

to boiling and the contents of the jar were allowed to come to the temperature of the bath. The motor was then started and continued at high speed for exactly five minutes. The bath was removed, the jar was removed and allowed to stand for five minutes. If oil separated, an insufficient amount of emulsifying agent was present. The operation was then repeated with more sodium oleate and less water.

Ten cc of the oil were again measured out, 3.5 cc of *N*/10 sodium oleate and 86.5 cc of water were added. The temperature was again raised to 100° and the mixture stirred five minutes. If there still appeared unemulsified oil at the end of five minutes, the operation was repeated with the addition of 4 cc of *N*/10 sodium oleate. If this amount of sodium oleate produced an emulsion it was apparent that at least enough had been added, but it may have been more than was necessary to accomplish emulsification. Therefore the experiment was repeated with 3.8 cc, etc., until the minimum amount of soap necessary to produce emulsification was ascertained. The data are shown graphically in Figs. 1–3.

TABLE I

Emulsification of Cottonseed Oil with Sodium Oleate

cc Oil	cc Oleate Sol'n	cc Oleate	gm Na Oleate
10	4.0	86.0	0.122
20	5.2	74.8	0.158
30	6.8	63.2	0.207
40	7.5	52.5	0.228
50	12.3	37.7	0.374
60	40.0	—	1.216 (No emul.)

TABLE II

Emulsification of Corn Oil with Sodium Oleate

cc Oil	cc Oleate Sol'n	cc Water	gm Na Oleate
10	6.0	84.0	0.182
20	6.0	74.0	0.182
30	6.0	64.0	0.182
40	12.0	48.0	0.365
50	25.0	25.0	0.760
60	40.0	—	1.216 (No emul.)

TABLE III
Emulsification of Olive Oil with Na Oleate

cc Oil	cc Oleate Sol'n	cc Water	gm Na Oleate
10	4.5	85.5	0.137
20	4.8	75.2	0.146
30	5.3	64.7	0.161
40	8.0	52.0	0.243
50	9.6	40.4	0.292
60	40.0	—	1.216 (No emul.)

TABLE IV
Emulsification of Linseed Oil with Sodium Oleate

cc Oil	cc Oleate Sol'n	cc Water	gm Na Oleate
10	5.0	85.0	0.152
20	7.5	72.5	0.228
30	9.2	60.8	0.280
40	13.0	47.0	0.395
50	19.0	30.7	0.587
60	40.0	—	1.216 (No emul.)

TABLE V
Emulsification of Peanut Oil with Sodium Oleate

cc Oil	cc Oleate Sol'n	cc Water	gm Na Oleate
10	5.2	84.8	0.158
20	7.8	72.2	0.237
30	10.3	59.7	0.313
40	14.0	46.0	0.426
50	20.2	29.8	0.614
60	34.8	5.2	1.058

TABLE VI
Emulsification of Rape Seed Oil with Sodium Oleate

cc Oil	cc Oleate Sol'n	cc Water	gm Na Oleate
10	3.0	87.0	0.091
20	5.3	74.7	0.161
30	7.5	62.5	0.228
40	9.0	51.0	0.274
50	11.0	39.0	0.334
60	40.0	—	1.216 (No emul.)

Table VII

Emulsification of Castor Oil with Sodium Oleate

cc Oil	cc Oleate Sol'n	cc Water	gm Na Oleate
10	5.3	84.7	0.161
20	9.8	70.2	0.298
30	12.5	57.5	0.380
40	12.0	48.0	0.365
50	12.3	37.7	0.374
60	40.0	—	1.216 (No emul.)

Table VIII

Emulsification of Sesame Oil with Sodium Oleate

cc Oil	cc Oleate Sol'n	cc Water	gm Na Oleate
10	4.8	85.2	0.146
20	4.8	75.2	0.146
30	6.8	63.2	0.207
40	7.8	52.2	0.237
50	8.3	41.7	0.252
60	40.0	—	1.216 (No emul.)

Table IX

Emulsification of Sperm Oil with Sodium Oleate

cc Oil	cc Oleate Sol'n	cc Water	gm Na Oleate
10	15.0	75.0	0.456
20	18.0	62.0	0.547
30	20.0	50.0	0.608
40	22.0	38.0	0.669
50	22.0	28.0	0.669
60	40.0	—	1.216 (No emul.)

The results obtained with the various oils are in general the same for each oil. With small amounts of oil, each 10 cc increase in the oil requires but slight increase in the amount of soap required for emulsification, but above 40 cc the amount of soap required for emulsification increases rapidly.

The "dirt" that the laundryman has to deal with is in large part oils from one source or another. The present data seem to be added information that emulsification is at least one of the most important factors in the detergent action of soap.

NEW BOOKS

Fats and Fatty Degeneration. *By Martin H. Fischer and Marion O. Hooker. 23 × 16 cm; ix + 155. New York: John Wiley and Sons, 1917. Price: $2.00.*—Dr. Martin Fischer's severest critic could never accuse him of being dull. His recent work on "Fats and Fatty Degeneration," published in conjunction with Dr. Marion O. Hooker, is no exception to the rule. Possessed of the pen of a ready writer, the skill of a special pleader, a conviction regarding the infallibility of his own point of view that amounts almost to fanaticism, Dr. Fischer ignores or sweeps aside that which does not harmonize with his theme, and blends without acknowledgment the work and ideas of others with his own in such a manner as to convey the impression of originality and to create a favorable effect on the minds of those of his readers who do not happen to possess a technical acquaintance with this highly specialized subject.

The principal purpose of this book is to throw light on the problem of protoplasmic equilibrium, particularly as regards the physical state of the fats present in living cells under normal and pathological conditions, by studying the conditions under which emulsions of oil dispersed in water, like cream, and water dispersed in oil, like butter, may be produced, broken down and transformed into one another. In borrowing from earlier investigators the idea of tackling the problem of protoplasmic balance by studying the reversal of phase relations in emulsions, Dr. Fischer failed to make himself acquainted with the data already available regarding the conditions under which emulsions of water in oil may be formed, and emulsions of this type transformed into those of oil in water and *vice versa*. His failure to secure a clear conception of this the very keystone of the whole structure has led Fischer into considerable difficulties. He ignores Pickering's emulsification of 99 percent of one phase in 1 percent of the other; Bancroft's demonstration that the formation of one or the other type of emulsion depends not upon the relative volumes of oil and water, but simply upon whether the emulsifying agent employed is preponderantly hydrophilic or lipophilic, soaps of sodium and potassium, for example, causing the formation of emulsions of oil in water, while those of calcium and magnesium produce emulsions of water in oil; and Clowes' experiments in which emulsions of one type were readily converted into emulsions of the opposite type, or *vice-versa*, by modifying the emulsifying agent or by varying the proportions of certain antagonistic electrolytes in the system. These simple and easily repeated experiments were presented in papers referred to by Dr. Fischer and were carried out years before he commenced his experiments. In spite of this, Fischer adheres to the old contention that the formation of an emulsion of water in oil, is caused by raising the proportion of oil to water above a somewhat nebulous critical ratio at which, according to his point of view, an emulsion of oil in water will tend to go over to water in oil.

He starts out with the perfectly correct statement (page 1), which is subsequently repeated (page 21): "From the same quantities of oil and water, for example, two entirely different types of emulsions may be produced which have totally different properties. There may be made an emulsion of the oil in the water, or of the water in the oil." This statement scarcely harmonizes with one in the same chapter which is repated frequently throughout the book (pages 12, 13, 41, 63, 90, 94, 105). "When the fat in an oil-in-hydrated colloid emulsion is steadily increased, a point is finally reached at which the emulsion breaks over to one of the opposite type, namely, one of hydrated colloid-in-oil. In the case of the adipose tissues and of the fat secretions, the fat figures rise to 50, 60, and even 85 or 90 percent. The adipose tissues, too, are emulsions, but the increase in the percentage of fat has been carried beyond the critical point and so they are emulsions of the type of water-in-fat."

This statement is somewhat surprising in the face of Pickering's emulsification of 99 percent of oil in 1 percent of an aqueous soap solution, and Fischer's own data and illustrations (page 40 and 78) of emulsions (borrowed without acknowledgment from Pickering even to the stick standing up in the jelly) in which 20 parts of oil are emulsified in one part of the water phase; considering that the adipose tissues referred to seldom contain fat in a higher ratio to water than 5 or 10 to 1.

Fischer's own data (page 41) and the unsatisfactory accompanying photographs indicate that he does not differentiate sufficiently clearly between the mere breaking down of an emulsion to form separate layers of water and oil and the conversion of an emulsion of oil in water to one of water in oil. In fact Dr. Fischer's work is greatly marred by the extremely poor illustrations which make it almost impossible to differentiate between these two types of emulsions. This difficulty might have been overcome by staining the oil phase with some fat-soluble dye like Sudan III.

Fischer lays great stress on the fact, which has long been well established, that emulsions of oil in water may best be produced by employing hydrophilic colloids like soaps of sodium or potassium or alkaline casein, but nowhere does he recognize the obvious converse of this that emulsions of water in oil may be produced by employing as the emulsifying agent lipophilic substances which are readily dispersed in oil. Fischer appears to believe that the hydrated colloid which acts as the emulsifying agent is evenly distributed throughout the water phase in a definite chemical union with the water and appears to oppose the idea of a concentration film at the oil-water interface, in spite of the evidence presented by Bancroft, Briggs, Clowes, etc., of the formation of such a film. Subsequently he is forced to acknowledge that such an interfacial film must be formed in the case of milk to account for the stability of the emulsion and the facility with which it may be diluted, but the reader is rather led to conclude that he considers this as a special case.

Turning now to the biological and pathological aspects of the case, it is somewhat amusing to note (page 30), "We long ago gave up the notion of lipoid membranes about cells and the complex notions of their changing permeability to which Clowes and many authors still hold," and (page 9) "The smallest amounts of fat ever found in cells suffice to prove that the cell contents are not aqueous solutions of various salts and non-electrolytes contained in a semi-permeable bag, as is so often believed by the adherents of the osmotic conception of cell constitution." And then to turn to a subsequent section (page 118) in which he uses particles of acacia surrounded by oil as a model of protoplasm, and states, "While the oil which contains the acacia particle may not be compared directly to protoplasm from the chemical point of view, it does, in its 'liquid' behavior, act like it physically. Protoplasm, too, is best conceived of as a physical mixture of several mutually immiscible liquids."

It is doubtful if the most enthusiastic exponent of a continuous external lipoid film for protoplasm would ever make use, for purposes of analogy, of a system in which the oil phase is more obviously continuous than in that employed by Fischer.

In the opinion of the writer of this review, existing experimental evidence indicates that the greater part of the interior protoplasmic structure consists of a system in which the non-aqueous phase is dispersed in the aqueous. The protoplasmic margin appears to approximate more nearly to an emulsion or jelly system in which both the aqueous and non-aqueous phases are continuous, a crude analogy for which is a porcelain bougie, but in which the relative continuity of the two phases is continually fluctuating with a consequent intermittent variation in the permeability of the system to water and water-borne substances. This is very far from stating that protoplasm is surrounded by a continuous lipoid or fat film, as suggested by Fischer, who has not apparently made himself sufficiently acquainted with the paper which he criticizes. In fact Fischer's frequent, would-be humorous, references to the biologists' conception of protoplasm as a sack or bag containing salts in solution only go to prove his entire failure to grasp the significance of the work accomplished in this field in the last decade.

In the chapter on fatty degeneration, Fischer fails entirely to give credit to Alonzo E. Taylor, who simultaneously with Athanasiu recognized the true nature of this process as early as 1899. Taylor demonstrated that when animals were subjected to phosphorus poisoning, causing fatty degeneration of the organs, not only was there no increase in the fat content at the expense of the protein, as had previously been believed to be the case, but that an actual loss of fat took place. Furthermore Taylor recognized that the increased visibility of the fat, which had led previous investigators to believe that there was an actual increase in the fat content of the cell, was attributable to the aggregation or deposition of the extremely finely dispersed fat particles with the formation of globules sufficiently large to be readily recognized. When an emulsion of oil in water is exposed to the action of some agent, like acid, capable of destroying the emulsifying agent, the partial separation of oil which results appears in the light of Taylor's observation to afford an accurate model of the process of fatty degeneration.

In considering Fischer's data regarding fatty infiltration and secretion it is well to bear in mind that there is a profound difference between the mere destruction of an emulsion of oil-in-water, resulting in the separation of oil in which a certain amount of water may be mechanically enmeshed, but not truly emulsified, and the production of a true emulsion of water-in-oil, such as is obtained when water is shaken with oil containing a calcium or magnesium soap in which additional mechanical admixture simply improves the emulsification of the water in the oil. It is by no means easy to determine whether smears or sections of the fatty deposits of adipose tissue afford an accurate picture of their original physical condition in living cells, but even if it be conceded that these deposits are real emulsions of water in fat, exception must be taken to

Fischer's contention that emulsions of fat in water may be converted into those of water in fat by raising the ratio of fats to water either by addition of oil to the system or by evaporation of a portion of the water. Fischer's illustration (page 99) of the effect of evaporation on an emulsion of oil-in-water does not indicate a change to an emulsion of water in oil, but rather a gradual breaking down of the oil-in-water emulsion with a consequent aggregation of the previously dispersed phase. Neither does his illustration (page 100) of the clarification of an emulsion of oil-in-water by evaporation indicate any change from the original form of emulsion. While the change from an oil-in-water emulsion to one of water-in-oil cannot be effected by simply destroying the hydrophilic emulsifying agent by means of acid, it is perfectly conceivable that if suitable hydrophilic and lipophilic colloids were both present in such a system, the hydrophilic predominating over the lipophilic sufficiently to maintain an emulsion of oil-in-water, the destruction of the hydrophilic colloid should cause the predominance of the lipophilic colloid and the formation of an emulsion of water-in-oil.

Errors and misstatements which might well be excused in a preliminary communication should scarcely occur in a work like this which poses as the last word on the subject and in which, from the first page to the last, there is never a reservation made or a doubt expressed regarding the absolute and final correctness of the author's conclusions. Dr. Fischer's statements in the preface of his book (dated July 20, 1916) that "this detailed study of the fat in the cell is less than two years old," and in his first paper on the subject (*Science*, March 31, 1916), "we have been engaged during the past few months in the study of the conditions which determine the making and breaking of emulsions," are significant when coupled with his references to, and presumably knowledge of, work published in 1913 in which a description was given of means whereby emulsions of oil-in-water may be transformed into those of water-in-oil, and *vice-versa*, and attention was drawn to the probable significance of these observations from a biological standpoint.

While the writer of this review would certainly not charge Dr. Fischer with any deliberate intention to mislead, the obvious haste with which this somewhat pretentious work has been constructed suggests an attempt to skim the cream of a new idea in a promising field of research. *G. H. A. Clowes*

Cours de Physique. *Part II. By E. Rothé. 25 × 17 cm; pp. xv + 328. Paris: Gauthier-Villars et Cie, 1917. Price: 13 francs.*—The preface was written in July, 1914; but the book has evidently been held up by the war because the title page bears the imprint of 1917. This volume is devoted to thermodynamics as an experimental science and is intended for scientific and engineering students. The chapters are entitled: principle of equivalence; variations of energy; general remarks on transformations and graphical representations; ideal gases; determinations of the specific heats of gases; Joule's law; different types of expansion and compression; reversible and irreversible changes; the second law of thermodynamics; irreversible changes; applications of thermodynamics; different diagrams of the thermodynamics of fluids; application of thermodynamics to solids and liquids; application of Clapeyron's equation in determining the latest heats; special study of vapors; Boulvin's diagram and the steam engine cycle.

Wilder D. Bancroft

ALTERNATING CURRENT ELECTROLYSIS WITH MERCURY ELECTRODES

78.

BY HARRY B. WEISER

When a solution of sodium thiosulphate is added to solutions of certain metallic salts, notably lead, mercury, silver, copper,[1] zinc and cadmium,[2] the metals are precipitated as the sulphides. By electrolysis of sodium thiosulphate solutions with a direct current, using anodes of any of the above mentioned salts, the electrodes dissolve with the formation of sulphides of the metals. Richards and Roeppler[3] have prepared cadmium sulphide by electrolyzing a solution of sodium thiosulphate with alternating current between cadmium electrodes; and they have taken out a patent covering this phenomenon as a method for preparing cadmium yellow. LeBlanc and Schick[4] have continued the work of Richards by studying the effect of frequency of alternation on the efficiency. With high frequency they found that little cadmium sulphide was formed but with lower frequencies the yield rose to as much as 77 percent. That any cadmium sulphide at all was obtained with an alternating current was due to the continuous removal of a part of the dissolved cadmium from the reducing action of the next current impulse. Under these conditions it is evident that the greatest yield will be obtained at the lowest frequency. Similar effects were observed with zinc and silver electrodes in thiosulphate solution and with copper, silver, zinc and nickel electrodes in cyanide solution.

LeBlanc and Schick determined the efficiency both in thiosulphate solution and in cyanide solution from the loss in weight of the specific electrodes after the electrolysis had pro-

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[1] Faktir: Zeit. anal. Chem., 39, 395 (1900).

[2] Vohl: Liebig's Ann., 96, 242 (1855).

[3] Richards and Roeppler: Zeit. Elektrochemie, 6, 275 (1899); Richards: Trans. Am. Electrochem. Soc., 1, 221 (1902).

[4] Zeit. phys. Chem., 46, 213 (1903).

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ceeded a definite interval of time. Similar efficiency measurements in alternating current electrolysis have been made by Brochet and Petit,[1] Wilson[2] and others. Since the ease of corrosion of an anode is dependent in large measure on the electrode surface and since the electrode surface is likely to be very different in different experiments with the same metal, we should expect to encounter difficulties in attempting to duplicate any set of experiments on electrolytic corrosion. A few observations will be cited to show that this is the case:

Brochet and Petit[3] found that the solubility of platinum and of iron electrodes under the influence of the alternating current in cyanide solution varied but little with the current density, whereas the solubility of cobalt increased with the current density. The explanation of this difference is probably to be found in a later observation of the same investigators,[4] namely, that cobalt electrodes in cyanide solution under the influence of the alternating current dissolve irregularly and the electrodes become pitted.

In a continuation of the work of LeBlanc and Schick,[5] with electrodes of copper, iron, zinc and nickel in cyanide solution Löb[6] made the interesting observation that in all cases the quantity of metal dissolved under similar circumstances depended to a large extent on the electrode surface. In all cases the smoother the surface the smaller the quantity dissolved in a given time. He found further, that the loss in weight of the electrodes was increased by raising the current density; by increasing the concentration of cyanide solution and by decreasing the frequency. Iron and nickel were exceptional in that at higher current densities they became passive.

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[1] Comptes rendus, 138, 359, 1095 (1904); Bull. Soc. chim. Paris, [3] 31, 1257, 1261 (1904).

[2] Trans. Faraday Soc., 1, 305 (1905).

[3] Comptes rendus, 138, 1095 (1904).

[4] Brochet and Petit: Bull. Soc. chim. Paris, [3] 31, 1257 (1904).

[5] Loc. cit.

[6] Zeit. Elektrochemie, 12, 79 (1906).

White[1] made some particularly striking observations that indicate to what extent the electrode surface may determine the degree of corrosion. In an attempt to determine the effect of current density and temperature on the efficiency in the electrolysis of thiosulphate solution between cadmium electrodes using an alternating current of constant frequency, he found that the efficiency of corrosion varied between 0.8 percent and 36 percent, under constant conditions of temperature, current and frequency. The obvious conclusion reached was that the efficiency was practically independent of the current strength of the temperature and of stirring and was dependent almost entirely on the electrode surface. It is interesting to note that the lowest efficiency obtained by White was greater than that obtained by LeBlanc and Schick for approximately the same frequency.

In discussing White's paper Bancroft[2] sums up the situation as follows:

"It is not safe to draw any conclusion as to the effect of current density or concentration or temperature from any single set of experiments. I have no doubt that all these factors affect the yield to a certain extent; but as that variation is probably very small it disappears absolutely in comparison with fluctuations from fifteen to twenty-five percent, or even more, depending on minor changes in the electrodes which you cannot represent quantitatively. Until someone can devise a method for making an absolutely reproducible electrode the changes in efficiency due to the other factors have simply to be classed under the head of not being measurable."

Similar observations were later made by White[3] in a study of electrolytic corrosion of metals using a direct current:

"A very important factor was the electrode surface and care was taken to file and scour each anode with carborundum paper before beginning the electrolysis, to ensure a new and clean surface for each run. Even then it was impossible to

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[1] Trans. Am. Electrochem. Soc., 9, 305 (1906).

[2] Ibid., 9, 314 (1906).

[3] Jour. Phys. Chem., 15, 723 (1911).

duplicate the results exactly. Experiments with freshly deposited copper showed that there were discrepancies in the results even with this precaution to ensure a uniform surface."

Since attempts to make a reproducible electrode of solid metal have proven unsuccessful, it was thought that mercury electrodes would prove satisfactory for studying the effect of current density, concentration of the electrolyte, temperature, stirring, etc., on the efficiency of electrolysis with an alternating current of constant frequency. The results of this investigation are contained in the following pages.

When a solution of sodium thiosulphate is electrolyzed with an alternating current using cadmium electrodes, cadmium sulphide is precipitated and hydrogen is evolved from both electrodes. A similar phenomenon takes place when thiosulphate solution is electrolyzed with mercury electrodes and this solution was accordingly used in these experiments. Mercuric sulphide is formed at both electrodes but relatively little hydrogen is evolved because of the lower discharge potential of sodium ion at a mercury electrode. Under these conditions a part of the liberated sodium is dissolved by the mercury before being subjected to the oxidizing action of the next current impulse.

Since the surface tension of mercury varies with the electrical charge upon it, the surface of mercury electrodes under the influence of an alternating current undergoes rhythmical vibrations or pulsations. This vibration of the mercury keeps the electrode surface perfectly clean—a factor which is of distinct importance in determining the amount of corrosion. The phenomenon also keeps the solution agitated in the region of the electrodes.

The electrolysis was carried out in the following manner: A 400 cubic centimeter beaker was supplied with a wire support suitable for suspending it firmly in a larger beaker of boiling water. For the electrodes approximately 60 grams of carefully cleaned and dried mercury were accurately weighed into each of two crystallizing dishes, 3.3 cm internal diameter and 1.8 cm deep. Each electrode thus contained approximately the same volume of mercury and presented a surface of about 8.5 square centimeters. Electrical connection was made with the mercury by means of a small mercury-filled glass tube, into the end of which was sealed a piece of platinum wire that projected about 2 millimeters and was bent at right angles to the length of the tube. The glass tubes were held firmly in place by fitting them snugly in holes bored in a strip of wood which rested on the edge of the beaker and which was tied to the wire support above mentioned. The mercury was covered with water to prevent any vaporization of the metal before the addition of the electrolyte to the cell. After suspending the cell rigidly in the beaker of boiling water, the boiling electrolyte was poured into it and electrical connection was made with the source of current through a sliding contact rheostat whereby the current was maintained constant. The current employed was an alternating current of 60 cycles or 7200 alternations per minute. Westinghouse meters of the PM type were employed for reading the current. In some experiments the electrolyte was stirred and this was accomplished by an electrically driven stirrer.

At the conclusion of the electrolysis the cell was immediately removed from the boiling water, placed under a water tap, and a small stream of water allowed to flow into it. This very effectually washed the electrolyte and the flocculent precipitate of mercuric sulphide from the cell. The tubes containing the platinum contacts were removed with particular care to avoid any loss of mercury, after which the mercury cups were removed and the contents of each was transferred to tall, narrow beakers of 50 cc capacity. The mercury was next thoroughly washed by allowing a stream of water to flow into the beaker which was turned at an angle and constantly rotated. The nature of the precipitate of mercuric sulphide was such that the washing was usually accomplished with relatively little difficulty. The most of the supernatant water was sucked off with a pipette and all but a trace was taken up with strips of filter paper touched to the edge of the mercury surface. The almost dry mercury was then washed with two 10 cubic centimeter portions of absolute alcohol, the most of which was removed in the same way as the water. To remove the last trace of alcohol the beaker was gently rotated at an angle of 45° for three minutes, after which it was placed in a vacuum desiccator and suction applied for three minutes. It was weighed immediately and the loss in weight determined.

In the entire process particular care was taken to avoid any loss of mercury. The bottom of the cell was always carefully explored for mercury that occasionally splashed out of the containers during an electrolysis. Since all of the flocculent mercuric sulphide was readily washed from the beaker in the manner described, even a minute drop of mercury could

Table I

Time (Minutes)	Current (Amperes)	Electrode loss (Grams)			Efficiency (Percent)	Remarks
		a	*b*	Sum		
60	1	0.3110	0.2994	0.6104	16.89	stirred
60	1	0.3164	0.3100	0.6264	17.33	stirred
60	1	0.3080	0.3092	0.6172	17.08	not stirred
60	1	0.3063	0.3075	0.6138	16.98	stirred
60	1	0.2960	0.2991	0.5951	16.46	stirred
60	1	0.2969	0.2949	0.5918	16.38	stirred
30	1	0.1679	0.1650	0.3329	18.45	not stirred
30	1	0.1442	0.1433	0.2875	15.85	not stirred
30	1	0.1558	0.1570	0.3128	17.31	not stirred
60	2	0.5584	0.5604	1.1188	15.47	stirred
60	2	0.5860	0.5806	1.1666	16.14	stirred
60	2	0.5426	0.5438	1.0864	15.03	stirred
60	2	0.5219	0.5216	1.0435	14.44	stirred
60	2	0.5370	0.5400	1.0770	14.90	stirred
60	2	0.5943	0.5916	1.1859	16.40	stirred
60	2	0.5576	0.5630	1.1206	15.50	not stirred
60	2	0.5465	0.5442	1.0907	15.09	not stirred
30	2	0.2560	0.2543	0.5103	14.12	not stirred
60	1.75	0.4411	0.4438	0.8849	13.99	not stirred
60	1.75	0.4554	0.4546	0.9100	14.37	not stirred
60	1.75	0.4786	0.4770	0.9550	15.10	stirred
60	1.75	0.4305	0.4290	0.8595	13.59	stirred
60	1.75	0.4470	0.4452	0.8922	14.17	stirred

be detected and recovered. Fortunately, this did not often happen; but in case it did, the recovered mercury was added to the electrode marked *a* in the tables.

The current for a run was multiplied by the time in seconds and this by 1.0039,—the electrochemical equivalent of mercury in milligrams per ampere second. This value was taken as 100 percent and the efficiency of the electrolysis was calculated from the sum of the observed losses of the two electrodes.

In the first series of experiments approximately 15 percent solutions of sodium thiosulphate were electrolyzed at a temperature of 100° and with varying current density. The results are recorded in Table I.

In the above series of experiments it will be seen that in any given electrolysis the electrode losses were very nearly the same but that in different determinations, the total losses and hence the efficiency of the electrolyses varied considerably even when particular care was taken to keep the temperature and the current constant. At first it was thought that the variation was due to fluctuation in frequency, but tests with a frequency indicator showed that this was not the case. It was not caused by a difference in the rate of stirring for similar variations were observed when the electrolyte was not stirred. The concentration of the electrolyte was the only remaining variable. The solution was prepared separately for each experiment and as before stated, it was made only approximately 15 percent since it was thought that small differences in the concentration of the electrolyte would have relatively little effect. Subsequent experiments showed, however, that the failure to maintain the concentration of the electrolyte constant was responsible for the variation in efficiency under otherwise constant conditions.

The Effect of Concentration of the Electrolyte

In determining the effect of the concentration of the electrolyte on the efficiency of corrosion, the current was maintained constant at one ampere for one-half hour since the electrode loss under these conditions was quite sufficient for accurate determination and since the current could be read with a high degree of accuracy on a two-ampere meter that was available. The electrolyte was not stirred since the previous experiments showed that the effect was not particularly marked and since it was thought that more constant conditions could be maintained without mechanical agitation which would vary somewhat with the speed and position of the stirrer. The temperature was kept at 100° by suspending the cell in boiling water as before described. The level of the solution was maintained constant by replenishing the water lost by evaporation. Two or three cells were usually connected in series. The results of a series of determinations at different concentrations of electrolytes are recorded in Table II and are shown graphically in Figure I.

Table II
Effect of Concentration of Solution

Time (Minutes)	Concentration (Percent)	Electrode loss (Grams)			Efficiency (Percent)	
		a	*b*	Sum		Average
30	5	0.0374	0.0373	0.0747	4.14	4.17
30	5	0.0378	0.0378	0.0756	4.18	
30	5	0.0381	0.0377	0.0758	4.20	
30	15	0.1412	0.1426	0.2838	15.70	15.69
30	15	0.1422	0.1410	0.2832	15.67	
30	15	0.1420	0.1405	0.2825	15.63	
30	15	0.1428	0.1422	0.2850	15.77	
30	25	0.2191	0.2210	0.4401	24.36	24.37
30	25	0.2192	0.2217	0.4409	24.40	
30	25	0.2187	0.2213	0.4400	24.35	
30	35	0.2710	0.2741	0.5451	30.16	30.14
30	35	0.2770	0.2673	0.5443	30.12	
30	35	0.2712	0.2734	0.5446	30.14	
30	50	0.0494	0.0468	0.0962	5.32	5.23
30	50	0.0450	0.0476	0.0926	5.13	
30	50	0.0525	0.0433	0.0958	5.25	

The above results show the marked influence of the concentration of electrolyte on the efficiency. Tests carried out in the absence of electrolysis showed that the increased efficiency with increased concentration was not due to solubility of the metal in the electrolyte.

When a given electrode is acting as anode the liberated thiosulphate ion attacks the mercury with the formation of mercuric thiosulphate which readily decomposes with the formation of mercuric sulphide. However, this decomposition is not absolutely instantaneous, otherwise all the mercuric ions would be removed from the sphere of action of the next current impulse just as fast as formed and the electrolytic corrosion would be 100 percent efficient, which we know is not the case. For the brief interval before the mercuric ions are removed as insoluble mercuric sulphide, both mercuric and sodium cations exist. With the next impulse the electrode under consideration becomes cathode and the current is carried by both cations. The factors chiefly instrumental in determining which of the ions will be liberated are the discharge potential of the ions and the relative concentrations of the ions. With a given temperature, current, and frequency of alternation, the concentration of mercuric ion will be approximately constant whereas the concentration of sodium ion will vary enormously with marked change in the concentration of the electrolyte. With a low concentration of sodium ion, that is in dilute thiosulphate solution, mercuric ions are chiefly discharged because of their lower discharge potential and their relatively high concentration. Under these conditions the electrode loss will be relatively small, for the mercury dissolved by one impulse will be largely reprecipitated by the next. However, with increased concentration of thiosulphate the proportion of sodium ions relative

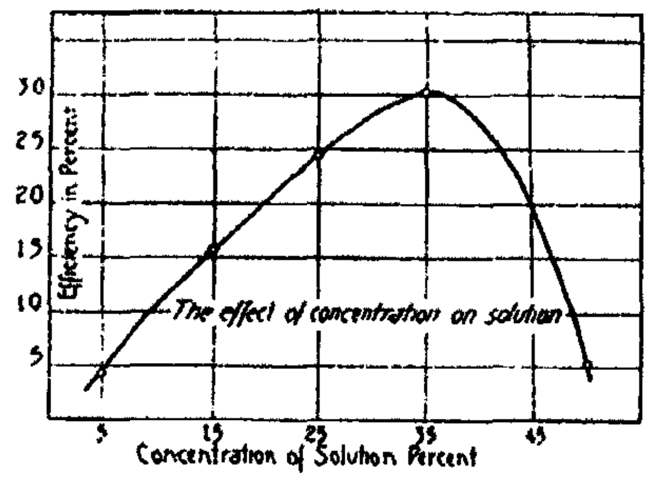

Fig. I

to mercuric ions liberated is increased and the quantity of mercuric ions thrown down as sulphide of mercury is correspondingly increased. In line with this explanation it will be seen by referring to the above table, that the efficiency increases almost in direct proportion to the concentration,—rising from 4 percent in a 5 percent thiosulphate solution to 30 percent in a thirty-five percent solution. This fact explains the variation in the results in the first series of experiments where no particular care was taken to maintain the concentration of the electrolyte constant.

With too high a concentration of thiosulphate, another factor was introduced that caused the efficiency to fall off very fast, as shown in the above table. Attention has been called to the fact that the electrode kept itself clean by the rhythmical vibration of the surface under the influence of the alternating current. If this vibration were prevented by the formation of a film of sulphide over the mercury surface, the corrosion would be materially diminished. Such a condition was actually realized in highly concentrated solutions. The formation of a film over the mercury surface in highly concentrated solutions and not in more dilute solutions was caused by the chemical action of thiosulphate on metallic mercury. As before intimated, when mercury was subjected for a half hour to a 15 percent boiling solution of thiosulphate there was relatively little action. As a matter of fact, however, a very thin film of sulphide was formed. With a saturated solution of thiosulphate a visible film formed immediately. After allowing a saturated solution of thiosulphate to stand for a few minutes in contact with mercury electrodes, one ampere was passed through the cell. There was no vibration of the electrodes and the corrosion was very slight. In a 50 percent solution an invisible film probably formed over the mercury surface and this cut down the vibration to such an extent that the film gradually grew in thickness until the vibration was almost entirely prevented. This resulted in the relatively low efficiency observed.

An interesting quantitative experiment was carried out showing the effect of the presence and the absence of a film of sulphide on the corrosion of two electrodes in the same cell. A thick film was formed over two electrodes by electrolyzing a highly concentrated solution of thiosulphate for five minutes with a current of one ampere. The electrodes were then removed from this solution and the film was washed from one of them and was allowed to remain on the other, after which the electrolysis was continued for 25 minutes in a 15 percent solution of thiosulphate at a temperature of 100 degrees and a current of one ampere. The results are recorded in Table III.

TABLE III

Time (Minutes)	Current (Amperes)	Electrode loss (Grams)		Efficiency of corrosion (Percent)		
		with film	without film	with film	without film	total
30	1	0.0445	0.1392	2.47	7.15	9.62

It is evident that the corrosion of the electrode with the film was relatively very slight compared to that from which the film was removed. The fact that the efficiency of corrosion of the electrode from which the film was removed was slightly less than in the previous experiment under similar conditions (Table II) was due to the film formation in the concentrated solution and the consequent decreased corrosion during the first five minutes.

The Effect of Current Density

The effect of current density on the efficiency of electrolysis was determined with currents varying from one-half ampere to five amperes. The electrolyte was not stirred and the temperature was kept at 100 degrees as before. To prevent boiling of the electrolyte when 5 amperes were passed, the cell was surrounded by water at room temperature.

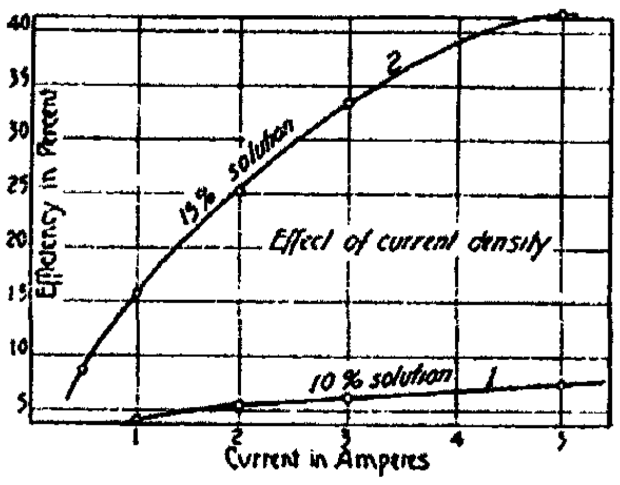

Fig. II

Two concentrations of electrolyte were employed—5 percent and 15 percent. The results are recorded in Tables IV and V and are shown graphically in Figure II.

TABLE IV
Effect of Current Density
5 Percent Solution

Time (Minutes)	Current (Amperes)	Electrode loss (Grams)			Efficiency (Percent)	
		a	b	Sum		Average
30	1	0.0374	0.0373	0.0747	4.14	4.17
30	1	0.0378	0.0378	0.0756	4.18	
30	1	0.0381	0.0377	0.0758	4.20	
30	2	0.0483	0.0498	0.0981	5.42	5.44
30	2	0.0505	0.0489	0.0994	5.50	
30	2	0.0484	0.0489	0.0973	5.39	
30	3	0.0581	0.0583	0.1164	6.44	6.41
30	3	0.0572	0.0577	0.1149	6.36	
30	3	0.0580	0.0578	0.1158	6.41	
30	5	0.0659	0.0684	0.1343	7.43	7.44
30	5	0.0672	0.0676	0.1348	7.46	
30	5	0.0668	0.0674	0.1342	7.42	

The results in Tables IV and V show that under otherwise constant conditions the efficiency increases with the current density. However, the increase in efficiency is not in direct proportion to the current density but is proportionately less at the higher current densities. This is what we should expect from the previous considerations on the effect of the concentration of the electrolyte. The total change in the concentration of the electrolyte is relatively small but the concentration is always greater in the body of the solution than it is in the immediate region of the electrodes where the ions are constantly being removed. All other conditions being the same, the concentration of thiosulphate in the immediate region of the electrodes (which is what counts), is less the higher the current

TABLE V
Effect of Current Density
15 Percent Solution

Time (Minutes)	Current (Amperes)	Electrode loss (Grams)			Efficiency (Percent)	
		a	*b*	Sum		Average
30	0.5	0.0810	0.0794	0.1604	8.93	8.75
30	0.5	0.0785	0.0777	0.1562	8.65	
30	0.5	0.0821	0.0747	0.1568	8.68	
30	1	0.1412	0.1426	0.2838	15.70	15.69
30	1	0.1422	0.1410	0.2832	15.67	
30	1	0.1420	0.1405	0.2825	15.63	
30	1	0.1428	0.1422	0.2850	15.77	
30	2	0.2270	0.2304	0.4574	25.31	25.24
30	2	0.2289	0.2291	0.4580	25.34	
30	2	0.2263	0.2267	0.4530	25.08	
30	3	0.2955	0.3100	0.6055	33.51	33.47
30	3	0.3018	0.3071	0.6089	33.69	
30	3	0.2969	0.3029	0.5998	33.20	
30	5	0.3749	0.3772	0.7521	41.62	41.76
30	5	0.3786	0.3794	0.7580	41.89	

density. Therefore at higher current densities the quantity of mercuric ions reprecipitated on the electrode will be correspondingly greater and the efficiency of corrosion correspondingly less than at lower current densities. This is in accord with the experimental results.

Since the concentration of thiosulphate in the immediate region of the electrode at a definite current density will be correspondingly greater in concentrated than in dilute solutions we should expect to find the efficiency proportionately greater with the higher concentrations. That this is the case is evident from the above results. The corrosion in the 5 percent solution with a current of 5 amperes is less than twice what it is with a current of one ampere, whereas in the 15 percent solution the corrosion with 5 amperes is nearly three times what it is with one ampere.

The Effect of Stirring

From the above considerations it follows that if it were possible to maintain an absolutely uniform concentration of the electrolyte at all times during an electrolysis, the efficiency of corrosion would increase in direct proportion to the current density. Since stirring the electrolyte would tend to keep the concentration more uniform, the efficiency should increase by agitating the solution. This was tried by electrolyzing a 15 percent solution at 100° and stirring the electrolyte vigorously with an electrically driven stirrer. The result obtained is recorded in Table VI. That the efficiency is increased is shown by comparison with the results obtained without stirring.

TABLE VI
Effect of Stirring

Time (Minutes)	Current (Amperes)	Electrode loss (Grams)			Efficiency (Percent)	
		a	*b*	Sum		
30	1	0.1443	0.1453	0.2896	16.02	stirred
30	1	—	—	—	15.69	not stirred

The Effect of Temperature of the Electrolyte

The effect of the temperature of the electrolyte on the efficiency of the electrolysis was next studied. Since the migration velocity of the ions and the rate of diffusion is materially decreased by lowering the temperature, it is evident that the concentration of electrolyte in the immediate region of the electrodes, after the electrolysis has run a definite length of time, will be less the lower the temperature. From previous considerations we should expect, therefore, that the efficiency of the electrolysis would decrease with decreasing temperature of the electrolyte. This was verified experimentally.

Fifteen percent thiosulphate solutions were electrolyzed for one-half hour with a current of one ampere and the temperature of the electrolyte was varied. In order to maintain the temperature approximately constant throughout an experiment the cells were suspended in a large metal container filled with water heated to the desired temperature. Experiments were carried out at 25 degrees and at 75 degrees. No determinations were attempted at zero because of the difficulty of maintaining this temperature constant with one ampere passing through the solution. The results are recorded in Table VII.

TABLE VII
The Effect of the Temperature of the Electrolyte

Time (Minutes)	Temperature (Degrees)	Electrode loss (Grams)			Efficiency (Percent)	
		a	*b*	Sum		Average
30	25	0.1155	0.1132	0.2287	12.66	12.67
30	25	0.1153	0.1144	0.2297	12.76	
30	25	0.1137	0.1137	0.2274	12.59	
30	75	0.1248	0.1225	0.2473	13.68	13.63
30	75	0.1245	0.1210	0.2455	13.58	
30	75	0.1187	0.1277	0.2464	13.63	
30	100					15.69

Experiments with Zinc Electrodes

The results of LeBlanc and Schick's[1] electrolysis experiments with electrodes of different metals in thiosulphate solution might lead one to believe that the efficiency of corrosion is affected but slightly by the composition of the electrode. In order to show that the efficiency may differ widely with different metals some experiments were run with electrodes of zinc. The electrodes, which were cut from a piece of pure sheet zinc, were approximately 1.7 cm wide and 12 cm long. After thorough cleaning and polishing they were immersed in 15 percent thiosulphate solution to a depth of

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[1] Loc. cit.

10 cm and were clamped firmly against the sides of the beaker in such a way that the back was scarcely attacked during the electrolysis. In this way an electrode surface was obtained that was approximately double that used in the electrolysis with mercury electrodes. Two amperes were passed through the solution which was kept at 100° by immersing the cell in boiling water. Three cells were connected in series and the electrolysis was continued for one hour since the efficiency of corrosion was very small. At the conclusion of one run the same electrodes were polished and a second set of determinations made. The results are recorded in Table VIII.

TABLE VIII
Electrolysis Experiments with Zinc Electrodes

Time (Minutes)	Current (Amperes)	Electrode loss (Grams)			Efficiency (Percent)
		a	*b*	Sum	
60	2	0.0139	0.0151	0.0290	1.23
60	2	0.0126	0.0144	0.0270	1.15
60	2	0.0150	0.0131	0.0281	1.19
60	2	0.0222	0.0159	0.0381	1.67
60	2	0.0146	0.0196	0.0342	1.45
60	2	0.0150	0.0217	0.0367	1.56

The above results show that the efficiency of corrosion may vary widely with different electrodes. Under approximately the same conditions of current density, temperature and concentration of the electrolyte, the efficiency of corrosion with mercury electrodes is twelve times greater than with zinc electrodes. In order to show that this difference was not due to a protecting film over the surface of the electrode, subsequent experiments were carried out with rotating zinc electrodes constantly brushed with a tooth brush to keep the surface clean. The results obtained under these conditions were approximately the same as with stationary electrodes. A lower efficiency with zinc electrodes is exactly what we should expect since zinc thiosulphate is considerably more stable than the corresponding mercury salt and hence relatively few zinc ions are precipitated as sulphide. It is interesting to note that with apparently identical electrodes there is considerable variation in the amount of corrosion and that the corrosion is appreciably greater with electrodes that are used the second time. These differences merely serve to emphasize again the importance of the electrode surface in determining the efficiency of electrolytic corrosion. The same effects are unquestionably produced by variations in temperature, current density, concentration, etc., with zinc electrodes that are quantitatively measurable with mercury electrodes; but these effects are negligibly small in comparison with that resulting from slight differences in the electrode surface.

The results of this investigation may be summarized as follows:

1. The efficiency of the electrolytic corrosion of solid metallic electrodes with the alternating current varies so widely with minor differences in the electrode surface that the results of a given set of experiments cannot be reproduced.
2. The mercury electrode in thiosulphate solution under the influence of the 60 cycle alternating current is reproducible.
3. The effect of widely varying conditions on the efficiency of electrolytic corrosion with the alternating current of constant frequency has been studied with mercury electrodes in sodium thiosulphate solution.
4. The efficiency of corrosion increases almost directly as the concentration of thiosulphate solution. With too high a concentration, however, a film of sulphide forms over the electrode which cuts down the corrosion.
5. The efficiency of corrosion increases with the current density but not in direct proportion. The variation from strict proportionality is greater in dilute than in concentrated solution.
6. Mechanical stirring increases the efficiency of corrosion.
7. The efficiency of corrosion decreases with decrease in temperature.

8. Any variation in conditions that affects the concentration of electrolyte in the immediate region of the electrodes correspondingly affects the efficiency of corrosion.

9. Under like conditions zinc electrodes corrode much less readily with the alternating current than do mercury electrodes.

10. The effect on the efficiency produced by variations in current density, stirring, temperature and concentration of thiosulphate solution is of the same character with solid metallic electrodes as with mercury; but with the former these effects are negligibly small compared with that resulting from slight differences in the electrode surface.

Department of Chemistry
The Rice Institute
Houston, Texas

SOME STUDIES OF SOAP SOLUTIONS. III

BY VICTOR LENHER AND GEORGE M. BISHOP

W. Spring[1] in his work on the behavior of soap solutions with lampblack, colloidal ferric hydroxide, silicic acid and clay, found what he described as an adsorption compound formed between the carbon (lampblack) and the acid radicle of the soap. His view is that the lampblack hastens the decomposition of soap in water by causing the formation of an acid salt, and considered the colloidal or adsorption compound due to the difference of electrical polarity of its constituents by water. Spring found that the ash of a solution so treated is greater than that of the original soap solution, and concludes that the formation of this adsorption compound is the active feature in the detergent action of soap.

A series of experiments have been conducted by us to ascertain, if possible, whether or not any surface condensation of soap takes place on carbon. It is well known that when one's hands or clothing are grimed with graphite there is no better way to cleanse than by washing with soap. Certainly the highly refractory chemical character of graphite would preclude its being attacked by so mild a chemical agent as a soap solution.

Obviously, different forms of carbon should adsorb the soap to different degrees. This we have tested experimentally by treating a soap solution with various forms of carbon, such as Ceylon graphite, willow charcoal, and animal charcoal.

Experimental.—A glass tube 34 cm long and 3 cm in diameter was closed at the lower end with a rubber stopper fitted with a short, glass delivery tube. The tube was filled with powdered Ceylon graphite, in the first experiment, which had been heated for four hours at a bright red heat in an electric muffle. This heating served to remove any organic

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[1] Spring: Zeit. Kolloidchemie, **4**, 161 (1909); **6**, 11, 109, 164 (1910); Rec. Trav. chim. Pays-Bas., **28**, 120, 424 (1909); **29**, 1 (1910); Bull. Acad. roy. belg., **1909**, 187, 949; Arch. Sci. phys. nat., **30**, 561 (1911).

or volatile impurities in the graphite. As soon as it was cool it was introduced into the tube.

The graphite column, about 30 cm long, was separated from the stopper at the bottom of the tube by a $2^1/_2$ cm layer of glass wool, which also served as a filter. The glass tube was clamped in an upright position and was closed at the top with a rubber stopper carrying a separatory funnel. The solution, after passing through the graphite, was collected in 50 cc portions in a small filter flask and analyzed for its oleic acid content.

The soap solution used was an approximately $N/10$ solution of very pure sodium oleate, which had been allowed to stand for eighteen months in order to allow hydrolysis to become complete. Portions of the clear slightly yellow solution were allowed to pass through the column of graphite. The graphite was inclined to settle and pack a little, so that it required about ten days for 200 cc of the solution to pass through the tube. Each 50 cc portion as it came through was drawn off and analyzed. The first fraction came through colorless, but each succeeding fraction was colored, until the last which had the same color as the original solution.

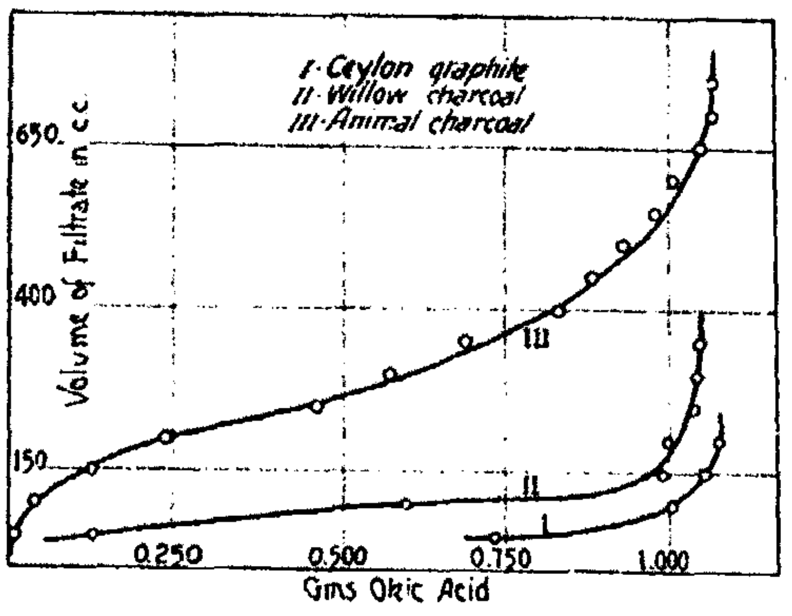

Fig. 1

The oleic acid content of the various fractions was determined by the Hanus method. While oxidation of the oleic acid had undoubtedly taken place to a certain extent in the eighteen months of standing, yet the relative values obtained are of more real importance than the absolute amount of oleic acid present. All of the determinations in Table I and in succeeding tables represent determinations made in duplicate.

TABLE I
Action of Ceylon Graphite on Soap Solution

Fraction	Gm oleic acid per 50 cc fractions	Fraction	Gm oleic acid per 50 cc fractions
Sodium oleate soln.	1.077	III	1.058
		IV	1.080
I	0.735		
II	1.007		

Experiments with Sodium Oleate Solution and Willow Charcoal.—Columns of willow charcoal were treated in the same way as the Ceylon graphite. The material was powdered and ignited at a red heat for four hours, and immediately introduced into the tubes. It was very light and showed no tendency to pack in the tubes, yet the filtration of the soap solution required nearly as long a time as with the graphite. The results obtained with willow charcoal show that this form of amorphous carbon has a greater adsorption capacity than graphite. It required only about 150 cc of soap solution to reach a point where no more measurable adsorption took place.

TABLE II
Action of Willow Charcoal on Soap Solution

Fraction	Gm oleic acid per 50 cc fractions	Fraction	Gm oleic acid per 50 cc fractions
Sodium oleate soln.	1.050	IV	0.998
I	0.123	V	1.043
II	0.595	VI	1.046
III	0.989	VII	1.050

Animal Charcoal and Soap Solution.—The animal charcoal used in the third series of experiments was found to contain considerable calcium carbonate and phosphate. It was purified by long digestion with moderately strong hydrochloric acid, after which it was thoroughly washed until free from chlorides. It was dried and heated to redness for three hours just before filling the tubes.

This particular form of carbon shows greater adsorptive powers than either Ceylon graphite or willow charcoal. The first fraction showed almost complete adsorption and a total of 750 cc of soap solution was passed through the column of animal charcoal before adsorption ceased.

TABLE III

Action of Animal Charcoal on Soap Solution

Fraction	Gm oleic acid per 50 cc fractions	Fraction	Gm oleic acid per 50 cc fractions
Sodium oleate soln.	1.068	VIII	0.778
I	0.008	IX	0.879
II	0.038	X	0.928
III	0.123	XI	0.975
IV	0.241	XII	1.009
V	0.458	XIII	1.049
VI	0.572	XIV	1.068
VII	0.687	XV	1.069

SOME EXPERIMENTS ON THE MANIFESTATION OF OSMOTIC PRESSURE WITH MEMBRANES OF CHEMICALLY INERT MATERIALS[1]

BY S. L. BIGELOW AND C. S. ROBINSON

The direct observation of osmotic pressure requires the use of a so-called semipermeable membrane, the function of which has been the cause of much discussion among investigators interested in osmotic phenomena. When two bodies of matter are separated by a layer of a third which is of such a nature that the others pass through it at unequal rates, osmotic pressure results and the intermediate layer constitutes a semipermeable membrane. Usually the material on one side of the membrane is called the "solvent" and that on the other side the "solution." Generally the latter consists of a solution of some solute in the "solvent." Under suitable conditions, with the proper apparatus, the solvent passes more readily through the membrane into the solution until finally a state of equilibrium is reached when a certain pressure is developed in the solution which pressure is called osmotic pressure. Without the semipermeable membrane the solvent and solution merely diffuse into each other until a solution of uniform concentration is produced. No difference in pressure results. Generally speaking, the membrane "allows of a pressure being exerted on a solution in contact with a solvent, without exerting a pressure on the latter."[2]

Previous Work and General Theories Involved

While such is essentially the acknowledged function of the membrane the mechanism of its action is a matter of doubt. The theories in regard to it may be divided into two classes in which the membrane has respectively a passive and an active function in the phenomena. The former includes such

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[1] The experiments described in this article were performed in the Chemical Laboratory of the Michigan Agricultural College Experiment Station and the results are published with the permission of the Director.

[2] Findlay: "Osmotic Pressure," p. 66 (1913).

theories as Traube's "atomic sieve" theory and Poynting's hydrate theory while the latter includes the various solution theories, the electrostatic theories of Perrin and of Girard, etc.

The first detailed consideration of the passive function of the membrane was given by M. Traube,[1] who was the first investigator to use precipitation membranes. He conceived membranes to be sieve-like structures, the openings being molecular interstices (as distinguished from the pores of other membranes). He prepared membranes of various materials including the precipitate of gelatine and tannic acid, ferrocyanides of copper, iron, mercury and lead. Some of his attempts failed to yield precipitates capable of acting as membranes and to explain this in the light of his theory, he formulated the rule that "any precipitate whose interstices are smaller than the molecules of its components must assume the membrane form on contact of the solutions of its components."

He also clogged the pores of some of his membranes with other materials in order to reduce the size of the interstices. Such membranes varied in permeability and exhibited certain properties which substantiated his theory.

Ostwald[2] studied the permeability of membranes for ions in the light of Traube's theory. From his work it follows that a membrane is permeable for a salt only when it is permeable for *both* ions of that salt; and if a membrane is impermeable for an ion it is impermeable for all salts containing that ion.

Tammann,[3] however, disproved the above statements and declared himself opposed to Traube's theory.

Likewise Walden[4] after an exhaustive investigation of several precipitation membranes says (p. 718) "precipitation membranes cannot act as atomic sieves."

Pickering[5] attempted to substantiate Traube's theory.

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[1] "Arch. Anat. Physiol. und Wissen. Med.," 1867, p. 87.

[2] Zeit. phys. Chem., 6, 71 (1890).

[3] Ibid., 10, 255 (1892).

[4] Ibid., 10, 699 (1892).

[5] Ber. deutsch. chem. Ges., 24, 3629 (1891).

He suggested that solute molecules possess a certain affinity by which they attract solvent molecules and hold them in a more or less unstable manner. These clusters of molecules pass through the pores of the membrane less readily than single solvent molecules.

This work was later discredited by Barlow[1] who demonstrated the defectiveness of the experimental methods upon which it was based.

The simple sieve theory has been more or less modified in the minds of later workers especially as regards the mechanism of its action. For instance Poynting[2] assumes a combination between solute and solvent molecules which decreases the mobility of the latter. His conception of osmosis is as follows: "The solvent molecules are entering the membrane from both sides, but the mobility or number set free per second from the pure solvent is greater than the number set free from the solution. The membrane goes on absorbing the solvent from each side till it becomes saturated, *i. e.*, holds so much that it returns as many molecules as it receives. It is receiving more from the pure solvent side, and therefore when saturated for that side is supersaturated for the other. Consequently more molecules are sent into the solution than are received from it, and the solution grows until the growing pressure so much increases the mobility that it is equal on both sides of the membrane."

Later Larmor[3] while believing that "each molecule of the dissolved substance forms for itself a nidus in the solvent; that is, it sensibly influences the molecules around it up to a certain minute distance, so as to form a loosely connected complex in the sense not of chemical union but of physical influences" still criticized Poynting's theory as follows: "that Prof. Poynting's recent suggestion with a view to evading the necessity of the ionic dissociation hypothesis, cannot

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[1] Phil. Mag., [6] 10, 1 (1905); Findlay and Short: Jour. Chem. Soc., 87, 819 (1905).

[2] Phil. Mag., [5] 42, 289 (1896).

[3] Nature, 55, 545 (1897).

avail, as it would not lead to the desired value for the osmotic pressure; the pressure depends on the number of molecular complexes involving the dissolved substance that exists in the dilute solution, but not on their individual degrees of complexity."

Still another variation of the sieve theory is that of Sutherland[1] who states that "if we seek to picture to ourselves how a membrane allows water molecules to pass, but not sugar molecules, our simplest conception of its structure is that of a mesh, amidst the threads of which the water molecules are packed in such a manner as to give way before one another almost as in ordinary water, while the sugar molecules are held back by the mesh. Thus the mesh forms a solid or quasi-solid framework through which water can pass with high viscous resistance, while the sugar molecule is absolutely blocked. Now if the framework turns back the sugar molecules, it must take the force of their blows and shield the water molecules from them. If then we suppose a semipermeable membrane separating water and a dilute solution of sugar in water the sugar molecules are to be regarded as replacing some water molecules, but their collisions on the water in the membrane are rendered inoperative by the shielding action of the framework so that the water molecules in the membrane receive more impacts on the side of the pure water than on the side of the solution and therefore water flows through the membrane until in the solution there is enough excess of hydrostatic pressure established to compensate for the inoperative impacts of the sugar molecules. This inequality of pressure which can be hydrostatically balanced is the osmotic pressure."

M. Traube's conception of the action of the semipermeable membrane was subjected to emphatic adverse criticism by J. Traube[2] who cites the work of Overton.[3] Overton

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[1] Phil. Mag., [5] 44, 493 (1897).

[2] Ibid., [6] 8, 704 (1904).

[3] Zeit. phys. Chem., 22, 189 (1897); Vierteljahreschr. d. Naturf. Geselsch. Zurich, 40, 1 (1895); 44, 88 (1899).

showed that permeability increased in homologous series by the substitutions of CH_3, for H, C_2H_5 for CH_3, etc. This was contrary to M. Traube's hypothesis which postulated that an increase in the size of the molecule should cause a decrease in the readiness with which a substance should pass through a membrane.

Also Barlow[1] after demonstrating the defects in Pickering's work states that "It may justly be concluded that these experiments prove that the part played by the membrane in osmotic phenomena is not a sieve-like one." He claimed that pure alcohol passed through a copper ferrocyanide membrane easier than pure water although when these two are separated by such a membrane the water flows into the alcohol.

Kahlenberg[2] also opposes the sieve theory. He says: "When we think of a large molecule like that of copper oleate rapidly travelling through vulcanized caoutchouc as in No. 35, and that under like conditions cane sugar, $AgNO_3$, and LiCl do not pass through the septum, it certainly must convince us that the membrane does not act as a sieve."

Finally in connection with this theory attention may be called to the recent work of Tinker[3] who examined, with the ultramicroscope, precipitation membranes made according to Traube. He says (p. 368): "Since the smallest pore diameter in a copper ferrocyanide membrane is about 8 millimicrons, it follows that from 100 to 200 water molecules could be placed in a chain from one side of such a pore to the other, and that several thousand could be travelling across the cross section of the pore at the same time. A selective mechanical blocking of even large hydrated crystallized molecules is hence out of the question, and this hypothesis for accounting for osmotic effects—already largely rejected—is no longer tenable."

A second series of theories ascribing a more active part to the membrane, assign to it a capillary structure. Chrono-

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[1] Loc. cit.

[2] Jour. Phys. Chem., **10**, 169 (1906).

[3] Proc. Royal Soc., **92A**, 357 (1916).

logically this was apparently the first to be advanced. From subsequent articles it seems probable that Fischer[1] must have had this conception of the organization of the membrane. Likewise Poisson[2] attempted to show that osmosis was due to capillarity rather than electric action as suggested by Dutrochet. The latter denied that capillarity could explain the phenomenon although he later[3] stated distinctly that osmotic phenomena were observed when two liquids were separated by a membrane with capillary pores.

Draper[4] states emphatically his belief in the capillary structure of osmotic membranes and gives details of his conception of the action of such a membrane.

The real development of this theory however dates from an article by Brücke.[5] He devised a cell consisting of a glass tube pressed against a glass plate and obtained osmotic effects through the crack thus formed.[6] He attributed the results to the difference in the attraction of the walls of the capillaries for the two liquids and explained in detail the mechanism of the action. Evidence tending to confirm his views was contributed later by Ludwig[7] who showed that membranes actually did take up less solution than solvent. Fick[8] discusses both of these articles at some length. He does not, however, favor the capillary theory. Some years later Baranetzky[9] investigated the relations between membranes of parchment, bladder, cellulose and collodion and the quantities of various salts taken up by them and claimed to have added experimental proof for Brücke's theory.

Pfeffer,[10] after a thorough consideration of the whole

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[1] Gilberts Ann., **72**, 298 (1826); see also Pogg. Ann., **10**, 481; **11**, 126 (1827).

[2] Pogg. Ann., **11**, 134 (1827).

[3] Ann. Chim. Phys., **49**, 412 (1832).

[4] Jour. Franklin Inst., **17**, 177; **18**, 27 (1836).

[5] Pogg. Ann., **58**, 77 (1843).

[6] See also Fischer (Loc. cit.) and Dutrochet (Ann. Chim. Phys., **35**, 393 (1827); **49**, 411 (1832)) for osmosis through cracks in glass.

[7] Pogg. Ann., **78**, 307 (1899).

[8] Ibid., **94**, 59 (1855).

[9] Pogg. Ann., **147**, 195 (1872).

[10] "Osmotische Untersuchungen," Leipzig (1877).

subject, expressed himself as favoring the capillary theory.

Moore[1] attempted to show that osmosis "may be produced by difference in surface tension acting along the exceedingly fine capillary openings of almost molecular dimensions which place the solution in connection with its solvent in the pores of the semipermeable wall which separates them." He says: "It seems reasonable to suppose that after such a process (the precipitation of a membrane) communication takes place only in the intramolecular spaces or meshes of the precipitate."

The work of Tinker[2] may again be cited in connection with the capillary theory. He measured, microscopically, the sizes of the particles composing the precipitation membranes made from the same materials that Traube used and found a distinct connection between the diameters of the membrane pores, as calculated from the sizes of the particles, and the osmotic activity of the various membranes. He says (p. 370): "The relation between the extent to which the capillaries of a membrane are controlled by the surface forces and the osmotic properties of the membrane is, however, an apparent and noteworthy one. Copper ferrocyanide and Prussian blue—the most perfect of membranes—have their pores completely under control; the tannate and silicate membranes, which are not so efficient, have a central space within their capillaries throughout which the surface forces are comparatively weak, while membranes such as gelatin and parchment, which are permeable to all crystalloids, have pores which possess central canals outside the surface force range."

The capillary theory, as Bigelow[3] has pointed out, serves as a compromise between the strictly mechanical "sieve" theory and the purely chemical "solution" theory. This last theory ascribes to the membrane a still more active part in the process of osmosis. It postulates that a membrane is permeable to such substances as are soluble in it and imper-

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[1] Phil. Mag., 38, 279 (1894).

[2] Loc. cit.; see also Pfeffer: "Osmotische Untersuchungen," p. 43.

[3] Jour. Am. Chem. Soc., 29, 1675 (1907).

meable to those which are not. This theory, now probably the most generally accepted one, was anticipated by Liebig[1] as early as 1848 when he said: "The volume changes of two miscible liquids which are separated from each other by a membrane depends upon the unequal wetting or attraction which the membrane exerts on the two liquids."

In view of Liebig's own assertion later that his conception of osmosis appeared to be identical with Graham's it is certainly permissible to interpret "Anziehung" in a broad enough way to include "attraction of solution" in which case we have an exact statement of the present-day conception of the solution theory.

While Liebig's statement must be considered as exceedingly significant in view of later developments, the first important experimental work performed with the object of substantiating such a theory was carried out some years later by L'hermite.[2] He appears to have had a very clear idea of the possible relations between osmotic phenomena and solution and capillarity. He was the first to use the "three liquid layer" means of demonstrating that one liquid, soluble in a second liquid will pass into it through a layer of a third liquid in which the first is more soluble than the second. He pointed out the significance of this experiment from the standpoint of osmotic phenomena.

At almost the same time Graham in a series of articles dealing with the diffusion of liquids under various conditions formed practically the same idea of the process of osmosis, though his statements were hardly as clear nor were his experiments as conclusive, in the light of later work, as were L'hermite's. For instance in his early work[3] he found that the most pronounced osmotic effects were obtained with acid or basic substances while neutral salts and organic compounds were inert or showed very weak effects. This appears to

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[1] "Ursachen der Säftebewegung," Braunschweig (1848); also Liebig's Ann., **121**, 78 (1862).

[2] Ann. Chim. Phys., (3) **43**, 420 (1855).

[3] Phil. Trans., **144**, 177 (abs. in Phil. Mag., (4) **8**, 151 (1854)).

have been the basis for the formation of his first theory that osmosis depended on the interaction of the membrane and the liquids bathing it. In this article he opposes the capillary explanation of osmosis since he was unable to obtain results with membranes of various materials which he knew to be porous. Later he seems to have approached more nearly the pure solution theory as he says:[1] "The separation described (sugar from gum arabic by dialysis) is somewhat analogous to that observed in a soap bubble inflated with a gaseous mixture composed of carbonic acid and hydrogen. Neither gas as such, can penetrate the water film. But the carbonic acid, being soluble in water, is condensed and dissolved by the water film, and so is enabled to pass outwards and reach the atmosphere, while hydrogen being insoluble in water, or nearly so, is retained within the vesicle." Although this statement was made in regard to the process of dialysis, it is certainly suggestive of the tendency of thought, especially in view of his explanation of osmosis with aqueous solutions and colloidal membranes which he gives on p. 222 of the same article. "It now appears to me that the water movement in osmose is an affair of hydration and dehydration in the substance of the membrane or other colloidal septum." And on p. 223, "Placed in pure water, such colloids are hydrated to a higher degree than they are in neutral saline solutions. Hence the equilibrium of hydration is different on the two sides of the membrane of an osmometer. The outer surface of the membrane being in contact with pure water tends to hydrate itself to a higher degree than the inner surface does, the latter surface being supposed to be in contact with a saline solution. When the full hydration of the outer surface extends through the thickness of the membrane and reaches the inner surface it there receives a check. The degree of hydration is lowered, and water must be given up by the inner ayer of the membrane, and it forms the osmose."

Nernst[2] describes a "three liquid layer" experiment

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[1] Phil. Trans., 151, 183 (1861).

[2] Zeit. phys. Chem., 6, 37 (1890).

similar to those first performed by L'hermite which he used to illustrate the action of an osmometer. He separated ether from a solution of ether in benzol by a parchment membrane saturated with water, the water constituting the intermediate liquid layer or "membrane."

Tammann,[1] after citing experimental evidence against Traube's sieve theory, calls attention to the work of L'hermite and Nernst and definitely compares precipitation membranes to their three liquid layers, saying (p. 263), "In exactly the same manner one can also explain the semipermeability of precipitation membranes.... Whether any substance, other than water can pass through the membrane depends only upon its solubility in the membrane (the third liquid layer)."

The same idea of the function of the membrane in narcosis was held by Overton.[2] His assumptions were later contradicted by J. Traube.[2] Likewise, Barlow,[3] working with gutta percha membranes and solutions of lithium chloride and camphor, decided "that for osmotic pressure to show itself, the membrane must be able to dissolve the solvent and have a distinct 'attraction of solution' for it."

Wilcox[4] concluded that experiments in osmosis are merely distribution experiments, thereby reiterating the views expressed some fifty years previous by Schumacher[5] who said (p. 338), "If we examine somewhat more closely the processes of endosmosis we can easily persuade ourselves that they are nothing more than distribution phenomena (Mischungserscheinungen)." Also in his statement on p. 339, that in order to be miscible the substances must possess a certain degree of chemical attraction, Schumacher anticipates a somewhat modified form of the solution theory which has recently been proposed by Kahlenberg[2] who has described many experiments in support of his ideas. Kahlenberg assumes not

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[1] Zeit. phys. Chem., 10, 255 (1892).
[2] Loc. cit.
[3] Phil. Mag., (6) 11, 595 (1906).
[4] Jour. Phys. Chem., 14, 576 (1910).
[5] Pogg. Ann., 110, 337 (1860).

merely a solution of the liquids in the membrane but a loose chemical combination. He says, "In this paper it has been shown that whether osmosis will take place in a given case or not depends upon the specific nature of the septum and the liquids that bathe it; and if osmosis does occur, these factors also determine the direction of the main current and the magnitude of the pressure developed. The motive force in osmotic processes lies in the specific attractions or affinities between the liquids used, and also those between the latter and the septum employed. These attractions or affinities have also at times been termed the potential energy of solution, etc. They are to the mind of the writer essentially the same as what is commonly termed chemical affinity."

In this connection Nelson[1] says: "This view (*i. e.*, 'The Chemical or Selective Theory') of the nature of osmosis carries with it the assumption of a labile compound formed between the membrane and the solvent on the one hand and between the solvent and the solute on the other, and ascribes the movement of liquid into the osmotic cell by assuming that the solute robs the membrane of its imbibed solvent, the membrane in turn imbibing more solvent which is again extracted by the solute, this process being repeated until equilibrium is established.... It is only by assuming a chemical attraction and loose chemical combination that these results become at all intelligible. The mechanism of the formation of such a labile chemical compound between the membrane and the solvent on the one hand, and the solvent and the solute on the other, cannot be conceived of simply as a 'solution' of solvent and solute in the membrane when that word merely implies an orderly filling of the membranous interstices or intermolecular spaces by solvent or solute by virtue of capillary attraction."

While Kahlenberg was guided in his work by L'hermite's experiments, most of his investigations were conducted with rubber membranes and organic solvents.

His methods and some of his conclusions were subjected

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[1] Jour. Am. Chem. Soc., 35, 658 (1913).

to severe criticism by Cohen and Commelin[1] who however were interested in his data more from the standpoint of its relation to van't Hoff's theories of osmosis than from his ideas of the action of the membrane.

Although the preceding brief review of the theories concerning the functions of the membrane in osmotic pressure phenomena is not complete, some details and minor variations having been omitted, it nevertheless gives concise statements of these theories and affords an idea of the main lines along which they have developed. A careful study of the subject leads one to agree with Fitzgerald that "the theory of semipermeable diaphragms is in a very doubtful state." In recent years serious consideration of the purely mechanical sieve theory seems to have been eliminated and the field left to the various explanations based upon solutions or chemical attraction and capillarity. A more detailed, critical discussion of these two will be taken up later. Suffice it to say here that while most of the results obtained by Kahlenberg were perhaps predicable, *a priori*, the assertion that they might serve as a basis for a general theory of the function of all semipermeable membranes appeared doubtful. The exact nature of the "labile compound" between the solvent and the membrane seemed to be anything but definite, and the assumption that a chemical combination between membrane and solvent was always a requisite for osmosis seemed hardly to be justified by the data presented.

In order to test this assumption, the experiments described in this paper were carried out, the intention being to obtain osmotic effects under such conditions as to preclude the possibility of chemical reaction between the membrane and the solvent. While it may be unsafe, in view of the various new types of compounds which modern chemistry has either discovered or invented to harmonize with its theories, to claim that no chemical action can take place between water and gold or carbon under ordinary circumstances, it must still be considered as a rather remote possibility.

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[1] Zeit. phys. Chem., 64, 1 (1908).

Materials

The materials used in the preparation of the membranes were selected with the object of securing substances which would be as inert as possible toward the liquids with which the membrane would come in contact, since, as has already been stated, the object of the work was to obtain osmotic effects under conditions which should preclude as far as possible any chemical reaction between the membrane and cell contents. For the same reason it was necessary that the materials should be exceptionally pure. Consequently all substances used in preparing membranes were carefully purified before use.

The following materials were chosen from which to make membranes: silica, carbon (graphite and amorphous), metallic copper, metallic silver and metallic gold. They were all in a state of fine powders with the exception of one sample of graphite and the gold, which were in the form of small flakes or plates. For use they were pressed into discs in the cells, these discs constituting the membranes.

Apparatus

Owing to the peculiar physical nature of the materials, *i. e.*, the fact that they were in the form of powders, special apparatus and technique had to be developed for the construction of the membranes. The type of cell finally adopted was patterned after that used by Bigelow and Bartell[1] in working with unglazed porcelain. It consisted of the following parts: (Fig. 1.) A base (A) for holding the membrane; a plate (B) covering the open side of the base to hold the membrane in place; a second plate (C) for holding the glass parts of the cell against the base; an attachment (D) for use in connecting the cell to the pressure tank and gauge for measuring pore diameters and saturating the membranes, threaded rods G, G, G, and nuts for holding the various parts together. The base and plate (B) were made of manganese bronze and all other metal parts of yellow brass. A cell

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[1] Jour. Am. Chem. Soc., 31, 1194 (1909).

similar in construction but about five-sixths as large, and made entirely of brass with the parts held together by screws was first used. This cell was not strong enough to stand either the pressures used in forming the membranes or to hold the parts together with firmness enough to prevent leakage. Also the screws were less satisfactory than the threaded rods and nuts. Two plungers (E and F) exactly fitting the cavities in the base were used in forming the membrane (see p. 115). For measuring pore diameters the cells were connected with a pressure tank and gauge through capillary brass tubing fitted with brass unions. The three pieces of apparatus, cell, gauge and gas tank were connected through a specially constructed brass T. The gauge was an accurate one graduated to 30 kilograms per cm^2 and reading directly to 0.25 kilogram per cm^2. The tank was a small oxygen tank with a valve capable of delicate adjustment. It was charged with pure nitrogen from a large tank holding fifty cubic feet.

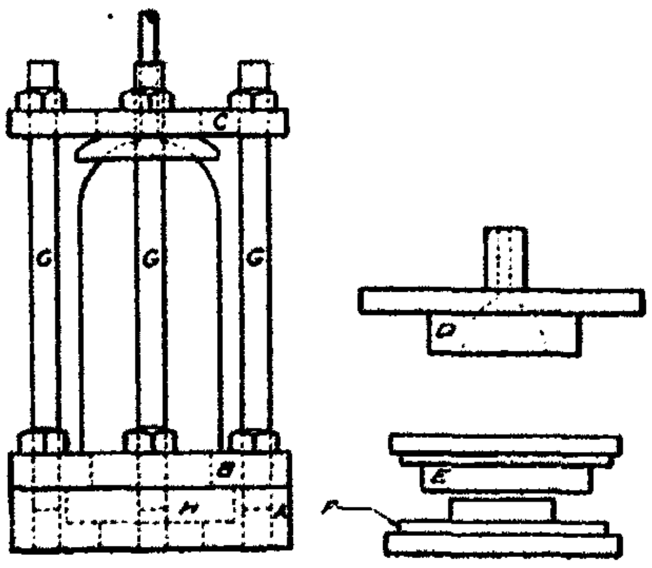

Fig. 1

These cells were used for membranes of all materials with the exception of metallic gold. Owing to the expense of preparing such a large membrane of this material, an attachment was designed which fitted the cavity in the base of the large cell and in effect reduced the size of this cavity. This attachment was made of brass, gold-plated. Suitable plungers, also gold-plated, were made to form the membrane in this modified base.

Much time was lost in attempting to make the gold membrane in a glass tube. Tubing of various sizes was tried, including that used in making high pressure gauges. This had a diameter of 30 mm with a bore of 12 mm. None withstood the pressure required to make the membrane of sufficient density to show osmotic effects.

In the early part of the work a good grade of rubber packing was used for the washers required to make the cells tight. It was noticed on taking apart cells which had stood for some time that this packing had swelled. This was objectionable since it would have a tendency to produce apparent osmotic effects by causing an increase in the volume of the cell contents. Also it was found that, on long contact under pressure, it caused a corrosion of the bronze parts of the cells and a discoloration of the surfaces of the metallic membranes. Since any such chemical action might produce soluble impurities which would give the very condition least desired, these washers were later replaced with filter paper saturated with paraffine. In the final form of cell the glass parts were ground to the metal and washers were entirely eliminated at these points.

In the early part of the work, the glass part of the cell consisted of a tube 40 mm in diameter and about 50 mm long held between the plates B and C, and filled with the solution under investigation. The opening in plate C was closed with a one-holed rubber stopper holding the manometer tube and the whole cell was set in a beaker of distilled water. In this way one side of the membrane was bathed with the solution and one side with distilled water. Although this arrangement was used throughout in saturating the membranes, measuring pore diameters, etc., it was found necessary later to change it in setting up the cells for observation in order to have equal volumes of liquid on each side of the membrane. Also continual trouble was experienced with the rubber stoppers leaking or changing their shape. To obviate these difficulties, the cell was set up as shown in Fig. 2. In

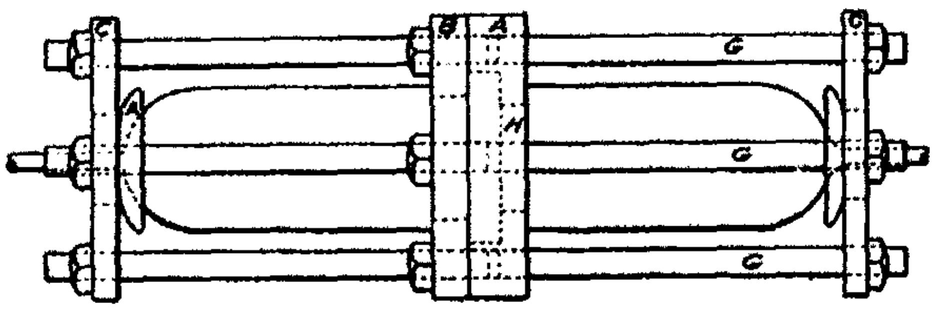

Fig. 2

this form the manometer tube was sealed to the large tube holding the liquid. The glass parts were held against the base as before by the plate C and protected from breakage through contact with it by means of the washers of rubber packing, KK. Instead of setting the cell in a beaker of water, the water was held in exactly the same sort of arrangement as was the solution, but against the opposite side of the cell base. The manometer tubes were bent at right angles to the long axis of the cell which was given a horizontal instead of a vertical position. The effect was that of a U-tube with the membrane at the bottom.[1] As the level of the liquid rose in one arm, it fell in the other. In addition to the advantages already cited this cell made it possible to detect any change in volume of the apparatus or its contents due to leakage, change in volume of the membrane, change in volume of the solution on dilution, formation of gas, etc. It has proven entirely satisfactory in every respect.

Preparation of Membranes[2]

Several methods of preparing the membranes were tried. The first one was by means of the centrifuge.[3] A high powered machine, capable of developing a speed of over 3000 r. p. m. and having a radius of 30 cm was used. A circular perforated plate of copper (H) was placed in the cell base covering the lower opening. This plate rested on a washer to prevent leakage between the membrane and cell. It was covered with a disc of ordinary filter paper[4] to prevent the material passing

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[1] U-shaped cells have been used by Vierordt: Pogg. Ann., 73, 519 (1848); Raoult: Zeit. phys. Chem., 17, 737 (1895); Comptes rendus, 121, 187 (1895); Lord Berkeley and Hartley: Proc. Roy. Soc., 73, 436 (1904); Barlow: Phil. Mag., (6) 11, 596 (1906); Bartell and Hocker: Jour. Amer. Chem. Soc., 38, 1043 (1916).

[2] As this work was nearing completion, an article by W. Spring (Zeit. phys. Chem., 2, 532 (1888)) was found which discussed the compression of powdered materials. The author's experiences with metallic substances, silica, kaolin, clay, etc., agree in general with those of Spring.

[3] See Lynde: Jour. Phys. Chem., 16, 763 (1912).

[4] Hardened parchment paper cannot be used as it alone will give osmotic effects.

through the perforations in the plates. The base was then placed in the centrifuge cup, a suspension of the material poured in and the cup whirled. This method was used only with silica, before a press was tried, and proved wholly unsatisfactory.

Next, the cell base, fitted with perforated plate and filter paper as above was used as a suction filter and the cavity filled with material before centrifuging. This procedure alone, however, was no more successful than the former.

The first successful membranes were made by filling the base with material by sucking a suspension into it, then clogging the pores by the addition of a suspension of very fine material of the same kind which did not settle for some time. The plungers E and F were placed in position and the membrane compressed by means of a mechanical press. The first press used was an ordinary letter press. Since there was no way of measuring the pressures used and inasmuch as only comparatively low pressures could be obtained, the chance to use a hydraulic press of the Buechner type was welcomed and this was used in all subsequent work.

A third method of procedure which gave very satisfactory results with some materials was to fill the cavity with the dry powder. The first portion was pressed at a pressure considerably lower than that to be finally used. The pressure was released at once, the cell removed and a second portion of material added. This was pressed at a somewhat higher pressure and the process continued till the desired thickness had been obtained. In some cases in order to avoid the subsequent separation of the layers with the consequent formation of air spaces, it was necessary to moisten each one before the addition of a fresh portion of the powder. In this way less material was squeezed out around the plunger. Also with some materials it was more convenient to work with the dry powder than to try to get a suspension.

In all cases after the formation of the membrane it was covered with a piece of filter paper, perforated plate and washers and held in place by the plate B. The perforated plate was necessary to prevent the rupturing of the membrane during saturation, measurement of pore diameters and washing.

The glass tube used to hold the water for saturating the membrane was next placed in position. In the first experiments this was just small enough in diameter to fit into the opening in the plate B and rested against a washer on the metal plate supporting the membrane. Owing to the fact that in some cases the membrane was slowly distorted by the pressure required to make the contact water-tight, a tube with a larger diameter was afterwards substituted. This rested against the plate B and thus removed all possibility of disturbing the membrane. The tubes used in this part of the work were approximately 50 mm long and 40 mm in diameter. They were held between the plates B and C by means of the nuts on the threaded rods, leakage being prevented by washers of rubber packing.

The next step was the saturation of the membrane. When it was sufficiently porous this was done by suction as the air could be more completely displaced by this means than by forcing it out with pressure. A high vacuum pump directly connected to the cell, or a gas tank evacuated by means of the pump, was used to draw the water into the membrane. Brass T tubes, attached to the cells through one-holed rubber stoppers inserted in the opening in the plate C and connected with each other and the pump by means of heavy-walled suction tubing made it possible to saturate several membranes at once. The distilled water used in saturation was held in heavy glass jars in which the cells were placed. Frequently it was necessary to use membranes so dense that suction failed to draw water through them. The cells containing these were filled with water and attached to the pressure tank and gauge used for the measurement of pore diameters and the water forced through the membranes at as low a pressure as possible. This pressure ordinarily was between four and eight kilograms per cm^2, though in a few cases it was higher. From one to two hundred cc of water were forced through each membrane before it was considered to be saturated.

Measurement of Pore Diameters

When the membrane was saturated the diameters of the largest pores were measured according to the method used by Bigelow and Bartell.[1] This consisted in connecting the cell supported with the bottom up, to the pressure tank and gauge, covering the surface of the membrane with water and gradually increasing the pressure, noting that at which bubbles appeared through the openings in the plate. This pressure represents that required to displace the water in the pores by air. From it, by means of Jurin's law, the pore diameters can be calculated. This law may be formulated as follows: $a^2 = hr$ where a^2 is a constant (14.823 for water at 20°), h the height to which water would rise on account of capillarity and r the radius of the pore. The appropriateness of the method has been discussed by Bigelow and Bartell.

The results given in the following experiments represent the diameters of the largest pores only. In following the procedure outlined above the pressure was gradually increased until bubbles were issuing from about one-third of the total number of openings in the plate covering the membranes.

After measuring the diameters of the pores, the membranes were again saturated. In the early part of the work the cells were at once filled with solution and set up. Certain anomalous results were obtained however which seemed to indicate that the process of saturation left the membrane in a state of strain. Its readjustment caused changes in the volume of the cell which obscured the results due to osmosis. In subsequent work the membranes were allowed to stand several days before setting up and then were tested with water on both sides before filling the cell with solution.

Preliminary Experiments

Before going to the trouble of carrying out all the precautionary measures which it was realized from the first

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[1] Loc. cit.

would have to be employed before final measurements could be made, it seemed desirable to determine whether or not any positive results at all could be obtained with the type of membrane and the materials which had been selected. With this in mind the preliminary experiments described in the following pages were conducted.

Silica.—Several samples of silica from various sources were investigated. The first positive effects were obtained with a sample prepared from sodium silicate by precipitation with HCl, washing free from Cl′ and ignition. It contained 97.85 percent SiO_2. With $M/1$ sugar solution it gave a corrected[1] reading of 28 mm at the end of 114 hours.

No measurements of the pore diameters were made on this membrane as it was prepared before the necessary apparatus had been obtained.

Carbon.[2]—The four samples of carbon which were used had the following characteristics:

No. 1 was a commercial graphitic powder 59.39 percent of which was lost on ignition.

No. 2 was a graphitic lubricant sold under the trade name of "Aquadag." When ignited 99.06 percent was volatilized.

No. 3 was a sample of carbon prepared by igniting cane sugar. It was completely volatilized on ignition but an analysis made by the Dennstedt combustion method showed it to contain 96.05 percent C and 1.00 percent H. Probably

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[1] The observed readings with the vertical type of cell had to be corrected for two factors, *i. e.*, the capillary ascension of the liquid in the measuring tube and the greater density of the sugar solution as compared with water. For the tubing used in these experiments the algebraic sum of these two corrections, the former of which would tend to increase the true reading and the latter to lower it was calculated to be 6 to 8 mm. for $M/1$ sugar solution.

With the U-shaped cell, the capillarity factor in the correction disappears because the levels of both water and solution are measured in tubes of equal diameters. The correction for the difference in densities of the sugar solutions and water for the lengths of the columns of liquid representing the initial readings in all experiments with these cells were as follows: $M/2$ solution 9 mm, $M/1$ solution 17 mm, and 2 M solution 31 mm.

[2] Graham (Phil. Trans., 1854, p. 177) attempted without success to obtain osmotic effects with a membrane of compressed charcoal.

the impurities consisted of adsorbed gases or vapors as will be shown later.

No. 4 was a sample of commercial graphite which was in the form of small flakes. It gave a loss on ignition of 90.64 percent.

The following are the final corrected readings obtained with membranes of these materials and $M/1$ sugar solution:

TABLE I

1	25 mm	3	86 mm
2	58 mm	4	35 mm

The last membrane was also tested with $2\,M$ sugar solution and gave a corrected reading of 110 mm.

The membrane prepared from sugar carbon was the first one on which pore diameter measurements were made. The first measurements showed an average pore diameter of 2.361 microns for the largest pores. No osmotic effects could be obtained. The cell was taken apart, the membrane pressed and again measured. The diameters of the largest pores then approximated 1.976 micrcns. The sugar solutions remained at the level of the water in the beaker indicating one of two things, either the membrane was too dense to allow the solution to flow through and assume the lower level which it should on account of its greater density, or a small osmotic pressure was produced. The next compression of the membrane reduced the pore diameters to 1.482 microns at which the above effects were noted.

Metallic Copper.—The material of which the first membranes were constructed was that used in making striping bronzes. It was an exceedingly fine powder and was supposed to be pure copper. The preliminary work was carried out on this assumption without making an analysis. Later an analysis showed it to contain only 95.76 percent Cu. This result is probably explainable by the fact that most commercial metallic powders are coated with stearin. For the later work this was almost completely removed by extraction with petroleum ether.

A membrane was prepared from this material and pressed till the pore diameters approximated 1.602 microns. It gave a final corrected reading of 20 mm with $M/1$ and 35 mm with 2 M sugar solution.

Metallic Silver.—The material used for this membrane was so-called "molecular silver" prepared according to Gomberg and Cone[1] from pure silver chloride.

The silver chloride was purified by repeated solution in ammonia and precipitation with HCl. After washing thoroughly with hot water it was placed in a glass crystallizing dish in which was also set a porous cup holding some pieces of granulated zinc. This cup was supported above the silver chloride by means of a glass triangle. A piece of platinum foil to which was attached a platinum wire was slipped under the silver chloride, and the free end of the wire was fastened to a piece of the zinc in the porous vessel. Distilled water was then added to both dishes, the level in the outer one being maintained somewhat above that of the inner one to lessen the outward diffusion of the zinc chloride. A few drops of HCl were also added to hasten the reaction. When the reaction appeared to be complete, the silver was removed, washed with ammonia to remove any unreduced silver chloride and then with hot water.

That used for the first membrane was not analyzed but from the method of preparation it undoubtedly was very pure. It was pressed into the cell base at a pressure of 250 kg per cm^2. Measurements showed the largest pores to be approximately 0.659 micron in diameter. When set up with $M/1$ sugar solution it gave a maximum corrected reading of 12 mm. Further pressing at 300 kg per cm^2 for three hours reduced the pore diameters to about 0.296 micron, after which a reading of 28 mm with $M/1$ sugar solution was obtained.

Metallic Gold.—The material was obtained in the form of nuggets from a manufacturer of dental supplies and was supposed to be pure. It was dissolved in aqua regia. A small residue was left which proved to be silver chloride. The

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[1] Ber. deutsch. chem. Ges., 39, 3286 (1906).

liquid was decanted off and the precipitate transferred to a filter and washed, the washings being added to the original mother liquor. The resulting solution was concentrated and the precipitate, if any was formed, was removed as before. This process was repeated till no more material came down. The nitric acid was removed and the metallic gold precipitated by means of pure oxalic acid in the presence of ammonium oxalate. It was not analyzed but from the method of preparation was assumed to be pure.

The membrane was formed between perforated plates of gold in the modified cell described above. The gold, including the plates, weighed 21.08 g and was 6 mm thick. In the formation it was pressed at 40 kg per cm^2 but the pores were too large to measure. No positive results were noticeable.

The membrane was alternately pressed and set up with *M*/1 sugar solution until the pore diameters had been reduced to 2.361 microns when a maximum reading of 11 mm was obtained. Further pressing at 100 kg per cm^2 for ten minutes reduced the pore diameters to 1.695 microns, at which point a reading of 197 mm was recorded. The level of the solution was apparently still rising but it became necessary to take the cell apart and the maximum value was not obtained. This membrane was later subjected to further pressure which caused a corresponding reduction in the measurable pore diameters. The final readings taken are given in the following table:

TABLE II

Pore diameters	*M*/2 sugar solution	*M*/1 sugar solution	2 *M* sugar solution
0.847 micron	13 mm	32 mm	68 mm
0.741 micron	14 mm	17 mm	103 mm

The above results are considered to be accurate and, except where noted, free from the influence of certain sources of error discovered during the performance of this preliminary work. They manifestly justified the labor of repeating the work, taking all the precautions necessary to insure thoroughly reliable results. Since the manipulation and method of procedure developed are for the most part new in their application to the study of osmotic phenomena, a more detailed discussion of the difficulties involved and of possible sources of error may not be out of place. Some of them are involved in the study of all membranes and all must be considered in dealing with membranes prepared from powdered or finely divided solid particles. For a more thorough consideration of the effects of some factors, especially temperature, upon osmotic processes, the reader is referred to the work of Morse and his co-workers, published in Publication No. 198 of the Carnegie Institution of Washington.

Factors Affecting Accuracy of Results

The following sources of error were observed in the preliminary work and guarded against as thoroughly as possible in the following experiments:

1. Changes in temperature.
2. Changes in volume of cell parts.
3. Changes in volume of cell contents.
4. Chemical reaction between materials used.

Changes in temperature: Temperature changes may produce errors in three ways, *i. e.*, by causing changes in the volumes of the solutions or of the parts of the cell or by causing a change in the rate of osmosis. Of these, the first is the only one of importance in these experiments because the range of temperature change was restricted to that of the room which would not produce a perceptible effect from the change in volume of parts of the cell, and the rate of osmosis was secondary though interesting. To remove error due to the first, the experiments were conducted in a thermostat, the temperature of which was held constant at 24.6 ± 0.1°. This was, however, only large enough to hold the cells, themselves. The measuring tubes projected above the water in the thermostat and consequently were exposed to changes in the room temperature. For the size of tube used and the usual height of column of liquid exposed, this factor, from careful observation, was found to produce an error of only about 3 mm under extreme conditions. This is too small to influence the final values of any of the experiments though it might be responsible for incongruities in two consecutive readings.

Change in volume of cell parts: Errors may arise from this cause on account of change in volume of the membrane; change in shape of the membrane causing corresponding changes in the volumes of the parts of the cell holding the liquids; and changes in the volumes of rubber stopper or washers.

Changes in volume and shape of the membrane may result from pressure applied in its formation, saturation and measurement. These effects in some cases were rather significant and to avoid any error arising from them, all membranes were allowed to stand at least 24 hours before setting up. They were also tested by filling both parts of the cells with water and allowing to stand until the levels in the measuring tubes remained constant.

No measurements were made of the changes due to disintegration of the rubber stoppers and washers used in the earlier part of the work, but from the appearance of some of them the effects might have been considerable. As has been previously stated, rubber parts were eliminated entirely in the later work so that this source of error does not concern the following results:

Changes in volume of cell contents: Errors may be introduced on account of evaporation, drainage from measuring tubes after filling the cells, changes in temperature, hygroscopicity of solutions and increase or decrease in volume of solutions with dilution. Experiments made to measure the magnitude of such errors showed them to be very small.

No loss due to evaporation could ever be detected except in one or two experiments conducted incidentally, in which the liquids nearly filled the tubes. This condition did not exist in any of the experiments included in this report.

The method of filling the cells necessitated the filling of the measuring tubes with liquid above the zero level of the experiment. This excess liquid was removed by means of a capillary tube when the levels in the two measuring tubes were equalized. When this was done rapidly the subsequent drainage caused the levels to rise a few mm just as the reading of a burette or pipette changes if either is emptied too rapidly. This error was eliminated by drying the inner surfaces of the tubes with absorbent cotton attached to a fine wire or by readjusting the levels after drainage had ceased.

The effect of hygroscopicity and increase in volume of solution on dilution were imperceptible in the results reported in this paper but were of sufficient magnitude to attract attention in certain experiments conducted incidentally. The effect of either becomes evident as an inequality in the changes of levels in the two measuring tubes. In either case the level of the solution rises faster than the level of the water sinks—providing of course that the diameters of the measuring tubes are equal.

Chemical reactions between materials used: Errors from this cause fall into two classes, those which may produce apparent changes in volume of the liquid contents of the cells and those which may give rise to negative osmotic effects as described later.

Two important ones of the first class were met with: first, fermentation with the liberation of carbon dioxide and, second, the production of hydrogen through the interaction of water and finely divided metals used in making membranes. When either of these occurred the gas production caused unequal changes in the liquid levels making it appear that the volume of the liquid was changing. Both are easily detected by the formation of bubbles. Fermentation did not occur in any experiments included in this article. The formation of hydrogen was observed when membranes were made of finely divided zinc and iron. Since it was obvious that no results which would be of value could be obtained under such circumstances, attempts to obtain osmosis with membranes of these metals were abandoned.

In spite of all the precautions taken to avoid reactions between the various cell parts, the greatest difficulty encountered during the whole work arose from this cause.

Among the materials used in the construction of membranes was kaolin, with which attempts were made to duplicate the work of Bartell[1] on negative osmose. The solution used was $M/10$ $MgCl_2$ and very pronounced negative effects were observed.

Later in trying to obtain data on the extent of deformation of the membranes under various pressure treatment, kaolin membranes were set up with water both inside of the cell and in the beaker, *i. e.*, on both sides of the membrane. In all cases there was a flow of liquid from the cell to the beaker. The obvious explanation in this case was that the membrane was somewhat soluble in pure water and since the volume of water in the cell was smaller than that in the beaker, a more concentrated solution was formed which gave a condition analogous to that in which the cell was filled with the $MgCl_2$ solution.

At this time similar experiments were being tried with copper membranes. Strange to say, similar results were obtained. The abnormal readings were small and at first were disregarded, being attributed to various things such as temperature changes, leakage, evaporation and other causes which were later demonstrated to be insignificant. However, several readings were obtained which were of such magnitude that it became evident that some undetermined force was at work. Every precaution conceivable was taken to obviate the errors which have been discussed but still the negative results were obtained. The conclusion was finally forced upon us that even with the copper membrane, negative osmose was possible, and that the difference in the volumes of water on the opposite sides of these membranes was causing it to operate through the production of solutions of different concentra-

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[1] Jour. Am. Chem. Soc., 36, 646 (1914).

TABLE III

Date	Time	T	No. 3 Cu	No. 4 Cu	No. 10 Cu	No. 13 Cu	No 20 Cu	No. 2 Kaolin	No 5 Kaolin	No. 14 Kaolin
3/25	5 P.M.	22° C	0	0	0	0	0	—	—	—
3/26	4 P.M.	21	—8	+10	—7	—4	—7	—	—	—
3/27	10 A.M.	21	—8	—13	—10	—2	—7	—	—	—
3/29	9 A.M.	21	—8	—20	—15	—4	—5	—	—	—
3/30	1 P.M.	23	—11	—23	—20	—3	—5	—	—	—
3/30	3 P.M.	24	0	0	0	0	0	0	0	0
3/31	9 A.M.	20	—5	—9	—5*	—5	—5	0	—30+*	—13
3/31	3 P.M.	22	—4	—7	0	—3	—1	+2	—11	—13
4/1	9 A.M.	21	—7	—12	—3	—6	—3	0	—30+	—19
4/2	9 A.M.	20	—11	—17	—7	—7	—5	0	—30+*	—24*
4/3	9 A.M.	19	—12	—19	—10	—7*	—4*	—1	—29*	—11
4/4	9 A.M.	20	—14	—24*	—12	—3	—3	0	—24*	—18
4/5	9 A.M.	22	—14	—4	—15	—4	—1	—4	—23*	—22
4/6	9 A.M.	23	—15	—7	—17	—5	—1	—3	—23*	—27
4/7	9 A.M.	19	—20	—16	—24	—9	—4	—11	—27*	—13
4/8	9 A.M.	22	—16	—16	—25*	—	—	—10	—20*	—18
4/9	9 A.M.	22	—20	—20	—4	—	—	—10	—24*	—26
4/10	9 A.M.	22	—20	—24	—9	—	—	—15	—23*	—10
4/12	11 A.M.	18	—24*	—30+*	—30*	—	—	—23*	—30+*	—28*
4/13	9 A.M.	19	—3	—1	—5	—	—	—2	—16	—8
4/14	9 A.M.	21	—6	—5	—8	—	—	—4	—30+*	—15*
4/15	9 A.M.	21	—10	—10	—10	—	—	—7	—24	—23
4/16	11 A.M.	20	—13	—15	—15	—	—	—9	—30+*	—28*
4/17	9 A.M.	20	—16	—16	—20	—	—	—12	—18	—8
4/19	9 A.M.	20	—18	—23	—27	—	—	—13	—30+	—23

* Set at 0 after this reading.

tions. To test this, two membranes which showed negative values were measured by Professor Bartell to determine the difference in electrical potential between opposite faces of the membranes. These measurements gave values of 0.1899 and 0.1605 volt, with the orientation that would be expected, *i. e.*, the "solution" side or inside of the membrane positive.

The above table shows some of the values obtained with eight different membranes, five of copper and three of kaolin. They are not at all quantitative since the minimum reading obtainable with the apparatus used was about —30 mm. When this point was reached it was necessary to raise the level to 0 by the addition of water. The experiments were carried out at room temperatures which are given in Column T. The readings are in mm and are uncorrected.

It will be observed that the results with the copper membranes were, as a rule, much smaller than those with kaolin and that in some cases a minimum was apparently reached. There are indications of a relation between the magnitudes of these results and the pore diameters as is shown by the following table, the values for which are taken from Table III:

TABLE IV

Cell No.	4	10	3	20	13
Pore diameters in microns	0.847	0.988	1.186	1.299	1.482
Observed reading 3/30 1 P.M.	—23	—20	—11	—5	—3
4/3 9 A.M.	—19	—10[1]	—12	—4	—7

The above described conditions were responsible for the development, at the suggestion of Professor Bartell, of the U type of cell used in all subsequent work. With this the volumes of liquid on both sides of the membrane were approximately equal and any solution of the membrane took place to the same extent on both sides.

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[1] Cor. reading = — 15 as it was set back to 0 after 25 hours.

ALCOHOL AND SODA-LIME

BY BURT H. CARROLL

Introduction

In 1840, Dumas and Stas[1] showed that sodium acetate and hydrogen are formed when alcohol and potash-lime are heated, the apparent reaction being $CH_3CH_2OH + KOH = CH_3CO_2K + 2H_2$. In four runs the following percentages of hydrogen and hydrocarbons were found in the gases given off:

Hydrogen	94.1	93.3	89.2	86.3
Hydrocarbons	4.4	4.4	7.2	6.3

If the experiment is not stopped when the alcohol is converted completely into acetic acid, the acetate will, of course, decompose to methane and potassium carbonate. No book on organic chemistry explains why hydrogen should be evolved under these circumstances; but the superficial analogy with Sabatier's work on the contact catalysis of alcohol is so striking that it was suggested by Professor Bancroft that I study this reaction in some detail as part of my senior research work. It seemed possible that soda-lime might cause the catalytic decomposition of alcohol into aldehyde and hydrogen, after which the aldehyde would react with the soda-lime, the reaction taking place in at least two stages, according to the reactions

$$CH_3CH_2OH + NaOH = CH_3CHO + NaOH + H_2$$
$$CH_3CHO + NaOH = CH_3CO_2Na + H_2.$$

Sabatier had already shown that some decomposition of alcohol into aldehyde and hydrogen is caused by lime, though this substance is a poor catalytic agent.

The plan of attack was to study the reaction at varying temperatures as a reaction between alcohol vapor and soda-lime. After this a test was to be made to see what parts were

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[1] Liebig's Ann., 35, 129 (1840).

played by the caustic soda and the lime, respectively. Finally, aldehyde vapor was to be passed over the heated soda-lime to see whether it reacted according to the hypothetical equation as written. In case lime alone split alcohol into aldehyde and hydrogen and if pure NaOH did not bring about this reaction, it could be assumed that the whole reaction depended on the catalytic action of the lime. If any aldehyde were found in the products of the alcohol reaction and if aldehyde reacted with soda-lime as hoped, this would be fairly conclusive that the reaction passed through the aldehyde stage. On the other hand a negative result with aldehyde and soda-lime would not necessarily justify the conclusion that aldehyde was not an intermediate step. It is possible that aldehyde vapor might react more readily as it was forming from alcohol than at other times. Fortunately, this particular hypothesis proved not to be needed.

Apparatus

The apparatus, shown in the following diagrams, Fig. 1–2, was largely designed by Mr. Engelder in a previous investigation. It was altered somewhat during the course of the term, and a large amount of time spent in its construction, in developing the manipulation, and in adapting it to the varied conditions. The modifications of apparatus and procedure necessary with the use of alcohol and aldehyde, and of the three solids, will be given in more detail under the account of the experimental work.

The liquid used was contained in the vertical tube at the left of the diagram, Fig. 1. When using aldehyde, after the first experiment, this was kept in ice. To the vertical tube, which was 14 × 1.5 cm, was sealed a capillary tube leading through a glass stopcock, to the vaporizer.

The vaporizer A was a box of asbestos board, 20 × 8 × 12 cm, through which the tube from liquid container to furnace, passed. It was heated by an 80-watt electric bulb, which, in the closed box, gave a temperature of over 150°. This temperature was more than sufficient for complete vaporization of the liquid slowly through to the furnace, the highest rate of feed for alcohol being nine grams per hour, and ten for aldehyde; the use of the light avoided an open flame. To aid in rapid vaporization, a length of ordinary glass tubing about 10 cm long was sealed in between the capillary tube used elsewhere on the liquid side of the furnace.

The tube furnace, Fig. 2, used was also heated by electricity, nichrome wire of a total resistance of 14.3 ohms being wound upon an alundum tube 40 cm long and 2.6 cm inside bore, and held in place by alundum cement. This was then put into a section of ordinary drain tile about 3″ in diameter, and loosely packed with asbestos cement as a heat insulator. The temperature was controlled by a lamp bank, by which the temperatures of 250° to 450° were easily obtained. The higher temperatures were measured by a Hoskins pyrometer and thermoelement, which checked with a good mercury thermometer up to 350°. Inside the alundum tube was placed a porcelain tube, closely fitting it; this is the tube in which the reaction took place.

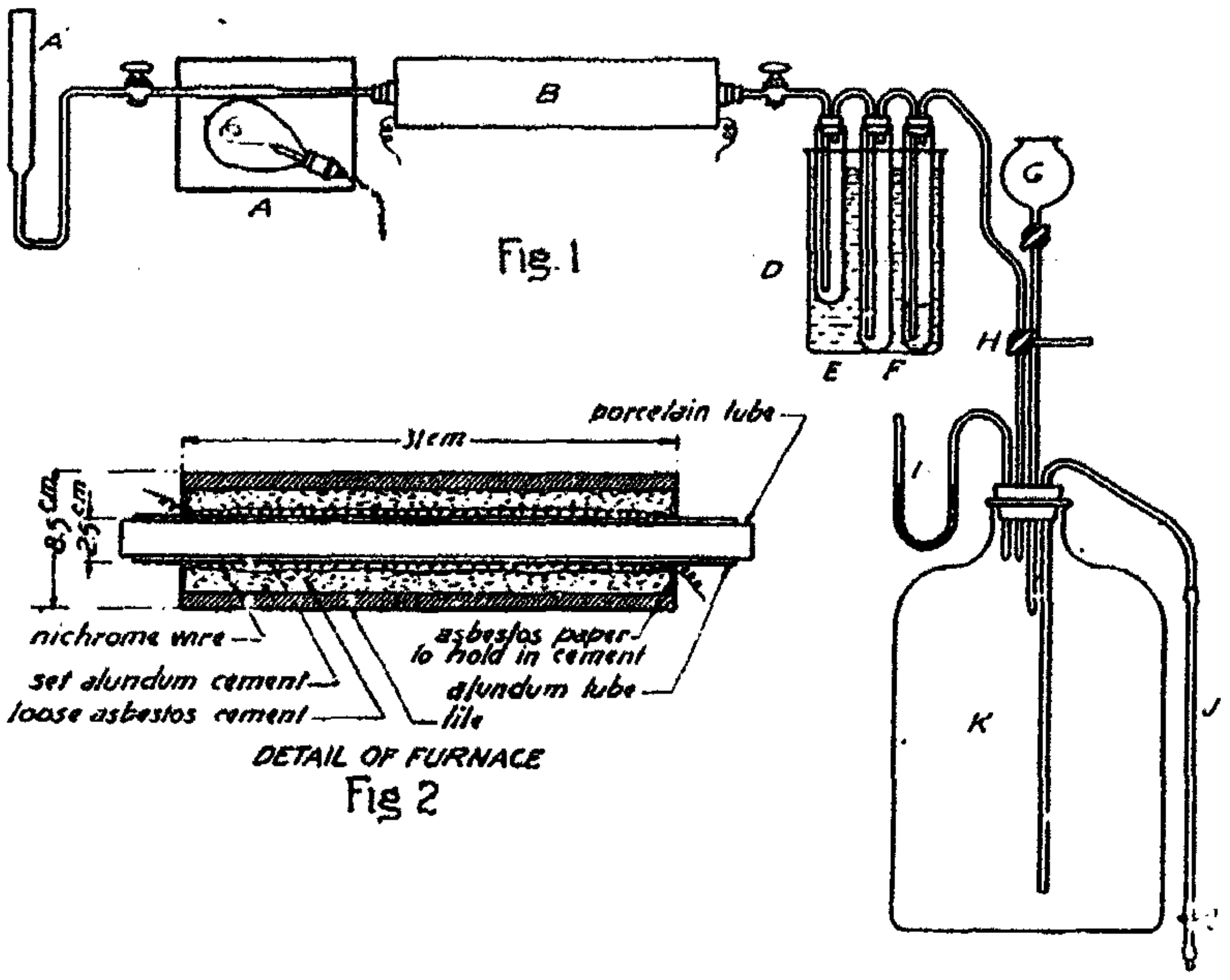

Fig. 1

DETAIL OF FURNACE

Fig 2

From the furnace the gases and vapors passed into the collecting and condensing apparatus shown. The two or three test-tubes were kept immersed in ice water; the first and second were empty, and served to condense vapors of alcohol, aldehyde, etc., the second also acting as a guard tube to protect the greater part of the liquid products from a NaOH solution sucked back from the third tube. This NaOH solution, through which the gases bubbled, prevented aldehyde vapor from passing on with the permanent gases. The gases were collected over water in a ten-liter bottle, the water being siphoned out and providing the suction for operation of the apparatus. For sampling the gas for analysis, a three-way stopcock was provided between the purifying chain and the collecting bottle. In this way a burette could be attached and draw a direct sample, uncontaminated by standing over water. In the latter part of the term, a sample of 200–300 cc was collected by means of a sample tube, with glass stopcocks at each end, and level bottle; 1 : 1 glycerine and water, in which the gases obtained are practically insoluble, being used as the confining liquid.

The solid material used in the reaction was contained in boats, in the porcelain tube of the furnace. For soda-lime and lime, porcelain boats were used; for NaOH, which fused at most of the temperatures employed, boats were made up of sheet copper or nickel, as it attacks porcelain when fused.

Methods of Analysis

Gas Analysis.—The Hempel apparatus was employed, using water-jacketed burettes, with mercury as the confining liquid. The methods given in Dennis' "Gas Analysis" were followed.

The determinations made were O_2, CO, unsaturated hydrocarbons, H_2, CH_4 and other paraffins, and N_2 by difference. CO_2 was removed by the NaOH used to take out aldehyde vapor. In experiments with Mr. Engelder, it was found that the aldehyde vapor was partially or wholly condensed by almost all the reagents used for the gas analysis, and, therefore, must first be removed before any accurate analysis was possible. All analyses, when sufficient gas was available, were made in duplicate; by checking analyses taken at all parts of the run with the average analysis of the gas obtained from that in the collecting bottle, it seems that the composition varied very little during the course of the reaction, and that representative samples were secured.

CO_2 was determined by one-minute standing over 1 : 1 KOH soln. O_2 was determined by three minutes' shaking with alkaline pyrogallol, made up as given in Dennis.

CO was determined by three minutes' shaking with ammoniacal cuprous chloride, and removal of NH_3 by 5 percent H_2SO_4.

C_2H_4 and other unsaturated hydrocarbons were determined by fuming sulphuric acid.

H_2 was most commonly determined by fractional combustion over CuO heated to 250°, as given in Dennis, flushing out the tube with nitrogen before and after the combustion. CH_4 and any other paraffins were determined by combustion in the Dennis combustion pipette.

Liquid Analysis.—Test for aldehyde in the liquid products was made with an ammoniacal solution of silver oxide, in the usual way.

Tests for unsaturated compounds, in the absence of aldehyde were made with 1 percent $KMnO_4$ solution.

Solid Analysis.—The solids after a run were analyzed for acetate (plus formate) by the method used in the course in organic analysis. Briefly, a two-gram sample is distilled with 15 cc syrupy phosphoric acid and 50 cc water, the water level being kept constant by means of a separatory funnel, until 250 cc have been distilled over. Further distillation was always carried out, but no measurable amount of acid found. 50 cc samples of the distillate were titrated with standard NaOH, giving acetate direct.

Materials

Alcohol.—Absolute alcohol, obtained from the department of organic chemistry, was used.

Aldehyde.—Aldehyde was made by the distillation of pure paraldehyde with small amounts of sulphuric or phosphoric acid, a Hempel fractionating column being employed. The boiling point varied from 21° to 29°, impurities being probably paraldehyde, certainly not alcohol.

Soda-Lime.—A finely divided granulated soda-lime, specially prepared for organic analysis, was used. The composition given was 33 percent Na_2O, 67 percent CaO.

NaOH.—After the first few runs, the NaOH was prepared by fusing the "C. P." sticks in a nickel crucible, until the water was driven off, and pouring while molten into the metal boats used. Considerable difficulty was found in expelling all the water, and there was considerable loss in all but the last case by sputtering as the soda heated up; even with all water removed, it seemed to creep around the edges of the boats in spite of all precautions.

$NaC_2H_3O_2$.—Fused sodium acetate, C. P., was fused again and poured molten into the boats.

NaOH Solution for Purifying.—About a 1 : 1 solution of the C. P. sticks was used.

Experimental Procedure

Supply of Alcohol.—The container A′ in the diagram was filled with alcohol to a mark. After the run it was refilled to the same point with alcohol from a burette, the amount used up thus being obtained directly.

Supply of Aldehyde.—Aldehyde was weighed up in a glass-stoppered weighing bottle, and poured into the container, which was kept in ice water. It was either entirely used, or the remainder after the run poured back into the bottle, and weighed.

The Vaporizer.—The vaporizer was always given at least ten minutes to heat up before starting generation of vapor.

The furnace was brought to constant temperature before starting the reaction. After a calibration in which temperatures with a given resistance had been determined, the furnace was frequently brought up to temperature by throwing on the line without resistance in series, until the pyrometer indicated the desired temperature; the appropriate resistance was then cut in. The boats with material were generally heated up with the furnace, and were never given less than twenty minutes to attain its temperature.

The condensing tubes and solution were thoroughly cooled before starting, and kept in ice water throughout the experiment; liquid products were measured by emptying the first tube, taken directly out of the bath, into a glass stoppered weighing bottle. *The collecting bottle* contained water which was saturated by shaking with the gases of the first few runs, and gave little change in the composition of gas standing over it, as checked by comparison of direct samples.

The furnace and vaporizer was first started up with a weighed amount of material in the boats. The liquid container was put in ice, if aldehyde was to be used, and the tubes in all cases. All connections were made, and the apparatus tested for leaks by opening the siphon tube on the collecting bottle, and thus applying suction to the apparatus as far as the stopcock which controlled liquid flow. The apparatus being found air-tight, fully heated, etc., and slight vacuum in the vaporizer, furnace and tubes, the first stopcock was cautiously opened so as to allow a slow flow of liquid (about 1 cm per second in the capillary tube) into the vaporizer. Increase of pressure and evolution of gas generally began almost immediately. The pinchcock on the siphon tube was now adjusted so as to allow a slight flow of the water with constant pressure indicated by the manometer. With active reaction such as the alcohol over NaOH it was possible to maintain a pressure of 1–2 inches of mercury in the apparatus; with others, especially at lower temperatures, a corresponding suction was used to keep up the feed of liquid. The liquid generally did not feed into the vaporizer continuously, but in small quantities, intermittently, giving a fairly constant supply of vapor. The end of the reaction was almost invariably marked by a rapid decrease in pressure and evolution of gas, a run of an hour's length frequently ending in a few minutes. When this stage was reached, the stopcocks at each end of the furnace were closed, the flow of liquid from the siphon shut off, power cut off from the furnace, and liquid products, gas volume and liquid used were measured. In the latter part of the term, after measuring the gas volume, vapors were swept out of the furnace and condensing tubes by passing one-half to one liter of air through them, either through the entire apparatus, all liquid being used up, or through a supplementary stopcock (not shown) inserted in the stopper in the "vaporizer end" of the furnace tube. The gas sample was collected during the run, generally at about the most active part, always late enough to allow all air to be removed from the furnace.

Reaction of Absolute Alcohol Vapor with Soda-Lime

Four preliminary runs were made, without complete analysis of gas or solid, which served to prove that the reaction went on very much as described by Dumas and Stas, except for some formation of tar; a comparatively large quantity of permanent combustible gas was liberated; temperatures of 280°–400° were used. As this work was chiefly to develop the methods of procedure, no further results will be given; no quantitative data were obtained, and the qualitative results were more fully confirmed later.

Three fairly quantitative experiments were made between Nov. 3 and Nov. 17, 1916. A tabulation of results is shown in Table I.

The lower temperature limit for the reaction seems to be about 250° C.

Some tar was always found, especially in the first part of the first boat, the entire half becoming semi-liquid in the lower temperature runs. The liquid products were largely unchanged alcohol, but always had a sharp acrid odor, and by 1 percent $KMnO_4$ solution indicated the presence of some unsaturated compound. No aldehyde test was obtained in any case; but the unsaturation test, and the fact that some tar always formed in the NaOH in the last test tube, similar to that formed later when aldehyde was known to be present, indicates that there was some present in the exit gases from the furnace.

TABLE I

Temperature	290° C	365° C	420° C
Alcohol fed in	6.8 gm	5.52 gm	1.94 gm
Liquid products	5.92	3.95	1.00
Alcohol apparently reacting	0.88	1.57	0.94
Gas produced, on air-free basis	550 cc	1750 cc	1100 cc
Time	2.75 hr.	1.75 hr.	0.75 hr.
Weight soda-lime at start	5.00 gm (approx.)	6.00 gm	3.47 gm
Gain in weight during run	—	0.63	0.16
Percent acetate (as $NaC_2H_3O_2$)	7.65	5.15	4.92
Weight acetate over weight NaOH at start	—	0.45	0.11
Gas analysis on air-free basis:			
C_2H_4	0.0%	0.3%	1.7%
CO	—	0.8	0.5
H_2	94.0	82.1	70.3
CH_4	6.0	15.9	27.5
Total volume H_2	510 cc	1420 cc	770 cc
Calculated volume H_2	950	1700	1000
Percent yield on H_2	54%	83.5%	77%
Volume methane	33 cc	292 cc	302 cc
$NaC_2H_3O_2$ corresponding to CH_4	0.11 gm	0.99 gm	1.03 gm
Percent acetate decomposed	abt. 25	75%	85%
Calculated gain in weight from total amount acetate formed	—	0.76 gm	0.44 gm
Actual gain in weight	—	0.63	0.16
Actual yield acetate	—	11.5%	8.0%
Yield on total acetate (calculated from CH_4)	35%	46%	82.5%
Ratio H_2 : CH_4	16.6 : 1	4.86 : 1	2.54 : 1
Indicating percent decomposition of acetate	12.5%	41%	90%
Alcohol fed per hour	2.45 gm	3.15 gm	2.48 gm
Alcohol apparently reacting per hr.	0.31	0.90	1.25
Gas formed per hour	200 cc	1000 cc	1460 cc
H_2 per hour (primary reaction)	185	810	1020
CH_4 per hour (secondary reaction)	12	167	400
Percent alcohol apparently reacting of that fed in	13%	29%	48.5%

As the furnace tube, with a capacity of nearly 200 cc remained full of the gaseous products at the end of the experiment, it seems probable that much of the low yield of hydrogen on the basis of alcohol apparently reacting (alcohol fed in liquid products) is due to unchanged alcohol vapor in the furnace. The yield of hydrogen and weight of acetate is calculated from the equation $C_2H_5OH + NaOH = NaC_2H_3O_2 + 2\ H_2$ and the amount of acetate formed and decomposed, and the gain in weight thereby, from the equation $NaC_2H_3O_2 + NaOH = Na_2CO_3 + CH_4$.

No determination of CO_2 in the soda-lime after the run was made, but from the violent effervescence, it seemed probable that the largest part of the soda was converted into acetate and carbonate. Judging by later results, the lime would be little affected.

Conclusions Regarding the Reaction

The reaction does not begin below about 250°. It was investigated up to about 450°, which is nearly the upper limit for the existence of alcohol vapor, some slight spontaneous decomposition beginning around the upper limit used. Beginning around 300°, such alcohol as reacts does so almost quantitatively, as shown by the yield of hydrogen, and the analysis of the gas. Such discrepancy as is shown in the first case is, as already explained, readily accounted for by unchanged alcohol vapor left in the furnace. The gas analysis, showing only traces of olefines and of CO, indicates that practically no secondary decompositions of the vapor take place. The formation of tar, however, proves that some other reaction takes place, and it would seem probable, in view of later work, that this is due to condensation of aldehyde, after this substance is formed with liberation of hydrogen. As would be expected, the velocity of the reaction increases greatly between the temperature limits used; the amount of alcohol apparently reacting per hour becomes four times as great at 420° as at 290°, and over five times as shown by hydrogen production; as more alcohol apparently reacting at the higher temperature is actually reacting, than at the lower, due to lower vapor density, these figures check very closely. The alcohol cannot be fed slowly enough to give complete reaction—some excess of vapor must be present; but much of the liquid products in these runs were formed by continuing feed of alcohol after the reaction had almost entirely stopped.

The secondary reaction, of sodium acetate with excess of alkali, while not bearing directly on the problem, is of interest. It begins at almost as low a temperature as the principal reaction, but its velocity increases much more rapidly with rise of temperature. Even at 300° some 25 percent of the acetate formed decomposes, while by 420° at least 85 percent breaks up. The decomposition takes place largely along with and not after the main reaction, as shown by the fact that the methane is given off at the same time as hydrogen. Gas analyses of direct samples taken during the run, and of the entire gaseous products from the collecting bottle, check within limits of error, provided the gas does not stand over the water for more than a few hours. The most favorable temperature for formation of acetate is about 300°; below this, the amount of tar, and above this the decomposition of acetate, rise.

A slight formation of ethylene is noticed; alcohol vapor begins to break up with heat alone at about 400°, and the decomposition goes either to ethylene and water, or to aldehyde and hydrogen; the aldehyde would also decompose somewhat to CH_4 and CO, thus accounting for the CO found.

Reaction of Absolute Alcohol Vapor with Lime

According to Sabatier "The pure CaO does not give any perceptible action on primary alcohols at 350°. It is only towards 400° that one begins to observe a little decomposition into aldehyde and hydrogen." This statement was checked to determine the part played by the CaO in soda-lime in causing the reaction. Four experiments were made, three of which were carried to completion; the gas sample from the third was lost in moving the apparatus to a new laboratory.

The appearance of the CaO was not changed in any case. On adding acid for analysis, a considerable effervescence indicated that some carbonate had been formed. There was no production of tar in any case. The liquid products gave unsaturation, but not aldehyde test in the first two runs; in the last two, a marked aldehyde test was obtained. With

TABLE II

Temperature	290° C	390° C	460° C	500° C
Alcohol fed in	2.53 gm	2.37 gm	2.45 gm	2.37 gm
Liquid products	1.86	1.74	1.98	1.49
Alcohol apparently reacting	0.67	0.62	0.47	0.88
Time	0.50 hr.	0.50 hr.	0.50 hr.	0.67 hr.
Gaseous products on air-free basis	65 cc	15 cc	100 cc	450 cc
Increase weight lime	0.18 gm	0.08 gm	0.24 gm	0.49 gm
Percent acetate in lime	0.0	—	—	1.0%
Gas analysis on air-free basis:				
CO	0.0%	0.0%	0.8%	8.4%
C_2H_4	3.4	0.0	2	6.3
H_2	79.9	91.8	—	80.9
CH_4	16.7	8.2	—	4.6
H_2 per gram alcohol apparently reacting	80 cc	20 cc	—	415 cc
Percent of calculated, assuming simply splitting to aldehyde	15%	4%	—	77%
Alcohol fed in per hour	5.06 gm	4.74 gm	4.90 gm	4.74 gm
Alcohol apparently reacting per hour	1.33	1.24	0.94	1.76
Hydrogen per hour	100 cc	30 cc	—	550 cc

the exception of the last run, almost all evolution of gas was over in about ten minutes; after this the action was simply distillation of alcohol through the furnace. In the last experiment evolution of gas continued for about forty-five minutes after the feed of alcohol was stopped, about 200 cc being liberated.

Conclusions

These results check with those of Sabatier, in that CaO is found to be a poor catalyst for alcohol, and gives largely aldehyde and hydrogen. The action does not begin until about 450°, and were it not for the fact that hydrogen so predominates over ethylene, might seem to be due to thermal decomposition alone. The small amount of CH_4 compared with H_2, and the almost total absence of any acetate from the lime after the run, show that it is a case of contact catalysis, largely without other reaction; the formation of CH_4 may be partly due to decomposition of aldehyde at above 400°. Increase in weight by the lime must be ascribed to adsorbed alcohol, or to moisture in the alcohol, as no compound is formed in sufficient quantity.

Combined with the following results on use of NaOH alone, it seems that the CaO plays no important part in the soda-lime reaction. Even with immediate reaction of the aldehyde formed, its catalytic effect is so small that it could not account for the main reaction; and as the reaction with NaOH was later proved to be more energetic than with soda-lime itself, it seems probable that the use of soda-lime instead of the pure NaOH, by Dumas and Stas, was due to the greater ease of handling; soda-lime is infusible at the temperatures used, while employment of fused NaOH would have given them great experimental difficulty.

Reaction of Absolute Alcohol Vapor with Caustic Soda

The next step was the use of the other constituent of the soda-lime-pure caustic soda. Four runs were made at different temperatures. The results are summarized in Table III.

The lowest temperature used (200°) gave no reaction, evidently. Liquid products were spoiled in the second run, but in the other very strong aldehyde tests were obtained, indicating that a large percentage was aldehyde rather than alcohol. There was no formation of tar in the solid products; the NaOH darkened somewhat, but only to a gray. There was no free NaOH evident at the end of the reaction; the material was no longer hygroscopic. In all these runs, except at 200°, there was a considerable loss of NaOH by spattering as it heated up, even though heated slowly with the furnace; the liquid also crept around the edges of the boats in which it was contained, and, of course, attacked the porcelain tube of the furnace, so that altogether no quantitative determination of acetate formation could be made. The rest of the NaOH, beside acetate, is accounted for as carbonate and silicate.

The alkali being contained in copper or nickel boats, it was feared that these might have some catalytic effect, so that

TABLE III

Temperature	200° C	305° C	410° C	450° C
Alcohol fed in	4.82 gm	2.84 gm	2.13 gm	6.79 gm
Alcohol apparently reacting	1.74	1.5 abt.	0.43	2.82
Gaseous products on air-free basis	0 cc	1.4 l	0.4 l	3.5 l
Time	0.75 hr.	0.67 hr.	1.0 hr.	0.25 hr.
Wt. NaOH at start	2.63 gm	1.82 gm	2.39 gm	7.46 gm
Percent $NaC_2H_3O_2$ after reaction	0.0	5.8%	—	Trace
Gas analysis on air-free basis:				
CO	—	0.6%	0.1%	1.9%
C_2H_4	—	1.4	2.6	2.1
H_2	—	79.0	85.1	65.9
CH_4	—	19.0	13.2	30.2
H_2 per gram alcohol reacting	0 cc	750 cc	550 cc	750 cc
Percent yield	0%	69.5%	51%	69.5%
Ratio $H_2 : CH_4$	—	4.1 : 1	6.4 : 1	2.2 : 1
Indicating by percent decomposition of acetate formed	—	48%	31%	92%
Alcohol apparently reacting per hour	0.0 gm	2.3 gm	0.43 gm	11.3 gm
H_2 per hour	0 cc	1.65 l	0.34 l	7.9 l
Percent alcohol fed in apparently reacting	36%	52%	20%	41%

alcohol was run through the hot furnace containing the empty boats. At 500° a slight aldehyde test was obtained. At 305°, out of 8.49 grams of alcohol passed through, 8.41 were recovered as liquid, and there was practically no gas production, the gas collected (not analyzed) being only 50 cc. There was a faint aldehyde test from the liquid products, but altogether the effect of the boats on the alcohol may be taken as negligible, as the alcohol always breaks up slightly at these temperatures.

The reaction was a most active one, pressures of 3.4 inches of mercury being readily obtained at 300° and above; the gas production in the run last recorded was at the rate of 12 liters per hour under a pressure of one to two inches of mercury.

The velocity increases rapidly with the temperature, as would be expected; the secondary reaction attains a high velocity at lower temperatures than with soda-lime. The apparently slow reaction in the third experiment was due to a deliberately very slow feed of alcohol, conditions in the other three runs being closely comparable.

Conclusions

Alcohol reacts very readily with caustic alkalis at temperatures of 300° up. The reaction is very like the reaction with soda-lime, and it may be concluded that in the soda-lime reaction the NaOH alone really takes part. A considerable quantity of aldehyde is found in the vapors from the furnace; aldehyde apparently is not condensed by the NaOH at this temperature, which is further evidenced by the non-formation of tar. This points to the formation of aldehyde during the progress of the main reaction.

As might be expected from the great activity of fused NaOH, the secondary reaction of the acetate with excess alkali begins with the main reaction and always results in the decomposition of the largest part of the acetate.

The side reaction of the alcohol, forming C_2H_4 and water, is slightly higher than with the soda-lime. Aldehyde formed and not immediately reacting seems to escape, rather than be condensed, as by soda-lime. The percentage of alcohol reacting of that passed through the furnace is again low. An experiment in feeding very slowly did not apparently raise the percentage at all, in fact, seemed to lower it; but as the liquid products were probably $^1/_3$ aldehyde, while assumed to be all alcohol in calculation, it was probably at least as high as before. However, the reaction reaches a state of equilibrium between alcohol vapor, NaOH and products of the reaction, which depends on temperature; so that if sufficient time is given for equilibrium to be reached, the rate of feed of the alcohol is not the factor which determines the percentage of alcohol converted, although if too fast, it may readily have its effect. It is interesting and rather puzzling to note the high production of aldehyde with slow feed of alcohol, as evidenced by aldehyde in the liquid products in the third run, and by low H_2 yield (formation of aldehyde gives only half the hydrogen of the complete reaction).

Altogether, from the last two sets of experiments, it seems thoroughly established that the sodium hydroxide in soda-lime is the substance which really reacts with the alcohol, and that the chemical effect of the lime may be neglected.

Reaction of Aldehyde Vapor with Alkali

The next step in the proof of the theory is to show that aldehyde, once formed, would react with the alkali with formation of acetate and H_2, a point of considerable interest, since alkali condenses aldehyde at ordinary temperatures. According to Sabatier, "Aldehyde is slowly condensed by soda-lime—sodium acetate—etc.," but it is not clear to what conditions he is referring. Three experinents were made passing aldehyde vapor over NaOH, and two using soda-lime. The results are tabulated for NaOH in Table IV.

TABLE IV

Temperature	Approx. 350°	350°	450°
Weight aldehyde fed in	4.90(?)	4.82 gm	5.13 gm
Liquid products	5.13(?)	1.0	2.58
Aldehyde apparently reacting	?	3.8	2.55
Gaseous products on air-free basis	270 cc	1700 cc	1200 cc
Time	0.50 hr.	0.50 hr.	1.3 hr.
Weight NaOH used	—	10.8 gm	8.0 gm
Percent acetate after reaction	—	11.1%	6.0%
Acetate formed	—	1.21 gm	0.48 gm
Gas analysis on air-free basis:			
CO	0.0%	—	0.0%
C_2H_4	1.7	0.6	0.5
H_2	96.4	70.0	96.8
CH_4	1.9	29.4	2.7
$H_2 : CH_4 =$	50.1	4.2 : 1	26 : 1
H_2 per gram aldehyde	—	315 cc	440 cc
Percent yield bases on hydrogen	—	56%	78%
Percent yield bases on acetate	—	17%	10%
Percent aldehyde fed in apparently reacting	—	80%	50%
Aldehyde apparently reacting per hour	—	7.6 gm	1.96 gm
Hydrogen per hour	0.52 l	2.4 l	0.90 l

The reaction assumed to take place in all cases is $CH_3CHO + NaOH = NaC_2H_3O_2 + H_2$, and the secondary reaction $NaC_2H_3O_2 + NaOH = Na_2CO_3 + CH_4$.

The free NaOH, as before, was all gone at the end of the reaction. It was prepared by fusing and pouring into the boats, for the last two runs, but loss could not be entirely prevented. Except at the lowest temperature, there was no formation of tar at all in the boats; in this it was slight. There was some carbonate, but not much, formed, as would be expected, from the small amounts of CH_4.

The furnace and tubes were flushed out by passing air through them after the reaction, so that no aldehyde vapor was left here, but owing to the great volatility of the substance, it could not all be condensed, and a large amount "apparently reacting" is accounted for by the strong formation of aldehyde tar in the NaOH solution used for purification of the gases.

Soda-lime was also employed, to make certain that the use of this substance instead of aldehyde would not prevent the reaction by condensing effect. One experiment was also made with pure fused sodium acetate, to determine its condensing power, and probable effect on equilibrium. The results of this are given with the soda-lime in Table V.

Gas samples from these experiments were collected over glycerine and water, and duplicate analyses made, the results being averaged. On the first runs with both NaOH and soda-lime (the first two made), there was difficulty in securing an even feed of the aldehyde, resulting in a sucking back of NaOH solution into the liquid products.

In both soda-lime runs, there was considerable blackening of the lime in the part first passed over by the vapor, and formation of more or less charred tarry products. As before, the presence of tar in the purifying tube accounted for a large proportion of aldehyde apparently reacting. With the exception of the formation of tar in the furnace, the reaction seemed very similar to that with NaOH.

TABLE V

			With $NaC_2H_3O_2$
Temperature	400°	400°	450°
Weight aldehyde fed in	10 gm(?)	4.50 gm	2.40 gm
Liquid products	?-spoiled	1.82	1.60
Aldehyde apparently reacting	?	2.68	0.80
Gaseous products on air-free basis	160 cc	525 cc	0 cc
Time	0.25 hr.	0.25 hr.	0.33 hr.
Weight soda-lime used	3.05 gm	2.35 gm	Fused sodium acetate used
Gain in weight	0.57	0.32	—
Percent acetate after reaction	6.1%	Analysis spoiled	—
Weight acetate after reaction	0.22 gm	0.2(?) gm	—
Gas analysis on air-free basis:			
CO	—	1.1%	—
C_2H_4	1.4%	1.2%	—
H_2	97.0%	89.1%	—
CH_4	1.4%	6.5%+	—
$H_2 : CH_4 =$	70 : 1	13.5 : 1	—
H_2 per gram aldehyde	—	180 cc	—
Percent yield based on hydrogen	—	32%	—
Percent yield based on acetate	—	4%	—
Percent aldehyde fed in apparently reacting	—	60%	33%
Aldehyde apparently reacting per hour	—	10.7 gm	2.40 gm
H_2 per hour	0.60 l	1.80 l	0.0 l

Using sodium acetate, there was no reaction, but a blackening of the solid, which was not produced when the salt was heated alone. It seemed to have a slight effect on the aldehyde, in condensing it, but not by any means a powerful one.

Conclusions

Aldehyde reacts with sodium hydroxide or soda-lime with the formation of sodium acetate, the reaction being represented by the equation

$$CH_3CHO + NaOH = CH_3CO_2Na + H_2.$$

Using NaOH, the reaction is nearly quantitative at around 450°; the yield falls off at lower temperatures, and the reaction does not begin until about 300°. The rate of the reaction is as high as that of alcohol with the same substances, as far as can be judged. With aldehyde a liberation of 2.4 liters of hydrogen per hour could be obtained at 350°; a higher production with alcohol was reached only at 450° (7.9 liters per hour), and the alcohol reaction liberates twice the volume of hydrogen. The rate of feed, amount of alkali, temperature, and other uncertain factors come into the reaction velocity; but, as far as can be determined, the two are almost the same.

Using soda-lime, the reaction of both is slower; but 1.8 liters of hydrogen per hour were obtained with aldehyde and soda-lime at 400°, while at 420° the alcohol reaction, yielding nearly twice the volume of hydrogen for a given weight of liquid, gave 1.02 liters. As has already been said, aldehyde reacts nearly quantitatively with NaOH; the yield with soda-lime is much poorer owing to the formation of condensation products. The yield of acetate is much better with NaOH, which is surprising. In both cases the yield of acetate was lower than when alcohol was used. The secondary reaction of acetate with alkali is much smaller when alcohol is present, the percentage of acetate decomposed to form methane being much smaller.

Dissociation of Aldehyde Vapor

Now that it has been shown that aldehyde is an intermediate product in the conversion of alcohol into acetate by means of soda-lime, it is necessary to consider what intermediate products there are in the reaction between aldehyde vapor and caustic soda.

$$CH_3CHO + NaOH = CH_3CO_2Na + H_2.$$

There are at least two possible reactions, though they are not equally probable. The aldehyde may split off one hydrogen, forming temporarily the free acetyl radical, which may react with caustic soda, setting free hydrogen and forming sodium acetate. Acetyl chloride reacts with caustic soda, forming acetate and chloride; and it is conceivable that the acetyl radical might set free hydrogen from caustic soda. There is no evidence, however, either that one hydrogen splits off from acetaldehyde or that the acetyl radical will react as suggested. It is therefore more probable to consider the second alternative, namely that the aldehyde dissociates to keten and that keten reacts with caustic soda, the two reactions being

$$CH_3CHO = CH_2CO + H_2,$$
$$CH_2CO + NaOH = CH_3CO_2Na.$$

Wilsmore prepared keten by the action of a hot platinum wire on acetic anhydride[1] or on acetone[2] while Schmidlin and Bergmann[3] obtained it by passing acetone vapor through a glass tube filled with pieces of earthenware and heated to 500°-600°. It is considered probable that acetone is an intermediate product in the formation of keten from acetic anhydride, in which case the reactions would be,

$$(CH_3CO)_2O = CH_3COCH_3 + CO_2,$$
$$CH_3COCH_3 = CH_2CO + CH_4.$$

I have not been able to find any evidence that keten is actually a decomposition product of aldehyde; but it is the normal product in case of a dehydrogenation, which is what we have; and keten reacts readily with water to form acetic acid. While it is not proved that keten is an intermediate product in the conversion of alcohol into acetate by means of soda-lime, this seems more probable than to assume that the intermediate product is the free acetyl group. While it might be difficult experimentally to show that aldehyde may yield keten and hydrogen, it ought not to be especially difficult to show the formation of the decomposition product ethylene, according to the equation

$$2CH_3CHO = 2CH_2CO + 2H_2 = C_2H_4 + 2CO + 2H_2.$$

Summary

The following general conclusions may be drawn from this paper:

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[1] Jour. Chem. Soc., 91, 1938 (1907).

[2] Proc. Chem. Soc., 24, 77 (1908).

[3] Ber. deutsch. chem. Ges., 43, 2821 (1910).

1. The reaction between alcohol vapor and soda-lime begins at about 250°, the primary reaction being represented by the equation

$$CH_3CH_2OH + NaOH = CH_3CO_2Na + 2H_2.$$

The secondary reaction

$$CH_3CO_2Na + NaOH = Na_2CO_3 + CH_4$$

begins at about the same temperature; its reaction velocity increases so rapidly with the temperature that at 450° practically all of the acetate decomposes as fast as it is formed. The primary reaction is nearly quantitative, not over ten percent at the outside estimate of the alcohol taking part in the side reactions which give aldehyde tars, ethylene and water, and methane and carbon monoxide from the high temperature decomposition of acetaldehyde. Under the experimental conditions the reaction does not run to an end, there being always a relatively large amount of unchanged alcohol. Increasing the rate of feed cuts down the percentage of alcohol decomposed; decreasing the rate of feed too much seems to make the secondary reactions relatively more important.

2. The caustic soda is the active constituent in the soda-lime. Lime itself has only a very slight effect on alcohol at the temperature used, whereas caustic soda reacts with alcohol at these temperatures with the primary formation of sodium acetate and hydrogen, and the secondary formation of sodium carbonate and methane, just exactly as soda-lime does. The only difference is that the reactions take place much more rapidly with caustic soda than with soda-lime, and that there is less tar formed. The reason for using soda-lime instead of caustic soda is that the latter is a liquid at the temperatures involved and is hard to handle.

3. The conversion of alcohol to acetate in presence of soda-lime takes place in at least three stages. The first stage is the dissociation of alcohol to aldehyde and hydrogen in presence of caustic soda as catalytic agent,

$$CH_3H_2OH + NaOH = CH_3CHO + NaOH + H_2.$$

Aldehyde is found in the liquid products when caustic soda is used; when soda-lime is used, some aldehyde tar is formed in the furnace and some in the NaOH washing bulb. At the temperature in question aldehyde reacts with caustic soda or soda-lime at least as rapidly as does alcohol.

The second stage of the reaction is the dissociation of aldehyde presumably to keten and hydrogen in presence of caustic soda as catalytic agent, according to the equation

$$CH_3CHO + NaOH = CH_2CO + NaOH + H_2.$$

The intermediate formation of keten has not been shown; but it is the most probable reaction and it does not seem probable that acetaldehyde splits off one of hydrogen, forming temporarily the free acetyl group.

The third stage in the reaction is the combination of keten with caustic soda to form sodium acetate acccording to the equation

$$CH_2CO + NaOH = CH_3CO_2Na.$$

Cornell University

NEW BOOKS

Principles of Agricultural Chemistry. *By G. S. Fraps. Second edition. 23 × 17 cm; pp. vi + 504. Easton: The Chemical Publishing Co., 1917. Price: $4.50.* The chapters are entitled: introduction; essentials of plant life; the plant and the atmosphere; origin of soils; physical composition and classes of soils; physical properties of soils; the soil and water; chemical constituents of the soil; chemical composition of the soil; active plant food and water-soluble constituents of the soil; chemical changes; soil deficiencies; losses and gains by the soils; manure, sources and composition of fertilizers; purchase and use of fertilizers; constituents of plants; composition of plants and feeds; digestion; utilization of food; maintenance rations and fattening; feeding work animals and growing animals; feeding milk cows; feeding standards and feeding.

There are a number of things in the book which are of especial interest to the physical chemist. On p. 173 the author discusses the interpretation of partial soil analyses. "The chemical analysis of a soil must be considered in connection with a knowledge of its location, depth drainage conditions, permeability to water and air, and, if possible, the amounts of crops it produces. Without consideration of the other factors which influence the fertility of a soil, the chemical analysis may not lead to satisfactory conclusions. * * * The interpretation of a chemical analysis unaccompanied by knowledge of the other soil conditions which affect its fertility may be unsatisfactory in a large proportion of cases. A careful interpretation of results with the aid of the knowledge referred to may sometimes be disappointing, but it is more often correct. Analyses of miscellaneous samples of soils are also of less value than systematic studies of definite areas. Analyses of virgin soils, or soils which have not been long under cultivation, or not treated with fertilizers, are more likely to yield satisfactory interpretations than analyses of soils whose properties have been modified by long-continued cultivation or by applications of fertilizers."

On p. 199 the author says that "as a rule, when two salts are present, which are required by the plant, their absorption is accelerated. For example, potassium salts are taken up in much larger quantity when a calcium salt is present. Potassium nitrate may be removed entirely from a solution containing calcium nitrate. In the presence of other ions, the potassium ion, nitrate ion, phosphate ion, and sulphate ion can be removed completely from the solution, while calcium or magnesium ions become more concentrated in the solution as a rule." It appears, p. 219, that an instance is on record in which corn took up so much nitrates from solution that crystals of potassium nitrate would fall out when the stalk was tapped on a table.

There is an interesting discussion of the action of antiseptics and heat on bacterial change, p. 233. "Carbon bisulphide, toluene, benzene, and other volatile antiseptics applied to the soil during the growing season may destroy or injure the crop; but, if an antiseptic is applied some time before planting, it increases the fertility of the soil to a decided extent. In an ordinary soil the bacteria have reached a condition of equilibrium. Antiseptics destroy protozoa and nitrifying bacteria, and injure other bacteria, and diminish the production of active nitrogen. In time, new bacteria develop, but along different lines, and there occurs both an enormous increase in number of bacteria and an abnormal predominance of certain species. The bacteria which produce ammonia are more energetic and the fixation of nitrogen also takes place to a greater extent than usual. The nitrogen is at first locked up in the bacterial bodies, and so is useless to the plants, but it becomes active when they decay. There is first a decrease in ammonia production, followed by a great increase. Hence the action of the antiseptic is depressing if applied to a growing crop; but they act like a nitrogenous fertilizer to a succeeding crop. After a longer or shorter time, the soil is more exhausted than it was at first. This is probably due not only to the rapid transformation of the more easily decomposed organic nitrogen of the soil into active nitrogen, but also to the abnormal mixture of soil bacteria due to the changed conditions. Heating the soil has similar effect to volatile antiseptics. The heat, however, itself changes the chemical composition of the soil, rendering both organic and inorganic material more soluble in water, and the soil more acid. Decomposition products of protein are produced and also some substances harmful to plants in water culture. Caustic lime in large quantities also kills protozoa and many bacteria and acts in a similar way to antiseptics, being injurious at first."

The author is not an enthusiastic believer in calories as the ultimate standard, p. 434. "The productive value of a food is the best measure so far devised for the net value of a food. Rations have heretofore been calculated on the assumption that all digestible nutrients of the same group have the same value to the animal, regardless of the origin of the material. We now know, however, that the net value of a food may vary very widely from its value based entirely on digestible nutrients, so that the value of a food for the purpose of producing energy is best measured by its productive value. It is quite possible that the kinetic energy of different feeds undergoes somewhat different losses when transformed into fat, so that the quantity of fat produced may not be the most exact possible measure of the net value of feeds. The energy used in digestion and given off as heat may also prove useful under certain circumstances, such as with an animal or a maintenance ration in cold weather.

"While the fat values of feeding-stuffs probably represent their comparative values for fattening purposes, and perhaps for milk production, it does not follow that they represent exactly the values of the feeds for productive work and for maintenance of the animal. The conversion of proteids, etc., into fat undoubtedly consumes energy, and a greater quantity of energy may be required to convert the proteids of one feeding-stuff into fat, than those of another; whereas, if the proteid is used directly for work or maintenance, these proteids might be equal in value for these purposes. We have seen that a feed-stuff possesses both kinetic and thermal energy, and that the thermal energy may be used to keep the animal warm. While the thermal energy fed to an animal on a heavy ration may be so excessive that differences in the thermal energy of feeds may have no significance, an animal on a small or maintenance ration, may be able to utilize the thermal energy. The use of the productive value of a feed is no doubt a decided advance in the science of animal nutrition, as it emphasizes the differences in the productive values of the digested nutrients of different classes of feeds. It is clear that the digested nitrogen-free extract, for example, of hays and fodders, does not have the same value to the animal as that of grains and other concentrates. * * *

"Certain pure proteins, such as gliadin from wheat and hordein from barley, cannot promote growth, while zein from corn can neither promote growth nor maintain body weight. On the other hand, active growth takes place with casein (from milk), ovalbumin, lactalbumin, edestin (from hemp seed), glutenin from wheat and glycerin. Zein does not yield the amino acids, lysin, glycocoll, or tryptophane, and when tryptophane is fed along with it, it will maintain weight but will not promote growth. Gliadin does not yield lysin, and additions of lysin to the gliadin renders it capable of promoting growth. The experiments were made on rats. Some substance in butter fat also seems essential to the growth of rats.

"These investigations make it appear possible that some single feeds may not furnish the amino acids necessary to the growth of young animals. On the other hand, a mixed diet would probably furnish the necessary amino acids, and even in single feeds the proteids are not alone, but are usually accompanied by others containing the necessary amino acids, though possibly not in sufficient quantity. Further investigation is necessary to clear up the bearing of the work on animal feeding. * * * Experiments at the Wisconsin Experiment Station, covering a period of four years, show that animals fed rations properly balanced from different plant sources, were not alike in general vigor, size, strength of offspring, and capacity for milk secretion. Animals fed from the products of the wheat plant exclusively were deficient in vigor; those fed from the corn plant were strong and vigorous; those fed from the oat plant were not as vigorous as those fed from the corn plant; while those fed a mixed ration were intermediate between the wheat and oat rations in vigor. These differences they now ascribe to the presence of toxic substances in the wheat germ. Thus other things than the protein and the other fodder groups are important in feeding."

Wilder D. Bancroft

SOME EXPERIMENTS ON THE MANIFESTATION OF OSMOTIC PRESSURE WITH MEMBRANES OF CHEMICALLY INERT MATERIALS II[1]

BY S. L. BIGELOW AND C. S. ROBINSON.

Final Experiments with Membranes of Pure Materials

The complete success attending the attempts thus far described to obtain osmotic effects with inactive materials of widely different chemical natures made it seem improbable that the results could be entirely due to the small quantities of impurities present. We therefore concluded that it would be worth while to repeat the preliminary experiments using all the precautions found necessary to obviate possible errors. These final results are given in the following pages.

Silica: The material was prepared from a commercial sample of chemically pure silicic acid. It was first dehydrated in a platinum dish over a blast lamp, then pulverized in an agate mortar, washed with hot water several times by decantation and finally filtered with suction. After being dried in the oven and again thoroughly ignited it analyzed as follows:

0.6342 g subst. : 0.0003 g residue : 99.95% SiO_2

The membranes prepared from it were made by alternately pressing at 350 kg per cm^2 and clogging the pores by sucking a suspension of fine material through the membranes. Two membranes were prepared in this way and tested for osmotic effects after each treatment. When the largest pores had been reduced in size to 1.4823 microns (No. 3) and 0.3488 micron (No. 9), respectively, the results shown in the tables were obtained.

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[1] The experiments described in this article were performed in the Chemical Laboratory of the Michigan Agricultural College Experiment Station and the results are published with the permission of the Director.

TABLE 5

No. 3

M/2 sugar solution

	Readings			Readings	
	Observed	Corrected		Observed	Corrected
1/27	0	9	1/31	14	23
1/28	9	18	2/ 1	14	23
1/29	14	23			

M/1 sugar solution

	Readings			Readings	
	Observed	Corrected		Observed	Corrected
1/12	0	17	1/20	42	59
1/13	—2	15	1/21	45	62
1/14	5	22	1/22	49	66
1/15	13	30	1/23	51	68
1/16	21	38	1/24	53	70
1/17	27	44	1/25	54	71
1/18	32	49	1/26	55	72
1/19	37	54			

2/*M* sugar solution

	Readings			Readings	
	Observed	Corrected		Observed	Corrected
2/2	0	31	2/10	78	109
2/3	15	46	2/11	78	109
2/4	35	66	2/12	79	110
2/7	66	97	2/14	79	110
2/8	71	102			

No. 9

M/2 sugar solution

	Readings			Readings	
	Observed	Corrected		Observed	Corrected
2/15	0	9	2/25	48	57
2/16	4	13	2/26	51	60
2/17	11	20	2/28	55	64
2/18	17	26	2/29	56	65
2/19	24	33	3/ 1	57	66
2/21	35	44	3/ 2	57	66
2/23	43	52			

M/1 sugar solution

	Readings			Readings	
	Observed	Corrected		Observed	Corrected
1/27	0	17	2/ 4	64	81
1/28	9	26	2/ 7	64	81
1/29	21	38	2/ 8	83	100
1/31	40	57	2/10	89	106
2/1	46	63	2/11	91	108
2/2	52	69	2/12	94	111
2/3	58	75	2/14	96	113

2 *M* sugar solution

	Readings			Readings	
	Observed	Corrected		Observed	Corrected
3/3	0	31	3/12	163	194
3/4	24	55	3/13	172	203
3/6	64	95	3/14	181	212
3/8	100	131	3/16	201	232
3/9	117	148	3/18	218	249
3/10	133	164	3/20	232	263
3/11	147	178	3/21	236	267[1]

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[1] The maximum reading with this membrane and solution could not be obtained because the level of the liquid on the water side sank into the cell.

At the conclusion of the above experiments the cells were taken apart, washed and pressed at 350 kg per cm^2 after clogging the pores. The membrane in No. 9 was so cracked by this treatment that it was useless for further work. The diameters of the largest pores in No. 3 were slightly reduced. The following results were obtained with it:

TABLE 6

No. 3

M/2 sugar solution

	Readings			Readings	
	Observed	Corrected		Observed	Corrected
2/27	0	9	3/ 8	42	51
2/29	6	15	3/ 9	45	54
3/ 1	13	22	3/11	49	58
3/ 2	18	27	3/12	52	61
3/ 4	28	37	3/14	54	63
3/ 5	34	43	3/15	55	64
3/ 6	36	45	3/17	56	65

M/1 sugar solution

	Readings			Readings	
	Observed	Corrected		Observed	Corrected
3/17	0	17	3/30	140	157
3/19	19	36	3/31	147	164
3/21	45	62	4/ 2	159	176
3/24	85	102	4/ 4	168	185
3/25	96	113	4/ 6	175	192
3/27	115	132	4/ 7	178	195
3/28	123	140	4/10	185	202

2 M sugar solution

	Readings			Readings	
	Observed	Corrected		Observed	Corrected
4/10	0	31	4/20	175	206
4/11	10	41	4/22	201	232
4/12	30	61	4/24	222	253
4/13	52	83	4/26	241	272
4/14	74	105	4/28	257	288
4/16	114	145	5/ 1	277	308[1]

It will be observed that in the first series, No. 9, having smaller pore diameters than No. 3 gave larger values, and that after the diameters of the pores in No. 3 had been reduced the values obtained with it were larger than before.

Carbon

Aquadag: The material after being acidified and washed was digested with aqua regia. After again washing, it was dried and ignited. This process was carried through twice, after which it was digested in a platinum dish with hydrofluoric acid, washed and again ignited.

A sample weighing 0.5880 g was then burned to constant weight of residue. The residue weighed 0.0022 g corresponding to a loss on ignition of 99.63% of the sample.

Two membranes were made from this material. The largest pores showed diameters of the following order of magnitude:

No. 9 = 0.593 micron. No. 14 = 0.624 micron.

The membranes were first set up with water on both sides. No movement of the liquid was noticeable. One side of each cell was then filled successively with $M/2$, $M/1$ and 2 M sugar solution and placed in the thermostat. The following corrected results were obtained:

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[1] Maximum reading not available owing to liquid sinking into the cell on water side.

TABLE 7

M/2 sugar solution

No. 9

	Readings			Readings	
	Observed	Corrected		Observed	Corrected
6/12	0	9	6/14	7	16
6/13	5	14	6/15	7	16

No. 14

5/ 8	0	9	5/11	—46	—37
5/ 9	—16	—7	5/12	—48	—39
5/10	—37	—28	5/13	—46	—37

M/1 sugar solution

No. 9

6/15	0	17	7/ 6	46	63
6/16	8	25	7/ 8	48	65
6/19	16	33	7/11	52	69
6/21	24	41	7/14	55	72
6/23	30	47	7/17	58	75
6/26	31	48	7/19	60	77
6/28	35	52	7/22	62	79
6/30	38	55	7/26	64	81
7/ 3	41	58	7/27	68	85

No. 14

	Readings			Readings	
	Observed	Corrected		Observed	Corrected
5/19	0	17	5/24	9	26
5/22	4	21	5/25	10	27
5/23	6	23	5/27	11	28

2 *M* sugar solution

No. 9

	Readings			Readings	
	Observed	Corrected		Observed	Corrected
8/ 1	0	31	10/6	103	134
8/ 4	6	37	10/12	109	140
8/ 8	13	44	10/18	117	148
8/10	17	48	10/24	125	156
8/12	20	51	10/30	133	164
8/16	27	58	11/ 5	141	172
8/23	39	70	11/11	146	177
8/28	48	79	11/17	152	183
9/ 2	57	88	11/24	159	190
9/ 9	70	101	11/29	165	196
9/13	78	109	12/ 5	169	200
9/22	95	126	12/ 9	160	191
9/30	99	130			

No. 14

5/31	0	31	6/20	127	158
6/ 2	22	53	6/22	131	162
6/ 4	47	78	6/24	133	164
6/ 6	66	97	6/27	140	171
6/ 8	81	112	6/29	143	174
6/10	93	124	7/ 1	145	176
6/13	107	138	7/ 5	150	181
6/15	113	144	7/ 7	151	182
6/17	119	150	7/10	153	184

The membranes were next washed out with water and again subjected to a pressure of 350 kg per cm^2. They were tested with water alone without showing any signs of osmotic effects, after which they gave the following results:

TABLE 8

M/2 sugar solution

No. 9

The results of this portion of the experiment are without value because of the development of a leak in the cell. Through an oversight the work was not repeated.

No. 14

	Readings			Readings	
	Observed	Corrected		Observed	Corrected
8/4	0	9	8/10	—37	—28
8/5	—1	8	8/11	—39	—30
8/8	—29	—20	8/12	—39	—30
8/9	—34	—25			

M/1 sugar solution

No. 9

	Readings			Readings	
	Observed	Corrected		Observed	Corrected
6/16	—8	9	7/ 6	46	63
6/19	16	33	7/10	50	67
6/21	24	41	7/13	54	71
6/23	30	47	7/15	56	73
6/26	37	54	7/18	59	76
6/28	35	52	7/21	61	78
6/30	38	55	7/24	63	80
7/ 1	39	56	7/26	64	81
7/ 3	41	58	7/28	65	82

No. 14

	Readings			Readings	
	Observed	Corrected		Observed	Corrected
10/2	0	17	11/ 7	37	54
10/ 6	5	22	11/11	39	56
10/10	12	29	11/15	40	57
10/14	17	34	11/20	41	58
10/18	21	38	11/24	42	59
10/22	26	43	11/28	43	60
10/26	29	46	12/ 1	43	60
10/30	32	49			
11/ 3	35	52			

2 *M* sugar solution

No. 9

	Readings			Readings	
	Observed	Corrected		Observed	Corrected
8/ 2	1	32	7/30	99	130
8/ 5	7	39	10/ 4	101	132
8/ 8	13	44	10/10	107	138
8/11	19	50	10/18	117	148
8/14	25	56	10/28	131	162
8/23	39	60	11/ 7	143	174
8/30	52	83	11/17	152	183
9/ 9	70	101	11/28	164	195
9/13	78	109	12/ 5	169	200
9/22	95	126	12/ 9	160	191

No. 14

12/ 5	0	31	1/11	152	183
12/ 8	18	49	1/14	158	189
12/11	35	66	1/17	166	197
12/14	50	81	1/20	174	205
12/17	63	94	1/23	180	211
12/20	75	106	1/26	188	219
12/23	87	118	1/30	197	228
12/30	113	144	2/ 2	203[1]	234
1/ 2	124	155			
1/ 5	132	163			
1/ 8	143	174			

Sugar charcoal: For this work carbon was prepared from sugar by the following method which differs from that used in the preliminary work in that more care was taken to prevent the introduction of impurities and in the substitution of an alcohol burner for the gas burner used before. The

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[1] Further readings were impossible owing to the liquid sinking into the cell.

sugar was placed in a silica dish and thoroughly charred. The crusty mass was then removed and finely powdered in an agate mortar. It was returned to the silica dish and re-ignited, during which process it was constantly stirred with a platinum wire so that all parts of the mass were raised to a dull red heat. It will be recalled that the product obtained before was apparently impure as indicated by its analysis by the combustion method. The suggestion was made at that time that these impurities consisted of adsorbed oxygen and hydrogen. It seems impossible that other substances could be present. In the first place the original material used was a pure sucrose. During the process of carbonization it came into contact with nothing but pure silica, platinum and agate. Pure alcohol was used as the source of heat and the charred material was held at red heat for five to ten minutes, during which time it was so thoroughly stirred that all particles were exposed to the air. It is hardly probable that any organic decomposition products could have withstood the treatment. Since no inorganic matter was originally present, and from the precautions taken there was little likelihood of any being introduced during the manipulation, it seems safe to assume that the product finally obtained must have been in a high state of purity.

Two membranes were prepared from this material. The cavity in the cell was filled by sucking material through in a water suspension. The cake so formed was pressed and the pores clogged with a suspension of finer material. Much difficulty was encountered with these membranes and the above process had to be repeated many times before a membrane was obtained which gave signs of osmotic activity. The membranes were pressed, measured and tested with water alone and then with $M/1$ sugar solution on one side until osmotic effects were observed. No. 6 failed to show signs of such effects with approximate pore diameters of 1.976 microns and No. 11 with pores measuring 1.185 microns in diameter. The following figures were obtained with cells when the pore diameters had been reduced to 1.185 and 0.423 microns, respectively:

TABLE 9

M/2 sugar solution

No. 6

	Readings			Readings	
	Observed	Corrected		Observed	Corrected
3/3	0	9	3/10	23	32
3/4	13	22	3/12	25	34
3/5	15	24	3/13	26	35
3/6	16	25	3/15	27	36
3/7	19	28	3/16	27	36
3/9	21	30			

No. 11

	Readings			Readings	
	Observed	Corrected		Observed	Corrected
3/ 7	0	9	3/11	1	10
3/ 9	1	10			

M/1 sugar solution

No. 6

3/17	0	17	3/25	6	23
3/19	3	20	3/27	7	24
3/20	4	21	3/28	7	24
3/24	5	22			

No. 11

4/ 3	0	17	5/16	79	96
4/ 5	8	25	5/20	85	102
4/10	18	35	5/25	92	109
4/14	27	44	6/ 2	102	119
4/18	34	51	6/ 7	106	123
4/22	41	58	6/13	112	129
4/27	49	66	6/20	117	134
5/ 2	57	74	6/23	119	136
5/ 6	64	81	6/28	122	139
5/11	71	88	6/30	122	139

2 *M* sugar solution
No. 6

3/28	0	31	4/ 4	8	39
3/29	—2	29	4/ 5	10	41
3/30	0	31	4/ 6	12	43
3/31	0	31	4/ 7	14	55
4/ 1	2	33	4/ 9	17	48
4/ 2	4	35	4/10	17	48
4/ 3	6	37			

No. 11

	Readings			Readings	
	Observed	Corrected		Observed	Corrected
6/30	0	31	7/14	28	99
7/ 1	4	35	7/15	73	104
7/ 3	15	46	7/17	81	112
7/ 5	25	56	7/18	86	117
7/ 6	31	62	7/19	91	122
7/ 7	36	67[1]	7/21	103	134
7/ 8	38	69	7/22	102	133
7/10	51	82	7/24	102	133
7/11	55	86			
7/12	60	91			
7/13	64	95			

The cells were taken apart and the membranes washed out, clogged with fine material and again pressed at 350 kg per cm^2 for several hours. They then gave the results shown in the following tables:

TABLE 10
M/2 sugar solution
No. 6

	Readings			Readings	
	Observed	Corrected		Observed	Corrected
6/ 5	0	9	6/ 9	30	39
6/ 6	9	18	6/10	34	43
6/ 7	18	27	6/12	37	46
6/ 8	25	34	6/13	37	46

---

[1] Bath temperature rose 1° here.

No. 11

	Readings			Readings	
	Observed	Corrected		Observed	Corrected
8/12	0	9	11/ 5	105	114
8/14	4	13	11/11	110	119
8/23	15	24	11/17	116	125
8/30	21	30	11/24	120	129
9/ 9	33	42	11/29	125	134
9/18	45	54	12/ 5	128	137
9/30	62	71	12/11	133	142
10/ 6	69	78	12/17	137	146
10/12	77	86	12/22	140	149
10/18	85	94	12/24	142	151
10/24	92	101	12/31	146	155
10/30	99	108	1/ 3	142	151

M/1 sugar solution

	Readings			Readings	
	Observed	Corrected		Observed	Corrected
6/14	0	17	6/21	50	67
6/15	8	25	6/22	52	69
6/16	20	37	6/23	55	72
6/17	30	47	6/24	57	74
6/19	42	59	6/26	57	74
6/20	47	64			

No. 11

1/ 5	0	17	2/26	110	127
1/ 6	4	21	3/ 3	119	136
1/11	21	38	3/ 8	127	144
1/16	30	47	3/13	136	153
1/21	40	57	3/18	145	162
1/26	50	67	3/23	152	169
2/ 1	62	79	3/28	159	176
2/ 5	71	88	3/31	163	180
2/10	81	98	4/ 5	170	187
2/15	90	107	4/11	177	194
2/20	100	117			

2 *M* sugar solution
No. 6

6/26	0	31	7/ 7	138	169
6/27	18	49	7/ 8	146	177
6/28	34	65	7/10	162	193
6/29	50	81	7/11	170	201
6/30	62	93	7/12	177	208
7/ 1	94	125	7/13	184	215
7/ 3	97	128	7/14	191	222
7/ 5	118	149	7/15	200	231
7/ 6	128	159	7/17	214[1]	245

Flaky graphite: The flaky graphite used in preliminary work was subjected to much the same treatment in purification as was the "Aquadag." It was digested several times with HCl and with HNO_3, washed thoroughly after each digestion with hot water until free from acid and finally it was treated twice with HF. After washing and drying it analyzed as follows for loss on ignition:

a. 0.6409 g : 0.0001 g residue : 100.00% volatile
b. 0.7969 g : 0.0005 g residue : 99.95% volatile
Av. = 99.98% volatile

Owing to the small amount of material, only one membrane was made up. It was repeatedly pressed at 350 kg per cm^2 and tested for osmotic activity but showed none until the pore diameters had been reduced to 0.494 micron when it gave the following:

TABLE 11
2 *M* sugar solution

	Readings			Readings	
	Observed	Corrected		Observed	Corrected
2/22	0	31	3/ 8	3	34
2/28	1	32	3/12	4	35
3/ 4	3	34	3/14	4	35

Copper: The material for this work was at first purified by shaking out repeatedly with petroleum ether. It analyzed as follows:

0.2196 g subst.; 33.0 cc *N*/10 $Na_2S_2O_3$; 99.15% Cu.

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[1] Further readings impossible owing to level of solvent sinking into cell.

One membrane was made from it by pressing at 300–350 kg per cm^2 for approximately sixty hours. It showed pores having maximum diameter of 0.741 micron. When this membrane was set up with $M/1$ sugar solution on one side and the water and solution levels were equalized, the latter sank till a value of 0, corrected for density, was attained.

Subsequent pressings reduced the maximum pore diameters to 0.423 micron when it gave the following results with 2 M sugar solution:

TABLE 12

	Readings			Readings	
	Observed	Corrected		Observed	Corrected
3/ 4	0	31	3/10	10	41
3/ 5	3	34	3/11	11	42
3/ 6	5	36	3/12	13	44
3/ 7	6	37	3/13	13	44
3/ 8	7	38	3/14	13	44
3/ 9	7	38			

Later the impure copper powder was ignited and then reduced by heating in an atmosphere of hydrogen. This product analyzed as follows:

0.8689 g subst.; 1.0838 g CuO; 99.65% Cu

The following results were obtained with two of the membranes prepared from it by pressing at 350–400 kg per cm^2 for several days.

TABLE 13
$M/2$ sugar solution
No. 5

	Readings			Readings	
	Observed	Corrected		Observed	Corrected
3/15	−3	6	3/19	−6	3
3/16	−5	4	3/20	−7	2
3/17	−5	4	3/21	−7	2
3/18	−6	3			

No. 16

3/ 3	0	9	3/ 6	—7	2
3/ 4	—4	5	3/ 7	—7	2
3/ 5	—6	3			

M/1 sugar solution
No. 5

3/22	—8	9	3/25	—12	5
3/23	—10	7	3/26	—12	5
3/24	—12	5	3/27	—13	4

No. 16

3/ 8	—4	13	3/14	—14	3
3/ 9	—8	9	3/15	—14	3
3/10	—9	8	3/16	—16	1
3/11	—11	6	3/17	—16	1
3/12	—13	4	3/18	—15	2
3/13	—14	3	3/19	—15	2

2 *M* sugar solution
No. 5

3/28	16	47	4/ 1	32	63
3/29	24	55	4/ 2	33	64
3/30	28	59	4/ 3	33	64
3/31	31	62	4/ 4	33	64

No. 16

3/20	10	41	3/24	17	48
3/21	16	47	3/25	16	47
3/22	18	49	3/26	14	45
3/23	18	49	3/27	14	45

After washing, pressing, and saturating the membranes they were again set up in the cells. The following results were observed:

TABLE 14

M/2 sugar solution
No. 5

	Readings			Readings	
	Observed	Corrected		Observed	Corrected
4/12	0	9	4/14	8	17
4/13	10	19			

No. 16

4/12	0	9	4/14	4	13
4/13	5	14			

M/1 sugar solution
No. 5

4/24	0	17	4/26	10	27
4/25	7	24	4/27	9	26

No. 16

4/24	0	17	4/26	7	24
4/25	5	22	4/27	6	23

2 *M* sugar solution
No. 5

4/30	0	31	5/ 6	65	96
5/ 1	19	50	5/ 7	68	99
5/ 2	34	65	5/ 8	71	102
5/ 3	45	76	5/ 9	73	104
5/ 4	54	85	5/10	74	105
5/ 5	60	91	5/11	74	105

No. 16

4/30	0	31	5/ 6	60	91
5/ 1	16	47	5/ 7	63	94
5/ 2	30	61	5/ 8	66	97
5/ 3	42	73	5/ 9	68	99
5/ 4	50	81	5/10	69	100
5/ 5	56	87	5/11	70	101

Silver: The material was prepared by dissolving pure silver chloride in ammonia and precipitating with HCl. This process was repeated several times. The silver chloride was reduced as before. The resulting product was treated with ammonia to dissolve any unreduced salt and analyzed. It gave the following results:

0.4200 g subst.; 0.5574 g AgCl; 99.93% Ag

A membrane was prepared by pressing at 200 kg per cm^2 but failed to show signs of osmotic activity. It was alternately pressed at 350 kg per cm^2 and tested until the pore diameters were less than 0.329 micron. Their exact magnitude was undeterminable owing to the high pressure required to displace the water in the pores. The following results were observed:

TABLE 15

M/2 sugar solution

	Readings			Readings	
	Observed	Corrected		Observed	Corrected
6/14	0	9	6/17	—3	6
6/15	5	14	6/19	—7	2
6/16	0	9			
		M/1 sugar solution			
6/20	0	17	6/22	—6	11
6/21	2	19	6/23	—10	7
		2 *M* sugar solution			
6/28 9 A.M.	0	31	6/29	21	52
6/28 5 P.M.	17	48	6/30	14	45

The membrane was washed, pressed, and after testing with water, was again set up with sugar solution. It gave the following results:

TABLE 16

Silver membrane *M*/2 sugar solution

	Readings			Readings	
	Observed	Corrected		Observed	Corrected
7/13	0	9	7/15	15	24
7/14	26	35			
		M/1 sugar solution			
7/17 11 A.M.	0	17	7/18	8	25
7/17 5 P.M.	4	21	7/19	8	25
		2 *M* sugar solution			
7/24	0	31	7/27	28	59
7/25	6	37	7/28	31	62
7/26	19	50	8/ 1	25	56

Gold: The membrane giving the following results was prepared as previously described except that the rubber packing was replaced by paraffined filter paper. The material was purified as before. The membrane when formed weighed 13.5 g and was between 3 and 4 mm thick. Owing to the presence of one large pore which caused the formation of bubbles which interfered with the observations, the pore diameter measurements of this membrane were not made. The pore diameters were not greater than 0.984 micron however. The following results were noted:

TABLE 17

Gold membrane $M/2$ sugar solution

	Readings			Readings	
	Observed	Corrected		Observed	Corrected
3/ 3	0	9	3/ 6	3	12
3/ 4	1	10	3/ 7	3	12
		$M/1$ sugar solution			
3/15	0	17	3/17	—1	16
3/16	—1	16			
		$2\ M$ sugar solution			
4/ 1	0	31	4/ 7	8	39
4/ 2	4	35	4/ 9	9	40
4/ 3	6	37	4/10	8	39
4/ 4	6	37			
4/ 5	7	38			

The membrane was washed and again pressed at 200 kg per cm^2 for an hour and a half. The pores then were less than 0.912 micron in diameter. It gave the following results:

TABLE 18

$M/2$ sugar solution

No change in level. Corrected reading = 9 mm

$M/1$ sugar solution

	Readings			Readings	
	Observed	Corrected		Observed	Corrected
5/ 1	0	17	5/ 6	4	21
5/ 2	1	18	5/ 8	5	22
5/ 4	3	20	5/10	5	22
		$2\ M$ sugar solution			
5/10	0	31	5/13	5	36
5/12	3	34			

After another pressing which reduced the pore diameter to less than 0.591 micron, it gave the following results:

Table 19

M/2 sugar solution

	Readings			Readings	
	Observed	Corrected		Observed	Corrected
6/30	0	9	7/ 5	5	14
7/ 1	2	11	7/ 6	5	14
7/ 3	4	13			
M/1 sugar solution					
7/ 6	0	17	7/ 8	5	22
7/ 7	4	21	7/10	6	23

2 *M* sugar solution

No change in level. Corrected reading = 31 mm

Discussion

The above results are summarized in the Table 19 which contains the maximum observed readings. They possess only a rough quantitative value since in many cases the maximum possible reading was not obtained because the rate of change became too slow to warrant the expenditure of time necessary for the cell to reach equilibrium. In a general way, however, the figures are comparable. In case results are cited with two different membranes, the fact is indicated by the headings Cell A and Cell B. As was previously stated, the general method of conducting the experiments from which these results were obtained was as follows:

When the membrane had been pressed it was set up with water on both sides. If no change in the levels of the liquid resulted the water on one side was replaced with *M*/2 sugar solution. The resulting reading is that given in column *a* under *M*/2 sugar solution. The cell was next taken apart, the faces of the membrane washed off with distilled water and the cell set up with *M*/1 sugar solution in place of the *M*/2 solution. The reading thus obtained is recorded in column *a* under the corresponding sugar solution. The same procedure was followed in obtaining the *a* reading for the 2 *M* solution. When this last reading had been taken, the cell was taken apart and the membrane washed out by forcing distilled water through it, after which it was pressed as indicated in the descriptions of the various experiments. It was then again set up with water on both sides and, if no change in level occurred, put through the same procedure as above, giving the values recorded in the *b* columns. Thus the readings in columns *a* and *b* with any one membrane indicate the results obtained with this membrane before and after reducing the diameters of its pores. In other words, the *b* readings represent the results with membranes having pores of smaller diameters than the membranes giving the corresponding *a* readings but differing from them in no other respect.

TABLE 20

Preliminary Experiments

Solution	SiO_2	Tech. graphite	"Aquadag"	Sugar carbon	Flaky graphite	Copper	Silver		Gold				
							a	*b*	*a*	*b*	*c*	*d*	*e*
M/2 sugar	—	—	—	—	—	—	—	—	–	—	—	13	14
M/1 sugar	28	25	58	86	35	20	10	28	6	11	197	32	17
2 *M* sugar	—	—	—	—	110	35	—	—	–	—	—	68	103

Final Experiments

Solution	Cell A						Cell B					
	M/2 sugar		*M*/1 sugar		2 *M* sugar		*M*/2 sugar		*M*/1 sugar		2/*M* sugar	
	a	*b*	*a*	*b*	*a*	*b*	*a*	*b*	*a*	*b*	*a*	*b*
Silica	23	65	72	202	110	308+	66	—	113	—	267+	—
"Aquadag"	16	—	85	—	200	—	—37	—30	28	60	184	234
Sugar carbon	36	46	24	74	48	245	10	155	139	194+	133	—
Flaky graphite	12	—	25	—	—	—	—	—	—	—	—	—
Copper	6	19	9	27	64	105	9	14	13	24	49	101
Silver	14	35	19	25	52	62	—	—	—	—	—	—
Gold	12	9	17	22	40	36	—	—	—	—	—	—

Bearing of the Results on the Cause of Osmosis and the Function of the Semipermeable Membrane

In the review of the literature given in the first pages of this article the theories concerning the cause of osmosis may be divided into comparatively few classes, namely those attributing osmosis to.

1. A difference in the surface tension of solvent and solution.
2. A difference in the solubility of the solvent and the solution in the membrane.
3. An attraction of the solute molecules for the solvent molecules.
4. The so-called kinetic theory.
5. A difference in the vapor pressures of the solvent and solution.
6. A chemical reaction between the membrane, solvent and solution.
7. A difference in electrical potential between the opposite faces of the membrane.

The advocates of these theories and their various modifications advanced them as applying to osmotic phenomena in general and, if later, certain exceptions were found for any one theory, that theory was thrown into more or less disrepute. The main endeavor of investigators has been to find *one* theory to explain omosis, by osmosis being meant the flow of one liquid through a membrane permeable for it, into another liquid, for which the membrane is less permeable, until a certain difference in hydrostatic pressure is produced on opposite sides of the membrane. Yet the conditions under which "osmosis" takes place differ greatly in different experiments.

Thus, membranes range from a layer of liquid to a layer of solid such as metallic gold or unglazed porcelain and include rubber, parchment and various other animal, vegetable and inorganic membranes. The liquids used in producing osmosis vary as widely in character. When these things are considered it seems improbable that the phenomena in question should all be traceable to a single cause. It is more probable that we are dealing with several which manifest themselves in the same way, *i. e.*, in causing a transference of liquid through the membrane. Nor is this contrary to experience. In a "three-liquid layer" experiment for instance, the force is undoubtedly the difference in the "attraction of solution" between the liquids involved. The corresponding result may be brought about with a porous wall and two solutions under the influence of an electric current, *i. e.*, in electric osmose. Yet in the latter case we have no "attraction of solution" between the liquids and the membrane. In the case of sugar solution and water separated by a membrane of unglazed porcelain we have but little evidence of either of these forces being operative. The difference between ordinary osmosis and electrical osmose is that in the former the energy is derived from the system itself while in the latter it comes from an external source. That this same kind of energy may also be developed internally for the production of strictly analogous phonomena is fairly evident from Bartell's work on "negative osmose."[1]

If we grant then that "attraction of solution" may produce osmosis in a three-liquid layer experiment and difference in electrical potential may produce it in either electrical osmose or "negative osmose," we have differentiated "osmose" into at least two phenomena and, unless we conceive of "solution" as the filling of membrane pores of capillary dimensions with the liquid, we must apparently admit the existence of still a third class of osmotic phenomena obtainable with aqueous solutions of sugar, water and membranes of the inert materials used in the present work. Many of the various theories advanced appear plausible under certain circumstances and the fact that they are not always so should not cause their complete rejection. For instance, the relationships between surface tension and osmotic effect pointed out by Traube[2] seem too consistent to be attributed to coincidence and their significance should not be entirely denied because Barlow[3]

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[1] Jour. Am. Chem. Soc., 36, 646 (1914).

[2] Phil. Mag., (6) 8, 704 (1904).

[3] Ibid., (6) 10, 1 (1905).

later found them incapable of universal application. It is quite conceivable that difference in surface tension should under some circumstances produce liquid movements across a diaphragm but it is quite unnecessary to conclude therefrom that all such movements are due to this cause. It is equally absurd to postulate that since this explanation is not always tenable it is never so. It seems fairly obvious therefore that osmosis may be due not to one but to a variety of causes.

Nevertheless, several of these groups of theories which ascribe to the membrane an active role in the phenomena of osmosis and which are apparently at first sight irreconcilable, prove to be, upon closer scrutiny, very closely related to each other.

According to these theories osmosis takes place:

1. Through capillary spaces in the membrane,
2. By the solution of the solvent in the membrane, and
3. By the formation of a labile chemical compound between the membrane and the solvent.

That osmosis can take place through capillaries, as distinguished from molecular interstices, seems probable from the fact that it has been observed to occur when two liquids are in contact only through fine cracks in glass tubes,[1] through the pores in unglazed porcelain, through the various membranes described by Tinker[2] and through those used in the experiments reported in the present article. The limits of these pore diameters between which osmosis can take place are not definitely known but Bigelow and Bartell[3] and Bartell[4] have shown that with unglazed porcelain clogged with various materials the upper limit seems to be about 0.9 micron, a figure much too large to represent the dimensions of molecular interstices. This work has been corroborated by Tinker[5] and is in agreement

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[1] See in this connection, Fischer: Pogg. Ann., 10 481 (1827); Dutrochet: Ann. Chim. Phys., 35, 383 (1827); 49, 411 (1832); Brucke: Pogg. Ann., 58, 77 (1843).

[2] Loc. cit.

[3] Jour. Am. Chem. Soc., 31, 1194 (1909).

[4] Jour. Phys. Chem., 15, 318 (1911); Dissertation, Univ. of Mich., 1910.

[5] Loc. cit.

with that of Draper[1] on osmosis as applied to gases. That the lower limit may be of the dimensions of molecular interspaces is equally certain from the results of various investigators who have used the three-liquid layer arrangement, and in these cases there is certainly a solution of the liquids in the membrane.

The validity of the last of the three suggestions, namely the formation of a labile chemical compound between the membrane and the solvent, has not been so certainly demonstrated. It is however a possibility as will appear later.

As has been pointed out by Bigelow,[2] these views have always been held to be "mutually exclusive," although this was not at all necessary and in reality it is possible to bring them all into harmony. He showed that "the rate of passage of liquids through molecular interstices is expressible by the same laws which formulate the rate of passage of liquids through capillary tubes," thus affording experimental proof that there is no essential difference between capillaries and molecular interstices in this respect. Theoretically, interspaces of all dimensions from macroscopic capillaries down to infinitely small interstices are capable of existence. All phenomena which result from forces inherent in such interspaces should also manifest themselves and furthermore in a continuous fashion except as they may be influenced by certain secondary factors. There is really no basis for assuming that between the pores of solid membranes of capillary structure on the one hand and the molecular interspaces of liquid membranes on the other there exists a region of osmotically inactive spaces. It is far more logical to suppose that osmotic phenomena with the membranes are but extremes of one and the same process. From this it follows that there is no sharp line between the changes occurring in ordinary capillaries and in intermolecular interstices.

Furthermore, it is entirely conceivable that in the latter category may be included the formation of certain chemical compounds such, for instance, as certain so-called molecular

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[1] Jour. Franklin Inst., 17, 177 (1827).

[2] Jour. Am. Chem. Soc., 29, 1690 (1907).

compounds. Some investigators, while apparently realizing this, have failed to apply it to the phenomena in question with the possible exception of Lhermite.[1] Thus Graham[2] admits "that chemical affinity of the lowest degree may shade into capillary attraction" and Fitzgerald[3] states that "When we come to deal with really molecular magnitudes it is impossible to draw a hard and fast line between physical and chemical permeability." For many years there has been accumulating in chemical literature, evidence in support of this view in the tendency to class solution processes with chemical reactions and many investigators have pointed out that some of the criteria of the formation of true chemical compounds apply equally well to certain of these processes.

It appears evident, therefore, that there may not be such an impassable gulf between the capillary, solution and chemical theories of the membrane function as their respective advocates have believed.

Effects of Various Factors on the Efficiency of Osmotic Membranes

As mentioned above, the experiments described in the present report demonstrate conclusively that osmotic pressure can be obtained through the action of capillary attraction alone without the aid of either solution or chemical action. Theoretically, a certain solution tendency must be ascribed to all metals, even including metallic gold, but it is scarcely conceivable that such solubility effects could produce osmotic pressure and this conception is still more difficult in the case of carbon which apparently differs in no way from the other materials as regards its action as an osmotic membrane. From these considerations, ordinary solution effects may be excluded as the universal cause of osmosis.

Effect of the size of the pore diameters: If, then, in certain cases, the manifestation of osmotic pressure is de-

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[1] Loc. cit.

[2] Phil. Trans., 151, 222 (1861).

[3] Jour. Chem. Soc., 69, 897 (1896).

pendent upon the discontinuous state of the membrane, it would seem to be a necessary consequence that the magnitude of the results should increase with the decrease in the diameters of the pores of the membrane until these diameters became so small as to offer resistance to the passage of the molecules of the liquid. Assuming for the moment that all the pores in the membrane have the same diameter, it would be expected that, with pores of larger diameters than those at which the molecules of the liquid meet with resistance in their passage through the membrane, both the magnitudes of the results obtainable and rates of flow of liquid would continue to increase with decrease in the pore diameters, but that, when these pore diameters became small enough to offer resistance to the passage of the liquid, the rate of flow of the liquid would diminish. Finally a point would be reached at which the membrane would become impervious to the liquid. At this point the magnitude of the osmotic effects would reach a maximum but the velocity at which this maximum would be reached would be infinitely small. On the other hand, if the pores of the membrane are not all of the same diameter, a condition which, of course, is the one existing in the membranes used in the present work, the results obtained would represent the resultant of the action of pores ranging in diameter from those just small enough to give osmotic effects to those giving the maximum effects. When the membranes are pressed or the pores clogged the number of pores capable of giving osmotic effects is increased and the diameters of those already showing osmotic activity are decreased, with the result that the total magnitude of the osmotic effect is at first increased. As the process is carried further, however, more and more pores will become impervious to the liquid while these still permeable will permit only a slow passage of liquid and thus a gradual decrease in the observed effect will result. In brief then, as the diameters of the pores of a membrane are progressively decreased we should expect the osmotic pressure produced to increase to a maximum and then decrease to nil as the membrane finally becomes impervious to the liquid.

In Table 19 it will be observed that in practically all cases the *b* reading is larger than the corresponding *a* reading. Since, between the taking of these two readings, the membranes were pressed and in some cases clogged with fine material, it may be safely assumed that the *b* readings were made with membranes having smaller pores than those giving the corresponding *a* readings. Apparently then, for the ranges of pore diameters in these experiments, osmotic activity does increase with a decrease in pore diameters.

That the osmotic pressure finally reaches a maximum and then decreases is indicated by the results obtained with the gold membrane used in the preliminary experiments with which successive compressions of the membrane caused it to give osmotic pressures of 6, 11, 197, 40 and 25 mm. respectively. It is possible that this accounts for the small effects noted with the second gold membrane which was prepared and used in the later work. This membrane was subjected to somewhat higher pressures than was the former one and appeared to be much denser. The same is true of some copper membranes prepared for the second series of experiments. These results are substantiated by the actual measurements of the pore diameters.

It must be distinctly understood, however, that the importance of the pore diameter measurements in this work must not be overestimated. The values given represent only the diameters of the largest pores and these constituted but a small proportion of the total number in the membrane. The following table shows the smallest of these maximum values at which positive effects were obtained with the various materials:

TABLE 21

Material	Pore diameter	Material	Pore diameter
Silica	0.349 micron	Copper	0.423 micron
Aquadag	0.593 micron	Silver	0.329 micron
Sugar carbon	0.423 micron	Gold	0.984 micron
Flaky graphite	0.494 micron		

But whatever the actual sizes of the largest pores which exhibit osmotic activity, the first effect of reducing their sizes is to cause an increase in the osmotic pressure produced by them.

Effect of the chemical composition of the membrane: This factor is perhaps the most important one from the standpoint of this investigation, since its study was the original aim of the work herein described. The results obtained show, as do those of Bigelow, Bartell, and Tinker that there is a relation between the physical condition of the membrane and the osmotic effects obtained, but that the influence of the chemical composition of the membrane is, at most, of secondary importance. They also show that chemical reactions, in the ordinary sense of the term, between the membrane and the liquids bathing it are certainly not the only deciding factors in the manifestation of osmotic phenomena. The results with silica are perhaps inconclusive because of its tendency to combine with water to form silicic acid and because its well known colloidal properties may make possible certain complications. Such considerations however, seem scarcely applicable to metallic gold and silver and to carbon, all of which apparently differ in no way from each other and from other materials as regards their action as osmotic membranes. The very universality of the ability of substances to act as semipermeable membranes argues against this property being due entirely to the chemical constitution of these substances. It seems to be a property more colligative than constitutive in its nature.

Effect of concentration of the solution: A study of Table 19 shows that, as would be expected, the magnitude of the observed osmotic effects increases with an increase in the concentration of the sugar solution, other factors, of course remaining constant. In some cases, however, surprisingly large values were noticed with the 2 *M* solution as compared with the other two. While an increase would be expected, such a distinct difference in behavior of two solutions as concentrated as *M*/1 and 2 *M* was rather surprising. It may be that this is a scrap of experimental evidence in support of those theories which postulate that the size of the liquid units in solution exceed those in the pure solvent and are responsible in some cases, for the phenomena of osmosis.[1] This suggestion assumes an added importance in the light of the work of deBruyn and Wolff[2] whose results indicate that concentrated sugar solutions exhibit some of the properties of colloidal solutions, notably the Tyndall effect. Inasmuch as the particles which produce such effects are usually considered to exceed molecular dimensions *i. e.*, to consist of molecular aggregates, it may be concluded that in such concentrated solutions we are dealing, not with single molecules of water and of sugar, but with masses consisting either of sugar molecules alone or of sugar molecules which have attracted to themselves water molecules to form a hydrated complex.

These statements are offered merely as suggestions since obviously the experimental data are altogether too scanty to permit positive conclusions being drawn.

Summary

The results of the investigations reported in this paper may be briefly summarized as follows:

1. A method and apparatus have been devised for the study of osmotic phenomena with membranes of powdered materials.

2. Osmotic effects have been obtained with materials which have heretofore never been used successfully for this purpose, *viz.*, silica, amorphous carbon, graphite and metallic copper, silver, and gold.

3. The results of other investigators indicating that the magnitude of osmotic effects increases with a decrease in the diameters of the pores of the membrane have been corroborated.

4. It has been demonstrated that osmotic pressure can be produced through the agency of capillary forces alone without the aid of solution processes or chemical reactions.

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[1] See in this connection references to work of Pickering and of Poynting on pages 3 and 4, respectively.

[2] Rec. Trav. chim. Pays.-Bas., 23, 155 (1904).

Acknowledgments

In conclusion the writer wishes to express his gratitude to Professor S. L. Bigelow for his interest in the work and for many helpful suggestions in overcoming the numerous difficulties which were met with; to Professor F. E. Bartell for his kindly advice regarding certain phases of the work, and to the C. M. Warren Committee of the American Academy of Arts and Sciences for financial assistance.

ACETONE AND LIME

BY M. E. FREUDENHEIM

When calcium acetate is heated alone, the reaction takes place chiefly as in the equation

$$Ca(CH_3CO_2)_2 = CaCO_3 + CH_3COCH_3.$$

When calcium acetate is heated with an excess of lime the reaction takes place chiefly according to the equation

$$Ca(CH_3CO_2)_2 + Ca(OH)_2 = 2CaCO_3 + 2CH_4.$$

From this it would seem to follow that when acetone is passed over heated lime, we should get the reaction

$$CH_3COCH_3 + Ca(OH)_2 = CaCO_3 + 2CH_4.$$

If this reaction does not take place the acetone is not an intermediate product in the second equation.

Hoffman[1] obtained mesityl oxide by heating acetone with CaO in an extraction apparatus. The temperatures used were from 60° to 100° and if he did obtain any gaseous products he did not consider them. P. N. Raikow[2] placed acetone and lime in a flask and let them stand for 10 days. He obtained mesityl oxide and phorone. Since these experiments were done at too low temperatures to prove anything in regard to the reaction between acetone and heated lime, I took up the study of this problem as my senior research work under Professor Bancroft.

When work was first started the apparatus consisted simply of a distilling flask filled with acetone heated in a water bath. The outlet of the flask was connected to a combustion tube containing slaked lime and the other end of the combustion tube was connected to the sample bottle. Various difficulties kept coming up which necessitated changes in the set-up until that shown in the diagram resulted. This has proven very satisfactory and with it all the data given here have been obtained.

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[1] Jour. Am. Chem. Soc., 31, 722 (1909).

[2] Chem. Ztg., 37, 1455.

About 300 cc of acetone were run into the distilling flask. This was heated by means of a hot plate and the flask and plate were wrapped with asbestos board to ensure more even heating. The flow of vapor into the combustion tube was regulated by stopcock (1), (Fig. 1). Since this was but partially open there was a "piling up" of pressure in the flask. On account of this pressure a considerable "head" was necessary to replenish the acetone in the flask, as I did not wish to interrupt the run by cooling the flask. Accordingly, a reservoir was put up which gave a pressure of about six feet of acetone. This was very satisfactory and the flask could be replenished under all conditions. This excess pressure in the distilling flask would also become so great at times (seldom however) as to blow the stopper out. If a non-flexible tube were used to connect the flask to the reservoir this "blow out" would wreck the reservoir. Hence a spring made of glass tubing was inserted in the connecting line. Rubber could not be used, due to the solvent action of the acetone on it.

At the start of the experiment the apparatus was of course filled with air, the greatest volume of which was in the flask. To get rid of this cocks (1) and (3) were closed and cock (2) opened, current turned on and the acetone boiled. The vapor passed through cock (2), the condensing coil, and into the small flask. When no more bubbles were seen in the coil or tube leading to the small flask all the air was out of the still.

A standard 27″ laboratory combustion furnace was used with a 45″ tube of Jena glass. A long tube was used in order to avoid contamination from the rubber stoppers. These were faced with cork washers and the ends of the combustion tube were wound with wet rags at these places. At the ends of the inlet and outlet tubes in the combustion tube tufts of glass wool were inserted to keep out any particles of lime which might be blown in and clog the tube. Between 40 and 50 grams of $Ca(OH)_2$ were placed in the combustion tube before each run. The temperature of the combustion could be read by means of the pyrometer.

From the combustion tube the gaseous and volatile products passed through cock (5) and into the cylinder (A). This was so connected up that in event of any suction in the tube gas and not liquid would return. Cylinders (A) and (B)

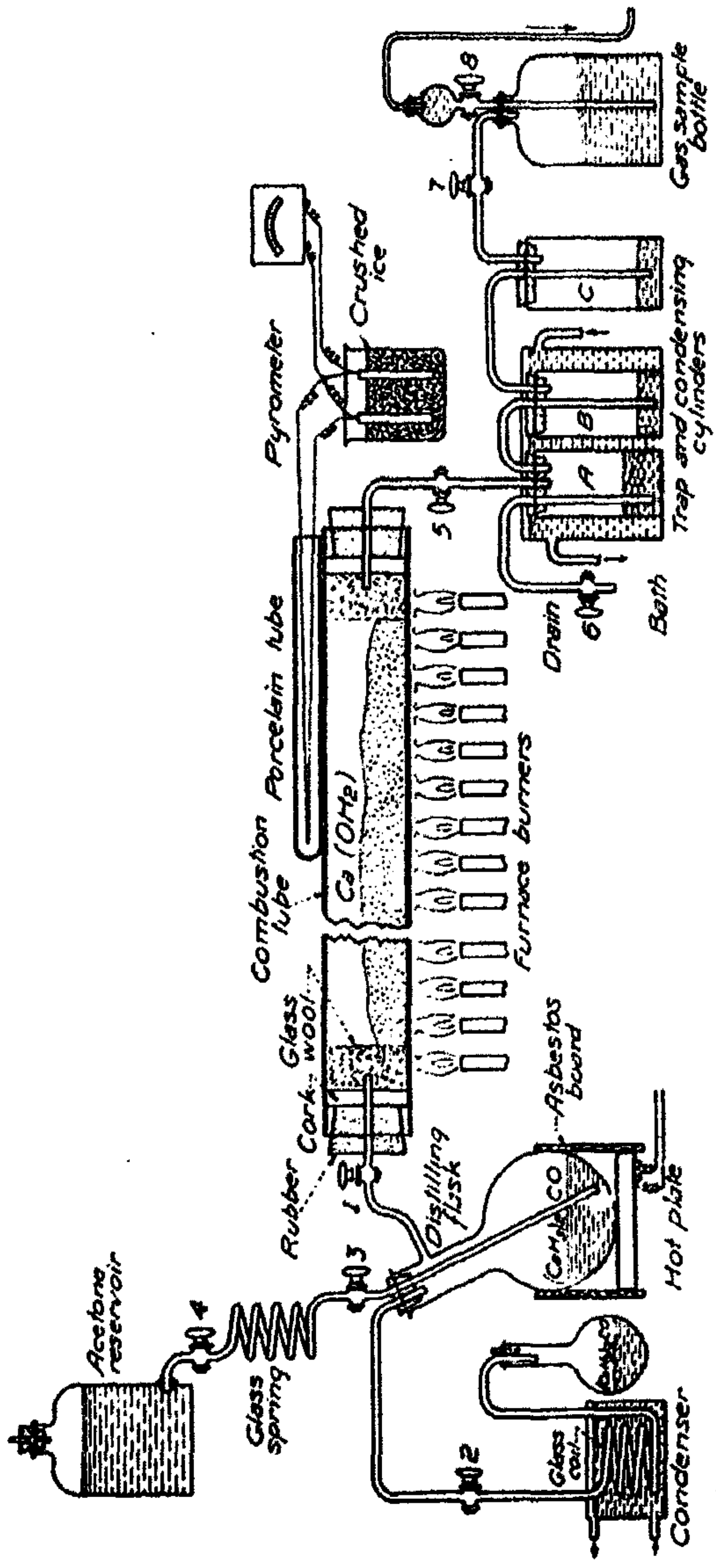

Fig. 1

were water-cooled and took out practically all of the volatile products. Cylinder (C) was for the same purpose but there was practically no condensible matter left at that point. Cylinder (A) was provided with a drain so that as it filled, the products could be forced out by closing cock (7) and opening cock (6). From (C) the gas passed into the sample bottle where it was trapped over water by simply closing cocks (8) and (9). These sample bottles were calibrated so that the rate of gas evolution could be measured.

Procedure

To make a run with apparatus described in the preceding pages the following procedure was used: With the still closed off from the combustion tube by means of cock (1) the furnace was started low to avoid cracking of the tube by sudden heating and then gradually run up till the desired temperature was recorded by the pyrometer. During this cocks (5) and (7) are open so that the gas expansion caused no internal pressure. Now with the still one-fourth full of acetone, cocks (1) and (3) closed and cock (2) open the hot plate was started and the acetone brought to boiling. The vapor passed through the condenser and when no bubbles could be seen in the coil cock (1) was opened sending the acetone through the combustion tube and cock (2) closed. The still was replenished as needed from the reservoir by opening cocks (3) and (4).

The gaseous products were allowed to exhaust into the air for from 15 minutes to one-half hour so that all the air was swept out of the combustion tube, traps, and condensers. Samples were now taken at stated intervals in bottles as shown in the diagram.

Cylinder (A) was drained as necessary.

The samples obtained were analyzed in the following order:

CO_2 KOH pipette
Oleofines $H_2S_2O_7$ pipette and KOH pipette to absorb acid fumes
O_2 alkaline pyro pipette.

CO first an old and then a new acid cuprous chloride pipette + KOH pipette

CH_4 and H_2 by combustion with O_2

CH_4 = CO_2 taken up by KOH

H_2 = two-thirds (total contraction, $2CH_4$)

These analyses were correct to ±0.4 percent.

When all the desired samples had been taken the heat was shut off, the apparatus allowed to cool and then cleaned and the reagents replenished.

Using the foregoing apparatus and procedure three classes of products were obtained. These were:

(1) In the combustion tube $CaCO_3$ and C were left in the form of black lumps. The carbon deposition varied with the temperature being slight at low temperature and very heavy at high temperatures.

(2) Liquid products (of a yellow color) which were condensed in the cylinders. The greatest portion of this was acetone since an excess was continually being passed through the tube.

(3) Gaseous products—consisting of CH_4, H_2, CO, olefines, traces of air and CO_2—the ones with which we are concerned in this experiment and the only ones considered.

The rate of evolution of the gases was dependent on the temperature of the experiment and on the length of a run. As shown in some tables which follow the higher the temperature the more rapid the formation of the gases and the longer the run the less rapid the formation of the gases. This last is explained by the fact that the charge in the combustion tube is gradually being converted to $CaCO_3$ and C. The first is what we would naturally expect since heat as a general thing increases the reaction velocity.

Analyses of the samples obtained at the same temperature were fairly constant, all things considered. Samples taken from 1 to 2 hours after the acetone vapor had been started through the combustion tube analyzed practically the same. A slight amount of air in the apparatus made a great difference in the results. In the course of a run there was a slight tendency for the H_2 content to drop off and the

CH_4 content to increase. Here is a typical set of analyses showing this and the variation in rate.

Sample No.	1	2	3	4
CH_4	29	30	32	34.7
H_2	48.5	39.4	39.4	38.6
Rate cc/min	140	100	8.5	70

These are data from a run made at 550°. The CO and olefine content remained practically constant around 16 percent and 4 percent, respectively. These samples were taken every one-fourth hour, as was done in the majority of cases for from 1 to 2 hours. In a few runs samples were taken every one-half hour over the same period. This is the period of even decomposition. Samples taken later were given off at a very slow rate and their analyses varied over a wide range.

The following table is really a summation of the results. These values were obtained by averaging the analysis of samples obtained during the second hour of the run. The same values were obtained—within 1 or 2 percent in the case of H_2 and CH_4 and 0.5 percent for CO and olefines—by averaging all the analyses made on all the samples taken during a run or runs at a definite temperature.

Temperature	% CH_4	% H_2	% CO	% olefines	Rate of evol. cc/min.
350°	9.5	78	0	< 1	5
450	20.8	67	2.5	2	30
530	31	45	10	5	140(?)
550	32	40	16	4	110
600	36	30	17	4	150
630	54	10	23	5	170

These data are shown graphically in Fig. 2. There are two distinct points to be accounted for. One is the increasing formation of carbon monoxide and ethylene at high temperatures and the other is the fact that hydrogen is relatively so important a product at low temperatures and is relatively so unimportant at high temperatures. The first point is quite simple. Schmidlin and Bergman[1] passed acetone vapor through a glass tube filled with pieces of earthenware and heated to 500°–600°. They obtained 10–15 percent yield of keten, according to the equation

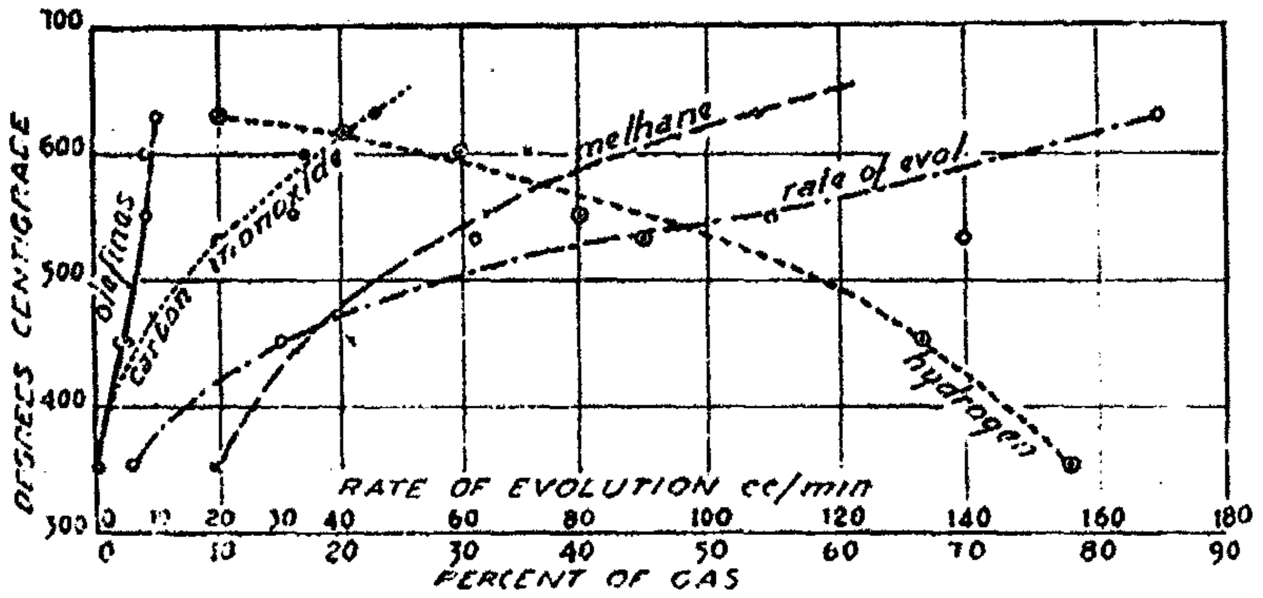

Fig. 2

$$CH_3COCH_3 = CH_4 + CH_2CO.$$

At higher temperatures the keten decomposed into carbon monoxide and ethylene.

$$2CH_2CO = 2CO + C_2H_4.$$

Barbier and Roux[2] obtained a similar decomposition by passing acetone vapor through a copper tube heated to 1000°.

$$2CH_3COCH_3 = 2CH_4 + 2CO + C_2H_4.$$

We may also get carbon monoxide through dissociation of acetone,[3] according to the equation

$$CH_3COCH_3 = CH_4 + CO + C + H_2.$$

By assuming a judicious combination of these two reactions with the normal one, it is possible to account for the relative amounts of methane, carbon monoxide, and ethylene in any of the experiments.

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[1] Ber. deutsch. chem. Ges., 43, 2821 (1910).

[2] Bull. Soc. chim. Paris, (2) 46, 268 (1886).

[3] Nef: Liebig's Ann., 318, 19 (1901).

It is more difficult to account for the production of hydrogen and methane alone at 350°. There is one point to be mentioned first about the hydrogen curve. Although the percentage of hydrogen in the gas mixture decreases with rising temperature from nearly eighty percent at 350° to about ten percent at 650°, the rate of evolution of hydrogen increases with rising temperature. Since the total evolution of gas at 350° is about 5 cc/min., the rate of evolution of hydrogen is about 4 cc/min. At 650° the total evolution is at a rate of 170 cc/min. which corresponds to a hydrogen evolution of about 17 cc/min., over four times the rate at the lower temperature. There are several possible ways of accounting for the evolution of hydrogen without any carbon monoxide; but they are all unsatisfactory. One would like to assume that acetone behaved like an alcohol and split off hydrogen to some extent under the catalytic action of heated lime; but then we ought to name the other product. It would be nearly hopeless to look for a small amount of liquid product in the condensed portion because that contains so much acetone and the condensation products of acetone. I have also been unable to get any organic chemist to make any prediction as to what the hypothetical product might be. Another suggestion that has been made is that the lime retains some of the carbon monoxide as formate which might perhaps be stabilized somewhat by the presence of an excess of acetone; but the curves for hydrogen and carbon monoxide do not offer any encouragement for this view. Diels and Meyerheim[1] obtained some carbon suboxide, C_3O_2, by treating malonic acid with phosphorus pentoxide.

$$CH_2(CO_2H)_2 = C_3O_2 + 2H_2O$$

but there is nothing to warrant the belief that lime causes acetone to break down into hydrogen and either a new carbon suboxide or into carbon suboxide plus carbon. When sodium acetate is electrolyzed in aqueous solution, the anode products may be ethane and carbon dioxide.

$$2CH_3CO_2 = C_2H_6 + 2CO_2.$$

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[1] Ber. deutsch. chem. Ges., 40, 355 (1907).

In presence of sulphates, chlorates, or carbonates, methyl alcohol and carbon dioxide may be formed in nearly quantitative amounts, apparently according to the equation

$$CH_3CO_2 + OH = CH_3OH + CO_2.$$

It is conceivable, though not very probable, that a reaction takes place.

$$2CH_3COCH_3 + CaO_2H_2 + 2H_2O = (CH_3CO_2)_2Ca + 2CH_3OH + 2H_2.$$

As a matter of fact, there is no satisfactory explanation as yet for this evolution of hydrogen. A similar phenomenon apparently occurs when sodium acetate is heated with soda-lime, because Gill and Hunt[1] report that the methane may contain up to ten percent hydrogen.

Regardless of where the hydrogen may come from, it may be asked why it does not increase relatively with rising temperature. One possible answer is that the other reactions have much higher temperature coefficients; but the more satisfactory answer is that the hydrogen is probably used up more and more as the temperature rises, reducing some of the excess acetone to isopropyl alcohol. The reason for this belief is that Mr. Engelder has since passed acetone vapor over heated nickel and obtained isopropyl alcohol together with a precipitation of carbon. The time at my disposal did not permit of my clearing up the question of the hydrogen much as I should otherwise have liked to.

The following conclusions may be drawn from this work:

1. When acetone is passed over lime heated to 650°, the chief gaseous product is methane.

2. There is nothing, therefore, to prevent acetone from being an intermediate product when calcium acetate and lime are heated together.

3. The presence of carbon monoxide may be due in part to the dissociation of acetone into methane, carbon monoxide, carbon, and hydrogen.

4. The presence of ethylene is probably due to the dis-

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[1] Jour. Am. Chem. Soc., 17, 986 (1895).

sociation of acetone into methane and keten, the keten breaking down into carbon monoxide and ethylene.

5. At 350° the gaseous products are nearly eighty percent hydrogen and about twenty percent methane. There is no really satisfactory explanation for this hydrogen formation.

6. It is known that hydrogen is also set free when sodium acetate is heated with soda-lime.

7. When acetone is passed over lime heated to 350° relatively little carbon is formed. At higher temperatures the amount of carbon increases rapidly.

8. When acetone is passed over heated nickel, a good deal of carbon is precipitated and some of the excess acetone is reduced to isopropyl alcohol.

9. It is probable that isopropyl alcohol is also formed when acetone is passed over heated lime; but no tests have been made.

10. Although the percentage of hydrogen in the gas mixture decreases very rapidly with rising temperature, the rate of evolution of hydrogen increases with rising temperature from about 4 cc/min. at 350° to about 17 cc/min. at 650°.

Cornell University

POTENTIAL MEASUREMENTS ON THE COPPER-NICKEL SERIES OF ALLOYS, AND SOME OBSERVATIONS ON BRASSES

BY NEWELL T. GORDON AND DONALD P. SMITH

The present experiments are a continuation of the study of the factors affecting the potential difference between a binary (solid) alloy and an electrolyte containing the corresponding ions, with regard to which a preliminary publication was recently made.[1]

With the extension of the experiments upon copper-zinc alloys from the single ingot previously discussed to a much larger number of samples, and particularly with prolongation of the time during which each sample was kept under observation, from a few hours to many days, it developed that no treatment which could be employed was sufficient to insure, with the alloys of this series, the desired degree either of reproducibility or of constancy in the "steady" potential finally attained. The account of these experiments will therefore be deferred until after the discussion of those made upon the copper-nickel alloys, in which a system was found remarkably free from the accidental variations shown by the brasses.

The System Copper-Nickel

The copper-nickel ingots were prepared from electrolytic copper and the best grade nickel in finely divided form. The weighed portions of the two metals sufficient to make about twenty-five grams of alloy were thoroughly mixed, introduced into a porcelain crucible of test-tube form about one centimeter in diameter, covered with borax, and melted in a carbon resistance furnace of the Tammann type. After the melt had been well stirred for some time with a porcelain rod it was allowed to cool in the furnace. The ingot was then inverted in the crucible and again fused and stirred under borax. Upon the second solidification the alloy was obtained in a state highly homogeneous and free from oxide, as was confirmed by microscopic examination. From this ingot small bars 2 × 2 × 5 mm were sawed longitudinally and then cut transversely into halves. The end surfaces produced by this last cut constituted portions of horizontal planes through the middle of the ingot, and were the ones later exposed to the action of the electrolyte.

The composition of each ingot was determined by analyzing the middle portions of some of the small bars not employed for potential measurements. To this end copper was deposited electrolytically from sulphuric acid solution, while the nickel was in most cases found by difference. In several instances however, the result was controlled by rendering the solution alkaline with ammonia, after the removal of the copper, and depositing the nickel also electrolytically. The errors of analysis, and those due to differences of composition between the samples analyzed and those taken for experiment, may be taken together as not over 0.3 percent in the composition of the alloy. The six ingots prepared had, respectively, 6.8, 10.9, 65.5, 74.3, 83.4, and 94.7 percent by weight of copper.

Each test-piece was annealed in a close-fitting, hard glass tube which was three times filled with nitrogen and evacuated, and finally sealed when the pressure of nitrogen equaled approximately 160 mm of mercury. Commercial nitrogen, which had been freed from oxygen by means of copper and an ammoniacal solution of ammonium carbonate, in an apparatus similar to that described by Van Brunt,[2] insured bright annealed test-pieces exhibiting no evidence of oxidation. The alloys of 6.8 and 10.9 percent copper were annealed in naphthalene vapor at 218° C, below the magnetic transition of nickel, while all the others were embedded in sand and heated in an electric furnace at 600° C. Each annealing continued for one week.

The electrolytes employed were all 1-normal in copper sulphate and nickel sulphate combined, some of them being in addition 1-normal in sodium sulphate. They were prepared by mixing and diluting 1.4-normal stock solutions made from the best obtainable "C. P." salts, with the use of volumetric apparatus calibrated at 20° C.

Figure 1 shows in cross-section the half-cell in which the test-piece was placed for observation of the potential. The whole apparatus was of glass, and consisted of a cylindrical outer vessel A, closed by the ground-glass stopper B, which carried the other parts.[4]

In preparation for a series of observations one end of a fine copper wire was twisted tightly around the test-piece, and the latter, together with the adjacent part of the wire, was heavily lacquered with an alcoholic solution of marine glue, leaving exposed only the end surface of the test-piece, which has previously been referred to as formed by the last cut in the preparation of the sample. The free end of the copper wire was joined by fusion to a small loop of platinum.

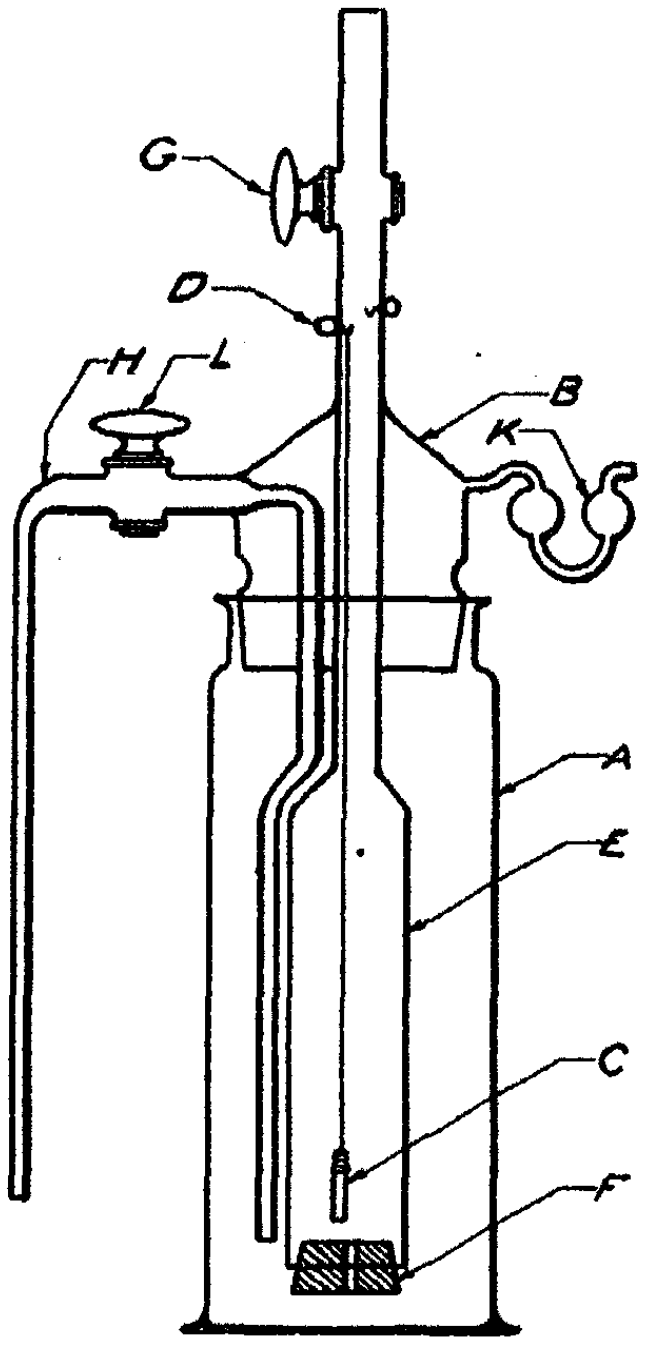

Fig. 1

The lacquer having dried, the stopper B and its attachments were removed, the test-piece C was suspended by its wire from the platinum hook D, so as to hang near the bottom of the inner cylinder E, and the one-hole rubber stopper F was put in place. After the electrolyte had been added to A the part B was replaced, the stopcock G being closed so that the pressure of air in E prevented the electrolyte from entering and coming in contact with the test-piece.

Nitrogen, which had been freed from oxygen by the method previously mentioned, was next admitted to the half-cell through the stopcock G and allowed to pass for five minutes, bubbling out through the trap K, which contained a portion of electrolyte.

The cell was now put into the thermostat and allowed to remain for fifteen minutes. Thereupon, by opening the stopcock G and applying a slight pressure of nitrogen at K, the electrolyte was caused to enter the inner cylinder E and come into contact with the test-piece. The stopcock L was then at once opened, establishing connection with the calomel electrode through the siphon H, containing the cell-electrolyte, and an intermediate vessel, containing 1-normal potassium chloride; the electrical circuit was now completed through the hook D and observations were begun with as little delay as possible.

All potentials were measured at 25° C against a normal calomel electrode by means of potentiometer and galvanometer. Other experimental arrangements were such as were described in the preliminary publication.

From the curves of Figure 2 may be seen the general character of the results obtained with each of the six alloys of the copper-nickel series. The observed points are inclosed by

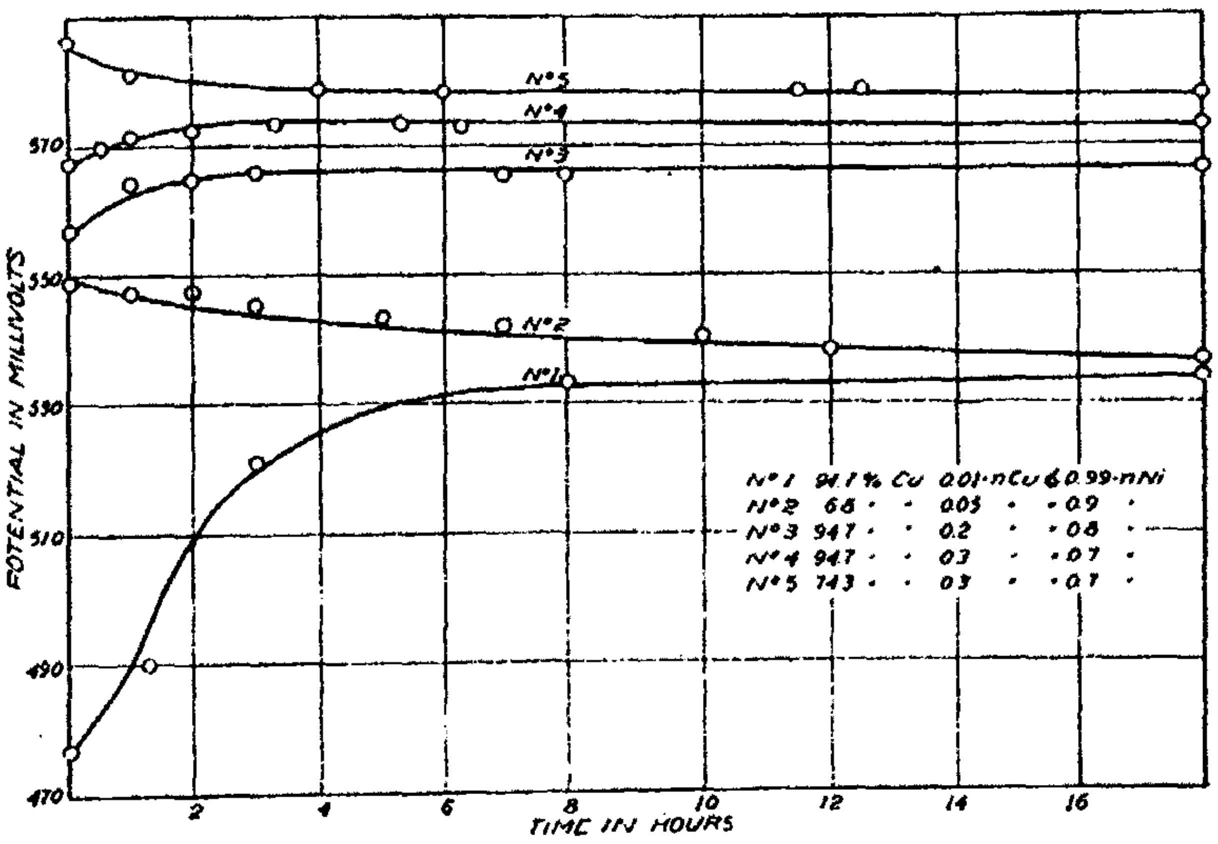

Fig. 2

circles which have a radius equal to the estimated error. For some time after the immersion of a test-piece in the solution the potential changed rapidly, although the direction of the change appeared to be accidental. It varied likewise in magnitude, being sometimes too small to be observed by any method less sensitive than that employed, while in other instances it amounted to as much as sixty millivolts. In every case, however, a steady value was reached, which thereafter remained constant to within three millivolts or less during the period of observation, which was usually from twelve to eighteen hours but in some instances was extended to eighty-five hours. The conditions obtaining in the five typical experiments represented by the curves of Figure 2 are stated in Table I.

TABLE I

Curve	Test-piece	Composition of electrolyte
No. 1	Ingot II (94.7% Cu)	0.01 *N* Cu and 0.99 *N* Ni
No. 2	6.8% Cu	0.05 *N* Cu and 0.95 *N* Ni
No. 3	Ingot I (94.7% Cu)	0.2 *N* Cu and 0.8 *N* Ni
No. 4	Ingot I (94.7% Cu)	0.3 *N* Cu and 0.7 *N* Ni
No. 5	74.3% Cu	0.3 *N* Cu and 0.7 *N* Ni

The variations at the beginning of the run may be accounted for in two ways: by the process of adjustment of the surface compositions of the two phases; and by irregularities due to superficial conditions such as films of oxide or possibly adsorbed gas. It is evident that the "steady" value of the flat portion of the curve is the important quantity and not the changeable readings of the first hours. This will be referred to as the "steady" value, and has in every instance which follows been derived from curves such as those shown in Figure 2.

It may be pointed out that the constancy of the steady value indicates that the method of measurement with a galvanometer as a zero instrument, in place of the electrometer often employed, produced no drift in the values observed.

In a search for the best method of treating the alloy to obtain uniform potentials numerous experiments were carried out with sawed, emeried, polished, etched, and annealed surfaces. These experiments show that surfaces carefully annealed while protected from oxidation by an atmosphere of nitrogen yield results which are the most nearly constant in any given experiment and which are reproducible within the narrowest limits. Test-pieces cut from an ingot containing 94.7 percent copper, and having annealed surfaces, were investigated in electrolytes of different compositions. Table II exhibits the characteristic values of the potentials for different electrolytes and also the agreement of the values in electrolytes of the same composition.

TABLE II

Test-piece	Composition of electrolyte	Steady potential (Calomel electrode = 0.5642)
No. 1	0.1 *N* Cu and 0.9 *N* Ni	0.5602
No. 2	0.1 *N* Cu and 0.9 *N* Ni	0.5601
No. 3	0.1 *N* Cu and 0.9 *N* Ni	0.5587
No. 4	0.2 *N* Cu and 0.8 *N* Ni	0.5692
No. 5	0.2 *N* Cu and 0.8 *N* Ni	0.5682
No. 6	0.2 *N* Cu and 0.8 *N* Ni	0.5687
No. 7	0.2 *N* Cu and 0.8 *N* Ni	0.5695
No. 8	0.2 *N* Cu and 0.8 *N* Ni	0.5682
No. 9	0.2 *N* Cu and 0.8 *N* Ni	0.5666
No. 10	0.3 *N* Cu and 0.7 *N* Ni	0.5742
No. 11	0.3 *N* Cu and 0.7 *N* Ni	0.5782
No. 12	0.3 *N* Cu and 0.7 *N* Ni	0.5732

The steady values, constant to within a millivolt, were confirmed by frequent observations during intervals of at least twelve hours and in several cases during forty-eight hours. It will be noticed that the potentials for test-pieces immersed in the same composition of electrolyte agree within three millivolts except in one instance, and usually within 1.5 millivolts.

These experiments showed that for alloys from a given ingot the steady potential was definitely determined by the composition of the electrolyte.

An ingot was next prepared showing the same analysis as the foregoing to within 0.2 percent, and the values of its potential were compared with those of ingot I. The results are given in Table III.

TABLE III
Electrolytes: 0.2 *N* in Cu and 0.8 *N* in Ni, 1.0 *N* in Na_2SO_4
(Calomel electrode = 0.5642)

	Ingot II	Ingot I
Initial potential	. 0.5397	0.5619
Steady potential	0.5680	0.5691
Steady potential after 24 hrs.	0.5688	0.5697

The steady potentials, observed during an interval of twenty-four hours, were constant within 1.5 millivolts, and the experiment showed that the values for the potentials of the two ingots were the same within less than three millivolts.

Among previous investigations of the changes of solid alloy potentials we may mention the researches of Puschin,[3] in which he used an electrolyte containing only one of the metal ions and measured potentials at room temperature against a rod of the baser metal immersed in the same electrolyte. Obviously the variations of the standard are reflected in the potentials of the alloys. The exact degree of constancy and reproducibility which he reached cannot be ascertained from the abridged German publication of his work.

Broniewski[1] in his measurements of alloy potentials, used as his reference electrode a carbon rod depolarized by manganese dioxide and seems to have been content with a variation of several centivolts. It is possible that variations caused by the nature both of the alloy and of the reference electrode are responsible for the alternating maximum and minimum values of his potentials, which he concluded to be characteristic of alloy potentials in general. However this may be, the results previously cited show that there is no such ambiguity in the potentials of the copper-nickel series.

The next experiments related to the influence of the surface condition of the alloy. They were made upon surfaces rubbed with emery or upon those which had been polished with rouge on a broadcloth-covered wheel. The amount of abrading or polishing being very difficult to regulate, it is not surprising that the measurements showed considerable variation. The test-pieces, numbered 1 to 6 in the following table, were obtained from two ingots of approximately 95 percent copper.

The results displayed in Table IV show no regular differences between the steady potentials of annealed and of emeried surfaces, although the latter appear to exhibit the greater accidental variations. Between the annealed and the polished surfaces, however, there is a difference which, while variable in amount, is always of the same quality, the polished surfaces having in every instance a greater tendency to give ions to the solution. This is made more evident by considering the fact that No. 1 and No. 5 were the most highly polished. It is not without interest that this fact seems to be in accord with Beilby's[6] "amorphous layer" theory of polished surfaces.

When the foregoing experiments had established the constancy and reproducibility, within the limits mentioned, of copper-nickel alloys having annealed surfaces, a new series of experiments was undertaken to show the relation between the potential and the compositions of the alloy and of the electrolyte. Potential measurements of copper-nickel alloys (94.7% Cu), immersed in electrolytes normal in copper and nickel sulphates combined and also normal in sodium sulphate, were continued until a steady value had been unmistakably attained. The values for each concentration, shown in Table V, are the average of from three to six experiments. The greatest deviation from the average obtained in a single experiment was less than three millivolts. Plotting these

TABLE IV
(Calomel electrode = 0.5642)

Alloy	Composition of electrolyte	Potential of annealed surface		Potential of emeried surface		Potential of polished surface	
		Initial	Steady	Initial	Steady	Initial	Steady
No. 1	0.01 N in Cu and 0.99 N in Ni	0.5067	0.5352	0.5110	0.5272	0.4971	0.5132
No. 2	0.03 N in Cu and 0.97 N in Ni	0.5606	0.5552	0.5642	0.5634	—	—
No. 3	0.1 N in Cu and 0.9 N in Ni	0.5487	0.5587	0.5472	0.5587	—	—
No. 4	0.01 N in Cu and 0.99 N in Ni	0.5030	0.5304	0.5179	0.5277	0.5122	0.5298
No. 5	0.05 N in Cu and 0.95 N in Ni	0.5207	0.5502	0.5372	0.5486	0.5302	0.5392
No. 6	0.05 N in Cu and 0.95 N in Ni	0.5217	0.5492	0.5262	0.5492	0.5407	0.5452

potentials against the logarithms of the copper concentrations gave the linear relation displayed in curve No. 4, Figure 3.

TABLE V

Composition of electrolytes	Steady potentials (averages) calomel electrode = 0.5642
0.3 *N* in Cu and 0.7 *N* in Ni	0.5752
0.2 *N* in Cu and 0.8 *N* in Ni	0.5682
0.1 *N* in Cu and 0.9 *N* in Ni	0.5602
0.05 *N* in Cu and 0.95 *N* in Ni	0.5498
0.01 *N* in Cu and 0.99 *N* in Ni	0.5332

A set of experiments conducted in a similar manner, but with the omission of sodium sulphate from the electrolyte, again indicated the same relation. It was found that while, for a given alloy composition, the potentials obtained with electrolytes containing sodium sulphate differed from those observed when sodium sulphate was omitted, the differences corresponded merely to a parallel displacement of the lines representing the dependence of potential upon the composition of the electrolyte. Hence in subsequent experiments sodium sulphate was not employed.

The potentials of the series of copper-nickel alloys containing 6.8, 10.9, 65.5, 74.3, 83.4, and 94.7 percent copper were investigated in electrolytes 0.3 *N* in copper and 0.7 *N* in nickel; 0.1 *N* in copper and 0.9 *N* in nickel; 0.05 *N* in copper and 0.95 *N* in nickel; and 0.01 *N* in copper and 0.99 *N* in nickel. Two test-pieces were used for each determination and the values to be recorded are the steady potentials obtained by the method illustrated in Figure 2. For every pair the steady potentials agreed within three millivolts. In the case of each alloy composition the linear relation between the potential and the logarithm of the copper concentration of the electrolyte was found to apply. Several of these curves are shown in Figure 3, and the complete summary of values is given later in Table VI, Curve No. 1 represents the average slope of the curves corresponding to all the alloy compositions investigated, each slope having been determined by finding graphically the intercept on the axis of potentials and that on the axis of logarithms of copper concentrations. The value for the average slope so determined is 30.14, and curve No. 2 having a slope of 41.43 represents the greatest observed deviation. Curves Nos. 2, 3, 5, and 6 show, respectively, the dependence of potential on the logarithm of the copper concentration for alloys containing 6.8, 10.9, 74.3, and 83.4 percent copper. The points on curve No. 4 are in each case the average of from three to six determinations of the potential of a 94.7 percent copper alloy immersed in an electrolyte normal in copper and nickel combined and normal also in sodium sulphate.

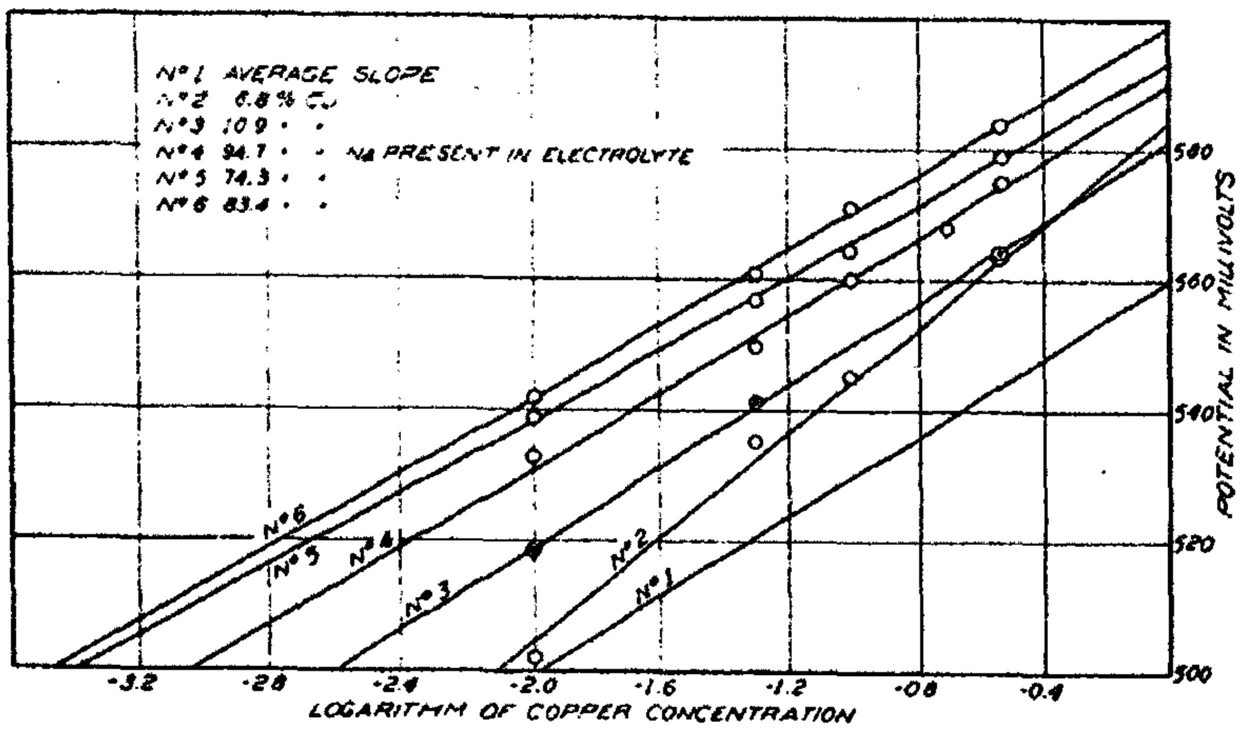

Fig. 3

In the foregoing paragraphs the linear relation between alloy potential and the logarithm of the copper concentration of the electrolyte has been established by experimental evidence. It is of interest to consider how this relation compares with the requirements of the well-known thermodynamic relation due to Nernst.[6] According to his application of the theory to binary alloys the equation

$$(1) \qquad E = \frac{RT}{nF} \ln \frac{P_1}{p_1} = \frac{RT}{nF} \ln \frac{P_2}{p_2}$$

holds for metals forming homogeneous solid solutions. We shall designate absolute potentials by E, those referred to a calomel electrode by E and the absolute value of the calomel electrode by E_c. Then $\mathrm{E} + E_c = E$. Instead of Equation 1 we may write

$$(2) \qquad E = \frac{\mathrm{RT}}{n\mathrm{F}} \ln \frac{[\mathrm{Cu}^{\cdot\cdot}]}{[\mathrm{Cu}^{\cdot\cdot}]_0} = \frac{\mathrm{RT}}{n\mathrm{F}} \ln \frac{[\mathrm{Ni}^{\cdot\cdot}]}{[\mathrm{Ni}^{\cdot\cdot}]_0}.$$

Regarding only the copper concentrations, the nickel present being beyond the limits for the exact application of the laws of dilute solutions, we obtain instead of Equation 2

$$(3) \qquad E = -\frac{\mathrm{RT}}{n\mathrm{F}} \ln [\mathrm{Cu}^{\cdot\cdot}]_0 + \frac{\mathrm{RT}}{n\mathrm{F}} \ln [\mathrm{Cu}^{\cdot\cdot}].$$

When the substitution of values $\frac{\mathrm{R}}{\mathrm{F}} = 0.861 \times 10^{-4}$, $\mathrm{T} = 298°$, $n = 2$, and the conversion to Briggs' logarithms are made, Equation 3 takes the form

$$(3a) \quad E = -3 \times 10^{-2} \log [\mathrm{Cu}^{\cdot\cdot}]_0 + 3 \times 10^{-2} \log [\mathrm{Cu}^{\cdot\cdot}].$$

Since the logarithmic terms have throughout a negative value, confusion of signs may be avoided by regarding all quantities as positive and writing Equation 3*a* as

$$(3b) \quad E = 3 \times 10^{-2} \,|\log [\mathrm{Cu}^{\cdot\cdot}]_0| - 3 \times 10^{-2} \,|\log [\mathrm{Cu}^{\cdot\cdot}]|,$$

which is of the linear form

$$(4) \qquad E = b - \frac{b}{a} \,|\log [\mathrm{Cu}^{\cdot\cdot}]|.$$

Equations 3 and 4 express the dependence of potential upon electrolyte-composition for a given alloy, if $[\mathrm{Cu}^{\cdot\cdot}]_0$ is the concentration corresponding to the solution pressure for this alloy composition. They are based upon the assumptions:—(1) that the alloy does not alter composition as the result of changes in the electrolyte; (2) that the proportionality $\frac{[\mathrm{Cu}^{\cdot\cdot}]}{[\mathrm{Cu}^{\cdot\cdot}]_0} = \frac{p_{\mathrm{Cu}^{\cdot\cdot}}}{\mathrm{P}_{\mathrm{Cu}^{\cdot\cdot}}}$ is valid. This relation holds so long as the ion concentration is small enough to make the extension of the gas laws to solutions permissible. In applying the equations, $[\mathrm{Cu}^{\cdot\cdot}]$ is put equal to $[\mathrm{CuSO_4}]$. Since its dissociation is not complete in the range of concentrations considered, the justification for this substitution will be discussed in later paragraphs.

The first assumption certainly is not justified, as is shown by the manner in which E at first changes in a new solution but finally, as may be seen by referring to Table VI, becomes independent of renewal of electrolyte. Instead of the constant, $\log [\mathrm{Cu}^{\cdot\cdot}]_0$, characteristic of an alloy composition, the function $f\,[\mathrm{Cu}^{\cdot\cdot}]$ must be substituted, producing in place of Equation 3*b*

$$(5) \quad E = 3 \times 10^{-2} f\,[\mathrm{Cu}^{\cdot\cdot}] - 3 \times 10^{-2} \mid \log [\mathrm{Cu}^{\cdot\cdot}] \mid .$$

The combination of Equation 5 with Equation 4 produces the relation

$$(6) \quad f\,[\mathrm{Cu}^{\cdot\cdot}] = \frac{b}{3 \times 10^{-2}} + \left(1 - \frac{b}{a \times 3 \times 10^{-2}}\right) \mid \log [\mathrm{Cu}^{\cdot\cdot}] \mid$$

or

$$(6a) \qquad \log [\mathrm{Cu}^{\cdot\cdot}]_0 = k + m \mid \log [\mathrm{Cu}^{\cdot\cdot}] \mid .$$

In other words the linear dependence of potential on concentration, empirically found, is consistent with Equation 3*b* only on the supposition of a linear relation between the logarithm of ion concentration in the electrolyte and the apparent final solution pressure concentration in the alloy.

Comparing different alloy compositions we find empirically a variation in both intercepts and slopes of the curves corresponding to Equation 4. However, taking the calculated average slope (30.14), as shown in Figure 3, to redetermine the potentials at the intercepts, and plotting these potentials against the compositions of the alloys, we obtain as represented in Figure 4, the simple relation $y = c + hx$, showing the de-

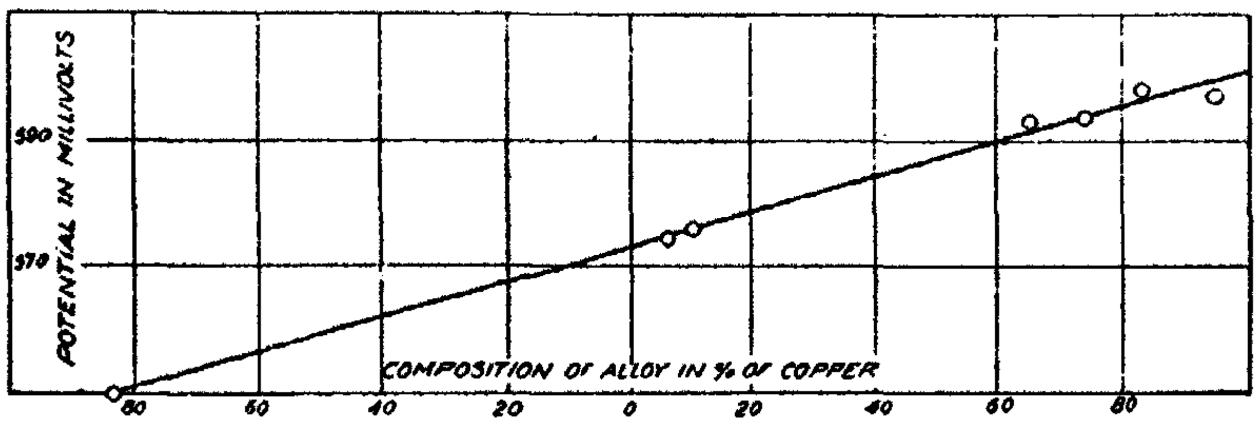

Fig. 4

TABLE VI
Calomel electrode = 0.5642

Composition of alloy in percent Cu	Composition of electrolyte	Potential in millivolts calculated (absolute)	Potential in millivolts observed (absolute)	Error	Percent Error
6.8%	0.3 *N* in Cu and 0.7 *N* in Ni	558.9	563.5	− 4.6	Average 0.87 (2.3 max.)
6.8	0.1 *N* in Cu and 0.9 *N* in Ni	544.76	545.2	− 0.44	
6.8	0.05 *N* in Cu and 0.95 *N* in Ni	535.7	535.3	+ 0.4	
6.8	0.01 *N* in Cu and 0.99 *N* in Ni	514.62	502.0	+12.62	
10.9	0.3 *N* in Cu and 0.7 *N* in Ni	560.02	564.2	− 4.18	Average 1.0
10.9	0.1 *N* in Cu and 0.9 *N* in Ni	545.88	556.0	−10.12	
10.9	0.05 *N* in Cu and 0.95 *N* in Ni	536.84	541.2	− 4.36	
10.9	0.01 *N* in Cu and 0.99 *N* in Ni	515.74	518.5	− 2.75	
65.5	0.3 *N* in Cu and 0.7 *N* in Ni	575.14	574.0	+ 1.14	Average 1.1 2.5 max.
65.5	0.1 *N* in Cu and 0.9 *N* in Ni	561.0	564.5	− 3.50	
65.5	0.05 *N* in Cu and 0.95 *N* in Ni	551.96	558.5	− 6.54	
65.5	0.01 *N* in Cu and 0.99 *N* in Ni	530.86	544.5	−13.64	
74.3	0.3 *N* in Cu and 0.7 *N* in Ni	577.8	579.0	− 1.2	Average 0.4
74.3	0.1 *N* in Cu and 0.9 *N* in Ni	563.8	564.5	− 0.7	
74.3	0.05 *N* in Cu and 0.95 *N* in Ni	554.6	557.0	− 2.4	
74.3	0.01 *N* in Cu and 0.99 *N* in Ni	533.5	539.0	− 5.5	
83.4	0.3 *N* in Cu and 0.7 *N* in Ni	580.15	584.0	− 3.85	Average 0.8
83.4	0.1 *N* in Cu and 0.9 *N* in Ni	566.01	571.0	− 4.99	
83.4	0.05 *N* in Cu and 0.95 *N* in Ni	557.0	561.0	− 4.00	
83.4	0.01 *N* in Cu and 0.99 *N* in Ni	535.87	541.8	− 5.93	
94.7	0.3 *N* in Cu and 0.7 *N* in Ni	583.2	585.2	− 2.0	Average 0.2
94.7	0.1 *N* in Cu and 0.9 *N* in Ni	569.06	568.5	+ 0.56	
94.7	0.05 *N* in Cu and 0.95 *N* in Ni	560.02	561.0	− 0.98	
94.7	0.01 *N* in Cu and 0.99 *N* in Ni	538.92	537.2	+ 1.72	

pendence of intercept in Equation 4 upon the composition x of the alloy. Equation 4 now takes the form

$$(7) \qquad E = c + hx - 30.14 \mid \log [CuSO_4] \mid .$$

The constants c and h are obtained graphically from the slope and intercept of the curve in Figure 4. Upon inserting their values we obtain finally the relation

$$(8) \qquad E = 573 + 0.277\,x - 30.14 \mid \log [CuSO_4] \mid$$

which represents the dependence of the potential upon the compositions both of the alloy and of the electrolyte.

The accuracy with which Equation 8 represents the observed values of potential, for the twenty-four experiments made with electrolytes not containing sodium sulphate, is shown by Table VI. This table contains complete information regarding the composition of the alloys; the potentials calculated from Equation 8; the experimentally determined values; the corresponding compositions of the electrolytes; and the percent error. The average error for each composition of alloy ranges from 0.2 percent to 1.1 percent which includes all the potentials observed, none having been omitted even when apparently in error. It is here shown that the dependence of potential both upon the composition of the alloys and upon the copper concentration of the electrolyte is represented by Equation 8 within an average error of less than 0.75 percent. Hence the empirical results are in close agreement with theory, and it will be shown, by considering actual ion concentrations, that the constants of Equation 8 compensate for the incomplete dissociation of the copper sulphate. The determination of the concentration of copper ions, in the solutions used, is rendered uncertain by the lack of conductivity measurements at 25° C and is furthermore influenced by the presence of nickel sulphate, but calculations were made using the data of Kohlrausch for conductivity and ionic mobilities at 18° C. Plotting the potentials of the series of alloys against the logarithms of the calculated ion concentrations produced straight line curves similar to those of Figure 3 but having different slopes and intercepts from those plotted against copper concentrations. From these curves an equation was developed in the same manner as Equation 8. This procedure produced the equation

$$(9) \qquad E = 587 + 0.4x - 37.65 \mid \log [\mathrm{Cu}^{\cdot\cdot}] \mid,$$

which corresponds with Equation 8, the value of the constants being changed and $[\mathrm{Cu}^{\cdot\cdot}]$ substituted for $[\mathrm{CuSO_4}]$. Equation 9 yields results, for the series of copper-nickel alloys, which agree with the observed values within an average error of one percent. Since, therefore, the employment of the copper sulphate concentration (in Equation 8) in place of the cupric ion concentration required by the theory of Nernst gives such excellent agreement with the observed potentials, it seems practically justifiable to avoid in this way the use of the imperfectly known concentrations of the cupric ion.

At this point a consideration may be inserted to show that the liquid potential between the normal potassium chloride solution of the electrode and the electrolyte normal in copper and nickel combined is not influenced to any disturbing extent by changing the ratio of the copper and nickel concentrations. If the liquid potential were *not* constant the variation would be reflected in the values of E when the equation

$$E = -0.5642 - 0.3 \mid \log [\mathrm{Cu}^{\cdot\cdot}]_0 \mid + 0.3 \mid \log [\mathrm{Cu}^{\cdot\cdot}] \mid$$

is applied to different concentrations of electrolytes. The values of E were found by experiment and the copper concentrations of the electrolytes being known it was possible to calculate the values for $\log [\mathrm{Cu}^{\cdot\cdot}]_0$ corresponding to each concentration. The calculated values are given in Table VII.

TABLE VII

Electrolyte	$\log [\mathrm{Cu}^{\cdot\cdot}]_0$
0.3 *N* in Cu and 0.7 *N* in Ni	—19.86
0.1 *N* in Cu and 0.9 *N* in Ni	—19.92
0.05 *N* in Cu and 0.95 *N* in Ni	—20.00
0.01 *N* in Cu and 0.99 *N* in Ni	—19.91

According to the theory of Nernst the value of $\log [\mathrm{Cu}^{\cdot\cdot}]_0$ should, for a given alloy, be independent of the composition of the electrolyte. If there were a variation in the liquid potential the values for $\log [\mathrm{Cu}^{\cdot\cdot}]_0$ calculated for different compositions of electrolytes should exhibit a progressive change. The constancy of log $[Cu^{\cdot\cdot}]_o$ in the table shows, therefore, that in this work the liquid potential may be regarded as constant.

The results which have been discussed show that the steady potential attained is determined by the composition of the alloy and the composition of the electrolyte jointly. It may be supposed, then, that when an alloy and an electrolyte not having compositions which would be in equilibrium with each other are brought into contact, the surface layers of both change their compositions in such a manner as to approach the equilibrium conditions. As a consequence concentration gradients and corresponding rates of diffusion are established in both phases. The steady potential will then be attained when a balance is established between the rates of diffusion in the two phases. On the basis of this conception it might be expected that the rate at which the potential changes on first immersion of the alloy would be determined by the comparatively slow rate of diffusion in the solid alloy and not by the more rapid processes in the electrolyte. This seems to be confirmed by results which will be described.

In these experiments, after the attainment of an unmistakable steady potential, the electrolyte was removed and replaced by a fresh portion having the same composition. Nitrogen was again bubbled through the apparatus and the potential observations were repeated. In one such experiment the steady potential upon first immersion was attained only after eight hours, while with renewal of electrolyte the steady value was reached before the first measurement, which was taken in less than three minutes. The conduct of the potential in this and in two other cases is shown in Table VIII.

TABLE VIII

Alloy	1st steady potential	Elapsed time	Steady potential with renewed electrolyte	Elapsed time
No. 1	0.5410	8 hrs.	0.5452	3 min.
No. 2	0.5672	19 hrs.	0.5675	1 hr.
No. 3	0.5678	19 hrs.	0.5678	1 hr.

It is of interest to note that similar conduct was shown by a pure copper wire immersed in a copper-zinc solution.

The foregoing experiments include the entire range of alloy compositions and the middle range of copper concentrations of electrolyte for the copper-nickel series, and it seems at first somewhat surprising that a single relation between alloy composition and potential (Equation 8) applies both to the right and to the left of the heterogeneous region due to the transition of nickel at 320° C, which is represented in the diagram of Guertler and Tammann.[7] This is not improbably accounted for by the enrichment of the alloy-surface in copper. Before the attainment of the steady potential electrolytes of such relatively high copper concentrations as those employed may be supposed to have converted even a test-piece having originally only five percent of copper into one having superficially a copper content higher than that which corresponds to the limit of the region of non-miscibility in the equilibrium diagram. The steady potentials would in that case all correspond to equilibria with the homogeneous solid solutions of the copper side of the diagram.

The appearance of the test-pieces on removal from the electrolyte in some degree supports this view; for with solutions 0.1 *N* in copper, or higher, the alloys presented the appearance of having been copper plated and must therefore have acquired a surface composition of not less than 85 percent copper, this being approximately the point at which the copper color begins to dominate in the alloys of this series; and while with electrolytes 0.05 *N* and 0.01 *N* in copper the test-pieces were not reddened, but only somewhat dulled in appearance, by contact with the solution, it is likely that the surfaces had acquired compositions higher in copper than the 45 percent[8] or less at which the transition interval ends. It may at least be said that the results of the potential measurements are not inconsistent with those which have been obtained by other methods.

The lower range of electrolyte compositions, below 0.01 *N* in copper, has not been included in this investigation.

Unfortunately the extension of the measurements to this interesting region, within which the equilibrium electrolytes of the entire series of alloys are doubtless to be found, has been rendered impossible by the very considerable loss of time experienced in endeavoring to obtain steady and reproducible results with the copper-zinc alloys.

The System Copper–Zinc

As was explained at the beginning of the paper, the continuation of the study of the binary brasses showed these alloys to be highly variable in conduct and unsuitable for an investigation of the kind contemplated. A brief account of the results may nevertheless be of interest, since they appear to conform to indications obtained by other workers that brasses are subject to changes of a sort not accounted for by the equilibrium diagrams hitherto proposed.

The materials used for the preparation of alloys and electrolytes, the methods of analysis, and the means for obtaining uniform test-pieces were identical with those described in the preliminary publication.[1]

Numerous conditions for annealing were investigated, with the employment both of an atmosphere of nitrogen and of other means of excluding air.

Annealing in sealed tubes filled with nitrogen was conducted both at the temperature of boiling sulphur, and at 560° C. The alloys treated at the lower temperature appeared entirely bright and clean, but were nevertheless unsatisfactory with respect to the constancy and reproducibility of potential, while those annealed at the higher temperature sometimes interacted with the glass, becoming covered either with a red scale or with a thin film resembling black dust. It was shown that this was not due to the presence of oxygen in the tube; but the introduction of alundum thimbles or calcined magnesium oxide between brass and glass, although preventing the formation of the red scale, did not obviate the production of the black film or cause the alloys to give satisfactory results in the subsequent potential measurements. If the tube instead of being filled with nitrogen was evacuated before sealing to a pressure of less than 0.01 mm of mercury, as indicated by a McLeod gage, the volatilization of zinc during annealing was sufficient to roughen the surface of the test-piece perceptibly, and hence to alter the surface composition of the alloy beyond permissible limits. Attempts to anneal by plunging the test-pieces into molten borax were equally unsuccessful because of the rapid loss of zinc.

On trying to eliminate the irregularities, shown by pieces annealed in nitrogen, through subsequent treatment with nitric acid, or by grinding or polishing, highly variable potentials were still obtained.

Nor did specimens of several commercial brasses, which were known to have lain undisturbed for more than twenty-five years, and hence might be regarded as annealed at atmospheric temperatures, show more regular conduct.

These irregularities were shown not to be due to variations in the illumination of the electrode, since they occurred in much the same degree with an open thermostat and with one from which light was carefully excluded.

That the variations were not due to differing orientation of the crystal grains seemed to be shown by the results of experiments made with a tapping electrode which made it possible to explore the potential at the faces of different crystals in the surface of the alloy, for the differences found in this way were of an altogether smaller order.

The range of variation between test-pieces which had formed adjacent portions of the same ingot, and had been annealed together in the same tube, was from 5 to 180 millivolts, and appeared to render necessary the conclusion that the copper-zinc alloys of the α solid solution series cannot be brought to a definite reproducible condition by any ordinary process of annealing. Furthermore, the continued irregular drift of the potential in the case of each alloy indicated that even after being annealed for from one to two weeks the system was still subject to a slow, progressive change; and this was observed even with alloys having as much as 80 percent of copper, which could hardly be supposed to contain anything but the pure α constituent.

It seems probable that these irregularities may be connected with various observations of other workers which appear to indicate that the α brasses are not so simple in conduct as would be inferred from the generally accepted equilibrium diagrams of Shepherd and of Carpenter. Among such previous observations may be mentioned the finding by Roberts-Austen[9] of a thermal effect at 473° C in an alloy with 75.6 percent copper and the peculiar effects of aging and subsequent annealing upon the mechanical properties of brasses which led Carpenter and Edwards[10] to make special assumptions as to the nature of these alloys, and of solid solutions in general.

Whether there is, in the region of the equilibrium diagram assigned to these alloys, a heterogeneous region not yet recognized or whether the changes indicated are to be accounted for merely by a slow attainment of equilibrium cannot be decided upon the basis of existing data.

Summary

A continuation of previous experiments upon the Copper-Zinc alloys shows these to be variable as regards electromotive force, but lends confirmation to indications obtained by others regarding unexplained changes to which these alloys are subject.

The Copper-Nickel alloys are shown to be very regular in electro-chemical conduct, it being possible to obtain values for their potentials which are reproducible and constant to within three millivolts and which remain constant, within the same limits, for many hours. They exhibit potential differences against mixed solutions of cupric sulphate and nickel sulphate of moderate copper concentrations expressible by a relation which is linear both with respect to alloy composition and to the logarithm of electrolyte composition.

It is shown that copper sulphate concentration may be employed without any sacrifice of accuracy in the representation of the empirical results, in place of the cupric ion concen-

tration required by the thermodynamic theory of Nernst, provided the constants of the equation be altered.

The tendency to give ions to the solution is increased as a result of polishing the surfaces of the alloys, while by coarser grinding only small accidental variations are produced from the steady values found with annealed surfaces.

The data for the copper-nickel alloys are of a higher order of constancy and reproducibility than those formerly obtained for solid alloys, and the experiments show that the employment of a calomel electrode and other refinements generally used in the study of amalgams is justified in application to this field of investigation.

REFERENCES

[1] Jour. Phys. Chem., **20**, 228 (1916).
[2] Jour. Am. Chem. Soc., **36**, 1448 (1914).
[3] Zeit. anorg. Chem., **56**, 1 (1908).
[4] Ann. Chim. Phys., **25**, 1 (1912).
[5] Proc. Roy. Soc., **72**, 227 (1903).
[6] Zeit. phys. Chem., **22**, 539 (1897).
[7] Zeit. anorg. Chem., **52**, 25 (1907).
[8] Guertler and Tammann: Loc. cit.
[9] Proc. Inst. Mech. Eng., **31** (1897); 4th Rept. Alloys Research Committee.
[10] Jour. Inst. Metals, **5**, 140–3 (1911).

THE TINTING STRENGTH OF PIGMENTS

BY T. R. BRIGGS

In a paper on the opacity and hiding power of pigments, G. W. Thompson[1] has considered briefly the question of the color strength or tinting power. I quote from the original:

"In many laboratories, tests for opacity have been conducted on the assumption that what is known as the strength or tinting strength of a pigment is a measure of its opacity. From numerous tests which we have made, we have come to the conclusion that strength is only an indication of opacity and that, working on pigments of the same composition, it is not safe to assume that the strength of a pigment is a measure of its opacity. By *strength* or *tinting power* we mean here:

" 'The relative power of coloring a given quantity of paint or pigment selected as standard for comparison,' which is the definition agreed upon by Committee D_1 of the American Society for Testing Materials. Much heated discussion has appeared in the *Farben-Zeitung* during the last year or more as to whether strengh is proportional to opacity . . . As far as the discussions have gone, it would appear that they have not led to any definite conclusion."

In an earlier paper,[2] Thompson put forward somewhat different views. "There has been a great deal of discussion, especially in a German periodical (Farben-Zeitung) recently on the relation between strength or tinting power and opacity, some claiming that there is a direct relation and others that there is an inverse relation. Most of these discussions are academic and not based on practical tests. There are reasons for believing that the relation between strength and opacity is a direct relation. The reasons are as follows: Strength increases as opacity does with the fineness of the pigment. In the case of white lead, for instance, its strength and opacity are both increased by grinding it finer . . . . . We hope with

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[1] Jour. Ind. Eng. Chem., 5, 121 (1913).

[2] Eighth Internat. Cong. App. Chem., 25, 802 (1912).

the opacity measuring apparatus referred to and the disc machine to determine the relation between strength and hiding power and opacity . . . ."

I have quoted from these two papers by Thompson because they show the interest which the practical paint manufacturer and chemist have in the physical properties of pigments and, beside this, they indicate how little is really known about one of these properties—the coloring strength or tinting power. The guess that there should be a direct relation between tinting strength and opacity is an obvious one; that this relation may be masked by other and disturbing factors is indicated clearly by the contradictory results obtained when the hypothesis was tested.

Tinting power is determined[1] usually by mixing the particular colored pigment with a white—ordinarily oxide of zinc. Equal weights of the pigments to be tested are mixed in linseed oil with one gram of a special zinc oxide, of uniform composition and *kept solely for the purpose.* The colored pigment should not exceed five percent by weight of the zinc oxide. By comparing the color depth of the different mixtures with that of a standard mixture, some idea of the relative strength of different samples of the same color may be obtained. Or one may follow Ostwald's suggestion[2] and determine how much white one must add to a certain weight of colored pigment before the color of the latter just disappears. It is possible, of course, to measure the tinting power of white pigments in an analogous manner.

In a recent paper, Ostwald[3] discusses the problem in some detail. He points out that Prussian blue seems to have one hundred times the coloring power of permanent green (chromium oxide) and that the coloring power is a function of the size of particles. "It is a fact," he writes, "familiar to every painter who knows his materials, that colors become

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[1] Cf. Walker: Chem. News, 102, 81 (1910); Holley: "Analysis of Paints and Varnish Products," 126 (1912).

[2] Zeit. Kolloidchemie, 16, 3 (1915).

[3] Ibid., 16, 1 (1915).

ever stronger as they are ground increasingly fine." Further than this, Ostwald does not commit himself, though he returns to the subject in a second paper[1] on lakes and lake pigments precipitated on an inert base. The following passages are worth quoting:

"For this reason a new type of precipitated color has been developed, consisting of a colorless base (Träger) on which there has been produced . . . an insoluble precipitate of the color lake. Such pigments, accordingly, exhibit under a powerful microscope an appearance which is quite different from that which the true lakes possess. The material of the base appears completely unaffected by the color and retains the same form and color peculiarities that it has in the pure state. Adhering, however, to the base are tiny masses of the insoluble precipitate, in amounts, indeed, that appear astonishingly small in comparison to the strength of the coloration. For these quantities, according to the usual authorities, amount as a matter of fact seldom to more than ten percent of the bases and often to very much less."

Ostwald proceeded to study the effect of precipitating a methyl violet-tannin-tartar emetic lake on a lithopone base. So little as one part of lake on 6400 parts of base reduced the brightness of the white from 1000 to 656, while one part on 100 of base reduced it from 1000 to 164.

He next studied the influence of the base, using one part methyl violet lake to 400 parts of the base. The data refer to brightness, pure white being equal to 1000. Each mixture was made into a tempera with 4 percent of glue.

TABLE I

Barytes, ground	99	Kaolin	225
$CaCO_3$, coarse ppt.	121	Chalk	226
Gypsum, ground	143	Blanc fixe (dried)	239
Gypsum, burnt	158	Lithopone	322
$CaCO_3$, fine ppt.	206	Zinc white	330
White lead	213	Magnesia	349
Blanc fixe (moist)	216		

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[1] Zeit. Kolloidchemie, 17, 65 (1915).

From the fact that heavy spar requires but $^1/_{15}$th the quantity of lake that magnesium carbonate does to give an equally dark compound pigment (Füllfarbstoff), it does not at all follow that, with the products obtained in this way, having an equal depth of color, one can cover equal surfaces. While a gram of the pigment compounded with magnesia is sufficient to cover 500 square centimeters, a gram of the barytes pigment suffices for only 40 square centimeters. These data are only round numbers but they indicate very clearly that the marked differences described above are bound up with a property of the carrier, which ordinarily is designated as *covering power*."

Ostwald concludes, in brief, that the tinting power of the white pigments varies directly as their hiding power and, inasmuch as hiding power is a function of the size of the particles, the finer the particles, under most circumstances, the greater the tinting power of a given white pigment. He makes the further assumption that as subdivision increases, the hiding power and strength pass through a maximum. It seems almost certain, however, that this maximum can never be reached with pigments, the particles of which are visible under the microscope. Throughout the discussion, Ostwald has overlooked the possibility that the fineness of the methyl violet lake itself may not be constant throughout his experiments. The importance of this point will become increasingly apparent as we proceed.

There have been reported from time to time various data on the colors of pigment mixtures. In nearly every case the author appears to be somewhat mystified by his results. According to Gardner[1] an equal weight of ground barytes may be mixed with red oxide of iron without diminishing appreciably the intensity of the red. The case of chrome green (lead chromate-Prussian blue) is even more striking, for a mixture containing 80 percent of barytes shows its green color practically unimpaired. No explanation for these phenomena is offered.

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[1] Proc. Am. Inst. Mining Eng., 50, 983 (1915).

Sabin[1] mentions another case. "Red lead has a very brilliant color, but little staining power; one part of dry lampblack in 500 of red lead changes it to a coffee color, and 1 percent to a dark chocolate."

A statement by Holley[2] is worth repeating: "Two chrome yellows may appear to possess identically the same tint and tone, yet when reduced with equal quantities of a white pigment, *e. g.*, white lead, one may be found to possess 25 percent more strength than the other and will still maintain a clear yellow tone while the other will appear dirty or may pass over into another tone or color altogether. Chemically these yellows may be the same and the difference is therefore due to the method of manipulation."

When two differently colored powders are mixed, the shade or tint of the mixture is not dependent solely upon the percentage composition. This point is beautifully illustrated by soils colored red and yellow by iron oxide.[3]

TABLE II

"Acid Digestion of Soils of Alabama and Arkansas"

Color	Percent Fe_2O_3 removed	Color	Percent Fe_2O_3 removed
Dark red	10.7	Red	9.3
Dark red	7.2	Red	23.6
Deep red	4.9	Red	5.0
Deep red	2.5	Red	2.6

It is apparent that the iron oxide content of these soils bears no direct relation to the depth of color. This fact led Robinson and McCaughey to make the following very interesting remarks:

"It is unfortunate that the mechanical analyses of these soils are not available, so that the depth of film of ferruginous material on the soil grains from the several samples might be compared with the color. It is evident that a film of coloring

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[1] "Technology of Paint and Varnish," 297 (1917).

[2] "The Lead and Zinc Pigments," 217 (1909).

[3] Robinson and McCaughey: Bur. Soils Bull., 79, 20 (1911).

matter of a certain depth over *large*[1] soil particles would contribute much less to the total percentage of the coloring matter than if the film of the same thickness was spread over the same weight of exceedingly fine particles; and since the film is postulated to be of the same thickness in each case, the color must be alike in the two instances. The following laboratory experiment will serve to illustrate this point: Samples of 20 grams each of coarse, white quartz sand, averaging 2 mm in diameter, and white quartz flour were treated with ferrous sulphate solutions of such a concentration that the dried material should contain from 0.1 percent Fe_2O_3 to 2.5 percent of Fe_2O_3, with five intermediate percentages. The material was evaporated to a paste and enough ammonia added to precipitate the iron present. Hydrogen peroxide was then added to oxidize the iron and the material was heated to a dull redness to drive off the ammonium sulphate and dehydrate the iron oxide. In this manner the iron was deposited upon the surface of the quartz grains. The quartz flour containing 2.5 percent Fe_2O_3 was very nearly matched in color by the coarse quartz sand containing 0.25 percent Fe_2O_3."

We have now reached a point where it is necessary to consider the general case of a mixture of two powdered substances. The simplest case is where one mixes together a white and a colored pigment. If the particles of one pigment are small compared with the particles of the other, there will be a tendency for the smaller particles (if dry) to coat or "dust over" the larger ones. This tendency will be more marked as the difference in size increases. Anything which increases the adhesion will also favor the coating of the large particles. It is obvious, therefore, that the color of the mixture is determined very largely by this coating effect; the more completely the large particles of one pigment are covered by the smaller particles of the second and the greater the hiding power or opacity of the second pigment, the more will the mixed pigments approximate the color of the small particles. If the colored pigment is coarse and the white is fine, a mixture of

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[1] [The italics are mine T. R. B.]

equal proportions of the two may be very nearly white; if the white is coarse and the colored pigment is fine, the mixture may be nearly indistinguishable from the pure colored pigment. The tinting strength of a pigment, besides depending upon the *absolute* size of the particles, is determined to a very great extent by the *relative* size of the particles compared with those of the second pigment. This, though perhaps obvious enough, has been overlooked almost entirely in previous work.

Since color is only one of many physical properties, we should expect to find other properties of mixed powders influenced largely by the relation between the size of particles. The electrical conductivity is such a property. This case has been discussed by Fink,[1] using mixtures of thoria and tungsten powders. He remarks that "the electrical conductivity of mixtures of finely divided substances is a function of the relative size of the components." His results also show how the appearance of the mixtures is affected in the same way, as the following table, prepared from Fink's data, indicates:

TABLE III

Fineness		Mixture	
ThO_2 (white)	Tungsten (black)	Appearance	Specific resistance
0.720	0.113	White	—
0.720	0.350	White	—
0.576	0.235	White	173 ohms
0.305	0.113	White	—
0.305	0.330	Nearly black	—
0.238	0.577	Nearly black	0.108 ohm

Equal parts by weight of thoria and tungsten were present in each mixture. The fineness was determined by a so-called "tap test," not a very satisfactory way. The conductivity data were obtained with rods fired at 1600° C for three hours. Since the resistance of the pure thoria was greater than 10^{12} ohms as compared with 0.016 for the tungsten, it may seem a

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[1] Jour. Phys. Chem., 21, 38 (1917).

bit surprising that a value so low as 173 ohms should have been obtained for the first mixture, as the color would indicate that the coarser tungsten particles (black) were very effectively coated over by the finer thoria (white). Sintering occurred during the firing of the rods, however, and this must have changed greatly the orientation and relative size of the particles, for the shade of *all* the mixtures became much more nearly uniform after firing.

As color is determined largely by the small particles coating the larger ones, so is the conductivity of the mixture very nearly that of the smaller particles, in case the coating is sufficiently complete. We have as an extreme case, metal gels[1] and deposits of finely divided metals containing an adsorbed substance of low electrical conductivity. Benedick's[2] "acetate copper" formed by electrolysis of cupric acetate owes its strikingly low conductivity to the fact that the copper crystals are coated with copper oxide. Faraday's mirrors[3] of colloidal gold were practically non-conducting as were similar mirrors of Lea's silver.[4] Fink[5] also points out that the low conductivity of copper containing sulphur, etc., may be due to sulphide films coating the copper crystals.

When the finely divided component constitutes only a small part of the mixture the question of adhesion becomes important. We do not know why powders adhere to surfaces[6] when powder and surface both are presumably dry, nor do we know to what extent adhesion occurs. We have carried out in the Cornell laboratory some preliminary experiments along this line and hope to be able to report progress before very long. It seems, however, that adhesion to the large particles increases as the small ones become still smaller and microscopic

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[1] Cf. Briggs: Jour. Phys. Chem., **17**, 281 (1913).

[2] Metallurgie, **4**, 5, 33 (1907).

[3] Phil. Mag., (4) **14**, 402, 512 (1857).

[4] Cf. Barus and Schneider: Zeit. phys. Chem., **8**, 278 (1891); Lüdtke: Wied. Ann., **50**, 678 (1893).

[5] Loc. cit.

[6] Cf. Tammann: Drude's Ann., **18**, 857 (1905); Biltz: Ibid., **31**, 1050 (1910).

examination indicates that the topography of the large surfaces is of great influence; the rougher the surface the more the tiny particles are caught and held. If the large crystals are covered with a thin film of moisture or oil, the adhesion will be greatly increased, of course, in case both powders are wetted by the liquid. On the other hand if the moisture or oil is present in sufficient amount, the apparent tinting strength of the fine pigment may become less, owing to the falling off in hiding power when one changes the medium surrounding the fine particles from air to liquid. Even when the oil is present in large excess, the same general relations will hold between size and orientation, for the small particles, especially if they form readily a suspension in the oil, will tend to surround and hide the larger ones. The high tinting power of the lakes precipitated on coarse bases such as barytes is due to the small size of the color particles in comparison with the base, and to the completeness with which the lake adheres to the base by adsorption, or mechanical adhesion.

It is possible to summarize the theory as follows: Tinting strength depends upon at least three factors—the relative size of the particles, the extent to which the smaller particles adhere to the larger ones and the hiding power *at constant size* of the small particles. Strength can be used as a measure of hiding power *in case the pigments under examination actually coat over or hide something*, and if the size relation and adhesion (coating) factor are kept constant throughout. Since little or no attention has ever been paid to these points, there is little wonder that nobody has been able to decide just what relation the data on strength and opacity (hiding power) indicate.

If strength tests are made to gain some idea of the hiding power of a pigment, it would seem that oxide of zinc is most unfortunately chosen as the standard white color. Few, if any, pigments consist of particles of smaller average size, so that the tendency will be to coat the other pigment with the zinc or else neither pigment will coat the other to any appreciable extent. As a result, the test may tell something about the coloring and hiding strength of zinc oxide, but does not necessarily indicate anything regarding the colored pigment. The white color should be relatively coarse; ground barytes ought to be preferable to zinc oxide.

On the other hand, we have seen that Ostwald interpreted his data with methyl violet lake on different white bases as measuring the hiding power of the white base, although the latter was coated with the violet lake. It seems to me, however, that the data indicate merely that the tinting power of a given percentage of lake grows smaller the greater the total surface to be covered and the smaller the particles of the base. In so far as the fineness of the base is a measure of its hiding power, Ostwald's conclusion is a just one; but fineness of subdivision is only one of the factors determining hiding power. As a matter of fact, Ostwald was measuring the extent to which a given quantity of a colored lake was able to hide surfaces whose total area differed within wide limits, and he was assuming that the data measured the hiding power of substances which were actually *hidden* more or less completely.

Gardner's statement about red oxide of iron and chrome green containing barytes is now perfectly simple. Red oxide of iron and the green are much finer than barytes, hence the latter are coated over and hidden more or less completely. The greater effect with chrome green indicates that the particular chrome green was finer than the red oxide, though adhesion or hiding power may have been greater as well. Sabin's data are easily explained by the theory, for red lead is reported to be rather coarsely crystalline (except in the form of orange mineral) while lampblack is extremely fine.[1] Holley's remarks concerning the tints of chrome yellow indicate merely that different samples have particles of quite different average size—which certainly is neither unexpected nor mysterious.

Experimental

During the summer of 1916, Mr. Tears carried out, as part of his senior research, some experiments of a preliminary

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[1] Cf. Kühn: Zeit. angew. Chem., 28, 126 (1915).

nature to test the hypothesis outlined above. Lacking at that time a white pigment of a suitable nature he used dolomite that had been analyzed mechanically by means of a set of standardized sieves. With dolomite as the white, the tinting power of various samples of "soluble" Prussian blue, lampblack, chromium oxide, and iron oxide was determined.

Ten grams of dolomite were taken for each test and the particular color added from a weighing bottle in minute quantities at a time until the mixture matched exactly a standard shade. Great care was taken to have the powdered substances dry and to see that the mixture was uniform and complete. Much trouble had been given in early experiments by the presence of lumps of the very fine coloring material; it was found necessary to rub up the mixture with a spatula or to grind it very gently until no further deepening of the shade occurred. The experiments were tedious and it was not easy to obtain good checks.

The data follow:

TABLE IV

Size of dolomite variable. Size of colored pigments constant

Dolomite (10 grams)	Weight Cr_2O_3	Weight Prussian blue	Weight lampblack
passed through 200	3.70	0.94	0.654
100–200	0.36	0.12	0.025
40–100	0.20	0.032	0.019
retained by 40	0.08	—	0.008

Although these data are striking enough in all three cases that were studied, they are particularly so in the case of lampblack. On glancing at the third column of data it will be seen that the finest dolomite required eighty times as much lampblack as the coarsest dolomite did to produce the same shade of grey. Someone may object that it is very hard to judge accurately the appearance of mixtures composed of very coarse and very fine dolomite, but even if one considers only the first two horizontal rows of data, the numbers are sufficient to compel attention. Thus the finer dolomite required ten times as much chromium oxide, eight times as much Prussian blue and twenty-six times as much lampblack as did the coarser dolomite (100–200 mesh). These numbers should be regarded as rough approximations only, but they do show that the results are in accord with the general theory.

A few months ago we were fortunate enought to receive from the National Lead Company, through the courtesy and coöperation of Messrs. G. W. Thompson and R. L. Hallett, samples of white lead and red lead, graded carefully according to size by means of the Thompson classifier.[1] Tests were made with these pigments by Mr. A. W. Ward, as part of his senior research, but the work was interrupted rather prematurely by Mr. Ward leaving to enter upon service in connection with the war.

A microscopic examination of the pigments was made for the purpose of measuring approximately the average size of the particles in the different samples. The necessary equipment was placed at Mr. Ward's disposal through the courtesy of Professor Chamot. The micrometer eyepiece was calibrated in the usual manner and the size of the particles was ascertained by averaging 100 readings. The data follow:

TABLE V

Microscopical examination of graded pigments. Size determined by averaging 100 readings. Ocular micrometer method

Thompson classifier Cone number	Average size in microns	
	White lead	Red lead
1	32	34
2	25	23
3	17	12
4	7	9
5	4	5

Preliminary experiments were carried out with dolomite and red lead. Tear's procedure was followed, except that one gram of dolomite was used in each run. Greater care was

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[1] Jour. Ind. Eng. Chem., 2, 90 (1910).

taken in adding the red lead and in making the mixture uniform. The data obtained confirm the previous results.

TABLE VI

Experiments with dolomite and red lead. Dolomite 1 gram. Cone No. 5 red lead added until each mixture had about the same shade

Dolomite	Read lead added (in grams)
Passed 350 mesh sieve	0.126
200–350	0.079
100–200	0.033
80–100	0.016

Next, mixtures of white and red leads were prepared. Owing to the limited supply of classified pigments, only one gram of the white was taken for each determination. The red was added from a weighing bottle slowly and with extremely careful intermixing, until the appearance and color of all the mixtures were as nearly as possible the same. The color matching was done with the eye and the pigments were mixed dry. The loss in weight of the weighing bottle containing the red lead was taken to be the amount of red added. Each experiment was run in duplicate.

TABLE VI

Experiment number	White lead (1 g) Cone number	Red lead Cone number	Red lead added (gram)			Percent red lead in mixture (Average)
			Original	Duplicate	(Average)	
1	1	5	0.0345	0.0345	0.0345	3.33
2	2	5	0.0478	0.0450	0.0464	4.43
3	3	5	0.0553	0.0510	0.0532	5.05
4	4	5	0.0636	0.0658	0.0647	6.08
5	5	5	0.124	0.110	0.117	10.47
6	5	1	0.887	0.905	0.896	47.31

Experiment 7—The mixture prepared in Experiment 6 above was ground in an agate mortar. The shade darkened to a very great extent, showing the effect of pulverizing the coarse red lead.

Experiment 8.—The mixture resulting from Experiment 1 was likewise ground. The effect was striking, the shade becoming much lighter and the light red of the original turning to a very pale brown.

The data confirm the theory in a very satisfactory way. The finer the red and the coarser the white, the less is the amount of red required to produce a given shade. Experiments one and six represent the most extreme cases. In one there is present more than fourteen times as much red lead, and yet the two mixtures have almost the same color and appearance.

The results of this paper may be summarized as follows:

(1) The ability of one pigment to impart its color to a mixture containing a second is greatly increased if the first pigment coats over and hides the particles of the second one.

(2) The smaller the particles of the first pigment relatively to those of the second, the less is required to coat the particles and the greater becomes the tinting strength of the first pigment.

(3) Anything which favors the adhesion of the fine particles to the coarse ones and thus promotes the coating-over effect, increases the tinting strength of the first pigment.

(4) For particles of the same size, and equal coating tendency (adhesion, etc.) the greater the hiding power the higher is the tinting strength.

(5) With proper control of the other factors, it ought to be possible to estimate hiding from tinting strength, in case the pigment to be tested is very fine compared with the one with which it is mixed and if it actually coats over and hides the latter.

(6) Other physical properties of mixed powders besides color are dependent very largely upon relative size of particles and the coating-over effect.

(7) Relative size of particles has an important bearing on the question of a mixture of two pigments, one of which is "inert." A larger amount of inert pigment may be added

without appreciably affecting the shade of the mixture, the coarser the inert pigment is in comparison with the other one. This observation helps to account for the fact that ground barytes, silex and asbestine are used so generally as inert fillers, for all three, in the form in which the paint manufacturer uses them, consist of particles which are far larger than is the case with the majority of the "true" pigments. The question of how far one should carry the addition of an inert pigment is of course another story.

Cornell University

NEW BOOKS

A Short History of Science. *By W. T. Sedgwick and H. W. Tyler. 22 × 15 cm; pp. xv + 474. New York: The Macmillan Company, 1917. Price: $2.50.*—"The present work aims to furnish the student and the general reader with a concise account of the origin of that scientific knowledge and that scientific method which, especially within the last century, have come to have so important a share in shaping the conditions and directing the activities of human life. The specialist in any branch of science is finding it more and more difficult to keep himself informed even to the indispensable minimum extent, as to current progress in his own field,—and hence his frequent neglect of all other branches than his own. It may reasonably be expected that some attention to the history of science on the part of students will give them a better understanding of the broad tendencies which have determined the general course of scientific progress, will enlarge their appreciation of the work of successive generations, and tend to guard them against falling into those ancient pitfalls which have bordered the paths of progress.

This is an admirable book, good in plan and good in execution. The chapters are entitled: early civilization; early mathematical science in Babylonia and Egypt; the beginnings of science; science in the golden age of Greece; Greek science in Alexandria; the decline of Alexandrian science; the Roman world and the Dark Ages; Hindu and Arabian science—the Moors in Spain; progress of science to 1450 A. D.; a new astronomy and the beginnings of modern natural science; progress of mathematics and mechanics in the sixteenth century; natural and physical science in the seventeenth century; beginnings of modern mathematical science; natural and physical science in the eighteenth century; modern tendencies in mathematical science; some advances in physical science in the nineteenth century—energy and conservation of energy; some advances in natural science in the nineteenth century—cosmogony and evolution.

It is rather surprising to read, p. 142, that in the fourth century the emperor Constantine wrote: "We need as many engineers as possible. As there is lack of them, invite to this study persons of about eighteen years, who have already studied the necessary sciences. Relieve the parents of taxes and grant the scholars sufficient means.

In view of the fact that Clausius is said to have refused even to look at Pfeffer's osmotic pressure experiments because they could not possibly be true, one is interested to learn, p. 222, that the principal professor of philosophy at Padua resisted Galileo's repeated and urgent entreaties to look at the moon and planets through his telescope, and that this same philosopher tried to convince the Grand Duke that the satellites of Jupiter could not possibly exist. "There are seven windows given to animals in the domicile of the head through which the air is admitted to the tabernacle of the body, to enlighten, to warm, and to nourish it. What are the parts of the microcosmos? Two nostrils, two eyes, two ears, and a mouth. So in the heavens, as in a macrocosmos, there are two favorable stars, two unpropitions, two luminaries, and Mercury undecided and indifferent. From this and many other similarities in nature, such as the seven metals, etc., which it were tedious to enumerate, we gather that the number of planets is necessarily seven. Moreover, these satellites of Jupiter are invisible to the naked eye, and therefore can exercise no influence on the earth, and therefore are useless, and therefore do not exist. Besides, the Jews and other ancient nations, as well as modern Europeans, have adopted the division of the week into seven days, and have named them after the seven planets. Now, if we increase the number of the planets, this whole and beautiful system falls to the ground." On p. 252, there is an apt quotation from Crew, "Leonardo da Vinci likens a scientific conquest to a military victory in which theory is the field marshal and experimental facts the soldiers. The philosophers who preceded Galileo had, in the main, been trying to fight battles without soldiers.

Arago says, p. 285: "The calculus of probabilities, when confined within just limits, ought to interest, in the equal degree, the mathematician, the experimentalist, and the statesman. From the time when Pascal and Fermat established its first principles, it has rendered, and continues daily to render, services of the most eminent kind. It is the calculus of probabilities, which, after having suggested the best arrangements of the tables of population and mortality, teaches *us to deduce from these numbers, in general so erroneously interpreted,* conclusions of a precise and useful character; it is the calculus of probabilities which alone can regulate justly the premiums to be paid for assurances; the reserve funds for the disbursements of pensions, annuities, discounts, etc. It is under its influence that lotteries and other shameful snares cunningly laid for avarice and ignorance have definitely disappeared.

In a series of appendices are given: the Oath of Hippocrates (about 400 B. C.); The Sixth Part of the Opus Majus of Roger Bacon (1267 A.D.); Dedication of The Revolutions of the Heavenly Bodies by Nicolas Copernicus (1543); William Harvey's Dedication of his work on the Circulation of the Blood (1628); Galileo before the Inquisition (1633); Préface to the *Philosophiae Naturalis Principia Mathematica,* by Isaac Newton (1686); An Inquiry into the Causes and Effects of the *Variolae Vaccinae,* by Edward Jenner (1798); Principles of Geology, by Charles Lyell (1830); some Inventions of the Eighteenth and Nineteenth Centuries.

The reviewer has found this a very interesting book and he feels certain that it will produce the same impression on others.

Wilder D. Bancroft

Laws of Physical Science. *By Edwin F. Northrup. 20 × 14 cm; pp. vii + 210. Philadelphia: J. B. Lippincott Co., 1917. Price: $2.00 net.*—In the preface the author says: "Exact knowledge consists of accumulated facts and sets of formulated propositions respecting facts. Data, Mathematical relations and Physical laws constitute the three firm supports of Physical Science and Engineering. The *data* of physical science are readily accessible in several published tables of physical constants. The *mathematics* used in physical science has been summarized, classified and formulated, for ready reference, in many published books. The author is not aware, however, of any hand-book or reference work which contains a full list of the *general propositions* or *laws of science.*

"Such reference lists are not without value, and this book has been prepared to fill an obvious gap in the literature of Physical Science. Furthermore, it appears to the author that students in any of the branches of Natural Science will not only find guidance, but will also derive inspiration by having before them under a single view the very epitome of the world's heritage of the fundamentals of its knowledge and wisdom. None will question that the fundamentals of science are its laws, principles, theorems, and precise statements of the general properties of matter; but it is not always easy for students in one branch of science to find and to know the literature on important principles and facts in an entirely different, or even in closely allied branches of science. The author hopes that what has been here gathered together and classified will help such students in their search and give them the means to broaden their view.

"We have chosen for a title, 'Laws of Physical Science;' but many general propositions, theorems, and mere statements of important facts have been included which perhaps, if strictly considered, could not be discriminated as laws. Indeed, it was found impossible, in many cases, to decide if certain propositions possess sufficient generality and validity to deserve the title 'law.' When, however, such doubts existed, a policy of inclusion has been followed in preference to one of exclusion."

The subject is arranged under the headings: mechanics; hydrostatics, hydrodynamics, and capillarity; sound; heat and physical chemistry; electricity and magnetism; light. The plan of the book is admirable. To have written it must have involved an enormous amount of work and we are grateful to the author for what was evidently a work of love. One must recognize, however, that in some parts the work could have and should have been done better. There may be a difference of opinion as to the advisability of speaking about the absorption of a gas by a solid, p. 84. Everybody has done it in the past; but adsorption is the proper term nowadays. On p. 91 the formula ascribed to Eötvös is really the Ramsay and Shields formula. On p. 93 is given what purports to be the Raoult formula for the lowering of the vapor pressure. It is not the original Raoult formula and leads to an absurdity for concentrated solutions. There is no objection to giving such a formula for historical reasons if one wishes to; but it is certainly wrong not to give the van't Hoff formula which Raoult himself accepted. The definition of the cryohydric temperature, as given on p. 99, would seem to limit it to sodium chloride and water, though of course that was not intended. There is no reference to eutectic temperatures although the cryohydric temperature is a special case under the general head. The statement of the phase rule on p. 100 is inaccurate. The formulation is true only when no other variables are considered but the pressure, temperature, and concentrations. In a book of this sort an accurate statement should be given. Under the grandiloquent title of the law of mutuality of phases, p. 100, we find the inaccurate statement that if two phases are in equilibrium with a third, they are in equilibrium with each other. As a matter of English one objects to the statement, p. 102, that the name catalysis "*means* an increase in velocity of reaction caused by the presence of substances which do not take part in it (or only to a secondary extent) although the reaction is capable of taking place without their presence." One should make a distinction between the definition and the meaning of a word. On the same page is the erroneous statement that substances can be divided into two classes, crystalloids and colloids. It scarcely seems worth while to say, p. 102, that "any substance is particularly transparent to radiation which has already been sifted by a plate of that substance." On p. 109 it is hardly fair not to qualify the statement that when light of the same kind is used, the photochemical action depends solely on the product of the intensity and the duration of the exposure.

This may seem hypercritical to some; but the essence of a book of this sort is accuracy. Inaccuracy is nearly as bad here as in a table of logarithms. Unfortunately, the author has taken statements from text-books without bothering himself very much whether they were right or not. Presumably the rest of the book is better than the part dealing with physical chemistry, though even there one cannot agree with everything. On p. 38 are two statements: "For the same liquid and the same temperature, the mean heights to which the liquid rises are independent of the forms of the capillary tube except at the meniscus. Provided the liquid moistens [wets] the tube, neither the thickness of the tube nor its nature has any influence on the height to which the liquid rises." The reviewer does not believe the first statement and there are physicists who do not believe the second. The experiments of Bigelow and Hunter prove that both cannot be true. On pp. 26 and 27 are given the principles of d'Alembert, Gauss, and Hamilton, in which case the Theorem of LeChatelier should have been referred to somewhere in the volume.

Wilder D. Bancroft

The Nature of Solution. *By Harry C. Jones. 23 × 15 cm; pp. xxiv + 380. New York: D. Van Nostrand Co., 1917. Price: $3.50.*—In the preface the author says. "No subject in chemistry has received more attention, especially during the last quarter of a century, than that of solution. This is due primarily to the fundamental significance of solution for chemical science. Solutions in the broad sense of the term are fundamental not only for chemistry, but for geology and the various branches of biology. Matter in the pure, homogeneous conditions is relatively inert. It becomes active when mixed in a certain way with other matter in the same or in a different state of aggregation—when dissolved. Since solution is so fundamental for the natural sciences in general, and for chemistry in particular, we must know what solutions are, if we would ever make these various branches of science exact. Since chemistry has to do largely with the science of solution, it can become an exact science only by the science of solution becoming exact. We must first know what is the real condition of matter in solution. What law does it obey? Is the dissolved substance combined with the solvent, and if so, with how much of it?

"As we shall see, many of the questions have now been answered and the relations between solutions and gases accurately established. This is of the greatest importance. We really know something about matter in the gaseous state, and we can now apply this knowledge to matter in the dissolved condition; and this has done more than any other one discovery to place the science of solution upon an exact basis."

As might be expected, the book is essentially a glorification of the solvate theory. That theory has been criticized so often that it is not necessary to discuss it here. About seventy pages have been given to colloidal solutions and this is a distinct advance, though one may not agree with the author's presentation, which is essentially non-committal even when the general conclusion is sound. The author concludes, p. 239, that emulsoids have an osmotic pressure but decides, p. 240, that it is impossible to determine the molecular weight of an emulsoid because "it is highly probable that in most cases the lowering of the freezing point and the rise of the boiling point observed were due to crystalloid impurities in the colloids. Further, if the colloids themselves actually produced the phenomena observed, it is not at all certain that these properties could be used to determine the molecular weights of these colloids. Before this can be done, it must be shown that Raoult's law of freezing-point lowering and depression of vapor tension, or rise in boiling point, hold for colloids as well as for crystalloids. If these methods cannot be used to determine the molecular weights of emulsoids, still less can they be employed with suspensoids, which show still smaller depressions of the freezing point and rise in the boiling point, if they have these properties at all."

The book is well written and is interesting reading. It furnishes admirable material for a psychologist wishing to study the foundations of scientific belief. The proof-reading has been a bit slack.

Wilder D. Bancroft

Organic Chemistry. *By W. A. Noyes. Third revised, enlarged edition. 23 X 16 cm; pp. xii + 292. Easton: The Chemical Publishing Co., 1916. Price: $2.00.*—In the preface to the first edition the author makes the following statement with regard to the purposes of the work: "Two distinct purposes have been kept in view. The first has been to furnish the beginner with sufficiently full and accurate directions and clear, concise, theoretical explanations of processes which have been found successful in practical laboratory experience. The second object has been to furnish the more advanced student and practical worker with a guide which will aid him in the selection of processes which are likely to be successful for the preparation of compounds which he may desire to use."

In the preface to the present edition—the third—the author makes a brief additional statement. "Comparatively few changes have been made in this edition. A few references to recent articles in the Journals have been added and a few corrections or changes on the basis of recent work have been inserted. Directions for a synthesis involving the use of malonic ester have been included. A table of atomic weights is given for the convenience of students."

The work is to be regarded as a manual of preparative organic chemistry and forms a fitting companion to Gattermann's very similar book, to which the author acknowledges his indebtedness. There are included detailed directions for some 132 organic preparations and syntheses together with chapters on the qualitative and quantitative analysis of the compounds of carbon. The original references that accompany each preparation form a particularly happy feature, though it is to be greatly regretted that the author has omitted the date in referring to the original journal articles. The present edition, however, constitutes a very satisfactory addition to a very useful work. *T. R. Briggs*

Les Allemands et la Science. *By Gabriel Petit and Maurice Leudet. 19 X 12 cm; pp. xx + 376. Paris: Librairie Félix Alcan, 1916. Price: 3 francs, 50.*—This volume consists of a number of short articles by distinguished French-men intended to show that the alleged superiority of Germany in science is a myth. The titles and authors are as follows: "In the Field of Art," by A. Alexandre; "Hermann the Liberator," by E. Babelon; "The Unworthiness of the German Scientists," by M. Barrès; "War and Paleontology," by M. Boule; "German Science," by E. Bontroux; "The Teaching in Medical Clinics in France and Germany," by A. Chauffard; "Science has its Roots in Liberty," by A. Chauveau; "The Limited Part Played by Germany in the Development of the Sciences," by Y. Delages; "German Surgery," by F. Delbet; "German Science and German Virtues," by P. Duhem; "Commercial Therapeutics of the Germans," by E. Gaucher; "Science and the German Mind," by A. Gautier; "Science and Scientists," by E. Gley; "Letter to Professor Gabriel Petit," by Dr. Grasset; "Germany and the Biological Sciences," by F. Henneguy; "German Erudition," by C. Julian; "German Medicine and French Medicine," by L. Landouzy; "The Bluff of German Science," by F. LeDantec; "German Science and the Government," by R. Lote; "Geology, Prussian Style," by S. Meunier; "Scientific Germany," by E. Perrier; "The History of Science and the German Claims," by E. Picard; "French and German Obstetrics," by Prof. Pinard; "The Mediocre Share of Germany in Scientific Discovery," by W. Ramsay; "Militarized Science," by S. Reinach; "French Science and German Science," by C. Richet; "Evolution of Medical Science in France and Germany," by H. Roger.

While these articles are interesting and while it is true that Germany has obtained a scientific reputation which is by no means warranted, the book is rather depressing reading. It is very difficult not to understate the German achievements and not to overvalue the French ones. It is also rather a shock to find a man like Sir William Ramsay saying what he does when one recalls his affiliations with Germany in the past. All that he says is probably true; but it would have been better for him not to have said it. On the other hand everybody knows that Germany's strength is not in the production of an occasional genius but in her development of a very large number of the highest grade of second-class men. No one would think of comparing Ostwald with van't Hoff for instance; but Ostwald is the man who developed physical chemistry and gave it the standing which it had at the time when he changed to metaphysics. It would be a pity to over-rate Ostwald; but it is foolishness to deny that the scientific world owes him a great deal and that he has a marvellous way of presenting things so as to get them adopted and believed.

It is probably a good thing to have a clear-cut statement of what people believe that Germany has and has not done in science; but one cannot welcome it with pleasure even though one may agree with much of what is said.

Wilder D. Bancroft

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ON THE MOLECULAR PHYSICS OF ORE FLOTATION[1]

BY WILL. H. COGHILL[2] AND C. O. ANDERSON[3]

Introductory

It is common practice to inquire into the efficiency of a process as soon as it has been made commercially successful. So it has been with the flotation process. Hoover[4] makes an erroneous statement about the force required to penetrate a liquid surface, and with it as a basis calculates and tabulates the actual and theoretical capacities of several types of flotation machines. Other writers have made similar efforts by using principles incorrectly. The most striking case is that of Van Arsdale.[5] He begins with the premise that "the maximum weight that can be supported on the surface of water is equal to the surface tension of the area supporting the weight." Beginning thus with a false premise, naturally he ends with false conclusions. It is scarcely hypercritical to say that for these fallacies to go unchallenged after receiving favorable editorial comments and being incorporated in a book, portends a tardy science of flotation.

In this discussion the underlying principles involved in calculating the floatability of solids and constructing profiles arising from surface tension will be pointed out and the calculation of "theoretical capacities" left to the more ambitious.

Maximum Depression against a Vertical Plate

Imagine a plate of unit horizontal length placed vertically with its lower edge below the surface of water with its faces so prepared that on one side $\theta = 90°$ and on the other, $\theta = 180°$, (θ is the angle of contact). It will appear in cross sec-

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[1] Published by the permission of the Director of the U. S. Bureau of Mines.

[2] Metallurgist, U. S. Bureau of Mines, Seattle, Wash.

[3] "Fellow," College of Mines, University of Washington.

[4] T. J. Hoover: "Concentration of Ores by Flotation," p. 77 (1914).

[5] G. D. Van Arsdale: "How Flotation Works," Eng. & Min. Jour., 101, 851 (1916).

tion at right angles to its length as shown in Fig. 1. Let h be the depth of the dimple in centimeters. It is obvious that the sum of the horizontal forces must be zero, otherwise there would be motion, and work would be done without the expenditure of energy, which is contrary to the laws of nature.[1]

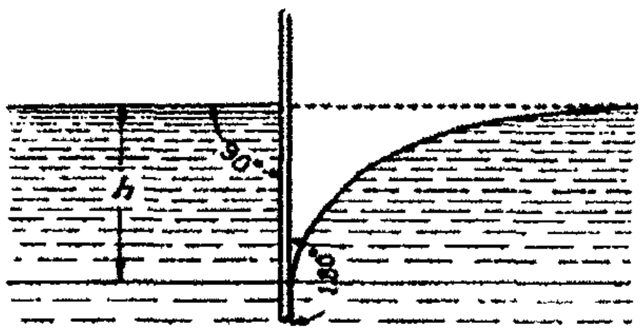

Fig. 1
Vertical plate with faces prepared so that θ is 90° and 180°

Since, on one side, the surface of the dimple meets the plate at 180°, the horizontal component of the pull due to surface tension is zero. On the other side, it is 0.0715 gram (the assumed tensile strength of the film). Opposite and equal to this force is that of the head of the water from a to b, which is

$$h \times \frac{h}{2} = \frac{h^2}{2};\ \frac{h^2}{2} = 0.0715.$$

$h^2 = 0.143.$

$h = 0.378$ centimeter, the maximum depth possible in pure water where the face is vertical.

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[1] The equilibrium of this system and the one in Fig. 2 was discussed by Le Conte and Riley in the Philosophical Magazine in 1883. Le Conte fell into a dispute with Young, who "insisted that according to Laplace's theory the horizontal molecular pressures on the opposite faces being unequal, the composite plate should be drawn in the direction of the center of concavity of the meniscus on the glass face (Fig. 2), and thus cause the entire system to take on a motion of translation.

He, therefore, "made the following arrangements with the view of experimentally testing the question: A plate of well cleaned glass and a plate of polished steel were cemented together so as to constitute a composite plate of these substances. This was floated in a vertical position by securing masses of cork to the two faces, and attaching a leaden sinker of the proper weight to the lower extremity of the plates. If such a composite plate is plunged vertically into alcohol contained in a large vessel, a concave meniscus will be formed by the ascending liquid on the glass face, while on the steel face no meniscus will be formed, and the adjacent surface of the alcohol will be horizontal." There was no evidence of unbalanced forces on the floating faces.

Riley investigated this principle and included conditions represented by Fig. 1 and found that in "every case the identity shows that the magnitude of these tensions is just the same as if the surfaces came up perpendicular to the plates without elevation or depression."

Maximum Rise against a Vertical Plate

The profile of the liquid surface wetting the glass, Fig. 2, is the inverted profile of the one where $\theta = 180°$ in Fig. 1, because hydrostatic pressure is the only variable, and it varies directly with depth—from the top of the meniscus in Fig. 2 to the bottom of the dimple in Fig. 1. The maximum rise is therefore 0.378 centimeter. The radius of curvature at any point is determined by the formula

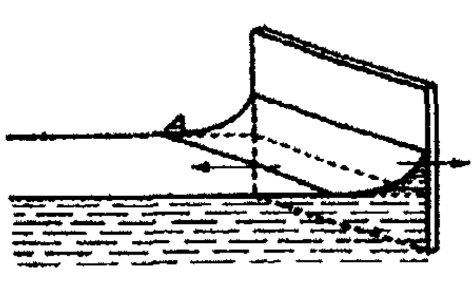

Fig. 2
Capillary rise against a vertical plate

$$P = \frac{T}{R}.$$

Note that in Fig. 1, where h was found to be 0.378 centimeter, the solid face was vertical. The maximum depth is obtained when the non-wetted face is horizontal. Let this depth be H.

Profile of a Drop of Water

If the liquid is resting on a solid which it meets at an angle of 180°, the drop will appear as shown in Fig. 3. The total

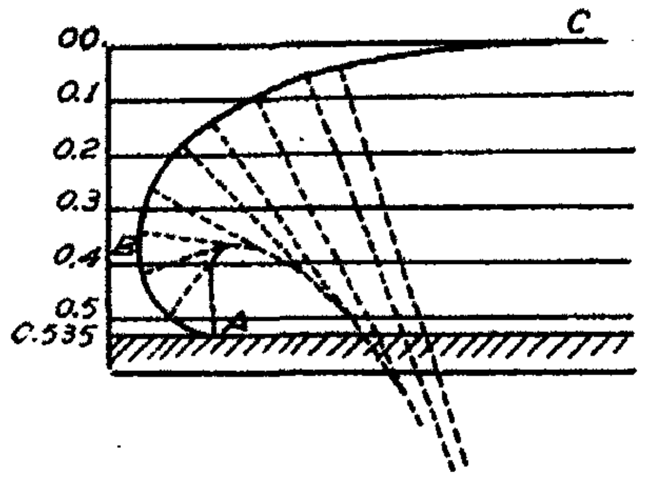

Fig. 3
The arc method of constructing the profile of drops of water

hydrostatic pressure against an imaginary vertical plane of unit horizontal length against the right end is $\frac{H^2}{2}$. The opposite and equal force is 2 T, where T is tensile strength in gram-weight per unit length of film.

$$\therefore \frac{H^2}{2} = 2T,\ H^2 = 4T = 0.286$$

$$H = 0.535 \text{ centimeter.}$$

To draw this, take a horizontal line to represent the upper plane surface. Having the value of H, take another line to represent the surface of the solid on which it rests. Let the surface of the water meet the solid surface at A. The radius of curvature R of the surface of the water where it leaves this solid is found by substituting in,

$$P = \frac{T}{R} = H:$$

$$0.535 = \frac{0.0715}{R}$$

$$R = 0.134 \text{ centimeter.}$$

From "A" measure a distance R vertically upwards, and with the point so chosen, describe a small circular arc of radius R, to represent the lowest arc of the profile. The remaining arcs of the profile are drawn as indicated by the figure.

It is not absolutely correct mathematically to apply the formula

$$P = \frac{T}{R}$$

in this case. It is correct only when a surface element is obtained by bending a flat surface about a straight line as an axis, *i. e.*, only one plane of bending, giving a cylinder. With the flattened drop there are really two planes of bending at right angles to each other, and when the radii are R_1 and R_2, the correct formula is

$$P = T\left(\frac{1}{R_1} + \frac{1}{R_2}\right).$$

Generally, however, R_2 is so large that $\frac{1}{R_2}$ may be neglected. When $R_1 = R_2$, we have, of course, the spherical drop.

The Proverbial Steel Needle

The following demonstration of equilibrium of the floating needle is taken from Edser:[1]

Let Fig. 4 represent the transverse section of a needle of radius r, floating on water. Let the surface of the water leave the needle tangentially at B, where the radius CB of the needle makes an angle A with the vertical. Let the point B be at a distance, h, below the flat surface of the water.

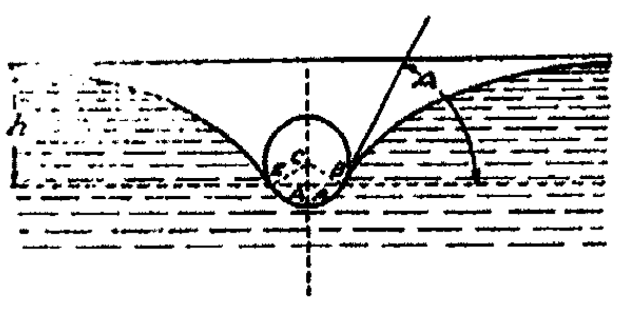

Fig. 4
Transverse section of wire floating on water when θ is 180°

The following are the upwardly directed forces acting on unit length:

The force due to the surface tension of the water is equal to

$$2\ T \sin A. \qquad (a)$$

If the portion of the needle below the horizontal plane EB were removed, the hydrostatic pressure of the water would exert an upward force equal to

$$2\ r \sin A\, h \qquad (b)$$

The additional upward force due to the segmental portion of the needle below EB is equal to the weight of the water displaced by this portion of the needle; that is,

$$r^2\left(\pi \cdot \frac{A}{180} - \sin A. \cos A\right) \qquad (c)$$

It is assumed that the length of the wire in comparison with the diameter is so great that the surface-tension pull upon the ends may be neglected.

The downward force is

$$7.7 \cdot \pi r^2. \qquad (d)$$

We now wish to eliminate h in Equation b. Inspection shows that for horizontal forces in FB to be in equilibrium,

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[1] Edwin Edser: "General Physics for Students," p. 340 (1911).

$$\frac{h^2}{2} = \mathrm{T} - \mathrm{T}\cos \mathrm{A}.$$

$$h = 2\sqrt{\mathrm{T}}\sqrt{\frac{1 - \cos \mathrm{A}}{2}}.$$

$$= 2\sqrt{\mathrm{T}}\sin\frac{\mathrm{A}}{2}. \qquad (e)$$

Substituting this value for h in Equation b and equating the upward and downward forces, we obtain the equation

$$2\mathrm{T}\sin \mathrm{A} + 4r\sin \mathrm{A}\sin\frac{\mathrm{A}}{2}.\sqrt{\mathrm{T}} +$$

$$r^2\left(\pi.\frac{\mathrm{A}}{180} - \sin \mathrm{A}\cos \mathrm{A}\right) = \pi r^2\, 7.7.$$

Setting sin A cos A equal to 0.5. sin 2A *(f)*

and transforming,

$$r^2\left(24.2 + 0.5\sin 2\mathrm{A} - \pi.\frac{\mathrm{A}}{180}\right) - 1.07\, r\sin \mathrm{A}\sin\frac{\mathrm{A}}{2}$$

$$= 0.143\sin \mathrm{A}. \qquad (g)$$

Fig. 5 shows the values of r for values of A lying between 0° and 120°. It will be noted that the maximum value of r corresponds to A = 100°, and is equal to 0.0995 centimeter, or roughly 1 mm. Thus the diameter of the largest needle that can float on water is equal to two millimeters approximately. The position of the needle relative to the surface is shown in Fig. 6. The curve in Fig. 5 shows that the needle is in unstable equilibrium when A is greater than 100°.

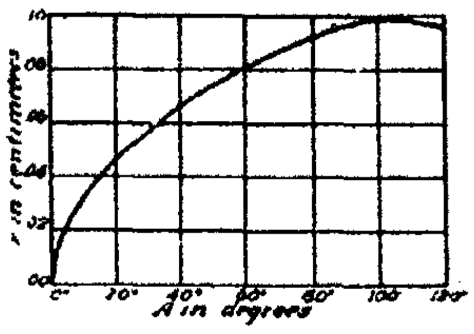

Fig 5
Graph exhibiting relation of r and A for steel wire on water where θ is 180°

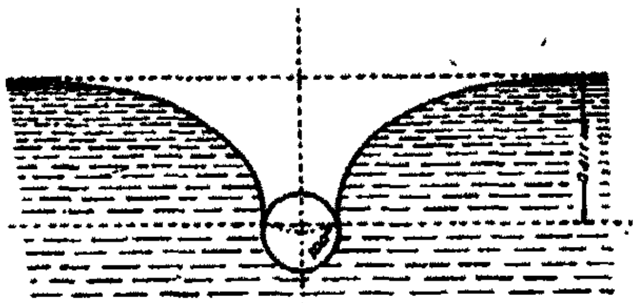

Fig. 6
Steel wire floating on water where θ is 180° and r is a maximum

Liquid Profiles

A method of constructing liquid profiles is shown in Fig. 3. Its inaccuracy becomes apparent when one attempts to apply it; there is a cumulative error which necessitates "fudging" the curve to make it become tangent at "C." An exact method of construction based on a coördinate system is therefore desirable.

A search of the scientific literature reveals the fact that some of the scientists have been unable to deal with this curve in a scientific manner, using instead "cut and try" methods. A striking example of this is found in the paper of Richards and Coombs,[1] where they made elaborate experiments to "discover" the "diameter necessary in order to attain the flat surface with which the capillary rise is to be compared" while measuring surface tension by the capillary rise method. After investigating the literature and making many tests, they decided that "in the 38 mm. tube, a portion in the middle, apparently about 5 mm. in length, appeared to be flat, coinciding exactly with the horizontal spider-line of the telescope." From this it appears that in a large glass receptacle where θ is zero, or nearly so, the meniscus would coincide with the plane surface of the liquid at a distance 16.5 millimeters $\left(\frac{38-5}{2}\right)$ from the wall. Since the upper portion of the profile (that above B) in Fig. 3 is like the inverted profile of the meniscus referred to, it would be expected therefore that the horizontal distance from B to C would be 1.65 centimeters. The error in the conclusions of Richards and Coombs is indicated below.

A comparison of the theoretical and observed positions of floating cylinders where the specific gravity, angle of contact and surface tension are known would add to the significance of these factors when applied to the study of floating minerals. To do this a correct liquid profile must be constructed by means of coördinates. Gray's[2] work aids in

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[1] T. W. Richards and L. B. Coombs: "The Surface Tension of Water and the Alcohols," Jour. Am. Chem. Soc., 37, 1656 (1915).

[2] A. Gray: "A Treatise on Physics," 1, 651.

this regard. Under the subject of capillarity he gives the equation of this curve but treats it so academically that one finds it difficult to make the technical application. His equation is

$$x = -(4a^2 - y^2)^{1/2} + a \log \frac{2a + (4a^2 - y^2)^{1/2}}{y} + \mathrm{C}.$$

It is interesting to note at this point that Lord Kelvin and Tait[1] have likewise applied this equation to the curve of a bent wire. Hall[2] has also used it. If we set $2a = 0.535$ (the value of H), $\mathrm{C} = 0.1427$ and change the Napierian logarithm to the common system by multiplying by 2.3, it takes the form

$$x = -(0.2862 - y^2)^{1/2} + 0.6152 \log \frac{0.535 + (0.2862 - y^2)^{1/2}}{y} + 0.1427.$$

Table I gives the x, y ordinates.

The remarkable coincidence of this curve (Fig. 7) with the portion of Fig. 3 in which the arc method of construction has the minimum error, and the deviation from it where the error is obviously maximum, dispels all doubt toward the application of the formula to the profile of a standing liquid with one plane of bending.[3]

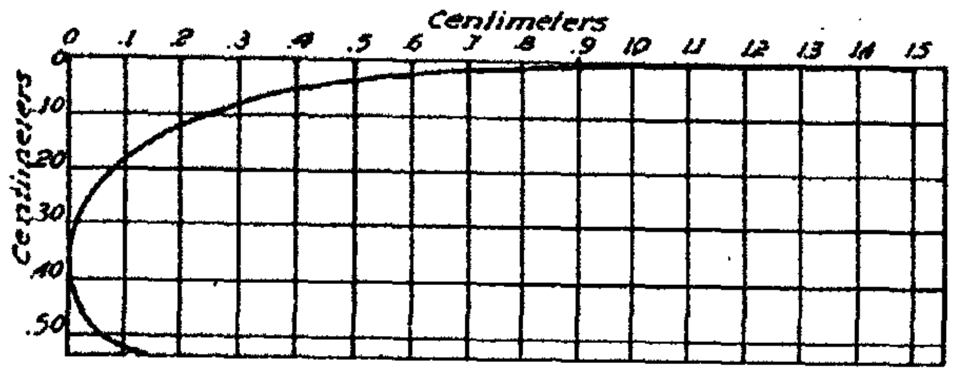

Fig. 7
Profile of standing water with one plane of bending.
T = 0.0715 gram

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[1] Lord Kelvin and P. Tait: "Treatise on Natural Philosophy," Part 2, p. 149.

[2] T. P. Hall: Phil. Mag., 36, 385 (1893).

[3] This equation will be treated in more detail by one of us (A) in another paper. There it will be shown how the two parameters used in the graphical construction of the curve are incorporated into the equation.

TABLE I

Coördinates for Liquid Profile where there is only One Plane of Bending

T = 0.0715 g, sp. gr. = 1

x	*y*	*x*	*y*
0.143	0.535	0.1828	0.13
0.0809	0.52	0.2032	0.12
0.0645	0.51	0.2240	0.11
0.0517	0.50	0.2479	0.10
0.0332	0.48	0.2749	0.09
0.0149	0.45	0.3052	0.08
0.0050	0.42	0.3409	0.07
0.0011	0.40	0.3799	0.06
0.0000	0.378	0.4278	0.05
0.0018	0.35	0.4768	0.04
0.0085	0.32	0.6714	0.02
0.0154	0.30	0.8663	0.01
0.0244	0.28	0.9331	0.0075
0.0421	0.25	1.0015	0.0050
0.0580	0.23	1.2266	0.0025
0.0746	0.21	1.3630	0.0015
0.0843	0.20	1.4710	0.0010
0.1199	0.17	1.5480	0.00075
0.1496	0.15	2.0866	0.00010
0.1671	0.14		

Reference to the last two values of y and x in Table I shows that the 1.65 centimeters, taken by Richards and Coombs as the distance from the solid at which the meniscus coincides with a plane surface, allows an error of less than 0.00075 centimeter and more than 0.00010 centimeter. This appears in Fig. 7 and Table I.

Having this curve, we can now consider the angle of contact.

The Practical Formula for Steel Wires Floating on Water

In the formula developed for the floating "needle," θ was taken as 180°. Since this value is likely never found in practice, it must be regarded as ideal. By a simple substitution a variable which will make it applicable for all values of θ

TABLE II

Values of A and r in Equation g'. Steel Wires

$\theta = 180^\circ$ $D = 0^\circ$		$\theta = 168^\circ$ $D = 12^\circ$		$\theta = 150^\circ$ $D = 30^\circ$		$\theta = 135^\circ$ $D = 45^\circ$		$\theta = 105^\circ$ $D = 75^\circ$		$\theta = 90^\circ$ $D = 90^\circ$		$\theta = 75^\circ$ $D = 105^\circ$		$\theta = 45^\circ$ $D = 135^\circ$	
A	r cm	A	r	A	r	A	r	A	r	A	r	A	r	A	r
0	0.0000	—	—	—	—	—	—	—	—	—	—	—	—	—	—
10	0.0320	—	—	—	—	—	—	—	—	—	—	—	—	—	—
—	—	12	0.0000	—	—	—	—	—	—	—	—	—	—	—	—
20	0.0461	20	0.0291	—	—	—	—	—	—	—	—	—	—	—	—
30	0.0572	30	0.0444	30	0.0000	—	—	—	—	—	—	—	—	—	—
40	0.0667	40	0.0563	40	0.0333	—	—	—	—	—	—	—	—	—	—
—	—	—	—	—	—	45	0.0000	—	—	—	—	—	—	—	—
50	0.0752	50	0.0660	50	0.0482	50	0.0234	—	—	—	—	—	—	—	—
60	0.0829	60	0.0753	60	0.0602	60	0.0421	—	—	—	—	—	—	—	—
70	0.0895	70	0.0829	70	0.0704	70	0.0553	—	—	—	—	—	—	—	—
—	—	—	—	—	—	—	—	75	0	—	—	—	—	—	—
80	0.0941	80	0.0896	80	0.0792	80	0.0668	80	0.0242	—	—	—	—	—	—
90	0.0976	90	0.0946	90	0.0864	90	0.0765	90	0.0435	90	0.0000	—	—	—	—
100	0.0994	100	0.0979	100	0.0921	100	0.0839	100	0.0573	100	0.0345	—	—	—	—
—	—	—	—	—	—	—	—	—	—	—	—	105	0.0000	—	—
110	0.0987	110	0.0989	110	0.0957	110	0.0897	110	0.0682	110	0.0510	110	0.0247	—	—
120	0.0961	120	0.0981	120	0.0974	120	0.0936	120	0.0767	120	0.0630	120	0.0446	—	—
130	0.0906	130	0.0946	130	0.0967	130	0.0947	130	0.0830	130	0.0721	130	0.0572	—	—
140	0.0824	140	0.0885	140	0.0946	140	0.0943	140	0.0869	140	0.0784	140	0.0669	140	0.0248
150	0.0714	150	0.0798	150	0.0880	150	0.0912	150	0.0886	150	0.0828	150	0.0739	150	0.0433
160	0.0570	160	0.0686	160	0.0801	160	0.0857	160	0.0879	160	0.0848	160	0.0784	160	0.0554
170	0.0388	170	0.0547	170	0.0701	170	0.0783	170	0.0853	170	0.0863	170	0.0803	170	0.0635
180	0.0000	180	0.0380	180	0.0580	180	0.0690	180	0.0807	180	0.0821	180	0.0807	180	0.0690

is introduced, after which theoretical and observed values may be compared.

The corrections are simple, though at first somewhat confusing.

Since, in practice, the angle of contact is always less than 180°, an angle D is introduced to represent this difference. Equation *a* then becomes,

$$2T \sin (A - D). \qquad (a')$$

Equation *e* becomes

$$2\sqrt{T} \sin \frac{A - D}{2},$$

and when this value is substituted in (*b*) we have

$$4r\sqrt{T} \sin A \sin \left(\frac{A - D}{2}\right). \qquad (b')$$

The expressions (*c*) and (*d*) are unchanged.

Equation *g*, which applies to steel wires, then becomes

$$r^2\left(24.2 + 0.5 \sin 2A - \pi \frac{A}{180}\right) - 1.07\, r \sin A \sin \left(\frac{A - D}{2}\right)$$
$$= 0.143 \sin (A - D). \qquad (g')$$

Table II gives the values of A and r for stated values of θ.

Fig. 8 shows the curves conforming to the coördinates given in Table II.

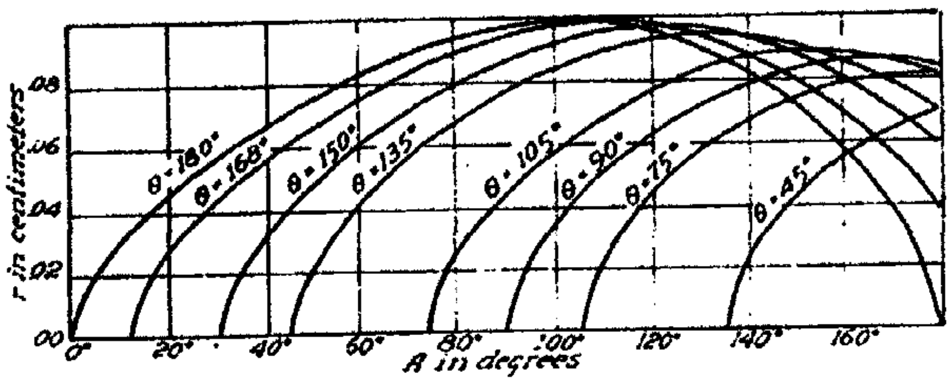

Fig. 8

Curves showing the theoretical values of A for steel wires for stated values of r and θ

The Relation of Angle of Contact to Floatability

We now have sufficient data to show the relation of the angle of contact to the floatability of cylinders. The subject begins to take the aspect of a science when we see from this figure that if r is sufficiently small a solid is floatable though θ may be as small, for example, as 45° or less. Previously, the fact that pieces of glass floated on water could be explained only by the "air cushion" theory. Such an hypothesis must now give way to facts. Consider, for example, a steel wire with a radius of 0.06 centimeter. Reference to Fig. 8 shows that when $\theta = 180°$, A = 33°; $\theta = 168°$, A = 44°; $\theta = 150°$, A = 60°; $\theta = 135°$, A = 74°; $\theta = 105°$, A = 102°; $\theta = 90°$, A = 117°; $\theta = 75°$, A = 133°; $\theta = 45°$, A = 165°. The very slight drop in the consecutive crests of the curves from left to right, while θ decreases from 180° to 45°, is striking. But this must not be taken to indicate relative floatability in practice. For, though it is true that increasing "A" brings the object near the point of unstable equilibrium (the descending portion of the curve), yet another factor of no less importance appears in practice. It is the position of the walls of water with reference to the object, and to each other. Note in Fig. 9, *a*, how the object rides safely on a disturbed surface, while in Fig. 9, *h*, there is continual danger of the walls overlapping and causing submergence. When they overlap and coalesce, the surface tension film, of course, vanishes. A little lycopodium powder or talc on the surface assists in maintaining the interface by preventing coalescence. Is it not probable that the insoluble oil used in flotation acts in the same manner, preventing the coalescence of the walls of the bubble whenever it is in danger of being separated from the mineral?

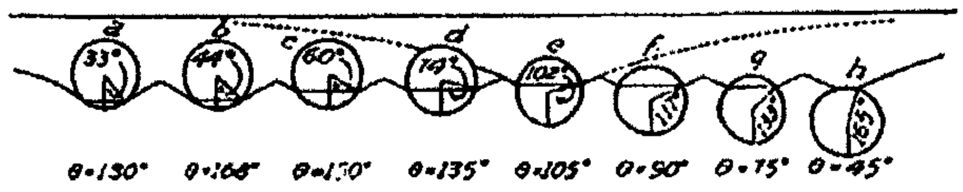

Fig. 9

Showing how a steel wire of given diameter (r = 0.06 cm) rides on pure water while θ decreases from left to right

These theoretical considerations would have greater significance if supported by physical measurements and observations. Such tests have been made with the cathetometer, and the agreement of observed and calculated values justifies the theory. Let us first consider the principles involved in constructing Fig. 9, after which we shall consider the physical measurements.

Take, for example, Fig. 9, *b*. The radius of the steel wire is 0.06 centimeter and θ is 168°. The angle D is therefore 12°. Look along the line (Fig. 8), corresponding to r = 0.06 cm and find where it intersects the curve marked "$\theta = 168$." Here the corresponding angle A is 44°. Now use the modified form of Equation *e*, which is,

$$h = 2\sqrt{T} \sin \frac{A - D}{2}.$$

This gives the value of h, which is then applied to Fig. 9. At the point on the curve so determined strike off the radius of the object so that "A" has the value desired, and draw the circle.

Of course, θ must be determined by test. The classic methods for this determination were considered, but discarded in favor of an indirect method in which the cathetometer was used. Here the capillary rise or depression against a vertical plane surface was determined, and θ was found by means of the above equation by solving for D after setting A equal to 90°. When there is capillary rise, θ equals D, and for capillary depression θ equals 180° minus D. Pure water gives an angle of contact of 168° against a surface prepared by dipping a solid into molten paraffin and sprinkling lycopodium powder on it before the paraffin congeals. Against solid paraffin the angle is 105°.

Table III shows that the observed and theoretical position of steel wires floating on pure water coincide with a satisfactory degree of accuracy. The cathetometer was used to measure the vertical distance from the plane surface of the water to the bottom of the floating wire. No correction was made for the thickness of the paraffin shell, which was found to be very thin—only 0.01 centimeter. Fig. 10 shows the theoretical position of these wires on the liquid profile. The liquid meets the heavy and dotted circles at 168° and 105°, respectively.

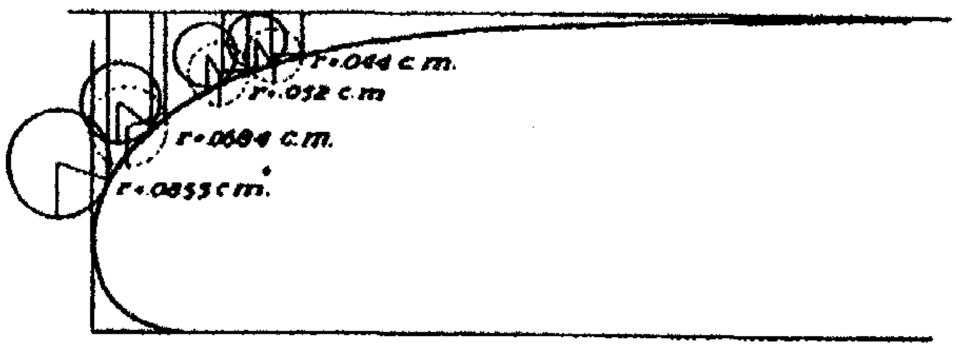

Fig. 10
Theoretical positions of steel wires floating on water where T is 0.0175 and θ is 105° and 168°, respectively

Table III

Showing the Observed and Theoretical Depth of Steel Wires Floating on Pure Water

Radii of wires in cm	$\theta = 168$ Depth in cm		$\theta = 105$ Depth in cm	
	Observed	Theoretical	Observed	Theoretical
0.0440	0.090	0.082	0.120	0.115
0.0520	0.125	0.129	0.160	0.156
0.0684	0.205	0.212	0.260	0.253
0.0855	0.330	0.335		

The Flotation of Aluminum Wires

From the standpoint of the metallurgist, we are still dealing with an ideal case because minerals cannot be obtained in the form of right circular cylinders; again, steel wires have a greater specific gravity than many of the metallic sulphides. In order to transform ideal conditions into the practical, let us make a further study of the effect of specific gravity, reserving the question of shape of the floating object for a later discussion.

Having made a study of the conduct of wires heavier than the average of the metallic sulphides, it seems that if we would make a similar study of those lighter than the minerals and find an agreement also between theoretical and observed values, we could use mathematical processes for predicting the conduct of any mineral. The following results deal, therefore, with aluminum wires:

When aluminum wires (specific gravity 2.7) are used, the equation corresponding to Equation g' is

$$r^2\left(8.4823 + 0.5 \sin 2A - \pi\frac{A}{180}\right)$$
$$- 1.07\, r \sin A \sin\left(\frac{A - D}{2}\right) = 0.143 \sin (A - D).$$

The values of A and r for stated values of θ are shown in Table IV.

TABLE IV
Values of r and A. Aluminum Wires

$\theta = 168°$ $D = 12°$		$\theta = 105°$ $D = 75°$		$\theta = 90°$ $D = 90°$	
A	r	A	r	A	r
12	0.0000	—	—	—	—
20	0.0499	—	—	—	—
30	0.0775	—	—	—	—
40	0.1004	—	—	—	—
50	0.1216	—	—	—	—
60	0.1422	—	—	—	—
70	0.1626	—	—	—	—
—	—	75	0.0000	—	—
80	0.1812	80	0.0446	—	—
90	0.1986	90	0.0835	90	0.0000
100	0.2129	100	0.1145	100	0.0686
110	0.2210	110	0.1410	110	0.1033
120	0.2262	120	0.1630	120	0.1312
130	0.2217	130	0.1795	130	0.1531
140	0.2083	140	0.1892	140	0.1686
150	0.1860	150	0.1931	150	0.1771
160	0.1564	160	0.1870	160	0.1769
170	0.1182	170	0.1761	170	0.1733
180	0.0744	180	0.1602	180	0.1631

These points are plotted in Fig. 11. The scale is the same as that of Fig. 8. Note how they have the same general form as those for steel, but run up much higher on account of the lesser density of the aluminum. The remarkable coincidence of the theoretical depth with the observed depth of the bottom of the wire below the plane surface of the liquid again substantiates the theory. See Table V.

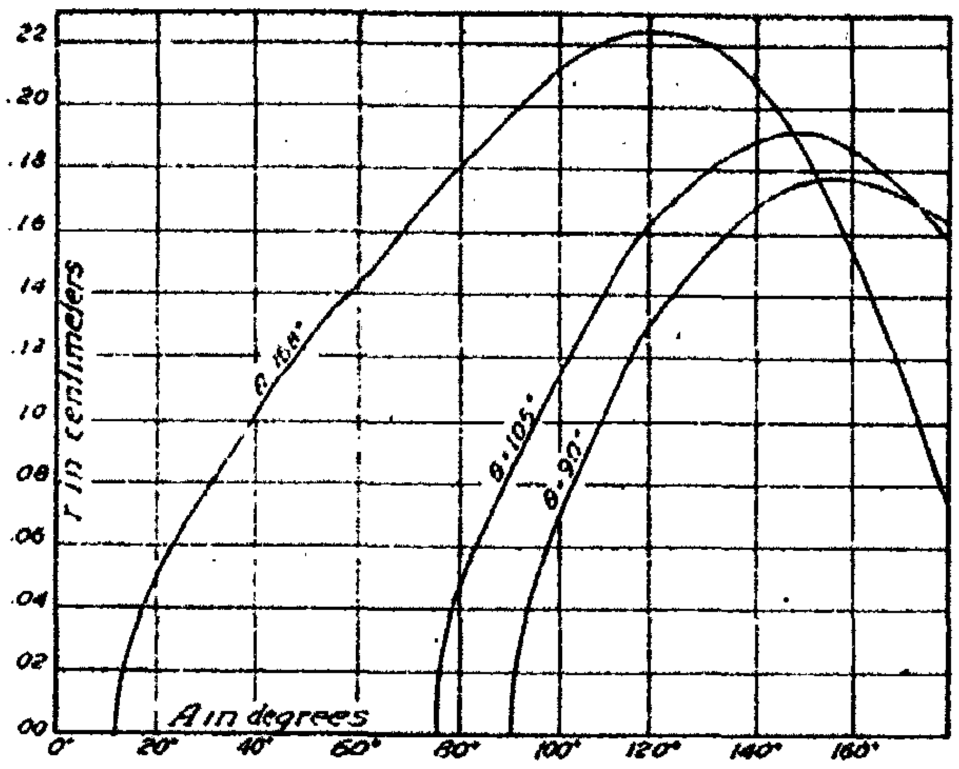

Fig. 11

Curves showing the theoretical values of A for aluminum wires for stated values of *r* and *θ*

TABLE V

Showing the Observed and Theoretical Depth of Aluminum Wires Floating on Pure Water

Radii of wire in cm	$\theta = 168°$ Depth in centimeters		$\theta = 105°$ Depth in centimeters	
	Observed	Theoretical	Observed	Theoretical
0.065	0.067	0.065	0.102	0.100
0.095	0.136	0.140	0.190	0.195
0.192	0.494	0.500	—	—
0.215	0.680	0 642	—	—

Fig. 12 shows the theoretical position of these aluminum wires on the liquid profile. The liquid meets the heavy and dotted circles at 168° and 105°, respectively, as in Fig 10, where the steel wires were shown.

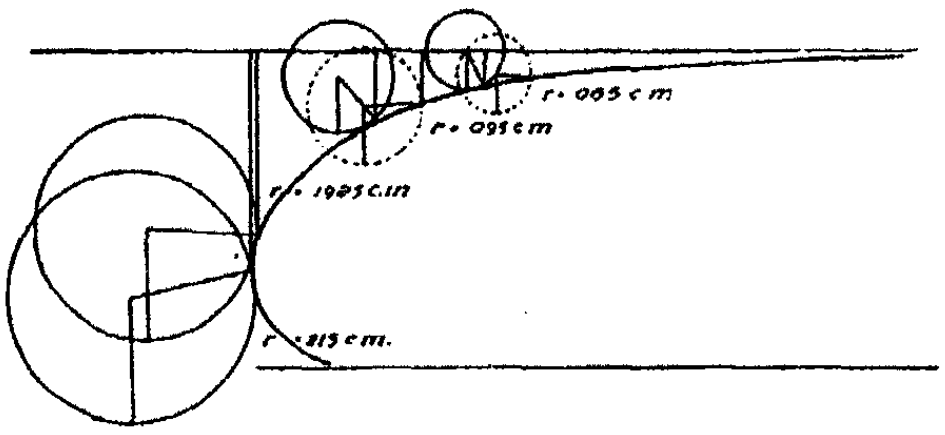

Fig. 12
Theoretical position of aluminum wires of given radii, floating on pure water, where θ is 105° and 168°, *respectively*

Anderson[1] says: "A needle, especially if slightly oily, will float if carefully placed upon water. We may note in passing that the weight of the water displaced by the sagging of the surface film is equal to the weight of the needle (Archimedes' Principle)." This statement will be discussed in another paper.

The Flotation of Galena

To compare the conduct of the mineral grains fed to a H. E. Wood flotation machine to a group of skaters where some glide over the ice and others break through, is an analogy that is fruitless. Ice breaks when the molecules are removed beyond the limit of influence, but at the instant when galena sinks the molecules in the surface of the liquid are under the same stress as those on an undisturbed surface. To speak of the membrane rupturing or breaking at the instant the galena becomes submerged, is as far from accuracy as is the North from the South. We must have the facts or continue the guessing process in flotation, which, it must be admitted, has, in some cases at least, produced such favorable results that a "small piece of cheese has been left for the cats after the monkey got his portion."

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[1] W. B. Anderson: "Physics for Technical Students."

What is the position of floating galena relative to the liquid profile? The angle of contact of pure water against cleavage face is approximately 45°. Is a mineral floatable when the water turns up at this angle to meet a vertical face? Figs. 8 and 9 show that wires are, and it seems consistent to assume that the same conclusion applies to minerals. Conjecture offers only one explanation—diagrammed in Fig. 13. Cathetometer observations show that this is a reality. The liquid profile meets the upper horizontal face (at 45°), the proof of which is shown in Table VI.

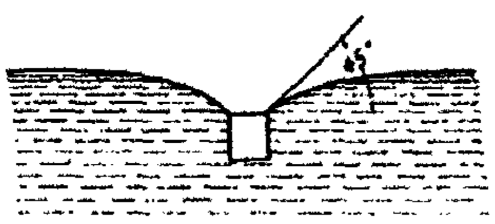

Fig. 13

Diagram showing how galena floats on water when θ is 45°

TABLE VI

Cathetometer Observations on Floating Galena

Approximate mesh	Vertical dimensions in centimeters	
	Of galena	Bottom of galena to intersection of liquid profile with galena
36-mesh	0.040	0.055
33-mesh	0.045	0.055
13-mesh	0.130	0.150
12-mesh	0.140	0.150

In each observation the readings showed that the mineral was wholly below the bottom of the dimple.

Summary

The maximum rise and depression of a given liquid against vertical plates are determined and shown to be the same for angles of contact of 0° and 180°, respectively. The horizontal pull of the film is independent of the angle of contact.

A graphical method of constructing a liquid profile with one plane of bending is reviewed.

A review is given of the mathematical discussion of the floating needle when the angle of contact is ideal.

A liquid profile with one plane of bending is constructed on a coördinate system, and compared with the arc and "cut and try" methods.

A practical formula for steel wires floating on water is developed from the ideal and theoretical and observed values are compared.

A formula is developed for calculating angle of contact from the cathetometer measurements of rise or depression of a liquid against a vertical plate. The relation of angle of contact to floatability is indicated by curves and checked by observations.

The flotation of aluminum wires is treated scientifically and practically.

The manner in which "floating" galena is suspended at the surface of water is shown.

ELECTRICAL ENDOSMOSE. II

BY T. R. BRIGGS, H. S. BENNETT AND H. L. PIERSON

The Apparatus

After a careful study of the literature on electrical endosmose, the results of which have been communicated in a previous article,[1] it was decided to construct an apparatus similar to the one used so successfully by Perrin.[2] There was finally developed[3] a modified electro-osmometer, possessing certain distinct advantages over Perrin's original apparatus. In the latter instrument there was no means of removing the gas that might be liberated from the electrodes on the passage of an appreciable current, and this gas, collecting in large bubbles beneath the vertical diaphragm, tended to cause a flow of liquid quite irrespective of electrical endosmose. In the apparatus to be described this difficulty was solved in a very simple way and there was added a somewhat novel means of measuring quantitatively the rate of flow through the diaphragm, by observing the speed with which an air bubble moved along a calibrated tube.

The electro-osmometer is constructed almost entirely of rather heavy glass and is essentially a horizontal tube with several vertical side arms. The complete apparatus is depicted in Figure 1. The horizontal electrolyzing chamber containing the diaphragm is about three centimeters in diameter and thirty centimeters long; the two vertical electrode tubes A_1 and A_2 are about ten centimeters apart. In these tubes are placed the platinum electrodes E_1 and E_2 which are held in position by being sealed into narrow glass tubes supported in corks grooved so as to permit the gases generated during electrolysis to escape. Midway between A_1 and A_2, the horizontal electrolyzing chamber is enlarged slightly for

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[1] Jour. Phys. Chem., 21, 198 (1917).

[2] Jour. Chim. phys., 2, 601 (1904).

[3] The early experiments were performed with the assistance of Mr. G. D. Kratz.

a distance of four centimeters; this enlarged section forms the chamber in which the porous diaphragm is constructed. There is a small vertical side arm in the upper part of this enlarged section, in order that a thermometer may be inserted into the diaphragm.

At R_1 and R_2 the "bubble tube" is joined to the electro-osmometer with short rubber connections. Attached to the horizontal chamber by ground glass joints, are two three-way cocks, C_1 and C_2, by the proper manipulation of which it is a simple matter to introduce the air bubble at B. The speed and direction of flow through the diaphragms are measured by the movement of this bubble, with the aid of a stop-watch and a scale divided into centimeters. Having determined the volume per centimeter of the bubble tube, one may calculate the volume of liquid transported in unit time through the diaphragm.

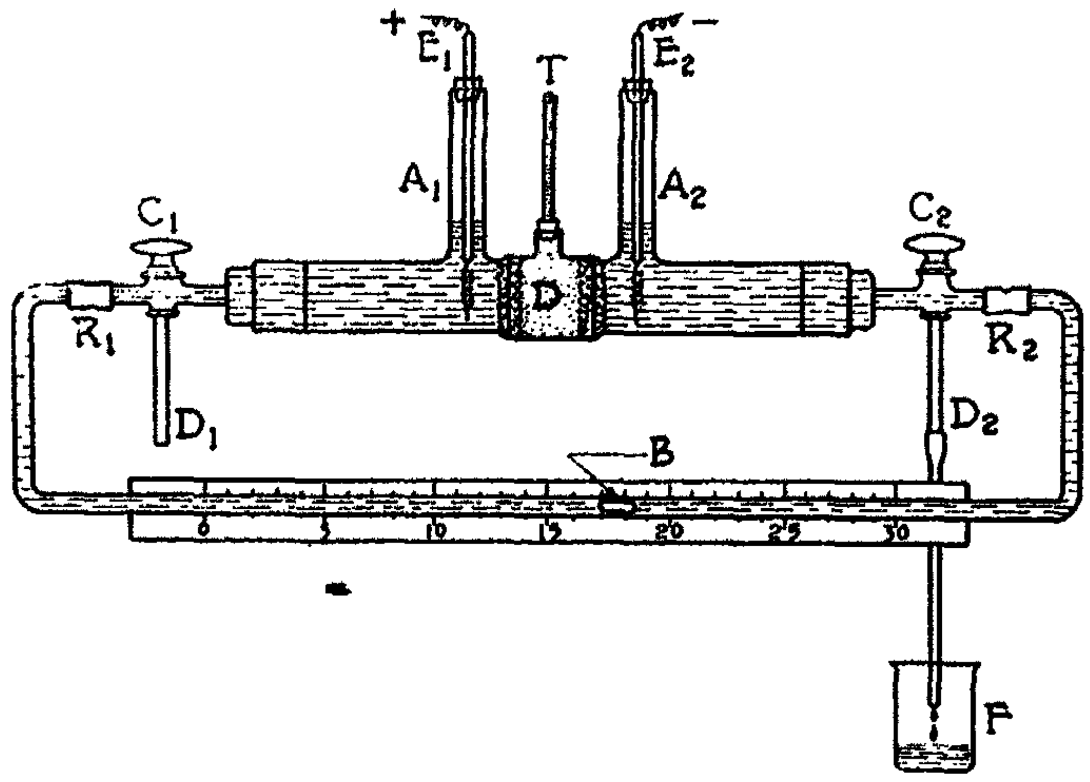

Fig. 1

The air bubble is introduced into the measuring tube as follows: After the diaphragm has been built up in the chamber D, the whole apparatus is assembled as shown in Figure 1 and the measuring tube is connected to the osmometer at R_1 and R_2. The whole system is filled with the solution to be employed by adding the liquid through the vertical arms A_1 and A_2 and properly manipulating the cocks at C_1 and C_2. Care is taken at this point to see that the exit tube D_2 (including the rubber tube connected thereto) is completely filled with liquid.

The second exit tube D_1 is now placed beneath the surface of *distilled* water in a beaker, connection is made between D_1 and the measuring tube through the three-way cock C_1 and the exit tube D_2 is likewise connected to the measuring tube through C_2. Owing to the siphon action of the long exit tube D_2, distilled water is sucked through the measuring tube from D_1 and out at D_2, into the beaker at F. When the original (conducting) liquid has been displaced completely by distilled water, C_1 is closed and the surface in the beaker at D_1 is lowered until the end of D_1 is free. By carefully manipulating C_1 an air bubble of the desired length is drawn into the exit tube D_1 and the latter is once again immersed in the beaker of water. On again opening C_2, the bubble is carried along the measuring tube into any desired position. Finally, the level of the liquid in the vertical electrode chambers A_1 and A_2 is adjusted and the osmometer proper connected with the measuring tube through C_1 and C_2.

The most difficult operation is forming the diaphragm. The finely powdered and carefully sieved material is treated several times with the solution to be employed and is then introduced into the apparatus in the form of a paste. The actual diaphragm formation is carried out with the aid of suction as follows:

The body of the apparatus, minus the connecting parts, is placed with the electrolyzing chamber vertical and is connected to the suction pump through one side arm, A_1 or A_2, the other being closed with a rubber stopper. The diaphragm is built up on a perforated cork or rubber plate, upon which is laid a compact layer of glass wool or pure cotton. Glass wool is the best substance for the purpose because it forms a comparatively strong and rigid plug. The rubber plate is kept in place by means of a glass rod which is in turn held in position by a rubber stopper inserted into the lower end of the electrolyzing chamber. The procedure is simply that of filtering with suction on an improvised, perforated plate and the diaphragm is prepared quickly and washed easily,[1] so long as the individual particles are not excessively small. On adding an upper plug of glass-wool or cotton, and after removing the perforated rubber plate, the diaphragm is complete.

By following this procedure it is easy to use the same diaphragm with a number of different solutions, for one is able to wash the diaphragm completely in a comparatively short time. This procedure as been followed throughout these experiments.

As I have observed already, the new electro-osmometer eliminates the possibility of gases evolved at the electrodes producing an apparent electro-osmotic flow. Special tests have proved beyond doubt that the free evolution of gas during the passage of the current has no measurable influence on the movement of the air bubble in the calibrated tube, so long as the evolution is not too copious and the electrode tubes are *clean*. Moreover, the air bubble being sensitive to extremely slight differences in level between the columns of liquid in A_1 and A_2 a very slight endosmotic flow through the diaphragm is rendered visible by a motion of the air bubble in one direction or the other.

In carrying out the experiments, one determines the time required for the bubble (having reached a maximum speed) to pass between two points on the scale, after which the direction of the currect is reversed and the time of transit in the opposite direction ascertained. After several readings, the mean is taken in case the temperature—as measured by the thermometer in the diaphragm—has not changed appreciably. From these observations the speed of the bubble is calculated in terms of centimeters per second. Likewise readings are taken of the temperature in the center of the

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[1] Care must be taken never to suck air into the diaphragm.

diaphragm and the voltage acrosss the electrodes. The subsequent calculations follow.

In the previous paper[1] we saw that

$$V_e = \frac{qE\epsilon D}{4\pi\eta l}. \qquad (1)$$

For a particular diaphragm of constant length and cross section, the volume of liquid V_e transported in unit time depends upon the potential drop through the diaphragm, the interface potential ϵ, and the values of D and η for the liquid. Since ϵ, D and η are constant for a given solution at a particular temperature, under such circumstances the rate of flow through the diaphragm should be proportional to the voltage drop between the two extremes.

When an appreciable current of electricity flows through the diaphragm, however, Joule heating occurs and the temperature rises. At constant voltages, accordingly, V_e will depend upon the variation of ϵ, D and η with the temperature. Since ϵ depends upon selective adsorption of ions and we know little regarding the way selective adsorption changes with the temperature, we cannot compute the temperature coefficient. It seems probable, however, that ϵ is approximately constant within narrow temperature limits *if equilibrium is established and the ion composition of the liquid phase does not change with time.* We know that the dielectric constant becomes smaller as the temperature increases. At 0°, D for water is 88; at 17° it is 81. If we call $1/\eta$ the fluidity of the liquid, the increase in the fluidity with the temperature is known for pure water or very dilute solutions and V_e is directly proportional to the fluidity.

Theoretically, the temperature coefficient of the fluidity is the predominating factor and one would expect V_e to increase strongly with the temperature. This is actually the case. But one should not expect the flow to keep pace with the increased fluidity of the liquid since the temperature coefficient of D is negative. Accordingly, it is not strictly accurate to assume that the rate of endosmose is inversely pro-

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[1] Jour. Phys. Chem., 21, 201 (1917).

portional to the viscosity, though for ordinary purposes this way of putting it is sufficiently close to the truth. These conclusions have been subjected to experimental test, in the manner to be described.

Varying the Voltage at Constant Temperature

Some glass tubing was pulverized and sieved, the portion passed by an 80-mesh sieve but retained by a 120 one being used to make a diaphragm. The diaphragm was built up in the usual manner and retained in position by plugs of glass wool. Distilled water was used as the liquid. To obtain a wide range of voltages, the current from a battery of storage cells (32 volts) was passed through a rheostat frame and the field coils of a small 0.11 kw generator, operated by an induction motor. By changing the current in the field coils the potential of the transformed current could be increased to 500 volts as a maximum.

After several preliminary experiments had been made by Mr. H. S. Bennett, to standardize conditions, the data of Table 1 were obtained.

TABLE 1

INFLUENCE OF APPLIED POTENTIAL ON RATE OF FLOW

Glass diaphragm in distilled water. Liquid flowed to cathode

Applied potential (Volts)	Time (Secs.)	Distance Cm	Temp. °C	Rate. Cm per second	Rate/potential
530	13.5	20	19.8	1.48	27.9×10^{-4}
500	13.8	20	19.9	1.45	29.0×10^{-4}
450	15.2	20	19.8	1.32	29.3×10^{-4}
416	16.1	20	20.0	1.24	29.8×10^{-4}
350	19.1	20	20.5	1.05	30.0×10^{-4}
300	22.2	20	19.7	0.90	30.0×10^{-4}
250	13.2	10	19.6	0.76	30.4×10^{-4}
200	16.8	10	19.7	0.60	30.0×10^{-4}
150	22.0	10	19.6	0.45	30.0×10^{-4}
100	32.8	10	19.5	0.30	30.0×10^{-4}

The data are shown graphically in Figure 2 by means of a curve drawn between bubble speed and applied potentials. The curve is a straight line except at very high voltages where the speed of the bubble was fairly great and the resistance to the flow of liquid through the apparatus began to complicate matters. A number of minor tests were also made. The length of the air bubble acting as indicator in the measuring tube was increased very considerably without appreciably affecting the speed. The diaphragm itself was next replaced by a solid plug, to ascertain whether the motion of the bubble might be due to something independent of electrical endosmose through the porous diaphragm; on applying 110 volts no motion at all occurred.

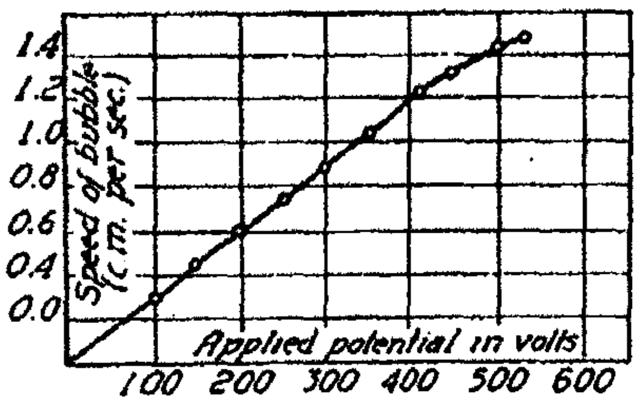

Fig. 2

Varying the Temperature at Constant Voltage

Measuring the temperature coefficient of electrical endosmose proved to be less easy. Some data obtained for me by Mr. H. L. Pierson, in Worcester (Worcester Polytechnic Institute), were fairly satisfactory. Alundum and carborundum diaphragms were used and V increased steadily with the temperature. When we came later to renew the work in the Cornell laboratory, we tried powdered glass and got very irregular results. Mr. Bennett found at first a *maximum* value for the bubble speed as the temperature rose from 20° to 65°, seeming accordingly, to corroborate the testimony of Cruse.[1]

On allowing the apparatus and its contents to cool, it was found on repeating the test that the rate of flow was now very different from what it had been at the beginning of the

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[1] Phys. Zeit., 6, 201 (1905).

experiment. There was a marked decrease even though the same voltage was applied. The current flowing between the electrodes was measured on a milliammeter and showed a pronounced increase, which grew rapidly when the temperature was kept for a time at 60°. The glass of the plugs and diaphragm appeared to dissolve and the ion composition of the liquid—which was originally distilled water or dilute alkali—changed appreciably. The adsorption equilibrium between liquid and diaphragm could no longer be regarded as constant and the rate of endosmose fell off. The maximum obtained in the first run was explained; at temperatures below the maximum, the increasing fluidity had more influence than the increasing ion concentration, while above the maximum point the reverse was true. This explanation is based upon the fact that the solid dissolved faster at high temperatures than at low temperatures.

After keeping the diaphragm in contact with the hot solution for several hours, then cooling and allowing the whole to stand overnight, the heating test was repeated. No maximum whatever was observed between the same temperatures; the rate of endosmose increased steadily with rising temperature, but did so much less rapidly than the fluidity.

Crystolon (carborundum) and alundum diaphragms held in position with glass wool gave irregular results also, so glass was eliminated as far as possible, and washed asbestos or macerated filter paper substituted. Distilled water was used as liquid, and was kept in contact with the diaphragm for 24 hours to insure equilibrium. The diaphragm was heated from the outside by pouring a steady stream of water from a heater over the central portion of the endosmometer. A special test showed that the speed of the bubble was not affected by having hot or cold water in the measuring tube. The data follow, the values of time recorded in the table being the mean of at least six readings in every case.

TABLE 2

INFLUENCE OF TEMPERATURE AT CONSTANT VOLTAGE

Asbestos diaphragm. Distilled water. Flow to cathode

Applied potential (Volts)	Time (Secs.)	Distance (Cm)	Temperature (°C)	Rate. Cm per second	Rate times viscosity
250	16.2	5	18.0°	0.308	32×10^{-4}
250	25.9	10	30.5°	0.386	31×10^{-4}
250	22.0	10	39.0°	0.454	30×10^{-4}
250	19.8	10	46.5°	0.505	30×10^{-4}
250	18.0	10	58.0°	0.588	30×10^{-4}
Cellulose in boiled water (air free)					
400	28.2	5	22.6°	0.177	16.7×10^{-4}
400	25.5	5	27.6°	0.196	16.7×10^{-4}
400	22.3	5	36.1°	0.224	15.9×10^{-4}
400	19.1	5	52.0°	0.262	14.0×10^{-4}
400	17.1	5	67.0°	0.292	12.5×10^{-4}

The following data with a crystolon (CSi) diaphragm had previously been obtained by Mr. Pierson at Worcester with the same apparatus:

TABLE 3

200-Mesh Crystolon in *M*/500 NaOH. Flow to cathode

Applied potential (Volts)	Time (Secs.)	Distance (Cm)	Temperature (°C)	Rate. Cm per sec.	Rate times viscosity
110	53	5	23.5°	0.087°	8.1×10^{-4}
110	49	5	27.0°	0.093	8.0×10^{-4}
110	47	5	29.0°	0.097	8.0×10^{-4}
110	44	5	32.5°	0.103	7.9×10^{-4}
110	45	5	33.5°	0.101	7.6×10^{-4}
100	43	5	35.5°	0.106	7.6×10^{-4}
100	46	5	36.5°	0.109	7.7×10^{-4}
100	40	5	38.5°	0.114	7.8×10^{-4}
103	44	5	38.5°	0.110	7.5×10^{-4}
110	38	5	40.5°	0.120	7.8×10^{-4}
110	37	5	41.5°	0.122	7.8×10^{-4}
104	38	5	45.5°	0.126	7.4×10^{-4}

If the rate of endosmose varied with the fluidity of the liquid and with nothing else, the product of rate into the coefficient of viscosity should be constant. Values of this product are given in the last column of data. These numbers decrease slightly as the temperature rises and the rate of decrease is more rapid apparently, the higher the temperature. The data show that some other factor comes into play and tends to counteract slightly the effect of rising fluidity in increasing the rate of flow. We have seen that this factor is theoretically the dielectric constant, to which the rate is proportional; since this decreases with rising temperature, we can account for the data recorded in the last column of Tables 2 and 3.

Nevertheless at room temperature and for moderate temperature changes the rate of flow is approximately proportional to the fluidity of the liquid. Assuming that the very dilute solutions employed in this work have the same viscosity as pure water, one can correct for temperature changes at constant voltage as follows:

$$\text{RATE}_{20^\circ} = \frac{\eta_{t^\circ}}{\eta_{20^\circ}} \textit{ times } \text{RATE}_{t^\circ} \qquad (2)$$

Since $\eta_{20^\circ} = 0.0100$ dyne per cm^2 almost exactly, the rates corresponding to 20° are very easily calculated from the rate determined at experimental temperatures.

The voltage correction is made in a similar manner. The rate corresponding to 100 volts may be computed as follows since at constant temperature

$$\text{RATE}_{(100 \text{ volts})} = \frac{100}{\text{E}} \textit{ times } \text{RATE}_{(\text{E volts})} \qquad (3)$$

This reduction has been carried out in Table 3.

By combining (3) and (4) we obtain the composite expression which allows the rate corresponding to 20° and 100 volts to be computed.

$$\text{CORRECTED RATE} = \frac{100\eta_{t^\circ} \textit{ times } \text{OBSERVED RATE}}{\text{E}\eta_{20^\circ}} \qquad (4)$$

Or, when water or dilute aqueous solutions are used, remembering that $\eta_{20^\circ} = 0.0100$ dyne per cm^2, nearly

$$\text{CORRECTED RATE} = \text{OBSERVED RATE} \textit{ times } \frac{\eta_{t^\circ} \times 10^4}{\text{E}}. \qquad (5)$$

Acid and Alkaline Solutions

A set of experiments was made under my direction by Mr. Pierson in Worcester, for the sake of duplicating approximately Perrin's work with dilute solutions of acids and bases. The degree of refinement of the work was by no means the maximum possible with the apparatus but the results obtained were quite satisfactory. The Norton Company was kind enough to furnish us with graded and purified samples of crystolon and alundum, with which we worked. The data which follow were obtained with a diaphragm of crystolon (120-mesh). The concentration of the solutions was determined only approximately and no great care was taken to use sodium hydroxide absolutely free from carbonates.

TABLE 4
ACID AND ALKALINE SOLUTIONS

Solution	Concentration	Average rate (corrected) Cm per sec.	Direction of flow
Water (distilled)	—	0.114	to cathode
NaOH	*N*/500	0.217	to cathode
NaOH	*N*/250	0.198	to cathode
NaOH	*N*/100	0.154	to cathode
Water (distilled)	—	0.159	to cathode
HCl	*N*/1000	0.070	to anode
HCl	*N*/500	0.102	to anode
HCl (check)	*N*/500	0.099	to anode
HCl	*N*/100	0.074	to anode

Figure 3 illustrates these data. In the experiments the same diaphragm was used throughout, for by arranging the apparatus as described previously, the diaphragm was washed easily and completely with water and solution at 50° or 60°. The first washing required more than a liter of hot water and this was followed with the solution to be studied, hot at first and then cold. The rates tabulated above represent the averages of many readings and have been reduced to 100 volts and 20° by means of Equation 5.

The results confirm Perrin completely and the curve is similar to the one drawn by Freundlich[1] from Perrin's data. The reversal is very sharply defined and the isoelectric point lies over on the acid side at concentrations of HCl, which are less than one thousandth normal. No allowance has been made for carbonates in the sodium hydroxide, although very pure alkali was used originally, and the water was ordinary distilled water of excellent quality.

On studying alundum a sharp acid-alkali reversal was found. Although these diaphragms were held in place with small plugs of glass wool, the trouble caused thereby was much smaller than when the temperature-effects were studied, doubtless because the temperature in the diaphragm was kept low and possibly because the glass was of better quality. At any rate, no current was observed in the milliammeter and a diaphragm of glass wool alone showed practically no endosmose. When *powdered* glass was used, however, there was always a strong flow to the cathode and no reversals were obtained in acid solutions—not even in $N/100$ hydrochloric acid. As the acid content increased, the flow to the cathode approached zero. On the other hand, reversals were obtained with diaphragms of gelatine and agar jellies.

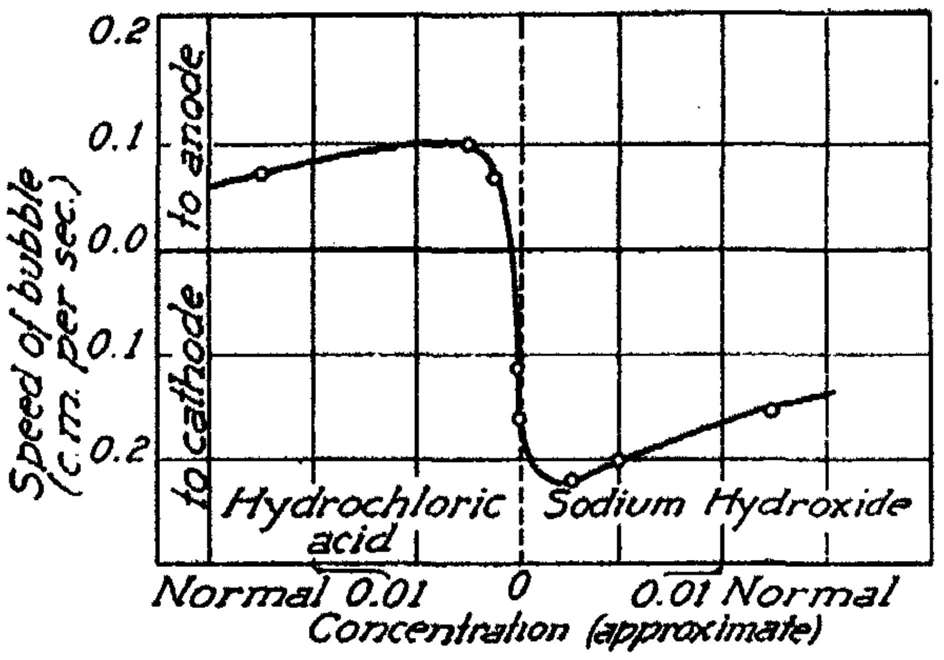

Fig. 3

The Volume of Solution Transported

Having made these measurements, Mr. Pierson ascertained the average volume per linear centimeter of the measur-

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[1] "Kapillarchemie," 236 (1909).

ing tube containing the bubble. Experiment gave 0.125 cc per centimeter. For *N*/500 NaOH in Table 4, the bubble rate was 0.217 cm per second or 13 cm per minute, corresponding to 1.6 cc for a potential drop of about 12 volts per centimeter through the diaphragm. With his apparatus Perrin rarely obtained more than 0.1 cc per minute with a potential gradient of 10 volts per centimeter.

Polyvalent Ions

A long series of experiments was carried out to duplicate, if possible, the data obtained by Perrin; the results confirmed in all the essentials what he found. For the particular salts studied, the so-called valence rule held satisfactorily. Barium was used as a typical divalent cation, sulphate, ferrocyanide and ferricyanide as anions. In alkaline solution adsorbed barium ions reduced the rate of endosmose and did so very much more strongly than did equivalent quantities of the alkali metals. In acid solution, barium was far less active, it being the polyvalent anions which reduced the endosmose most strongly.

Copper Salts

Using an alundum diaphragm, Mr. Pierson obtained some interesting results with solutions of certain copper salts. His data follow:

TABLE 5

COPPER SALTS

Solution	Normality	Rate (corrected) Cm/second	Direction
Copper acetate	0.1	0.048	to anode
Copper acetate	0.01	0.085	to anode
Copper acetate	0.004	0.098	to anode
Copper acetate	0.002	0.091	to anode
Copper nitrate	0.1	0.081	to anode
Copper nitrate	0.01	0.127	to anode
Copper nitrate	0.004	0.132	to anode
Copper nitrate	0.002	0.111	to anode
Copper sulphate	0.2	0.019	to cathode
Copper sulphate	0.1	0.020	to cathode
Copper sulphate	0.01	0.016	to anode
Copper sulphate	0.004	0.028	to anode
Copper sulphate	0.002	0.089	to anode
Copper chloride	0.002	0.113	to anode

The curves of Figure 4, illustrating these data, show clearly how the preferential adsorption of ions may change with the concentration. In many respects the data agree with Coehn's[1] except that he states that copper sulphate solutions *always* go to the cathode. We found a reversal as the concentration decreased, very dilute solutions flowing to the anode. Of course hydrolysis must be a disturbing factor. Leaving this out of account, copper as ion seems to be absorbed in preference to acetate, nitrate, chloride and sulphate in dilute solutions, but less readily than sulphate as the solution becomes more concentrated. These data account for the fact that copper sulphate solutions go to the cathode through a porous cup and copper nitrate solutions go to the anode.

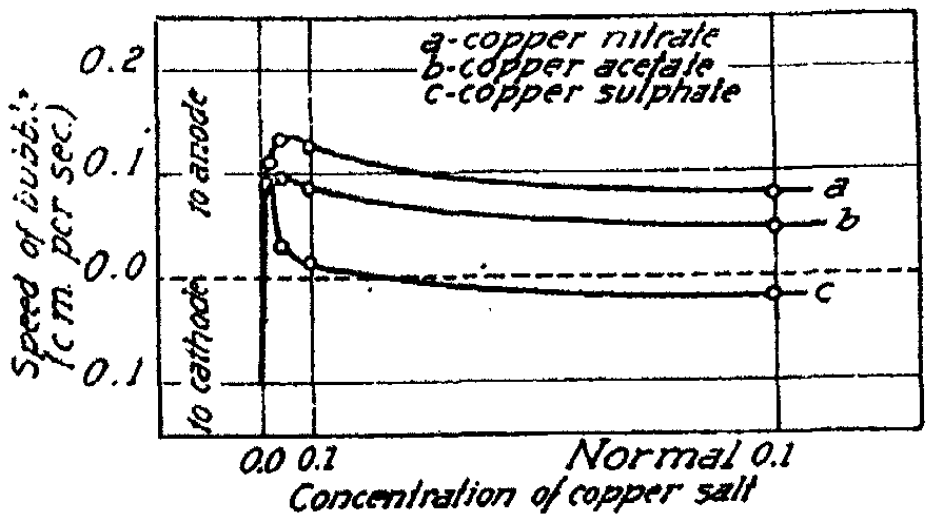

Fig. 4

Electrical Endosmose and Dyeing

Bancroft[2] has discussed the theory of dyeing with acid and basic dyes from the view-point of selective adsorption. So far as known, the adsorption of a dye by fibers or mordants depends, for a given adsorbent, upon the nature of the dye, its concentration, the other substances present in the dye bath, as well as upon the temperature. A basic dye is one having a colored basic radical, and an acid dye is one having

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[1] Zeit. Elektrochemie, 16, 586 (1910).

[2] Jour. Phys. Chem., 18, 1, 118, etc. (1914).

a colored acid radical. For the particular case of an acid dye, we have the following rules:

"(1) The dye is taken up most readily in an acid solution but may be taken up in a neutral or alkaline solution.

(2) A readily adsorbed anion decreases the amount of dye taken up.

(3) A readily adsorbed cation increases the amount of dye taken up."

For the case of a basic dye, the same rules hold, if one substitutes "alkaline" for "acid" and "cation" for "anion," and *vice versa*. A basic dye is taken up most readily in an alkaline solution. After all, rule (1) above is only a special case covered by (2) and (3) and would fail to hold in case the hydrogen ion of a particular acid were less readily adsorbed than its anion.

Mr. Pierson carried out a series of experiments designed to test the first of these generalizations. Alundum diaphragms were used and the following data obtained:

TABLE 6

Acid and Basic Dyes

Dye	Nature of dye	Solution (approx.)	Rate (corrected). Cm/sec.	Direction
Eosine	acid	*N*/500 HCl	(very slow)	?
Eosine	acid	*N*/500 NaOH	0.092	to cathode
Crystal ponceau	acid	*N*/500 HCl	(very slow)	?
Crystal ponceau	acid	*N*/500 NaOH	0.059	to cathode
Safranine	basic	*N*/500 HCl	0.077	to anode
Safranine	basic	*N*/500 NaOH	(very slow)	?
Methylene blue	basic	*N*/500 HCl	0.022	to anode
Methylene blue	basic	*N*/500 NaOH	(no flow)	?

(In each case concentration of dye was approximately *N*/5000.)

The results are quite in accord with the theory, and they emphasize certain points, particularly the marked effects of which small amounts of dye may produce and the difference between soluble acid and basic dyes. Alundum behaves as mordant essentially like hydrous alumina, except that the amount of dye removed by alundum is small and the dyed material is not fast to washing. When crystal ponceau was used in alkaline solution it was easily removed from the alundum by washing; after the dye was used in acid solution, however, it could be washed out only with difficulty. Methylene blue displayed the opposite behavior, for it was washed out easily after it had been used in acid solution but was removed with difficulty after it had been used with alkali.

The experiment is an excellent illustration of the neutralization of adsorbed ions. Alundum adsorbs hydrogen ions from an acid solution and becomes charged positively. If one adds a basic dye, neutralization of the adsorbed hydrogen can occur only by the adsorption of the colorless acid radical (usually chloride), which we have found by experiment to be only slightly absorbed. Some neutralization does occur, because the concentration of anions has been increased by adding the dye. But when we add an acid dye, the colored acid radical is adsorbed strongly and the positive charge on the diaphragm is neutralized. This neutralization is indicated by the fact that the solution no longer flows to the anode in acid solutions as it should do normally, but becomes almost stationary. Likewise, the adsorption of dye base from an alkaline solution is another example of the neutralization of adsorbed ions (in this case adsorbed hydroxyl).

The results of this paper may be summarized as follows:

(1) A new and convenient apparatus has been devised for studying electrical endosmose.

(2) The rate of electrical endosmose is proportional directly to the applied potential, other conditions being kept unchanged.

(3) The rate of electrical endosmose increases with rising temperature. It is not exactly proportional to the fluidity of the liquid but increases slightly less rapidly than the fluidity does with rising temperature. The results of experiment confirm the equation

$$V_e = \text{constant times } \frac{ED}{\eta}$$

for a given diaphragm and a given liquid.

(4) Perrin's data have been confirmed.

(5) Electrical endosmose has been studied with solutions of certain copper salts. Copper acetate, nitrate, and chloride flow to the anode, showing that copper as ion is adsorbed more than acetate, nitrate or chloride, but reversal occurs to the cathode with copper sulphate, indicating that sulphate is adsorbed more strongly than copper as ion at all ordinary concentrations.

(6) The relation of dyeing to contact electrification has been made evident by experiments on electrical endosmose.

Cornell University

BROWNIAN MOVEMENTS[1]

BY WILDER D. BANCROFT

If a stone be dropped into water, it sinks rapidly; but if it be ground into fine particles, the surface is much greater and consequently the particles sink slowly. If the stone were ground into very fine particles, we should expect them to sink very slowly, the rate being a function of the diameter and density of the particles. A formula,

$$V = \frac{2r^2(S - S')g}{9\eta},$$

for this case has been deduced by Stokes,[2] where V is the constant rate of fall, r the radius of the particles, S their specific gravity, S' the specific gravity of the liquid, η its viscosity coefficient and g the gravitational constant. Hatschek[3] has applied this formula to several special cases. For particles[4] of gold of 1 μ radius the rate of fall in water is calculated to be 2.4 mm per minute. With gold particles of 10 $\mu\mu$ radius the rate of settling in water is about 10 mm per month. For a particle of 10 $\mu\mu$ radius and a specific gravity of only 3 the calculated rate would be about 1 mm per month. Very small rates of fall have actually been observed. Even in air fine particles settle very slowly. Referring to a sandstorm in Grand Canyon, it is stated[5] that "the air, however, as is usual after these storms, was a brick-red color for two or three days." At the volcanic eruption of Krakatoa[6] on August 27, 1883, "an immense volume of dust and aqueous vapor was thrown to a

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[1] Under existing circumstances, it seems desirable to publish occasional and incomplete sketches of certain portions of the field of colloid chemistry, even though such papers involve no special research work.

[2] Mathematical and Physical Papers, 3, 1 (1901).

[3] "An Introduction to the Physics and Chemistry of Colloids," p. 24 (1913).

[4] Elutriation, or the difference in the rate of settling, is much used in grading powders such as emery, carborundum, ultramarine, kaolin, etc.

[5] Ellsworth and Emery Kolb: National Geographic Magazine, 26, 104 (1914).

[6] Moore: "Descriptive Meteorology," p. 245 (1910).

great height in the atmosphere above the Straits of Sunda. The antitrades spread this over the northern hemisphere, and winds higher up in the tropics carried it westward around the world and formed a layer from 5 to 15 miles above the earth's surface, consisting undoubtedly of minute particles. During the daytime the sun's disk appeared red, green, or blue, according to the thickness of the stratum through which the observer viewed it. This ring certainly was due to the diffraction of light penetrating through the layer of fine particles of ice or dust. After sunset, and by virtue of the diffusion of red light by this layer of particles, the whole western sky, even to near the zenith, glared with a lurid red as though lighted up from some great and distant fire. These remarkable sunsets continued, slowly diminishing in brilliance, through the years 1884 and 1885 in temperate latitudes, while their northern limit advanced slowly towards the pole, showing that minute particles of solid matter may float for years in the high upper atmosphere, so long as slowly rising currents buoy them up. Isolated clouds of such material may always be floating in the upper atmosphere and may give rise to the noctilucent or night-shining clouds that are occasionally observed at great altitudes when the observer looks northward in mid-summer."

If one may judge from some of the books that one reads, the dust in the air is one of the most striking characteristics of Asiatic scenery.[1]

"While stopping with the Khirghiz, we examined several old moraines. It is not necessary to discuss them, for their significance as indicators of pronounced, world-wide changes of climate in the most recent geological times is well known. The most peculiar quality of the Kwen Lun moraines is that they are shrouded in typical loess, a close-grained, yellowish deposit of the finest dust, unconsolidated, and yet so tenacious that for years a perpendicular face will hold the marks of the spade with which it is cut. Wherever the slopes outside the moraines were not too steep, they were likewise shrouded with

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[1] Huntington: "The Pulse of Asia," pp. 134, 147, 156, 191 (1907).

loess, and wherever there was loess, there was also vegetation. Our first day in the Lop basin happened to be unusually clear, but, as we saw from the Sanju pass, a yellow haze lay low over the desert fifty miles to the north. As the air grew hot, the haze gradually rose and expanded. That night a strong north wind came up. In the morning, as we looked out from our camp among the moraines, the whole country was enveloped in a haze of dust which we at first took for a thick, dirty fog or cloud. When the wind died down for a time, the haze began to settle, the mountain tops appeared, and the sky overhead showed a faint bluish tint, though the lower hills scarcely a mile away, were invisible; when the wind blew again, the dust was whirled upward, concealing the mountains and the sky. We could not see or feel the dust except as a haze, and were only positive as to its nature when the air, forced upward over the mountains by the north wind, became so cool that rain and hail began to fall. When the hailstones melted on a piece of dark cloth, each one left a spot of dust which it had gathered in the air, typical yellowish loess, of precisely the same nature as that which covered the moraines and mountain slopes. The dust could not have been of local origin, for the region nearby was well covered with grass, and was receiving accessions of loess rather than giving them up. Apparently, the dust came from the desert far to the north...

"The scenery was like that of Arizona, low, desert mountains covered scantily with weeds or low bushes of the sage type. The perpetual haze hemmed us in, making everything dull and uniformly brown or gray in color, and causing the sun, though bright and hot at noon, to fade into a molten ball and finally disappear an hour or more before sunset. Everywhere we found drifts of sand and deposits of loess half dissected by the wind. Evidently, at no remote date this region near the base of the mountains, at an elevation of seven or eight thousand feet, was more thickly covered with vegetation, so that loess could accumulate as it still does three or four thousand feet higher up among the moraines and grassy slopes of what may be called the loess-pasture zone. Within a few hundred or at most a few thousand years, there appears to have been such a change of climate that the vegetation has largely died, and the former region of aeolian deposition has been changed to one of erosion.

"Puski proved to be like Sanju, a fair green ribbon lying on two low terraces of loess beside a swift stream flowing in a broad flood-plain of cobblestones. On either side rise the low desert foothills; to the south, the mountains rise higher, and the stream is confined to a narrow gorge; while to the north, the vast naked beach of the zone of piedmont gravel slopes gently to the zone of vegetation. It took us a day to cross the gravel between Puski and Zanguya, the first town in the zone of vegetation. We grew sleepy in riding over the hot, monotonous plain. There was nothing to look at except pebbles, wonderfully smoothed and faceted by wind-blown sand, or dense columns of whirling dust, thirty or forty feet in diameter at the base and rising to a height of hundreds of thousands of feet, where they spread out after the manner of thunder-clouds. Twice I counted between twenty and thirty dust-whirls visible at one time, and there were always at least eight or ten. It was evident that, even if there were no wind, the air in summer would be full of dust continually...

"During the morning, every detail of the magnificent view was clearly visible. At noon, however, when a strong wind gave place to the usual afternoon breeze from the north, a change took place, and the process of the deposition of loess was vividly illustrated. The yellow band of haze, far away to the north behind all the mountains, had already expanded to a veil with a definite top, at the height, presumably, where the convectional currents of hot air rising from the desert had become so cooled by expansion that they spread out into a sheet at a position corresponding to that of the top of a thunder-cloud. Now the veil came slowly toward us, filling the lower gaps at first, and pouring into the Pisha basin, though the surrounding mountains and the sky remained clear. By two o'clock, the dust had been wafted upward so that the dark Tikelik plateau was hazy; and by four, even the highest of the white mountains to the south were dimmed. During the two succeeding weeks, which we spent in the Karatash valley east of Pisha, the air was thick with haze most of the time. Dust fell so fast, that even on a still day one was obliged to brush his letter-paper every ten or fifteen minutes to prevent the pen from becoming clogged. Almost every traveler speaks with exasperation or weariness of the persistence with which the haze shrouds the land for weeks at a time. I often felt as if my eyes were covered by a veil, which must somehow be torn off, or else I should drop into the apathetic mood of the natives. It would be rash, perhaps, to say that the apathy of the people, and their lack of curiosity and initiative, are due in any degree to an atmospheric haze. Nevertheless, when the traveler finds that this same haze tends to induce these qualities in himself, it is reasonable to question whether its continual influence upon generation after generation of Chanto natives may not, unconsciously to them, have been a factor in molding their character. Now they have reached a point where they are even more apathetic than most Orientals: a dull day is scarcely noticed; a clear sky inspired them but little; every vicissitude of life is received quietly; and nothing moves them greatly from the even tenor of their way...

"Our gaze went out far beyond them to where the last low hills gave place to a strange yellow band. It seemed at first to be the sandy desert of the heart of Asia; but during the two hours of our stay on the pass, it expanded and rose, and we then knew it for the inevitable dust-haze which shrouds the country more than half the year."

Ebell[1] states that ultramarine will stay suspended in pure water for months when obtained in a very finely divided state by grinding and elutriation. Mühlhäuser[2] found that when very finely ground carborundum powder is treated with water, a portion of it does not settle in months and be-

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[1] Ber. deutsch. chem. Ges., 16, 2429 (1883).

[2] Zeit. anorg. Chem., 5, 117 (1894).

haves in that respect like colloidal metallic silver. Brewer[1] points out the slow rate at which clays settle, and raises the question whether extremely finely divided particles settle at all.

"There is considerable difference as to details in the behavior of various clays in water. With some of them, if agitated and thoroughly diffused through the liquid and then allowed to stand at rest, the turbidity fades gradually and regularly in density from the bottom to the top, and the liquid gradually grows clearer until it becomes as clear as natural waters ever do. Usually however, and with the majority of clays (if the water be pure enough), the deposition is in quite a different manner. After some time, it may be a few hours or it may be only after some days, the suspended material disposes itself in layers or strata which are more or less obvious because of the different degree of turbidity of the liquid. There may be but two or three of these layers to be seen at once or there may be six or eight, the number depending in part on the composition and fineness of the material under experiment, in part on the freedom of the water from other dissolved material than the clay itself, and in part on the temperature. Some of these layers may be and usually are very obvious, others obscure and only to be seen in the best light; some are very sharply defined, others remain ragged and ill defined along the lines of separation. Some which may be obscure at one temperature become sharp and well defined if the temperature be slowly raised or lowered a few degrees, or well-defined strata at one temperature become first hazy and then disappear at a higher or lower temperature. Sometimes, with a change of temperature, what was before one uniform stratum will slowly resolve itself into several obvious strata, which remain distinct so long as the temperature is right, but which disappear again and become homogenous at another temperature. Thus, some suspended clays may be induced to exhibit a much larger number of these liquid strata in the aggregate than are visible at any one time.

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[1] Mem. Nat. Acad. Sci. 2, 165 (1884); Am. Jour. Sci., [3] 29, 1 (1885).

"These different strata, having unlike degrees of opacity, settle with very different degrees of rapidity, and if the temperature be kept nearly constant and the vessel entirely at rest, their number grows less and less from the more rapid settling of the lower and heavier. The lighter ones usually settle with extreme slowness, often but a millimeter per day, some even less than half that, and consequently, any cause, such as varying temperature, which sets up even very feeble currents, may so retard the ultimate clearing as to prevent it indefinitely.

"If the vessel be kept in the quiet and with as nearly constant temperature as is possible, the liquid finally becomes uniformly opalescent throughout. This opalescence gradually fades for a time, from the subsidence of some of the suspended matter, and if the water contains a sufficient amount (which may be a very minute proportion) of certain salts in solution, it becomes practically clear, that is, clear to the unaided eye in ordinary daylight—as clear as the clearest natural waters. If, however, the water be free from dissolved substances (other than the clay itself) the fading of the opalescence ceases after some time, it may be a few weeks, or it may be only after two or three years, and after that the liquid becomes no clearer by standing. The degree of opalescence may and often does vary with varying temperature, as if some of the sediment were again picked up, or as if a portion which had fallen and remained as a mobile liquid stratum on the bottom at one temperature were again raised by diffusion at another temperature. Certain very ferruginous clays under experiment, the latter suspensions from which are amber-colored, change thus very decidedly and obviously from summer to winter in a vessel which is kept in the temperature of my study. In pure water the subsidence is probably never complete. Some specimens under experiment, which have stood for more than seven years and which are obviously opalescent, have not become sensibly clearer for the last four years. The last portion of this time they have rested on a shelf fastened to a heavy wall in a deep cellar and further enclosed in a closet, in which changes of temperature are very slow, and jars or motion practically none."

If the very finely divided particles do not really settle at all, there must be some factor which neutralizes the action of gravity more or less completely. The experiments of an English botanist, Brown,[1] give us a clue to the difficulty, though the importance of these experiments was not appreciated until very much later. Brown was studying under the microscope the grains of pollen from *Clarckia pulchella.* "While examining the form of these particles immersed in water, I observed many of them very evidently in motion, their motion consisting not only of a change of place in the fluid, manifested by alterations in their relative positions, but also not unfrequently of a change of form in the particle itself, a contraction or curvature taking place repeatedly about the middle of one side, accompanied by a corresponding swelling or convexity on the opposite side of the particle. In a few instances the particle was seen to turn on its longer axis. These motions were such as to satisfy me, after frequently repeated observation that they arose neither from currents in the fluid, nor from its gradual evaporation, but belonged to the particle itself...

"Reflecting on all the facts with which I had now become acquainted, I was disposed to believe that the minute spherical particles or molecules of apparently uniform size, first seen in the advanced states of the pollen of *Onagiariae,* and most other Phaenogamous plants—then in the antherae of mosses and on the surface of the bodies regarded as the stamina of *Equisetum,* and lastly in bruised portions of other parts—were in reality the supposed constituent or elementary molecules of organic bodies, first so considered by Buffon and Needham, then by Weisberg with greater precision, soon after and still more particularly by Müller, and very recently by Dr. Milne Edwards, who has revived the doctrine and supported it with much interesting detail. I now therefore expected these molecules in all organic bodies, and accordingly on examining

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[1] Phil. Mag., 4, 161 (1828); 6, 161 (1829).

the various animal and vegetable tissues, whether living or dead, they were always found to exist; and merely by bruising these substances in water, I never failed to disengage the molecules in sufficient number to ascertain the apparent identity in size, form, and motion, with the smaller particles of the grains of pollen.

"I examined also various products of organic bodies, particularly the gum-resins, and substances of vegetable origin, extending my inquiry even to pit-coal; and in all these bodies molecules were found in abundance. I remarked here also, partly as a caution to those who may hereafter engage in the same inquiry, that the dust or soot deposited on all bodies in such quantity, especially in London, is entirely composed of these molecules. One of the substances examined was a specimen of fossil wood, found in Wiltshire oolite, in a state to burn with flame; and as I found these molecules abundantly, and in motion in this specimen, I supposed that their existence, although in smaller quantity, might be ascertained in mineralized vegetable remains. With this view a minute portion of silicified wood, which exhibited the structure of *Coniferae*, was bruised, and spherical particles, or molecules in all respects like those so frequently mentioned, were readily obtained from it in such quantity, however, that the whole substance of the petrifaction seemed to be formed of them. But hence I inferred that these molecules were not limited to organic bodies nor even to their products.

"To establish the correctness of the inference, and to ascertain to what extent the molecules existed in mineral bodies, became the next object of inquiry. The first substance examined was a minute fragment of window-glass, from which, when merely bruised on the stage of the microscope, I readily and copiously obtained molecules agreeing in size, form, and motion with those I had already seen. I then proceeded to examine, and with similar results, such minerals as I either had at hand or could readily obtain, including several of the simple earths and metals, with many of their combinations. Rocks of all ages, including those in which organic remains have never been found, yielded the molecules in abundance. Their existence was ascertained in each of the constituent minerals of granite, a fragment of the Sphinx being one of the specimens examined.

"To mention all of the mineral substances in which I have found these molecules, would be tedious, and I shall confine myself in this summary to an enumeration of a few of the most remarkable. These were both of aqueous and igneous origin, as travertine, stalactites, lava, obsidian, pumice, volcanic ashes, and meteorites from various localities. Of metals I may mention manganese, nickel, plumbago, bismuth antimony, and arsenic. In a word, in every mineral which I could reduce to a powder, sufficiently fine to be temporarily suspended in water, I found these molecules more or less copiously; and in some cases, more particularly in siliceous crystals, the whole body, submitted to examination appeared to be composed of them."

In the second paper[1] Brown says: "Although I endeavored strictly to confine myself to the statement of the facts observed, yet in speaking of the active molecules I have not been able, in all cases, to avoid the introduction of hypothesis; for such is the supposition, that the equally active particles of greater size, and frequently of very different form, are primary compounds of these molecules—a supposition which, though professedly conjectural, I regret having so much insisted on, especially as it may seem connected with the opinion of the absolute identity of the molecules, from whatever source derived. On this latter subject, the only two points that I endeavored to ascertain, were their size and figure; and although I was, upon the whole, inclined to think that in these respects the molecules were similar from whatever substances obtained, yet the evidence then adduced in support of the supposition was far from satisfactory; and I may add, that I am still less satisfied now that such was the fact. But even had the uniformity of the molecules in those two points been absolutely established, it did not necessarily

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[1] Phil. Mag., 6, 161 (1829).

follow, nor have I anywhere stated, as has been imputed to me, that they also agreed in all their other properties and functions.

"I have remarked that certain substances, namely, sulphur, resin, and wax, did not yield active particles, which, however, proceeded merely from defective manipulation, for I have since readily obtained them from all these bodies; at the same time I ought to notice that their existence in sulphur was previously mentioned to me by my friend Mr. Lister.

"The result of the inquiry at present essentially agrees with that which may be collected from my printed account, and may be there briefly stated in the following terms: namely,

"That extremely minute particles of solid matter, whether obtained from organic, or inorganic substances, when suspended in pure water, or in some other aqueous fluids, exhibit motions for which I am unable to account, and which from their irregularity and independence resemble in a remarkable degree the less rapid motions of some of the simplest animalcules of infusion. That the smallest moving particles observed, and which I have termed Active Molecules, appear to be spherical or nearly so, and to be between 1/20000 and 1/30000 of an inch in diameter [about one-thousandth of a millimeter]; and that other particles of considerably greater and various size, and either of similar or very different figure, also present analogous motions in like circumstances.

"I have formerly stated my belief that these motions of the particles neither arose from currents in the fluid containing them, nor depended on that intestine motion which may be supposed to accompany its evaporation. These causes of motion, however, either singly or combined with others—as, the attractions and repulsions among the particles themselves, their unstable equilibrium in the fluid in which they are suspenedd, their hygrometrical or capillary action, and in some cases the disengagement of volatile matter, or of minute air bubbles—have been considered by several writers as sufficiently accounting for the appearances. Some of the alleged causes here stated, with others which I have considered it unnecessary to mention, are not likely to be overlooked or to deceive observers of any experience, in microscopical researches: and the insufficiency of the most important of those enumerated, may, I think be satisfactorily shown by means of a very simple experiment.

"This experiment consists in reducing the drop of water containing the particles to microscopic minuteness, and prolonging its existence by immersing it in a transparent fluid of inferior specific gravity, with which it is not miscible, and in which evaporation is extremely slow. If to almond-oil, which is a fluid having these properties, a considerably smaller proportion of water, duly impregnated with particles, be added, and the two fluids shaken or triturated together, water drops of various sizes, from 1/50 to 1/2000 of an inch in diameter, will be immediately produced. Of these the most minute necessarily contain but few particles, and some may be occasionally observed with one particle only. In this manner minute drops, which, if exposed to the air would be dissipated in less than a minute, may be retained for more than an hour. But in all the drops thus formed and protected, the motion of the particles takes place with undiminished activity, while the principle causes assigned for that motion, namely evaporation, and their mutual attraction and repulsion, are either materially reduced or absolutely null.

"It may be here remarked, that those currents from centre to circumference, at first hardly perceptible, then more obvious, and at last very rapid, which constantly exist in drops exposed to the air, and disturb or entirely overcome the proper motion of the particles are wholly prevented in drops of small size immersed in oil, a fact which, however, is only apparent in those drops that are flattened, in consequence of being nearly or absolutely in contact with the stage of the microscope.

"That the motion of the particles is not produced by any cause acting on the surface of the drop, may be proved by an inversion of the experiment, for by mixing a very small proportion of oil with the water containing the particles, microscopic drops of oil of extreme minuteness, some of them not exceeding in size the particles themselves, will be found on the surface of the drop of water, and nearly or altogether at rest, while the particles in the centre or towards the bottom of the drops continue to move with their usual degree of activity."

These movements of suspended particles are known as Brownian movements. In regard to them, Perrin[1] says: "The singular phenomenon discovered by Brown did not attract much attention. Moreover, for a long time it remained ignored by the majority of physicists, and it may be supposed that those who had heard of it thought it analogous to the movement of the dust particles, which can be seen dancing in a ray of sunlight, under the influence of feeble currents of air which set up small differences of pressure or temperature. When we reflect that this apparent explanation was able to satisfy even thoughtful minds, we ought the more to admire the acuteness of those physicists, who have recognized in this, supposedly insignificant, phenomenon a fundamental property of matter.

"Besides, as happens most frequently when it is sought to unravel the genesis of a great directing idea, it is difficult to fix precisely how the hypothesis, which ascribes the Brownian Movement to molecular agitation, first appeared and how it was developed.

"The first name which calls for reference in this respect is, perhaps, that of Wiener,[2] who declared at the conclusion of his observations that the movement could not be due to convection currents, that it was necessary to seek for the cause of it in the liquid itself, and who, finally, almost at the commencement of the development of the kinetic theory of heat, divined that molecular movements were able to give the explanation of the phenomenon......

"It was established by the work of M. Gouy,[3] not only

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[1] "Brownian Movement and Molecular Reality," pp. 3, 6, 7 (1910).

[2] Pogg. Ann., 118, 79 (1863).

[3] Jour. de Phys., (2) 7, 561 (1888); Comptes rendus, 109, 102 (1889); Revue générale des Sciences, 1895, 1.

that the hypothesis of molecular agitation gives an admissible explanation of the Brownian movement, but that no other cause of the movement could be imagined, which especially increases the significance of the hypothesis. This work immediately evoked a considerable response, and it is only from this time that the Brownian movement took a place among the important problems of general physics.

"In the first place, M. Gouy observed that the Brownian movement is not due to vibrations transmitted to the liquid under examination, since it persists equally, for example, at night on a sub-soil in the country as during the day near a populous street where heavy vehicles pass. Neither is it due to convection currents existing in fluids where thermal equilibrium has not been attained, for it does not change appreciably when plenty of time is given for equilibrium to be reached. Any comparison between Brownian movement and the agitation of dust particles dancing in the sunlight must, therefore, be set aside. In addition, in the latter case, it is easy to see that the neighboring dust-particles move in general in the same sense, roughly tracing out the form of the common current which bears them along, whereas the most striking feature of the Brownian movement is the absolute independence of the displacement of neighboring particles, so near together that they pass by one another. Lastly, neither can the unavoidable illumination of the preparation be suspected, for M. Gouy was able abruptly to reduce it a thousand times, or to change its color considerably, without at all modifying the phenomenon observed. All the other causes from time to time imagined have as little influence; even the nature of the particles does not appear to be of any importance, and henceforward it was difficult not to believe that these particles simply serve to reveal an internal agitation of the fluid, the better the smaller they are, much as a cork follows better than a large ship the movements of the waves of the sea.

"Thus comes into evidence, in what is termed a *fluid in equilibrium*, a property eternal and profound. This equilibrium only exists as an average and for large masses; it is statistical equilibrium. In reality the whole fluid is agitated indefinitely and spontaneously by motions the more violent and rapid the smaller the portion taken into account; the statistical motion of equilibrium is completely illusory.

"The Brownian movement is explained, in the theory of M. Gouy and his predecessors, by the incessant movements of the molecules of the fluid, which striking unceasingly the observed particles, drive about these particles irregularly through the fluid, except in the case where these impacts exactly counterbalance each other. It has, to be sure, been long recognized, especially in explanation of the facts of diffusion, and of the transformation of motion into heat, not only that substances in spite of their homogeneous appearance, have a discontinuous structure and are composed of separate *molecules*, but also that these molecules are in incessant agitation, which increases with the temperature and only ceases at the absolute zero."

"There is, therefore, an agitation maintained indefinitely without external cause. It is clear that this agitation is not contradictory to the principle of the conservation of energy. It is sufficient that every increase in the speed of a granule is accompanied by a cooling of the liquid in its immediate neighborhood, and likewise every decrease of speed by a local heating, without loss or gain of energy. We perceive that the thermal equilibrium itself is also simply a statistical equilibrium. But it should be noticed, and this very important idea is again due to M. Gouy, that the Brownian movement is not reconcilable with the rigid enunciation too frequently given to Carnot's principle; the particular enunciation chosen can be shown to be of no importance. For example, in water in equilibrium it is sufficient to follow with the eyes a particle denser than water to see it at certain moments rise spontaneously, absorbing work necessarily at the expense of the heat of the surrounding medium. So it must not any longer be said that perpetual motion of the second sort is impossible, but one must say: 'On the scale of size which interests us practically, perpetual motion of the second sort is in general so insignificant that it would be absurd to take it into account.' Besides, such restrictions have long been laid down, the point of view that Carnot's principle expresses simply a law approximated to has been upheld by Clausius, Maxwell, Helmholtz, Boltzmann, and Gibbs, and in particular may be recalled the *demon,* imagined by Maxwell, which being sufficiently quick to discern the molecules individually, made heat pass at will from a cold to a hot region without work. But since one is limited to the intervention of visible molecules, it remained possible, by denying their existence, to believe in the perfect rigidity of Carnot's principle. But this would not longer be admissible, for this rigidity is now in opposition to a *palpable reality.* On the other hand, the practical importance of Carnot's principle is not attacked."

Smoluchowski[1] says: "The direct observation of this movement, by means of the microscope, produces an impression analogous to our imagination of molecular motions. It is not a vibration, nor a simple progressive movement, but it is rather a trembling, or, as Gouy expresses it, a swarming. The particles pursue an irregular zig-zag course, in all directions in space, as if they were pushed here and there by accidental collisions with the molecules. In reality their progress is very slow in spite of their feverish activity. Many physicists have considered this phenomenon as a visible proof of the truth of the kinetic theory. . . .

"We shall study here the simplest kinetic theory; we shall assume that what we see in this motion is the result of accidental collisions between the particles and the molecules of the liquid. One objection often considered as fatal to this theory was first raised by Nageli. He shows that the velocity transmitted to a spherical particle of diameter 0.003 mm by collision with one molecule of hydrogen is only 2×10^{-6} mm per second, which would not be visible in the microscope; in addition, the shocks received on the various sides of the particle would annul each other and give no perceptible result.

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[1] Burton: "The Physical Properties of Colloidal Solutions," p. 68 (1916).

"This conclusion is comparable to that error which one makes who pursues a game of chance, if he expects never to have a loss or a gain more than the simple wager. One knows that, in general, the chances do not balance exactly and that the amount of the sum lost or gained increases with the number of plays. We have in the problem before us to discuss the excess in the number of shocks given to a particle by the molecules in a certain direction. Now we have the simple result that the velocity transmitted to a particle of mass, M, in repose, by a direct collision with a molecule of mass, *m*, which is moving with a velocity, *c*, will be: $C = mc/M$ which is of the order given by Nageli; and further the absolute value along a fixed direction, X, will be still smaller. But it is necessary to consider that the particle M suffers more than 10^{16} collisions per second in a gas and more than 10^{20} in a liquid, of which the effect will be annulled in general, but there will always be an excess, + or —, of 10^8 or 10^{10} collisions, by virtue of which the particle will attain a velocity of from 10 to 1000 cms per second in the direction of X (+ or —).

"This proves that the objection of Nageli is not justified, but the final result, on the other hand, is not exact. For (*a*) the absolute value of the change in the velocity of M will not be the same for each collision, but will depend on the absolute value of C at the time, and (*b*) the probability of collisions retarding will be greater than that of collisions accelerating for large values of C. These two factors oppose an unlimited increase in the values of C; the final result which one can readily foretell for the kinetic theory is that the mean kinetic energy of translatory motion of M will become equal to the mean kinetic energy of the molecules. For the equalization of this value is precisely the characteristic condition of the thermal equilibrium of bodies, according to the theory of Boltzmann and Maxwell. In the same way we conclude that the particles play the rôle of highly polyatomic molecules of some dissolved substance, and that they would consequently have the same kinetic energy as a molecule of a gas at the temperature of the medium. Then one can calculate the value of C according to the ordinary formula of the gas theory

$$C = c\sqrt{m/M} \qquad (1)$$

which for a particle of the diameter equal to 0.001 mm and a density 1, gives for C, 0.4 cm per sec. How are we to reconcile this result with the observed values, which are of the order 3×10^{-4} cm per sec.? This obstacle seems at first sight a serious matter for the kinetic theory. However, the explanation is very simple. It would be impossible to follow the movement of such a particle if it were endowed with a velocity of 0.4 cm per sec., for in a microscope of magnification 500 it would be moving with a velocity of 2 meters per second.

"That which we see is the mean position of the particle, pushed 1020 times per second with this velocity, each time in a different direction. Its centre describes a capricious, zigzag path, composed of straight pieces each very small in comparison with the dimensions of the particle. Its displacement is visible only when the geometrical sum of its paths is raised to an appreciable value. In addition there is the minor correction that it is not the movement in space we observe but the projection of this movement on a plane; consequently, we shall have to multiply observed results by $4/\pi$."

The distance between the two end points as a particle zig-zags forward and back is usually defined as twice the amplitude. Svedberg[1] found that for different solutions the product of the amplitude A into the viscosity η is a constant and that the amplitude divided by the time which the particles take in passing through that distance is also a constant. These results are in qualitative agreement with a theoretical formula deduced by Einstein.[2] If one knows the amplitude and the time, one can calculate the speed of the particles. For platinum particles with a diameter of 10–50 $\mu\mu$, Svedberg found speeds of 200–400 $\mu\mu$/sec. Perrin[3] considers that errors of measurement vitiate these data. He says that the speed of

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[1] Zeit. Elektrochemie, 12, 835, 909 (1906).

[2] Drude's Ann., 17, 549 (1905); 19, 289, 371 (1906).

[3] "Brownian Movement and Molecular Reality," p. 22 (1910).

a granule in suspension is not accessible to measurement. "One method of proceeding appears direct; let us suppose that one has the power of measuring the mass of a microscopic particle directly; can we not hope to obtain at least an idea of its mean speed, and, in consequence of its energy by direct readings, possibly by dividing by the time of an observation the distance between the two positions it occupies at the commencement and at the end of the observation (apparent mean speed), possibly by following its trajectory in a *camera lucida* during a given time, and dividing the total length of this trajectory by this time.

"As a matter of fact, this was at first essayed,[1] and values can be found in different papers which are always some microns per second for the speed of granules of the order of a micron, and which will assign to these granules a mean energy about 100,000 times less than the kinetic energy indicated for the molecule, and this would completely overthrow the theory of the equipartition of energy.

"But such values are *grossly untrue.* The entanglements of the trajectory are so numerous and rapid that it is impossible to follow them, and the trajectory seen is always infinitely shorter and more simple than the real trajectory. At the same time the apparent mean speed of a granule during a given time (the quotient of the displacement by the time) varies *absurdly* in magnitude and direction without in the least tending toward a limit when the time of observation is decreased, as can be seen in a simple manner by noting the position in a *camera lucida* from minute to minute, then, for example, every five seconds, and better still by photographing them every twentieth of a second, as Victor Henri has done, by cinematographing the movement. As is well understood, the tangent at any point of the trajectory cannot be fixed even in the roughest manner. It is one of the cases where one cannot help recalling those continuous functions which do not allow of derivation, which are regarded simply as mathe-

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[1] Wiener, Ramsay, Zsigmondy and myself.

matical curiosities, wrongly since nature can suggest them equally as well as the derived functions."

Even though quantitative measurements may be inaccurate, it is desirable to have a general idea of the magnitude of the phenomenon. From Exner's[1] experiments it appears that particles with a diameter larger than 4 μ show no perceptible Brownian movements. Particles smaller than 0.1 μ begin to show lively movements,[2] while particles with diameters of about 10 $\mu\mu$ give apparent trajectories up to 20 $\mu\mu$.

Perrin[3] came to the conclusion that the gas laws apply to dilute emulsions. "Let us suppose that it is possible to obtain an emulsion, with the granules all identical, an emulsion which I shall call, for shortness, *uniform*. It appeared to me at first intuitively, that the granules of such an emulsion should distribute themselves as a function of the height in the same manner as the molecules of a gas under the influence of gravity. Just as the air is more dense at sea-level than on a mountain-top, so the granules of an emulsion, whatever may be their initial distribution, will attain a permanent state where the concentration will go on diminishing as a function of the height from the lower layers, and the law of rarefaction will be the same as for air."

To test this hypothesis, Perrin prepared a uniform suspension of purified gamboge in water by means of fractional centrifuging. The results confirmed the hypothesis. With gamboge particles 0.3 μ in diameter a rise of 30 μ was sufficient to lower the concentration to a tenth of its value, 10 μ in the gamboge suspension being equivalent to 6 kilometers in the air.[4] Similar results were obtained with mastic suspended in water. Satisfactory results have also been obtained by Zangger[5] for drops of mercury, by Brillouin[6] for gamboge in

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[1] Sitzungsber. Akad. Wiss., Wien, 56 II, 116 (1867).

[2] Zsigmondy: "Kolloidchemie," p. 18 (1912).

[3] "Brownian Movements and Molecular Reality," p. 22 (1910).

[4] Perrin: "Brownian Movement and Molecular Reality," p. 43 (1910).

[5] Ann. Chim. phys., (8) 27, 412 (1912).

[6] Zeit. Kolloidchemie, 7, 216 (1911).

glycerol solutions having a viscosity 160 times that of water, and by Iljin.[1]

Einstein[2] assumes that suspended particles will behave exactly like dissolved particles, exerting an osmotic pressure and diffusing through the solvent. Instead of the van't Hoff expression that the osmotic pressure P of a dissolved substance is given by the equation

$$PV = nRT$$

Einstein deduces the equation

$$PV = \frac{n}{N} RT,$$

where n is now the number of suspended particles and N is Avogadro's constant or the actual number of molecules in a gram-molecule. Following this up he deduces for the rate of diffusion the equation

$$D_x = \sqrt{\frac{RT}{N\pi} \cdot \frac{t}{3r\eta}}$$

where D_x is the displacement in a given direction, t is the time, R is the gas constant, T the absolute temperature, N is the Avogadro constant, r is the radius of the particles and η is the viscosity of the liquid. This has been confirmed quantitatively by Perrin[3] who gets a mean value of about 68×10^{22} for N. In regard to this he says:[4]

"Thus the molecular theory of the Brownian movement can be regarded as experimentally established, and, at the same time, *it becomes very difficult to deny the objective reality of molecules*. At the same time we see that the law of gases already extended by van't Hoff to dilute solutions, can be extended to uniform emulsions. The Brownian movement offers us, on a different scale, the faithful picture of the movements possessed, for example, by the molecules of oxygen dis-

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[1] Zeit. phys. Chem., 83, 592 (1913).

[2] Drude's Ann., 17, 549 (1905); 19, 289, 371 (1906). See also Smoluchowski: Drude's Ann., 21, 756 (1906).

[3] Perrin: "Die Atome," p. 123 (1914).

[4] Perrin: "Brownian Movement and Molecular Reality," p. 46 (1909).

solved in the water of a lake, which, encountering one another only rarely, change their direction and speed by virtue of their impacts with the molecules of the solvent.

"It may be interesting to observe that the largest of the granules, for which I have found the laws of perfect gases followed, are already visible in sunlight under a strong lens. They behave as the molecules of a perfect gas, of which the gram-molecule would weigh *200,000 tons*.

"I add lastly that all the measurements detailed in this paragraph have been made on dilute emulsions, which in the parts richest in granules only contain a thousandth part of resin, and where the osmotic pressure does not reach a thousand millionth of an atmosphere.

"This last figure shows to what a point I was removed from the conditions under which it has been possible to reveal (Malfitano) and then to measure (J. Duclaux) the osmotic pressure of colloidal solutions with very fine granules closely crowded together. It may be that a generalization, more or less analogous to that of van der Waals, will give, one day, by means of a reasoning from the kinetic theory, the osmotic pressure of such solutions."

If we substitute four times the amplitude for $D_x (D_x = 4A)$ in Einstein's formula, t will be the time required for the particle to make one complete oscillation.[1] Einstein's formula, therefore, becomes

$$(4A)^2 = \frac{RT}{N} \cdot \frac{t}{3r\eta}.$$

If we are considering particles of the same size in various liquids we may write the equation $A^2 = k.t/\eta$ if we are working at constant temperature. "Since, by this kinetic theory, the average kinetic energy of a particle is the same as the average kinetic energy of a molecule, and the molecules of all fluids at the same temperature have the same average kinetic energy, we should expect the average velocity of all the particles to be the same, provided their masses are the same, whatever the liquid in which they are moving." Einstein's formula,

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[1] Burton: "The Physical Properties of Colloidal Solutions," p. 76 (1916).

therefore, leads to the set of relations: $A\eta$ = const.; D_x = const.$\sqrt{T/\eta}$; and $D_x/\sqrt{t}$ = const.

As was pointed out previously,[1] Svedberg had discovered independently that the product of the amplitude into the viscosity was a constant at constant temperature. Exner[2] found that the ratio of displacements at 20° and 71° is 1 : 1.6, while the ratio of the corresponding values of $\sqrt{T/\eta}$ for water at these two temperatures is 1 : 1.7. "Seddig[3] has shown by means of a photographic method in conjunction with the microscope, that finely divided cinnabar in water obeys Einstein's formula, the greatest departure from the theoretical value being 6 percent. As is the case with nearly all the results, the observed velocity exceeds the calculated." These variations are due chiefly to the considerable amount of radiant heat emitted by the heating wire and absorbed to a great extent by the suspended particles thus raising their temperature. This rise of temperature is shared very rapidly by the film of liquid in immediate contact with the particles, which latter therefore, move more rapidly than one would expect from the mean temperature of the liquid as shown by the thermopile. The error is more the higher the temperature of the heating wire. In a suspension containing coarse and fine particles, it was noticed that fine particles very close to a coarse one moved much faster than particles of the same size which were not near a coarse particle and were, therefore, in a less superheated liquid.

"Chaudesaigues,[4] working with an emulsion of gamboge, varied the viscosity of a solution by adding sugar. In this way he carried out observations on two solutions containing the same-sized particles at the same temperature, the viscosities of which were in the ratio 1 : 4 and found that the motion was twice as fast in the less viscous solution as it was in the solution of higher viscosity....... Chaudesaigues also

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[1] See page 290.

[2] Burton: "The Physical Properties of Colloidal Solutions," p. 77 (1916).

[3] Phys. Zeit., 9, 465 (1908).

[4] Comptes rendus, 147, 1044 (1908).

observed the velocities of particles of gamboge with radii, respectively, 4.5×10^{-5} cm and 2.13×10^{-6}, practically a ratio of 2 : 1, and found that these velocities varied inversely as the square of the radii....... He also observed the distances described by 50 grains, each of radius 2.13×10^{-5} cm during successive intervals of 30 seconds each and obtained the following results: the particles moved over on the average 6.7, 9.3, 11.8 and 13.95 microns in 30, 60, 90 and 120 seconds. The square roots of the times are proportional to the numbers 6.7, 9.46, 11.6 and 13.4, giving an ideal confirmation of this point."

It was first pointed out[1] by Smoluchowski[2] that we should expect to have the Brownian movements in gases as well as in liquids and he quotes from Bodaszewski[3] and O. Lehmann[4] as to the dancing movements executed by the particles of fumes of ammonium chloride, acids, phosphorus, etc., which they compared to the Brownian movements in liquids and interpreted as molecular movements. The formula of Einstein and Smoluchowski are based on the Stokes' law which does not hold for gases under low pressure where the mean free path of the gas molecules is large relatively to the radius of the particles. For the case of a gas, Smoluchowski[5] deduces a special formula of which, however, we shall make no use. "Ehrenhaft[6] was the first to carry out direct measurements on the Brownian movement of particles in gases. He found that, as theory predicts, there is a much livelier motion in gases than in liquids; at the same time the action of gravity in causing vertical descent of the particles is also much more apparent in gases than it is in liquids. For comparatively large particles in the smoke of cigars and cigarettes and in the fumes of ammonium chloride, he observed an undoubtedly

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[1] Burton: "The Physical Properties of Colloidal Solutions," p. 85 (1916).

[2] Drude's Ann., **21**, 756 (1906).

[3] Kosmos, **7**, 177 (1882); Beibl., **8**, 488 (1883).

[4] Molekularphysik, II, 5.

[5] Drude's Ann., **21**, 769 (1906).

[6] Sitzungsber. Akad. Wiss., Wien, **116** *IIa*, 1139 (1907).

zigzag Brownian movement, while with smaller particles obtained by a spark discharge between zinc, platinum, or silver electrodes, Ehrenhaft concluded that he has proved without a doubt the existence of a motion in gases completely analogous to the Brownian movement in liquids.

"As was predicted by Smoluchowski, it is more difficult to recognize this motion in gases on account of disturbing convection currents and the action of gravity. For the heavier particles, the velocity due to the force of gravity completely overshadows that due to the molecular shocks, while the opposite is the case with the very small particles. In Table I are given the velocities impressed by molecular shocks and by the force of gravitation, respectively, on silver particles of various sizes (density 10.5). These numbers show that when we reach particles having diameters of the order of the wave length of light the two velocities do not differ materially. As we deal with smaller particles, the velocity induced by gravity soon becomes negligible, while with particles increasing above 0.1 μ, the motion due to gravity soon dominates the situation. This is in keeping with what Ehrenhaft found. Particles, the linear dimensions of which were of the order of the size of the mean free path of a gas molecule (0.1 μ), and somewhat larger particles fall in a zig-zag line, the velocity due to gravitation being greater than that due to molecular shocks. Particles, which are near the limit of visibility in the ultramicroscope (1 μμ), are in such lively molecular motion

TABLE I

Brownian Movements in Gases

Radius of silver particles	Velocity due to molecular shocks	Velocity due to gravity
1 μμ	6.3 μ/sec.	1.2 μμ/sec.
5 μμ	28 μ/sec.	30 μμ/sec.
10 μμ	20 μ/sec.	120 μμ/sec.
50 μμ	8.9 μ/sec.	3 μ/sec.
100 μμ	6.3 μ/sec.	12 μ/sec.
500 μμ	2.8 μ/sec.	300 μ/sec.
1 μ	2.0 μ/sec.	1200 μ/sec.

that the vertical gravitational velocity is completely masked. Ehrenhaft viewed silver particles that remained in lively motion in the air of his ultramicroscopic cell for some thirty minutes. His measurements on the cigarette smoke particles gave a mean velocity of 25 μ/sec., and on the smaller particles of silver, 46 μ/sec.

"Much interesting work has been done in this field by De Broglie.[1] Both Ehrenhaft and De Broglie have found that these silver particles, suspended in air, are charged and, by measuring the velocity impressed on them by a known electric field, have come to the conclusion that the charge is that of one electron. The values that they find for this charge,[2] e are, respectively, 4.6×10^{-10} and 4.5×10^{-10} electrostatic units."

It seems to be accepted pretty generally that the work of Perrin, Svedberg, and others has established the practical continuity between suspended particles and dissolved substances; but this seems to be an over-hasty conclusion. The molecular weight of a dissolved substance, as calculated from the osmotic pressure, means something quite definite. The molecular weight of a suspended particle, as calculated from any of Einstein's formulas means something entirely different, if it means anything at all. We can determine the molecular weight of liquid benzene approximately from a measurement of the surface tension; but it is absurd to say that suspending fine drops of benzene in water causes the molecular weight of benzene to be equal to 200,000 tons. We are talking about entirely different things in the two cases. What we mean is that liquid benzene has a molecular weight of 78, and that liquid benzene suspended in water behaves, or may behave, as if it were a dissolved substance having a molecular weight of 200,000 tons, more or less. As a matter of fact the experiments bring out clearly the enormous difference between a solution and a suspension.

The safe ground to take is: that the Brownian move-

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[1] Comptes rendus, 146, 624, 1010 (1908); 148, 1163, 1315 (1909).

[2] See also Millikan: Phil. Mag., (6) 19, 209 (1910).

ments are due to the incessant movements of the molecules of the fluid; that the Brownian movements tend to make finely-divided, suspended particles distribute themselves uniformly throughout the liquid; that the uniform distribution is affected by the force of gravity as in the case of a gas; and that the Brownian movements, though causing diffusion, give rise to no appreciable osmotic pressure.

Very finely divided particles (less than 0.5 μ for instance) will be kept in suspension indefinitely by the Brownian movements, so long as the particles remain finely divided. If, however, two or more particles agglomerate or coalesce, the force of gravity may cause the particles to settle to the bottom of the containing vessel.

Cornell University

SOME SOLUBILITY MEASUREMENTS

BY STEWART J. LLOYD

The solubility determinations recorded in the following note were made incidentally in the course of other work and are given here to prevent unnecessary labor on the part of those who may need such data. Trustworthy solubility measurements are none too common, especially those in non-aqueous solvents, as has recently been remarked by Hildebrand.[1] Interest in what, for lack of a better name, may be called the theory of solubility, has recently revived also,[2] and the more data made accessible to those working on the subject the more rapidly will essential relationships be established.

These substances whose solubilities in various solvents were examined comprise sulphur dioxide, aluminium chloride, barium chloride, and benzoic acid.

The sulphur dioxide determinations were made by bubbling the gas through the solvent in question until equilibrium was reached. It was found that a steady quiet stream of SO_2 suitable for this work could be made most easily by running concentrated sulphuric acid and a saturated aqueous solution of sodium bisulphite into a Wolff bottle from separate dropping funnels. The Wolff bottle may be freed from spent solution without admitting air to it by inserting in the third hole a glass tube reaching to the bottom of the bottle and bent over at right angles outside the bottle. Closing the stopcock in the delivery tube forces out the liquid without trouble. The sulphur dioxide was dried by passing it through two sulphuric acid wash bottles, and a tube of phosphorus pentoxide.

The solvent in each case was contained in a long graduated

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[1] Jour. Am. Chem. Soc., 39, 2301 (1917).

[2] Hildebrand: Jour. Am. Chem. Soc., 38, 1452 (1916); Tyrer: Jour. Phys. Chem., 16, 68 (1912); Langmuir: Jour. Am. Chem. Soc., 39, 1848 (1917); Harkins: Ibid., 39, 541 (1917).

tube of small diameter immersed in a thermostat. When saturation was attained the volume of liquid in the tube was read, the contents of the latter rapidly immersed in a large volume of water, and thoroughly mixed with it. Enough solvent was usually taken to give a final volume of about 5 cc. The sulphur dioxide was then titrated with iodine and the solubility expressed in grams per liter of solution.

In some cases saturation is not reached as rapidly as might be expected. Entire exclusion of air is very necessary, and much time is saved by first passing the gas through a tube of the solvent maintained at a much higher temperature than that of the thermostat. In every case saturation was reached from both sides, from a higher and a lower temperature.

The organic liquids employed were distilled, dried over calcium chloride and redistilled just before using. The barometer reading remained between 756 and 760 mm throughout the measurements.

Sulphur dioxide; grams per liter

Temp.	Benzol	Nitrobenzol	Toluol	*o*-Nitrotoluol	Acetic anhydride
—5	—	—	—	—	196
0	—	—	—	—	148
5	—	—	—	—	136
10	—	—	—	—	122
15	—	311.4	—	290.8	114
20	—	267.4	217.5	236.0	106
25	—	227.9	170.4	192.2	99
30	127.5	190.0	124.4	160.7	90
40	82.9	132.0	93.6	118.5	—
50	60.3	98.7	77.2	87.0	—
60	34.0	78.6	54.7	68.8	—

The specific gravity of the saturated acetic anhydride solution at zero is 1.22.

The solubility of freshly prepared anhydrous aluminium chloride in pure chloroform and carbon tetrachloride was measured in the course of some work on Friedel and Craft's reaction. The chloride was prepared by passing dry hydrochloric acid gas over heated aluminium strips, and was distilled directly into the tube where its solubility was to be measured. Volhard's method was used for analysis.

Aluminium chloride; grams per liter

Temp.	Carbon tetrachloride	Chloroform
—15	—	0.65
0	—	1.00
4	0.74	—
14	0.22	—
20	0.15	—
25	—	0.72
34	0.06	—

Some work on the partition coefficients of radium chloride rendered necessary a determination of the solubility of anhydrous barium chloride in nitrobenzol. Mohr's method of analysis was employed.

Barium chloride; grams per liter

Temp.	Nitrobenzol
20	0.167
50	0.33
100	0.40

A study of the electrolytic decomposition of benzoic acid in ethyl acetate involved the determination of its solubility in that solvent.

Benzoic acid; grams per liter

Temp.	Ethyl acetate
—6.5	8.0
21.5	37.7
75	95.7

University of Alabama
Dept. of Chemistry
and Metallurgy

NEW BOOKS

Technology of Cellulose Esters. *Vol. VIII. By Edward C. Worden. 24 X 17 cm; pp. xxxvi + 577. New York: D. Van Nostrand Company, 1916. Price: $5.00.*—This large volume is but one of ten planned by the intrepid and indefatigable author. It is much to be hoped that he will be able to finish the self-imposed task. This book deals with the cellulose acetates and formates and other non-inflammable cellulose esters. The subject is treated under the general headings: raw materials; manufacture of cellulose esters; cellulose acetate solvents, non-solvents, and plastic-inducing bodies; commercial application of the uninflammable cellulose esters; analysis of uninflammable cellulose esters; appendix.

Mr. Worden aims to tell us everything that is known about these cellulose esters and he seems to have succeeded. The results are mostly empirical and the time will come when this wonderful collection of material will be worked over primarily from the theoretical point of view. Whoever undertakes this task will bless the author. A few quotations will give a faint idea of the many interesting things in the book, pp. 2538, 2574, 2703, 2744, 2759, 2836, 2856, 2883, 2886.

"Knoevenagel found that the acetylation of hydroxyl groups with acetic anhydride can be accelerated and often carried out almost quantitatively at ordinary temperatures by the addition of 1 to 5 percent of certain substances (ferric, zinc and stannous chlorides, phosphorus trichloride, sulphuric acid, copper sulphate, ammonium sulphate, etc.) which behave, not as dehydrating agents, but in some unexplained way as catalysts. Substances containing carbonyl oxygen, and ethereal or anhydride-like bodies such as ethers, polysaccharides, celluloses and starches, and oxygen ring compounds as epichlorhydrin, cineol, etc., can also by the breakage of an oxygen linkage be similarly converted into diacetates (called "acetolysis" in contradistinction to hydrolysis). The catalysts appear to be specific in their action, so that by using a suitably selected catalyst with, for example, cellulose, it may be possible either to acetylate hydroxyl groups, or split the molecule by acetolysis at specific positions favorable for attack by the catalyst employed. The acetylation of a number of different types of substances has been studied in detail, using the catalysts mentioned above. All except ammonium sulphate convert aldehydes into diacetates. Quinone and unsaturated ketones react best in the presence of ferric chloride. Diethyl ether and three-membered oxygen carbon rings react only with ferric chloride, the former at 100°, the latter at the ordinary temperature. In contrast to this, six-membered rings, such as cineol, readily yield acetates, in presence of nearly all the catalysts, by the splitting of the ring at the oxygen atom. Salicylic aldehyde with acetic anhydride and phosphorus trichloride, copper sulphate or zinc sulphate, was converted into disalicylic aldehyde, while the other catalysts yielded mainly the triacetate......

"The following generalizations indicate the progress and degree of hydration of the acetated cellulose when a test sample is examined. If the partially hydrated cellulose is:

"(1) Soluble in cold chloroform and insoluble in pure acetone—insufficiently hydrated.

"(2) Soluble in both chloroform and acetone—insufficiently hydrated, but hydrated more so than (1).

"(3) Insoluble in chloroform, soluble in acetone—properly hydrated for films of maximum strength and flexibility.

"(4) Insoluble in chloroform and insoluble in acetone—an impossibility if the cellulose had passed into solution in the reacting mixture, for any cellulose acetate soluble in glacial acetic acid is at the same time either soluble in pure chloroform or pure acetone. Moreover, any hydrated acetate plastic in warm chloroform will dissolve in that chloroform by the addition of a small amount of ethyl alcohol, and at the same time be soluble in acetone.

"The same cellulose acetated by the same formula, if the temperature is allowed to rise to 65–70°, upon hydration will give rise to an ester which is obtained by precipitation in a very fine and soft powder, hard to wash, but easy to dissolve when dry. If the acetating and hydrating temperature was not allowed to rise above 49°, the hydrated acetate precipitates out in strings or flakes as a fibrous mass, porous and easy to wash. It, however, dissolves less readily. It is a noticeable fact that, whereas unmodified acetated cellulose is soluble in chloroform, and the addition of small amounts of alcohol will precipitate the ester, with modified or partially hydrated acetated cellulose which is on the border line between solubility and insolubility in chloroform, the addition of alcohol to such a solution will cause the ester to immediately pass into solution. The acetone-soluble form of acetated cellulose is readily dissolved by acetone oil and tetrachlorethane, but not by pentachlorethane, although partially gelatinized by it. Solubility in pentachlorethane is increased by the addition of small amounts of crystalline hexachlorethane. This form of cellulose acetate, and the cellulose acetates in general, differ from the corresponding cellulose nitrates in their greater antagonism to castor oil, so that castor oil in sufficient quantities to induce elasticity has not as yet been able to have been added to cellulose acetate. Although castor oil is soluble in acetone and acetylene tetrachloride, yet when, say, an acetylene tetrachloride solution of castor oil is added to an acetylene tetrachloride solution of cellulose acetate, the latter precipitates out, if enough castor oil has been added to induce plasticity and flexibility.

"After precipitating the hydrated acetate, it should be washed free from acid as quickly as possible so the acid contained in the acetate will not continue to hydrolyze. The acetic acid must be removed very carefully, for films containing minute amounts of free acid lose a considerable amount of their strength and become brittle upon storing....

"W. Lindsay has found that nearly all of the so-called camphor substitutes possess the property of dissolving acetyl-cellulose when used in conjunction with ethyl alcohol, and may, with propriety, be grouped in the following three classes:

"(1) Those substances which are non-solvents when melted or dissolved in either methyl or ethyl alcohol in the cold or at room temperature, such as triphenylphosphate, tricresylphosphate and naphthalene.

"(2) Those substances which become solvents when melted but are non-solvents when dissolved in ethyl alcohol at room temperature, such as camphor, tetrachlorethyl acetanilid, trichlormethyl acetanilid, and trichlorpropyl acetanilid.

"(3) Those which become solvents when melted, and are also solvents when dissolved in methyl or ethyl alcohol in equal parts at room temperature, such as toluol-sulphonamid, ethyl-*p*-toluolsulphonamid, benzene-sulphonamid, ethyl acetanilid and methyl acetanilid. He claims a mixture composed of one part each by weight of ethyl alcohol and ethyl-*p*-toluolsulphonamid is a more powerful solvent for acetone-soluble acetyl-cellulose than a mixture of two parts by weight of ethyl alcohol and one part by weight of ethyl-*p*-toluolsulphonamid, a rapidly decreasing solvent action being shown if the alcohol is increased beyond this proportion. To produce flowable solutions in the cold the above camphor substitutes are diluted with methyl or ethyl alcohol, with one or more of the following: Chloroform, epichlorhydrin, acetodichlorhydrin, dichlorethylene, ethylene chloride, trichlorhydrin, acetochlorhydrin, ethyl chloracetate, ethyl acetate and di-acetochlorhydrin....

"Tetrachlorethane dissolves dammar, sandarac, and mastic readily, is a poor solvent of orange and bleached shellac, an excellent solvent of castor and many other vegetable oils, and dissolves the kauri copals in large amounts, especially upon the application of gentle heat. It has strong bacterial action and is an effective disinfectant. It is a non-solvent of the cellulose nitrates both of high and low nitration, although tetrachlorethane is a valuable ingredient in nitrocellulose mixtures, appearing to exert an effect similar to that induced by the presence of amyl alcohol, *i. e.*, the resplendency, lustre, and smoothness of the film is increased. And, although a high-boiling nitrocellulose non-solvent, there is but little evidence of precipitation. For instance, a mixture of 65 parts commercial acetone (b. p. 56°) and 35 parts (by weight) of tetrachlorethane (b. p. 147°) will dry to a clear and tough film without any external evidence of precipitation. It therefore is a valuable adjunct as a constituent of pyroxylin mixtures, its value heretofore having been imperfectly appreciated; is a direct substitute for refined fusel oil in pyroxylin mixtures at less than one-half the cost per volume. Tetrachlorethane is an excellent solvent for a wide range of cellulose acetates of partial hydration, its solvent action being increased by the presence of methyl, or preferably ethyl alcohol. It is especially applicable as a solvent for those cellulose acetates which have been partially hydrated, in which the hydration has not been carried to a solubility in absolute acetone, but has been carried beyond a ready solubility in chloroform. Tetrachlorethane will apparently dissolve a wider range of cellulose acetates than any other single solvent, and when ethyl alcohol, acetone, or the higher ketones are added in relatively small amounts, the solvent action is considerably increased....

"The inflammability, combustibility and explosiveness of the higher cellulose nitrates, coupled with the variety and value of the commercial products in which they wholly or partially enter, have naturally directed attention to attempts to conserve the desirable technical properties, while at the same time eliminating substantially the tendency to ready flammability. For this reason the entire field of the nitrocellulose industry has been invaded by the cellulose esters in endeavors to replace pyroxylin, celluloid, and the collodions by the difficultly burnable acetylated celluloses. In many of these instances the peculiar property of thermo-plasticity, so highly developed in celluloid, was evident only in a diminished degree in the corresponding acetates, which hampered the acetic esters from fields in which they otherwise would find many uses. The greater cost of production of the acetic esters was a barrier to technical development where competition due to price was the prime factor. A well-marked tendency to brittleness in cold weather has also been a point of imperfection that is not apparent with the pyroxylin plastics. From a theoretical view-point the acetic esters of cellulose have had a peculiar interest, in that they furnished an entirely different point of attack in endeavors to elucidate the inner structure of the cellulose aggregate.

"It appears quite probable that the cellulose acetates will never be able to successfully compete with the nitrated celluloses where cost of production is the main factor, but rather that their uses will be restricted to those fields where their specific properties of non-inflammability, resistance to mercerization, faint affinity for cotton dyestuffs, absence of notable tendering in the wetted condition, and low specific conductive capacity, counterbalance increased cost of production. The manufacturing costs hinge upon the price of acetic anhydride and effective methods for its recovery from the acylating bath.....

"It has been found that while water or alcohol separately exert but little influence in assisting the penetration of dyestuffs in cellulose acetate filaments, if the two be combined, dark tints of many colors are readily obtainable. For instance, from an aqueous solution of methylene blue, cellulose acetate filaments cannot be dyed at all, while an alcoholic solution of the same dyestuff produces feeble tints. On the other hand, full shades are obtainable from a bath containing equal volumes of both. Similar typical results are stated to occur with such dyestuffs as rhodamine, erica, chrysoidine, naphthol-yellow, or fuchsine (magenta). As a second solvent in addition to water may be mentioned methyl alcohol, acetone, or acetic acid. This generalization does not always hold good.....

"Until quite recently acetic collodion has been restricted to solutions of nitrocellulose in concentrated acetic acid, and has found its principal use as a dip to impregnate and stiffen Welsbach and similar incandescent gas mantles. Acetic acid solutions are considered more penetrative than amyl acetate or acetone solutions, and in addition are very uniform in drying, which preserves the shape of the finished mantle without distortion. It has been customary to modify the inflammability of the lacquer due to the presence of the nitrocellulose by the addition of difficultly inflammable material which was at the same time soluble in glacial acetic acid, gelatin being most satisfactory. The principal drawback to the use of gelatin in this connection is its hygroscopic tendency and ready solubility in water. The replacement of gelatin by cellulose acetate overcomes this objection, both the cellulose nitrates and acetates being soluble in glacial acetic acid. Variation in the amount of acetic ester to cellulose nitrate governs the speed of burning, whereby the inflammability may be varied within wide limits, the preparation being entirely water-insoluble, not hygroscopic, and permanent in the atmosphere under all normal weather conditions. Paraffin would undoubtedly be suitable, but it is insoluble in acetic acid. Where the speed of ignition of the mantle is too great, it has been found that often the interstices between the woven filaments expand to such an extent as to rupture the knitted fabric, or the rare earth salts which were deposited upon the ignition of the fabric.....

"In France it appears that acetate lacquer is used to a considerable extent in lacquering aeroplanes, especially for the wings and other portions of the canvas. It has been found that cellulose acetate when dissolved in a mixture of tetrachlorethane and acetone, furnishes a lacquer which renders the canvas thoroughly waterproof, and adds materially to the tensile strength of the craft. The lacquer is preferably applied to the parts after assembling rather than to the canvas before attachment to the wing frame-work. It may be applied two coats to the skyward side of the plane, or one coat to each side—preferably the former. Where the maximum softness and pliability is desired, small amounts of castor oil or acetin may be added to the lacquer, while the opposite effect of stiffness and rigidity may be imparted by the addition of resins as shellac, dammar or copal.....

"The idea suggested itself readily to employ the solution of the non-inflammable celluloid, 'Cellon,' for the production of impregnations and coatings for making the materials treated with it non- or difficultly inflammable. Cellon has become of importance in aeronautics, due to the non-inflammability (the newspapers reported the surprising fact that in a recent lamentable Zeppelin catastrophe the Cellon planes remained intact, while the balloon covers were totally destroyed). Certain other properties make it also valuable for the purpose mentioned. Owing to the high viscosity of the Cellon solution, it is possible to provide, with a single stroke, the carrying surfaces with a uniform, enamel-like, smooth coat of Cellon, penetrating in all the pores and making them not only waterproof but, in contradistinction to rubber cloth, almost completely benzine- and oil-proof; consequently they are not affected or softened by the oil splashing on them from the motors or propellers. The principal advantage is, however, the attainment, by the varnishing, of a smoothness of the surfaces, which materially reduces the resistance to the air and therefore greatly and favorably influences the speed. Cellon solutions have therefore attained considerable importance and are sold under the name of 'Cellon-Emaillit.'

"It is, however, a surprising fact that the fabrics treated with Cellon solution are not made non-inflammable and are not even as difficultly inflammable as the Cellon itself. It naturally was to be expected that, if a piece of cotton or linen fabric, by itself not readily combustible, would be treated by the practically non-inflammable Cellon, the material would become entirely non-inflammable, or, at any rate, show only a moderate combustibility. As a matter of fact, however, a cellonated fabric burns just as easily as a non-cellonated one, and not much less than rubber cloth or oil-impregnated fabric. If a piece of Cellon film is placed over a piece of cotton fabric it becomes possible to light the Cellon film with a flame, and it begins to burn with a luminous, smoky flame, as if it were a combustible material. Even if instead of the plastic Cellon a solution of pure cellulose acetate is used (which would be impracticable, as the cellulose acetate coats become brittle after the complete evaporation of the solvent, which, however, will only be the case after several months, and thus may cause a tearing of the aeroplane surfaces), a certain degree of combustibility of the cotton fabric nevertheless remains. A little may be done to remedy this defect by impregnating the fabric with the above-mentioned salts, but this is not practicable in the case of aeroplane and balloon fabrics, as these would be washed out again by the rain or even on cleansing the apparatus and because these impregnations weaken in time the carrying surfaces enormously. Apart from this, such an impregnation is furthermore entirely inadequate, if plastic acetate coats, which increase the carrying power of the planes, are used for aeroplanes, or soft rubber-like coatings for balloon covers. These flexible Cellon fabrics burn, even if the fabric has been preliminarily impregnated with metallic salts, as readily as rubber cloth, although they surpass the latter by their extraordinary impermeability to water and their dielectric constant.

"The phenomenon that a non- or hardly inflammable fabric becomes combustible by impregnating or varnishing it with the non-inflammable Cellon is not only most surprising—it might be explained by a kind of wick-action—but also very undesirable, because it deprives the cellonation of the fabrics of its chief advantage, the non-inflammability. Long and tedious experiments were necessary to eliminate this disadvantage and to produce a variety of Cellon which makes the fabrics really non-inflammable, but we have recently been successful in attaining this. It is now possible to produce washable Cellon collars and cuffs similar to the celluloid articles, which may be placed in direct contact with a flame without being affected in any other way than by getting black. It is also possible to produce an absolutely non-inflammable and non-combustible aeroplane and balloon fabric. By applying Cellon lacquer the carrying planes of aeroplanes are not only stretched like a drum head, but they also become fire-proof to such an extent that benzine may be poured over them and ignited without affecting the surfaces in any other way than that they become blackened and partially carbonized and swell up. One of the many sources of dangers which accompanied the conquest of the air seems thereby removed, namely, the complete destruction of the aeroplane or balloon by fire in case of the spreading of a benzine fire on the wings of an aeroplane. Whether it is possible to increase the safety of the dirigible by coating the outside covers with fire-proof Cellon lacquer cannot be decided without more extensive experiments."

Wilder D. Bancroft

Everyday Physics. *By John C. Packard. 27 × 20 cm; pp. vi + 136. Boston: Ginn and Co., 1917. Price: $1.00.*—This laboratory manual is intended to appeal to the student by giving him experiments dealing with things of everyday life. Thus he learns to read water, gas, and electricity meters, making tests on the water meter. He determines the specific gravity of sea water and studies the lifting power of a life preserver, incidentally learning that the average boy of high-school age, falling into the water fully dressed, requires an extra support on the part of the rescuer of 5 lbs. if kept on his back with his nose and mouth out, of 12 lbs. if in an upright position with his head out, and of 26 lbs. with his head and arms out. The hot air furnace, the alcohol stove, and the gas stove are subjects for experiments and the student is asked to estimate the comparative costs of cooking with kerosene, denatured alcohol, gas, coal, and electricity. There are tests on sewing-machines and tests for astigmatism. Altogether this is a pretty good book. *Wilder D. Bancroft*

A

SOME PROPERTIES OF FOG

BY WILDER D. BANCROFT

A fog consists of drops of liquid, suspended in a gas, usually air. To obtain a fog a vapor must be supersaturated suddenly, so that condensation takes place more or less uniformly throughout the mass. On a laboratory scale this cooling can best be brought about by an adiabatic expansion or by letting a jet of steam come into a cooler atmosphere. The first method is the more satisfactory for quantitative measurements and the second for qualitative determinations. If the supersaturation is excessive, the liquid comes down as a dense fog without presenting any specially interesting characteristics. If the supersaturation be slight, it is found that no fog forms unless "nuclei" are present in the air. One of the earlier experimenters[1] really covered the ground surprisingly thoroughly. "It is well known that if air, saturated with vapor, be rarefied, the vapor condenses in a cloud on account of the diminished temperature. But the amount of vapor precipitated is not constant, even when the rarefaction is the same. This led the author to experiment on the subject.

"The cloud consists of small drops of water, moving in rapid currents, which are easily seen by aid of a lens. If the air be allowed to remain in the flask for some time before compression, the vapor is not precipitated, and the air remains perfectly transparent on rarefaction. Or if the air be well shaken with water, the same result ensues. The condensation appears to be induced by fine particles of dust, which afford a nucleus for the particles of water to condense on; if the air is first filtered through cotton wool, no condensation of water vapor is produced. A trace of tobacco smoke renders the air extremely active. If the air is heated before passing into the flask, it is not rendered inactive; but this is probably owing to particles of carbon being drawn

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[1] Coulier: Jour. Chem. Soc., 29, 186 (1876).

into the flask. The heated air from a spirit-lamp or a Bunsen burner requires to be filtered through cotton before it becomes inactive; the first layers of the cotton assume a dark color and contain approximately $^1/_{14400}$ of a milligram of carbon.

"If the vapor be illuminated by a candle while condensing, rings of colors are seen round the flame, and it is possible to estimate approximately the relative amount of suspended matter in the air by the difference in intensity of the colored rings. Even in the country, the air is active, but during a storm the activity is hardly appreciable. Observations made during the winter and summer of 1874 tend to show that the air is rather less active in summer than in winter. M. Mascart has proved that other liquids, such as alcohol, benzene, etc., produce the same results.

"Ozonized air is very active, and this activity is not destroyed by filtration through cotton; from this it would appear that other sources must be looked for to explain the 'activity' of air, besides the presence of small particles. A fine platinum wire, heated to redness for a moment, renders air active; the flame of hydrogen has the same effect; and this is not due to arsenic, antimony, or carbon accidentally present. If the air be passed through a tube surrounded with Dutch foil, and moderately hot, it becomes active. Oxygen, hydrogen, and nitrogen become active when they are heated; but, in the case of hydrogen, care should be taken that it is free from air; the nebulosity disappears much more rapidly than in air. In the three last-mentioned cases, the activity of the air is not removed by filtration through cotton wool. This would appear to contradict the hypothesis that the nebulosity is due to solid particles."

In addition to the substances mentioned by Coulier, it was found by R. v. Helmholtz[1] that the vapors of sulphuric acid, hydrochloric acid, and sulphurous acid act as nuclei. In a later paper R. v. Helmholtz and Richarz[2] advance the view that condensation occurs frequently during chemical

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[1] Wied. Ann., 27, 508 (1886).

[2] Ibid., 40, 161 (1890).

reactions even though the reacting substances and reaction products do not act as nuclei. They point out that neither ozone nor oxygen acts as a nucleus but that nuclei are present while ozone is decomposing. A similar phenomenon was observed in the case of a number of slow oxidations and reductions. Hydrochloric acid and ammonia are said not to act singly nor does ammonium chloride; but ions are formed during the reaction. This statement in regard to hydrochloric acid contradicts a previous statement as to this substance but there is a difference of concentration and the authors are also willing to admit that some ammonia in the air may have reacted with the acid in the earlier experiments. On this statement of facts the authors conclude that the reactions pass through an intermediate stage in which ions are formed, and that these ions act as nuclei. This extremely interesting hypothesis is put on the defensive by the experiments of Engler and Wild[1] who claim that solid substances are the real nuclei in all these cases, iodine pentoxide in the oxidation of iodine, an oxide of phosphorus in the oxidation of phosphorus, ammonium chloride, etc. Helmholtz and Richarz made a good deal of the fact that the nuclei could not be suspended solids because they were not removed when the gases were bubbled through water. Engler and Wild point out that the solids in the center of the gas bubbles do not come in contact with the water at all and that it is a simple matter to carry suspended particles of phosphorus pentoxide through several wash-bottles in spite of its tremendously hygroscopic nature.

Tyndall[2] found it very difficult to get experimental tubes which were absolutely clean on the surface and which contained no suspended particles. "For however well the tubes might be washed and polished and however bright and pure they might appear in ordinary daylight, the electric beam infallibly revealed signs and tokens of dirt. The air was always present and it was sure to deposit some impurity. All chemical pro-

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[1] Ber. deutsch. chem. Ges., 29, 1929 (1896).

[2] Phil. Trans., 160, 337 (1870).

cesses, not conducted in a vacuum, are open to this disturbance. When the experimental tube was exhausted, it exhibited no trace of floating matter; but, on admitting the air through the U-tubes containing potash and sulphuric acid, a *dust-cone* more or less distinct was always revealed by the powerful condensed electric beam. The floating motes resembled minute particles of liquid which had been carried mechanically into the experimental tube. Precautions were, therefore, taken to prevent any such transfer. They produced little or no mitigation. I did not imagine at the time that the dust of the external air could find such free passage through the caustic potash and the sulphuric acid tubes. But the motes really came from without. They also passed through a variety of ethers and alcohols in the flask. In fact, it requires long-continued action on the part of an acid, first to *wet* the motes and then to destroy them."

Pringal[1] considers that the nuclei attributed to ozone are really oxides of nitrogen and believes that ozone oxidizes nitrogen to some extent. Bieber[2] concedes that oxides of nitrogen will act as nuclei; but shows that they are not formed by the action of ozone on nitrogen, and that the oxides of nitrogen do not form the stable, blue cloud which is observed so often when working with ozone. He attributes this stable, blue cloud to hydrogen peroxide, showing that the cloud is formed when hydrogen peroxide is present and that it does not occur under conditions which preclude the formation of hydrogen peroxide. Thus we do not get it with water-vapor alone or with water-vapor plus a gas other than oxygen. Now hydrogen peroxide can be formed by the action of ultraviolet light on water, especially on liquid water, according to the equation $H_4O_2 = H_2O_2 + H_2$. It may also be formed by the action of ultraviolet light on a mixture of hydrogen and oxygen,[4] according to the equation $H_2 + O_2 = H_2O_2$.

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[1] Drude's Ann., 26, 727 (1908).

[2] Ibid., 39, 1313 (1912).

[3] Kernbaum: Comptes rendus, 148, 705 (1909); Thiele: Ber. deutsch. chem. Ges., 40, 4914 (1907).

[4] Fischer and Wolf: Ber. deutsch. chem. Ges., 44, 2956 (1911).

This second reaction of course plays no part in the case under consideration. Bieber rules out the first one because no hydrogen is formed, and consequently he believes that the reaction is $H_2O + O = H_2O_2$, where the oxygen atom is the third one in ozone or is set free from oxygen by ultraviolet light. While this may be true, it is not necessarily so. It is quite as simple to consider that the ozone acts as a depolarizer to the nascent hydrogen since it is very improbable that the action of ultraviolet light could give rise to the reaction $H_4O_2 + O_3 = H_2O_2 + H_2O + O_2$, because we know that the intermediate product, electrically neutral monatomic hydrogen, reacts with ozone.

Haber and Just[1] have shown that when the alkali metals react with different gaseous substances such as water vapor, hydrochloric acid, iodine, phosgene, oxygen, thionyl chloride, etc., negatively charged particles are set free in the reaction zone and can be removed from it by an electric field. When the pressure of the reacting gas is very low, the negative particles pass out from the reaction zone of their own accord and prove to be chiefly free electrons. In presence of light there is an enormous increase in the emission of electrons. Similar results were obtained with silver, copper, and aluminum when heated or when the pressure of the gas was very low.

While these experiments of Haber and Just prove conclusively that electrons are emitted during some chemical reactions, they do not prove at all that there is always an intermediate formation of ions in every chemical reaction. On the other hand we do know that gaseous ions, if present, may act as nuclei. As Donnan[2] points out, the very interesting experiments of C. R. T. Wilson[3] on the condensation of water vapor in the presence of dust-free air and other gases, have rendered it extremely probable that this condensation occurs around electrical nuclei of some sort. It was found

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[1] Zeit. Elektrochemie, **16**, 275 (1910); Just: Ibid., **20**, 483 (1914).

[2] Phil. Mag., (6) **8**, 306 (1902).

[3] Phil. Trans., **189A**, 265 (1897); **193A**, 289 (1899).

that an adiabatic expansion produced no condensation in dust-free air saturated with aqueous vapor until the expansion reached the value of 1.25. This expansion (ratio) produced a small shower of fine rain, and expansions ranging from the above value up to 1.38 produce small fine showers of not much greater density. At an expansion of 1.38, however, the phenomenon changes in character, and a more or less dense fog is produced. Now air or any other gas exposed to Röntgen rays becomes a conductor; and the experiments of J. J. Thomson and his fellow-investigators have made it practically certain that this conduction is of a convective nature, due to electrically charged nuclei in the gas. The importance of this lies in the fact that Wilson's experiments showed that air which was saturated with water vapor and exposed to Röntgen radiations gives, when expanded adiabatically, no condensation before the expansion 1.25, and a dense fog instead of a fine rain at that point. The natural conclusion is that the rain-like condensation for expansions ranging from 1.25 to 1.38 is due to condensation on a comparatively small number of electrical nuclei either existing in the gas or produced by the sudden expansion. Donnan was especially interested in the fact that here is a "case of condensation of a vapor of a liquid of unique ionizing power round electrical nuclei. It becomes a matter of interest to compare with water vapor the vapors of other liquids whose ionizing powers are either much smaller or practically zero." He came to the conclusion that organic liquids condensed on ions less readily than does water.[1]

When a gas is previously saturated with water vapor, the lowering of the pressure necessary to produce condensation by adiabatic expansion[2] is about 15 cm for air, oxygen, and nitrogen, but about 21 cm for hydrogen. Condensation of water takes place more readily on negative ions than on positive ions;[3] the reverse is true for alcohol.[4] In dust-free and

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[1] Cf. Barus: Phil Mag., (6) 4, 262 (1902).

[2] Bieber: Drude's Ann., 39, 1313 (1912).

[3] Wilson: Phil. Trans., 193A, 289 (1899).

[4] Przibram: Physik. Z., 8, 561 (1907).

ion-free gases which do not react with water vapor, the condensation takes place much less readily, at an eight-fold supersaturation according to Wilson.

With water vapor the expansions 1.25, 1.28, 1.31 and 1.38 are the values: (*a*) to start catching the negative ions; (*b*) to catch all the negative ions; (*c*) to start catching the positive ions; (*d*) to catch the nuclei of cloudy condensation.[1]

Since gaseous ions act as nuclei[2] it is not surprising that condensation may take place when inert air is exposed to cathode rays, Röntgen rays, Becquerel rays or ultra-violet light; also when a spark discharge or a silent discharge passes through the air. The ions given off by heated metals may also act as nuclei.

Broadly speaking, the nuclei consist of very hygroscopic substances, solids and ions. The hygroscopic substances form solutions having a very low vapor pressure and the water vapor is excessively supersaturated when they are present, consequently condensation takes place. Freundlich[3] accounts for the behavior of suspended solids by postulating that they have concave surfaces on which water would have a lower vapor pressure than on a convex surface and consequently would precipitate more readily. This is very ingenious but carries with it the corollary that solid spheres would not act as nuclei. While this may be true, it is not probable. It seems much simpler to consider that water vapor is adsorbed by the suspended solid, forming the equivalent of a liquid surface on which the further excess of water vapor condenses. It has been shown by J. J. Thomson[4] that the effect of electrification of a drop of liquid is to decrease the vapor pressure of the liquid. Consequently water vapor will tend to precipitate on an ion as a nucleus, which is what happens experimentally.

While fog usually consists of condensed water there are

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[1] Quoted from Wilson by Owen and Roberts: Phil. Mag., (6) 23, 352 (1912).

[2] Freundlich: "Kapillarchemie," 294 (1909).

[3] "Kapillarchemie," 295 (1909).

[4] "Application of Dynamics to Physics and Chemistry," 166 (1888).

conditions under which we have special types occurring. Thus Frankland[1] describes what he calls dry fog. "It has often been noticed, especially in and near large towns, that a foggy atmosphere is not always saturated with moisture: thus on the 17th of October last, at 3.30 P. M., during a thick fog in London, the degree of humidity was only 80 percent of saturation; and Mr. Glaisher, in his memorable balloon ascents observed that in passing through cloud or fog the hygrometer sometimes showed the air to possess considerable dryness. In the ascent from Wolverhampton on July 17, 1862, at an altitude of 9882 feet, and when passing through a cloud so dense that the balloon could not be seen from the car, the dry bulb thermometer read 37.8° F and the wet 30.2°, indicating a dew point 17.9° below the air temperature. Again, on the 30th of July in the same year, when at an altitude of 6466 feet between the Crystal Palace and Gravesend, and while the balloon was passing through a "great mist," the dew point was 1.27° F below the temperature of the air. The following is a tabulated statement (Table I) of other instances in which there was comparative dryness of the air in the midst of cloud or fog:

"It is thus evident that the air closely surrounding the spherules of water in a mist, cloud or fog, is sometimes far from saturated with moisture; although, as is well known to persons occupied with gas analysis, when a perfectly dry air is admitted into a moist eudiometer it very rapidly assumes the volume indicating saturation, notwithstanding that the proportion of water surface to volume of gas is obviously far less than that afforded to the interstitial air of a fog.

"In a special experiment of this kind, it was found that air, dried over calcic chloride, became completely saturated with moisture in less than one minute and fifty seconds when it was passed into a moist glass tube over three-fourths of an inch in diameter. It appeared to me, therefore, interesting to inquire under what condition the evaporation from the surface of water can be so hindered as to cause this delay

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[1] Proc. Roy. Soc., 28, 238 (1879).

TABLE I

Date	Place of ascent	Altitude in feet	Temp. of air	Percentage saturation
1862				
August 18	Wolverhampton	5922	53.5° F.	61
1863				
March 31	Crystal Palace	3698	38.5	62
April 18		9000	32.5	52
"		8000	34.9	73
"		7000	37.8	87
"		6000	41.0	76
"		5000	45.0	67
June 26	Wolverton	11000	30.0	68
"	"	10000	31.5	46
July 11	Crystal Palace	3200	65.2	57
"	"	2600		53
"	"	1600		50
"	"	1000	64.7	53
1864				
April 6	Woolwich	6000	44.0	64
"	"	1000	41.7	75
1865				
February 27	Woolwich	4400	42.0	52

in the saturation of the closely surrounding air. Many years ago I became acquainted with the fact, first noticed I believe by Mr. P. Spence of Manchester, that the evaporation of saline solutions, kept just below their boiling point in open pans, can be almost entirely prevented by covering the liquid with a thin stratum of coal tar. It was thus that Mr. Spence effected a considerable saving of fuel in that part of the process of manufacturing alum in which burnt aluminous shale is digested for many hours with hot dilute sulphuric acid; much less fuel being, of course, required when the digestion was carried on without evaporation than when steam escaped from the surface of the hot liquid. This simple though important technical application suggested to me a condition of things under which the existence of so-called 'dry fog' would be possible. From our manufactories and domestic fires, vast aggregate quantities of coal-tar and paraffin oil are daily distilled into the atmosphere, and condensing upon, or attaching themselves to, the watery spherules of fog of cloud, must of necessity coat these latter with an oily film, which would, in all probability, retard the evaporation of the water and the consequent saturation of the interstitial air."

Experiments with water in platinum dishes showed, of course, that the water evaporated less rapidly when covered with a film. "The results of these experiments point out a condition of very common occurrence, competent to produce 'dry fog' while they also explain the frequency, persistency, and irritating character of those fogs which afflict our large towns; inasmuch as some of the products of destructive distillation of coal are very irritating to the respiratory organs, and a large proportion of them is scarcely if at all volatile at ordinary temperatures."

While Frankland's explanation of the dry fogs is probably the correct one, there are two possibilities which are not covered by the experiments. He has not shown that the oily matters condense on the drops of water. It is certain that, under some conditions, the water vapor might condense on the oily drops as nuclei, in which the water would be outside and not inside. He has also not considered the possibility of the "dryness" being due to a lowering of the vapor pressure of the drops by the dissolving in them of sulphur dioxide, sulphuric acid, etc. While it is not probable that sufficiently concentrated solutions would be formed in this way to produce so great an apparent dryness, yet it is very probable that this is at least a contributing factor.

At times a special state of things occurs at the seashore. If the wind blows very hard from the sea, a heavy surf springs up and salt spray is carried inland. Ordinarily this does no harm to vegetation because a wind of this sort is usually accompanied by rain which dilutes the spray sufficiently to make it harmless. One summer at Newport, R. I., the wind blew hard from the south for sixty hours without any rain. The result was that undiluted salt spray was carried inland in enormous quantities. Everything was coated with salt;

and trees, shrubs, and plants were burned brown for nearly half a mile from the shore.

Supercooled fogs seem also to occur at times. Pollock and Collier[1] describe frost formation on Dartmoor. "On the afternoon of Tuesday, December 30, 1884, about 3 P. M., we were on Yes Tor, near Okehampton, long reputed the highest point of Dartmoor, though it is understood that the new survey now in progress brings out the neighboring summit of High Willhayse a few feet higher. For about 200 feet below the Tor the ground was frozen hard. It was free from snow, the weather having been fine for several days, but everything was white with hoar-frost. On the rocks of the Tor this frost assumed a form of singular beauty, and, we think, not a common one. At least, neither of us can match it in either English or Alpine experience, or remember to have seen an account of anything like it.

"On the first impression the walls of the granite masses which make up the Tor looked as if covered with featherwork exquisitely wrought in congealed snow. The feathers (to call them so provisionally) overlaid one another as thickly as real plumage, and ranged in length from one inch or less to five or six inches, being smaller on the flat and recessed surfaces of the rock, and larger on the jutting and exposed ones. They lay almost wholly on the eastward, that is (as the weather then was, and for some days had been), the windward side of the Tor; and their tips pointed roughly in that direction, with the sort of uniformity one would get by laying down a great number of branches or feathers all one way. It is impossible to describe the richness of this natural decoration. Only the finest Oriental workmanship could come near the effect produced by the infinite and minute variety which this tapestry of frost-flakes combined with one dominant form direction. Something of the same sort, but far less perfect, may be seen on a mussel-covered rock at low water. Still more curious was the appearance of the Royal Artillery flagstaff which surmounts the Tor. It was loaded (on the

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[1] Nature, 31, 216 (1885).

windward side, like the rocks) with a solid fringe of the same formation, but in longer and thicker flakes. We judged it to be full six inches deep, and at first thought it must be supported by a string attached to the staff, but there was, in fact, no string at all.

"Close examination of the individual flakes revealed great beauty of structure. They were mostly of an elongated lozenge shape, like a squared spear-head, but sometimes more like tongues of flame. Their contours and delicate surface-markings showed them to be made up of laminae, into which they were easily resolved by a slight blow. These laminae again split up into crystalline needles parallel to the longer diameter of the flake, that is, in the line of the imaginary spear-shaft. Only photography or very careful drawing (for neither of which had we the means, time, or skill) would clearly convey the details of the formation.

"As to the physical explanation, we conceive that the process must have been set up by a thin layer of mist (probably in a very finely divided state to begin with) drifting against the rock and freezing to it. Successive accretions brought in the same way would gradually produce the display of giant hoar-frost which we have imperfectly described. The details of form and structure we leave to be considered by those who have made a special study of ice-crystals. But it seems fairly obvious that for such a result there must be a concurrence of many favoring conditions. There must be a clear frost without snow, which, of course, would destroy and obliterate these delicate forms. There must be a steady set of wind, enough and not too much of it, and the air must be saturated with moisture in a certain state of molecular division. Some of these data might, perhaps, with the resources of a modern laboratory, be settled by experiment. If the experiment succeeded, it would be an extremely pretty one."

A similar phenomenon was described the same year by Osmond.[1] "In addition to the fall of snow, hail, etc., there is on Ben Nevis a form of solid precipitation scarcely known

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[1] Nature, 31, 532 (1885).

on lower ground, but of almost daily occurrence here. In ordinary weather the top of the hill is enveloped in drifting fog, and when the temperature of the air and ground is below freezing this fog deposits small crystalline particles of ice on every surface that obstructs its passage. These particles on a wall or large sloping surface, so well described in a recent letter to "Nature,"[1] combine to form long feathery crystals; but on a post or similar small body, they take a shape more like fir-cones, with the point to windward. Whether this deposition is from the vapor of the fog directly or from actual particles of frozen water carried along in it is not very clear. The forms and arrangements of the crystals vary according to the form of the surface to which they adhere, but all belong to this feathery or cone type, the branches lying at an angle of 30° with the main axis pointing to windward. On a flat board they gather first and most abundantly near its edges, forming a most beautiful border around it; while the centre, which I suppose the wind does not directly reach, remains clear. A round post, on the contrary, has an almost uniform crop of these crystals all over its windward half, and so accurately do they point to windward that it is possible to trace changes in the direction of the wind from the successive layers of crystals lying at different angles. The rate of growth varies with the density of fog and the speed of the wind, but for the ordinary winds and fogs of this exposed position about half an inch per hour may be taken as rough average. I have never seen it exceed two inches per hour. If there is a damp feeling in the air, if in fact it is mist that is passing rather than fog, the crystals are icy and hard; but when the temperature is well below freezing and the fog feels comparatively dry, they are looser in texture, seem when first formed to be attached by a mere point to whatever they are on, and are pretty easily knocked off. There is practically no limit to their growth. Last winter during a long continuance of strong southwesterly winds and cold weather a post 4 inches square grew into a slab of snow some 5 feet broad and 1 foot thick in less than a

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[1] Pollock and Collier: Nature, 31, 216 (1885).

week; the crystalline mass then fell off by its own weight and a new set began to form....

"Since the above was written, I have made a rough attempt to measure definitely the rate of growth of these crystals. A cylindrical stoneware bottle 3.6 inches high and 2.25 inches in diameter was stuck upside down on a post 40 inches high for three hours at a time, the crystals formed on it melted down and the volume of the water measured. Assuming that the cylinder acted like a flat surface placed perpendicularly to the wind whose height and breadth are equal to its height and diameter—an assumption that appears to be very nearly true, at least for small surfaces—I find that with dense fog and strong wind (force 6 to 8 of Beaufort's scale) the rate of growth, as measured above, is about 0.125 inch per hour. That is to say, if the density of the snow be one-tenth that of the water, the crystals were growing at the rate of one and a quarter inch per hour. The crystals were quite loose and feathery, and contained practically no fallen or drifted snow; all had been formed directly out of the air."

McConnel[1] says in regard to this: "As far as I can judge from the above description the deposit is just what might be expected from liquid particles below 32° F, drifting with the wind. If the fog particles were dry ice how should they stick together to form the feathers? I may suggest, further, that in the upward deflexion of the wind by the slopes of the mountain we have an excellent reason for the cooling of the air after the drops were formed."

These supercooled fogs, if that is what they are, are quite different from the so-called ice storms which occur once or more every winter and which sometimes do so much damage to trees. In the ice storms, the moisture deposits as liquid water on the branches and twigs, freezing there to solid ice. These storms occur when the temperature is below freezing and a warm rain or mist comes down from above without getting chilled to the freezing point before it strikes the trees. The damage is caused by the weight of the ice breaking the

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[1] Phil. Mag., (5) 29, 461 (1890).

branches or by the wind breaking the branches when they are so encased in ice that they cannot bend.

The optical properties of suspended drops of water are very interesting, the best known case of this being the rainbow.[1] When direct sunlight falls upon a transparent sphere, such as a raindrop, some of it is reflected from the outer surface in all directions, and some of it is refracted from the outer surface in all directions, and some of it is refracted to the interior of the drop, where it suffers from one to many internal reflections, with more or less loss, dependent upon the angle of incidence, at each place of reflection. The refraction splits the original light into all its elementary colors, and these are sent out practically in every direction. That part of the light which leaves the drop in a diverging manner is spread over an area that increases as the square of the distance, and hence soon becomes imperceptible. The same is true also of that part which leaves the drop in a converging manner, because beyond the point of intersection it, too, becomes diverging. There are a few directions, however, in which the light leaves the drop in very nearly parallel beams, and along which it travels with but slightly diminished intensity. This light of practically constant intensity is the light of the rainbow.

"The several colors composing the original sunlight are refracted unequally, and therefore separated. Also, since the drops are spherical, whatever angle exists at one of them between the incident solar ray and a given colored ray that goes to the observer, must obtain for all other drops that do the same thing. Consequently the rainbow is along the circumference of a circle whose center is a straight line with the sun and the eye of the observer. Hence no two persons see strictly the same rainbow. One sees the light from one set of drops, while another sees that from a different set.

"Very generally two bows are seen simultaneously. The one with the smaller radius, the primary, is the brighter and is due to light that enters the upper portion of the drops,

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[1] Moore: "Descriptive Meteorology," 249 (1910).

and after one internal reflection leaves their lower portions. The larger and fainter bow, the secondary, is due to light that enters the lower portions of the drops, and after two internal reflections leaves their upper portions. The outer edge of the primary bow is red and the inner violet, while in the secondary the reverse is the case. Accompanying both the primary and the secondary, which are some distance apart, are often seen from one to many supernumerary bows, due to interference phenomena."

McConnel[1] has made a study of fog-bows. "When the sun is shining on fog or mist, a bow is often seen differing considerably in appearance from the ordinary rainbow—far broader and, though quite bright, nearly colorless. The breadth may be as much as 6° or 7° instead of 1.5° as in the rainbow, and the coloring seldom surpasses a faint dull red and orange at the outer border and a slight blue tinge at the inner. The mean radius is a few degrees less than in the rainbow. Verdet[2] considers this to be a degraded form of the primary rainbow. According to Airy's theory the radius would be diminished by smallness of the drops; and Verdet attributes the whiteness: (*a*) to the faintness of illumination; and (*b*) to the irregularity in size of the drops.......

"Out of eighteen bows [observed on Ben Nevis] no fewer than eighteen were double. In one case the outer bow was probably a form of the secondary rainbow; for the inner bow, according to the measurement, extended at one edge almost up to the normal radius of the primary rainbow. But in the other case, in which measurements were taken, both bows were within this radius and in five cases the inner bow had the red inside. Assuming that the two bows are the primary bow and its first supernumerary, the reversal of the normal order of colors is a direct result of Airy's theory.

"The divergence of the principal bow from its normal position, and of the first supernumerary from the principal bow, depends on the ratio of the radius of the drops to the

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[1] Phil. Mag., (5) 29, 453 (1890).

[2] "Leçons d' Optique physique," 1, 422.

wave-length of the light. As it is greater with a given kind of light, the smaller the drops, so with given drops it is greater the greater the wave-length. For red light it is greater than for blue. As long as it is small for both, it only brings the red bow rather nearer the blue; but, when it is greater, it may bring the red bow to coincide with the blue; and it may become so great—with the first supernumerary at any rate—as to put the red bow well within the blue."

The size of the bow depends on the size of the drops, the diameter of the bow being less with very small drops[1] than with large drops. "An interesting phenomenon[2] is seen by observers standing on a mountain top at sunrise or sunset, when the shadow of the mountain, or what appears like it, suddenly starts into view. The dark shadow is bounded on either side by ashen or rosy tints, and rises as the sun descends or *vice versa*. A still more startling cloud effect is known as the Specter of the Brocken, because it was first described as having been observed on the famous mountain of that name in Germany. It is seen when the sun shines past the observer, and he sees his own shadow cast upon the clouds, or more often on the thin fog while a circle of glory appears to surround his own head. The most beautiful pictures of these glories have been published in connection with descriptions of balloon voyages, as the aeronaut sees a similar but still more brilliant glory surrounding his shadow when projected upon the top of a cloud. These glories, or shadows, are, of course, due to the reflection of light from the interiors of the cloud particles, combined with the phenomena of interference, just as in the case of glories around the sun or moon, which are formed by light that has passed through the drops without reflection. But the glories seen by the aeronaut are more perfect than those seen by the ordinary observer, because the particles on the upper sides of the clouds are more regular in size."

Under suitable circumstances we may see coronas sur-

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[1] Wood: "Physical Optics," 346 (1911).

[2] Quoted from Moore: "Descriptive Meteorology," 254 (1910).

rounding the sun or the moon.[1] "They are due to the interposition of small spherules of water, which act the part of diffracting obstacles. In order to have the formation of a well-defined corona, it is essential that the particles be exclusively or preponderatingly, of one size....... By measurements of coronas it is possible to infer the size of the particles to which they are due, an application of considerable interest in the case of natural coronas...... the general rule being the larger the corona the smaller the water particles. Young employed this method not only to determine the diameters of cloud particles (*e. g.*, $^1/_{1000}$ inch); but also those of fibrous materials for which the theory is analogous."

Moore[2] says that "the glories or coronae, of a few degrees in diameter, seen around the sun or moon, exhibit a succession of colors, the red being on the outside of the circle and the blue on the inside. These colors are produced in accordance with an optical principal of interference of waves of light, and in this particular case the phenomena themselves are known as diffraction. In accordance with this principle, when two beams of light intersect at an extremely small angle, the point of intersection, being equally affected by the two systems of waves, may become a source of light or of darkness, according as the waves re-enforce or neutralize each other. The little spaces between the particles of all hazy clouds allow these separate beams of light to pass through, and as they converge upon the retina they interfere and produce alternate light and dark bands. The bands are broader and the radii of the corona are larger in proportion as the cloud particles are smaller [the reverse of what is true for the rainbow]; hence the angular diameter of the corona is an index to the size of the particles of the clouds.......

"Every one is familiar with the colored corona surrounding a bright object, as seen through a pair of spectacles freshly bedewed with moisture. These colors are due to the same principle of optical interference and are entirely analogous

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[1] "Encyclopaedia Britannica," 11th ed., 8, 244 (1910).

[2] "Descriptive Meteorology," 248 (1910).

to those seen through a fog. Such circles may be seen around the sun almost any day of the year if we view it by reflection from some poor reflecting surface, like water, in order to eliminate the blinding glare of the sunshine. In the case of the largest corona, known as Bishop's Ring, the average diameter of the particles[1] of this ring by diffraction was calculated to be about 0.00015 of an inch [about 4 μ].......

"A brilliant series of experiments was begun by Dr. Carl Barus for the Weather Bureau in 1891, and has been continued by him ever since, leading up to new views in regard to the atmospheric vapor. He calls this subject 'cloudy condensation,' the idea being to determine by what process the cloud particles form and how they join together to form rain. He has conveniences at hand for filling a small tube with any kind of vapor in any state of condensation. A beam of light is passed through it, and as condensation takes place it is immediately accompanied by magnificent displays of color. The size of the particles may be determined by the color and order of the spectrum, and the total range of sizes observed by him lies between 0.0004 and 0.00001 of an inch. These studies by Barus go far to show that the colored clouds and colored suns are truly interference phenomena...... not necessarily interferences by diffraction."

The production of coronas in the laboratory was observed by Coulier in the paper referred to and has been the subject of study for many years by Barus[2]. To get the best effects the drops should be uniform in size.

The brilliant sunset and sunrise colors are also due in part to the presence of suspended particles of water.[3] "In the lower half of the atmosphere there are frequently larger particles, probably of aqueous vapor, dust, and smoke, that absorb the blue but transmit the red, so that after sun-

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[1] [These were solid particles; but formed a corona and not a halo. A corona is due to diffraction and red on the outside. A halo is due to refraction and is red on the inside.]

[2] Smithsonian Inst., 29, No. 13 (1901); Carnegie Inst. Pub. No. 62 (1907); No. 96 (1908).

[3] Moore: "Descriptive Meteorology," 245, 255 (1910).

set or before sunrise beams of reddish light permeate the atmosphere above our heads. When we look at this light directly above the sun and at an altitude of from 10 to 20° above the horizon, while the sun is 10 or 15° below the horizon, we see a pinkish blotch on the sky; on either side of this for a long distance we perceive a delicate green tint shading above into the blue and below into the yellows and reds. Lower down nearer the horizon both before and after sunset, we frequently see horizontal bands of both red and yellow, the red being more prominent in warm, moist air, and the yellow in cold, dry air. In very dry air, such as occurs in areas of high barometric pressure and cloudless skies, the color is a light lemon-yellow, but this is only seen in temperate and northern latitudes, while the deeper yellows and red prevail in the tropical regions and in our moist summers and on the advancing fronts of areas of low pressure or storms.

"Paintings by eminent artists, such as Turner, often give us elegant representations of the lurid red that precedes a storm on the British coast or a hurricane or typhoon in the tropics. In such cases, the sun being near the horizon, its light reaches the observer's eye passing through many miles of the denser moisture of the lower air, or after being reflected from the particles of the lower clouds and has lost first the blue and then the yellow portion of the spectrum, until only the red remains."

"Although the clouds appear white in full sunlight, yet when illumined by the yellow and red rays that penetrate to them from the setting sun they form the most magnificent color displays that are to be found anywhere in nature. The upper part of a tall cumulus is often a delicate pink, while the lower portion is ashy gray; and below that the blue and green sky tints may be visible. A decided pink or straw-colored yellow is often seen when looking at the dazzling white on the sunny side of a cumulus cloud. Apparently the surface particles of the cloud are being evaporated in the sunshine, and the adjacent layer of air is supersaturated with moisture at a relatively high temperature; possibly minute particles of water are present and modify the orange and pink tints that are spread in spots over the cloud. The tints are seen only when cumuli are sending up great thunderheads like explosions of steam boilers.

"Still another color phenomenon is associated with the under sides of cumulus clouds, as in approaching thunderstorms, when the landscape beyond the cloud is brilliantly lighted by the sunshine; in such cases the observer may see patches of yellow or green on the lower side of the cloud, being light from the bright landscape, reflected by the big drops."

While fog is due to the production of very small drops, rain is due to the formation of larger drops which fall with perceptible speed. There is no absolute dividing line between the two because most people would classify as rain what a Scotchman might call a mist. According to the Weather Bureau, rain appears[1] to begin when the drops reach a diameter of 0.04 mm. The maximum rate of fall of these drops is very small. Larger drops fall faster. According to Lenard[2] drops of 1.28 mm diameter have a final velocity of 4.8 meters per second, those with a diameter of 3.49 mm reach a velocity of 7.37 meters per second, while drops from 4.50 to 6.36 mm show a practically constant rate of about 8 meters per second. This limiting value is due to the drops becoming deformed, so that they become flattened out, instead of retaining the shape of spheres. They, therefore, offer an increased resistance to the air through which they fall. In consequence of this deformation large drops break up rapidly in the air into smaller drops. Lenard found that drops of 4 mm diameter were stable under all conditions, but that drops of 5.5 mm diameter and over could not exist for more than a few seconds after attaining their final velocity relatively to the air. This is in harmony with the results of other observers. Wiesner[3] concluded that natural raindrops cannot have a diameter larger than 7.2 mm, while Ritter found that the largest drops of

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[1] Moore: "Descriptive Meteorology," 205 (1910).

[2] Met. Zeit., 21, 249 (1904).

[3] Moore: "Descriptive Meteorology," 208 (1910).

natural rain did not exceed 6.6 mm diameter. An independent confirmation is found in Bentley's experiments on the size and frequency of drops during rains in northern Vermont. His data are given in Table II.

TABLE II
Measurements of raindrops, diameter and frequencies

Apparent size	Diameter of drops in mm	Frequency of drops	
		No. observed	Percent
Very small	Under 0.8	149	17
Small	0.8–1.5	288	34
Medium	1.6–3.3	254	29
Large	3.4–5.0	141	16
Very large	Over 5.0		

It is possible that the very smallest drops often escaped observation and that the percentage of very small drops should be more than 17. In any case the mean diameter is not over 1.5 mm and the instructive thing is to see the very small percentage of drops larger than 5.0 mm diameter.

Simpson[1] has recently developed a very interesting theory in regard to thunderstorms.

"Lenard has shown that if air ascends with a greater velocity than 8 meters a second no water can fall through the current, for if the drops are below a certain size they are carried upwards with the air, while if they are above that size they are unstable and quickly break up into smaller drops, which are then carried upwards. Now, as will be seen later, it is exceedingly probable that during thunderstorms ascending currents much greater than 8 meters a second come into play, and these must, therefore, hold a considerable quantity of water in suspension. This water will be constantly going through the process of growing from small drops to large drops, only to be broken up into small drops again. If, therefore, the breaking up of a large drop is accompanied by a separation of

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[1] Phil. Trans., 209A, 379 (1909); Humphreys: Jour. Franklin Inst., 178, 751 (1914); Phys. Rev. (2) 6, 516 (1915).

electricity, thunderstorm electricity might owe its origin to such an effect."

Simpson showed that the breaking up of a large drop in an air current did give rise to electricity, the drop becoming charged positively. To get this effect one must use a fairly pure water. It could not be obtained, for instance, with the water from the Simla mains. Simpson next points out that horizontal velocities of 8 meters per second (29 kilometers, or 18 miles an hour) is defined as a moderate breeze and that we have evidence in the case of tornadoes that the ascending currents are quite comparable with the greatest horizontal winds known (approximately 100 miles an hour).

"In the formation of hailstones we have equally certain evidence of strong ascending currents. A hailstone cannot grow appreciably above the size which would be sufficient to cause it to fall to the ground through the ascending currents below it, so that the size of a hailstone gives a rough measure of the upward velocity of the air current in which it was formed. Now hailstones have been met with having all sizes between those of peas and those of melons. A hailstone as big as a pea would require a vertical velocity of at least 10 meters a second to hold it in suspension; thus the ascending currents which produce stones as large as oranges and melons must be enormous. It would, therefore, appear that those disturbances in the atmosphere which are accompanied by the greatest amount of electrical discharge are also accompanied by violent ascending currents, much larger in all cases than the 8 meters a second necessary to hold water in suspension, and so it cannot be considered to be an unwarrantable assumption that in all thunderstorms a velocity of 8 meters a second occurs.

"A strong vertical current in the atmosphere must have a form something like that of an hour glass, having a comparatively large cross-section at the bottom where horizontal currents are feeding into it, and spreading out at the top to allow of the escape of the air after ascension. For simplicity in the following discussion we will imagine an ascending current to consist of three parts: (*a*) a base in which the cross-section is large and the vertical velocities are small; (*b*) a column of ascending air of which the cross-section is comparatively small and the vertical velocities are large and more or less constant throughout; (*c*) a cap or crown in which the air rapidly spreads out in all directions so that the vertical velocities are very small a short distance above the head of the column. If the air in the base is saturated, then as it rises through the column it will have its temperature reduced at the rate of approximately 0.5° C for each 100 meters of ascent, and there will be considerable condensation of water, which will form drops and tend to fall. If, however, the vertical velocity within the column is 8 meters a second or over no water can fall, but it will all be carried upwards until it reaches the top of the column, where the vertical velocities diminish. Here the water will accumulate in the form of drops which will continually be going through the cycle of growing to 5.5 mm in diameter and then being broken up into a number of small drops, each of which will grow again. A rough approximation of the water accumulated can be formed by assuming certain simple conditions. Thus let us assume that the height of the column is 2000 meters, so that the air which enters the base will be cooled 10° C during the ascent, and let the initial temperature be 15° C. Then by the time the air reaches the top, approximately 6 grams of water will have been precipitated within each cubic meter of air, and if all this accumulates at the top of the column,[1] 6 × 8 or 48 grams of water will have collected over every square meter of the column in one second, that is, in 10 minutes the water accumulated would be equivalent to a layer of water 2.9 cm deep, or if the water is in the form of drops there would be at the end of ten minutes 36 drops, each of the maximum size of 5.5 mm

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[1] This of course is only assumed for purposes of a rough approximation; it is not intended to assert that all the water carried up by the current would accumulate at the top of the column; but as the accumulation which would result from rain falling from above has been neglected, the calculation will give some idea of the magnitudes with which we are concerned.

diameter, over every square centimeter of the cross-section. Thus, if the ascending current had a velocity of only 8 meters a second, enough water would be deposited for a considerable breaking up into drops.

"Turning now to the second point which the theory has to consider, a rough estimate will be made of the amount of electricity which could be separated under such conditions. For this purpose it will be necessary in order to simplify the reasoning to make several somewhat artificial assumptions. It will be assumed that the ascending current extends over a fairly large area, so that vertical distances may be considered as small in comparison with horizontal ones; that the separation of electricity takes place uniformly over a horizontal plane; and that all the positive electricity remains in the water near the place of separation, while all the negative is carried vertically upwards in the air stream. We will first consider how many drops must be broken in order to set up the potential gradient of 30,000 volts per centimeter which is necessary for a lightning discharge. This field is set up between two parallel plates having a surface density of 8 electrostatic units per square centimeter. Thus sufficient drops must break over each square centimeter to provide 8 electrostatic units before a discharge can take place, and as the breaking of each drop provides 5×10^{-3} electrostatic units, this will occur when $\frac{8}{5 \times 10^{-3}}$ or 1600 drops have broken.

"Thus if one drop breaks over each square centimeter per second, a discharge can take place after 27 minutes, or if 27 drops break, after 1 minute. Now it has already been shown that under certain conditions which are not at all improbable, 36 drops of water, each large enough to be broken up, will have accumulated in the course of 10 minutes over each square centimeter of the ascending current; hence it does not seem at all improbable that with even moderate values of the ascending current sufficient breaking of drops could take place to give the rapid electrical discharges observed in thunderstorms. In this connection it is important to realize that each electrical discharge only neutralizes the electricity over a small area of the region in which separation takes place. Thus suppose that the ascending current is 4 kilometers in diameter, and that each discharge neutralizes the charge over 1 square kilometer of area then it would take 12 discharges to neutralize the whole electricity over the whole surface. Under these conditions, if the potential gradient were being created at the rate of 30,000 volts per centimeter every minute, the lightning discharges would occur on the average every 5 seconds.

"It may also be considered how many times a given mass of water would have to be broken up in order to give to the rain which falls from the cloud the charges which are actually measured. The case of rain positively charged will be considered first....... The positive charge carried down by the rain is of the order of magnitude of one electrostatic unit per cubic centimeter of water. The laboratory experiments showed that water which has splashed once has a charge of the order of magnitude of 10×10^{-3} electrostatic units per cubic centimeter. Thus the water on the average would have to splash something like 100 times to give the charges measured. There is no reason for considering that this would be impossible with violent and widespread ascending currents.

"The air which passes through the accumulation of water at the head of the ascending current carries with it the negative electricity separated during the splashing. This electricity is rapidly absorbed by the cloud particles through which the air streams in its upward course, and it is very probable that the large negative charges could in consequence be accumulated in the cloud. Thus the cloud over the ascending current will consist of negatively charged water particles, and these will coalesce to form rain having a negative charge. There is no means of estimating what negative charge might be expected, but there is no reason for considering that it should be smaller than the positive charge brought down by the water which has been broken up several times at the head of the ascending current. Thus it would appear that the process could provide both the positively and negatively charged rain actually observed.

"The water which has become positively charged on the ascending current and then fallen as rain will be the heavy rain which occurs in the center of the thunderstorm. Advancing a step further, it will be necessary to consider what happens to the negative electricity which is separated when a drop breaks up. It is very probable that this charge is given to the air in the form of free negative ions, and it appears certain that these will, on formation, be carried upwards with the full velocity of the ascending air; they will then quickly leave behind the drops of water which retain the positive electricity.

"But the negative charge cannot exist long as free ions, for the latter will be rapidly absorbed by the cloud particles with which the air is filled. In this way the cloud particles may become highly electrified. Now within a highly electrified cloud there must be rapid combination of the water drops, and from it considerable rain will fall: this rain will be negatively charged and, under suitable conditions, both the charge on the rain and the rate of rainfall could be large. But it is important to notice that the negatively charged rain has an entirely different origin from that of the positively charged rain, and, therefore, the character of the rainfall might be expected to be different in the two cases. It has already been shown that the positively charged rain is likely to occur in heavy downpours in consequence of its intimate connection with the ascending currents; but the negatively charged rain is formed in the large cloud masses, which are more or less uniformly charged and extend over and around the ascending currents, the negatively charged rain is likely to have a much more uniform rate of fall, and also to occur in the intervals between the bursts of the positively charged rain.

"The observations bear out these considerations in a remarkable way. In storm after storm it was found that negatively charged rain fell in the lulls after a heavy downpour of positively charged rain. Negatively charged rain never occurred in heavy downpour, but was very often associated with steady rain from a lightly clouded sky. Also negative electricity was measured but rarely, and in large quantities never, in the region of the storms in which violent and frequent lightning discharges occurred.

"It will sometimes happen that the negatively charged cloud will be carried by the upper winds to some distance from the place when the separation of electricity was effected and will then give rain. In such cases rain charged with negative electricity would be likely to occur. The frequency with which negative electricity was observed by Elster and Geitel with rain associated with distant thunderstorms might be explained in this way."

It is interesting to note that while drops become positively charged on splashing, water vapor condenses more readily on negative ions[1] than on positive ones and that liquid drops take up negative ions more readily than positive ones.[2]

The precipitation of a fog or mist is an important problem; but can best be taken up in connection with the precipitation of smoke or dust because the technical methods are as yet the same in the two cases. Reference may, however, be made here to a process devised by Pelouze and Audouin[3] who force the gas through a series of small apertures and cause the streams to impinge on a flat surface placed opposite. They consider that by this means the drops are brought into contact with one another which coalesce then to larger drops, these latter adhering to the surface against which they are driven. The method has been used for the separation of tar, carbon bisulphide, etc., from coal gas. It is interesting as being the mechanical analogue of the Cottrell electrical method.

Cornell University

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[1] Wilson: Proc. Roy. Soc., 64, 127 (1898).

[2] Schmauss: Drude's Ann., 9, 224 (1902); Seeliger: Ibid., 31, 510; 33, 431 (1910); Lehnhardt: Ibid., 42, 45 (1913).

[3] Comptes rendus, 77, 264 (1873).

A RAPID PRESSURE METHOD FOR THE DETERMINATION OF MOLECULAR WEIGHTS AND HYDROGEN EQUIVALENTS[1]

BY W. H. CHAPIN

I. Molecular Weights

By means of the apparatus described below the molecular weight of any organic liquid boiling below 90° C may be determined very quickly and with a degree of accuracy fully comparable with that obtained by any of the common methods. The particular advantages of the apparatus are its simplicity, cheapness, and ease of construction. In these respects it differs strongly from Lumsden's apparatus.

The principle of the method is simple: A weighed sample of liquid is volatilized inside the apparatus, and the pressure of the vapor read off on a mercury manometer. From this pressure and the known volume and temperature the volume of vapor under standard conditions is calculated. The molecular weight is then calculated in the usual way.

Apparatus.—The main part of the apparatus is constructed from a 600 cc distilling flask by cutting off the side tube and sealing on in its place a small manometer. The latter should have a bore of 5 mm and a total vertical height of about 20 cm. With a tube of smaller bore the capillarity effect on the mercury tends to make the reading uncertain. With one of larger bore the change of volume due to movement of the mercury is too great. It is possible, of course, to correct for the latter, but this is not necessary with a tube of 5 mm bore, since it involves an error of not over 0.05 percent.

The rise of the mercury in the manometer tube is measured by means of a movable celluloid scale, graduated in millimeters. This scale is made from an ordinary 15 cm (6 in.) ruler by cutting out the side as seen in the sketch. It is attached to the manometer by means of sliding metal clips

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[1] Contribution from Severance Chemical Laboratory, Oberlin College.

which may be moved out of the way when reading. By this device the height of the mercury column may be read with an accuracy of about 0.25 mm.

The device at the top of the apparatus is the same as that commonly used with the Victor Meyer apparatus. The capsule containing the liquid first rests on the end of the rod projecting through the side tube, and later is allowed to fall by slightly withdrawing the rod. The upright tube should have a bore of 7 mm. The rod passes through a piece of pressure tubing where, to prevent sticking and secure a tight

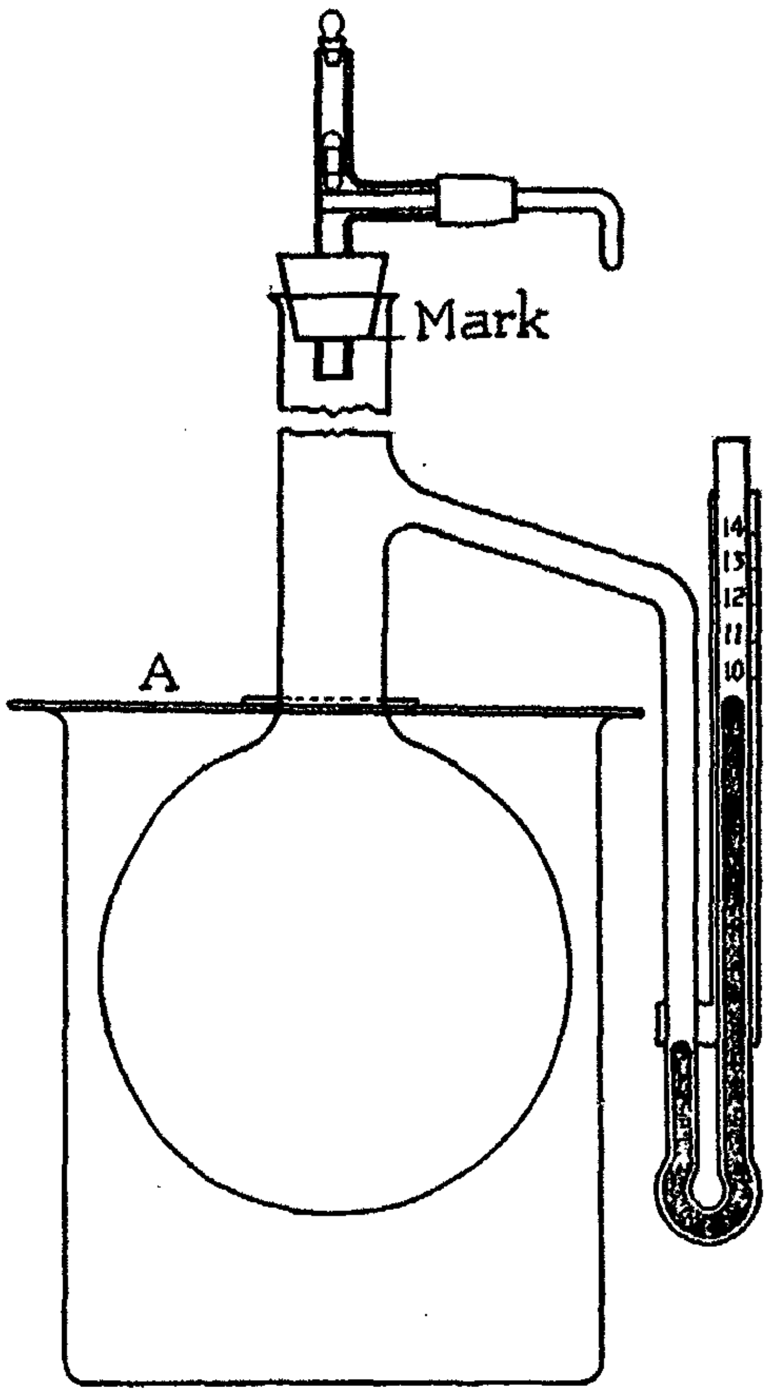

Fig. 1

joint, it is slightly moistened. The upright tube is closed by means of a plug made of a tapering piece of glass rod covered with rubber tubing. To secure a tight joint and definite volume the large stopper is moistened and then pressed in to a mark on the neck of the flask.

The large beaker below the flask serves as a steam jacket. It contains distilled water, which is boiled during a determination. The cover is made of sheet zinc, and is in two sections as seen in the sketch (A). The larger section has a slot in one side and passes astride the neck of the flask. The smaller section covers the slot.

Most liquids used in molecular weight determinations may be weighed out in the No. 3 gelatine capsules used by druggists.[1] These are of the proper size to slip through the vertical tube at the top of the apparatus. They usually give off a little moisture when heated, and in some cases they also give off formaldehyde (used in hardening the gelatine). To correct this tendency the capsules previous to use are placed in a flask which is then heated by steam as in the actual molecular weight determination, while a current of dry air is passed over them. After this treatment the capsules are kept in a glass-stoppered bottle until used.

Capacity and Temperature of the Apparatus.—The capacity of the apparatus is determined by filling with water and weighing. If the mercury is in place in the manometer the capacity thus determined will be the same as that actually used during an experiment. The capacity of the neck and of the bulb should be known separately for use as seen below.

Since a part of the apparatus is always outside the steam jacket it is necessary to determine experimentally the average temperature. Water is boiled in the jacket, and by means of a thermometer inserted in a stopper at the top of the apparatus the temperature is read off at different levels. In this way the average temperature of the neck is first determined and later that of the bulb. These two values are then averaged with

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[1] The idea of using the gelatine capsule was suggested by Mr. P. H. Fall of this laboratory.

due allowance for the fact that the bulb is several times as large as the neck. Thus, if the bulb is 11 times as large as the neck we multiply the average temperature of the bulb by 11, add that of the neck, and then divide the sum by 12. In three trials the average temperature of the apparatus was found to be 92° C. That of the bulb alone is nearly 100° of course.

Determination of a Molecular Weight.—It is first necessary to be sure that all joints are absolutely tight. This can be done as mentioned above.

Distilled water is placed in the jacket to a depth of two inches, and heated to rapid boiling. After the water begins to boil the plug is inserted at the top of the apparatus. The mercury in the manometer will rise at first due to further expansion of the air, but should finally remain stationary. Any leakage may be noted by a tendency for the mercury to fall after it has reached its maximum height, and any such leakage must, of course, be corrected.

When satisfied that the apparatus is ready a sample of the liquid whose molecular weight is to be determined is placed in a weighed capsule. This can be conveniently done by use of a small pipette made by drawing out a piece of glass tubing. Care should be taken not to fill the capsule too full or leakage will take place when the cover is put on. The size of the sample will take care of itself if the capsule is of the size recommended. When the loaded capsule has been capped it is weighed. While weighing, it must be kept in an upright position to prevent leakage. This can be done by placing between the arms of a small strip of metal bent into the shape of a U. After weighing, the capsule is slipped down the T-tube to the end of the rod, the plug is then tightly inserted, and immediately afterward the capsule is allowed to drop. In general the vapor generated inside the capsule pushes off the cover, and the liquid then evaporates within a minute. In some cases the time is a little longer, but this is usually with heavy liquids whose vapors diffuse slowly. No case has been encountered where any condensation occurred in the neck of the apparatus. This is due mainly to the large size of the flask. When the evaporation is complete the scale is adjusted so that the lower edge coincides with the meniscus in the near arm of the manometer, and the height of the mercury column is then read off. The tube must be tapped gently in the meantime to prevent any lag of the mercury, and parallax must be avoided. After taking the reading in this way it is always best to watch the manometer for further rise for about two minutes. Such rise is caused, of course, by the fact that the temperature of the vapor within the apparatus does not at once reach its maximum.

To repeat the determination it is only necessary to blow out the vapor in the apparatus by means of a current of dry air and then to drop in another loaded and weighed capsule. The temperature of the air within the apparatus will have reached its maximum while the process of filling and weighing the capsule is being carried out.

Calculation.—We now have the following data: (1) Volume of the vapor (capacity of apparatus). Call this V_t. (2) Temperature (average temperature of apparatus). On the absolute scale this becomes $273 + t$. (3) Pressure (rise of mercury). This may be designated as "Rise." (4) Weight of vapor (weight of sample taken).

We must first calculate the volume under standard conditions (V_0). For this purpose we make use of the common formula, thus:

$$V_0 = \frac{V_t \times \text{Rise} \times 273}{760 \times (273 + t)}. \qquad (1)$$

The weight of 1 cc of the gas under standard conditions equals

$$\frac{\text{weight of sample}}{V_0} \qquad (2)$$

and the molecular weight is the weight of 22,400 cc., or

$$\frac{22{,}400 \times \text{sample}}{V_0}. \qquad (3)$$

Putting the partial values 1, 2, and 3 into one equation, we obtain:

$$\text{Mol. Wt.} = \frac{\text{Sample} \times 22{,}400 \times 760 \times (273 + t)}{\text{Rise} \times V_t \times 273}$$

Of these values it will be noted at once that all are constant except "Sample" and "Rise." We may therefore work out once for all the value of the fraction

$$\frac{22{,}400 \times 760 \times (273 + t)}{V_t \times 273}.$$

This we may call K. The shortened equation then becomes:

$$\text{Mol. Wt.} = \frac{\text{Sample} \times \text{K}}{\text{Rise}}$$

By the use of logarithms the calculation in this simplified form may be made in three minutes. The time required in making a molecular weight determination, including the calculation, need not then exceed fifteen minutes.

Results.—Of the following results two in each case were obtained by a student who had never employed the apparatus for this purpose before, and who had only oral directions for its use:

Carbon tetrachloride	Benzene	Ether[1]	Alcohol
154.8	79.7	75.6	45.9
156.0	77.3	73.9	45.7
155.8	77.7	75.9	—
152.5	78.5	75.1	—
153.5	—	—	—
Accepted values 153.8	78.1	74.1	46.1

II. Hydrogen Equivalents

Apparatus.—For the determination of hydrogen equivalents the apparatus is essentially the same as that described above. In some cases a slight modification is required, but

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[1] This ether left a slight residue on evaporation, hence the high values.

this can be described without a sketch. In the case of sodium and magnesium the apparatus needs no change, since the samples may be dropped through the T-tube as described for molecular weights. In the case of metals obtained in sheet form the T-tube is replaced by an ordinary stopcock tube, and the sample is suspended by means of a thread caught in the stopcock.

The following cases represent the necessary differences in procedure:

Zinc and Aluminum.—The pure sheet metal is first cleaned with emery cloth and then cut into small rectangular pieces, (0.05 g for aluminum and 0.2 g for zinc). After the piece is weighed it is wrapped closely in a small piece of brass or copper gauze and then suspended by means of a thread as noted above. The gauze promotes the rapid solution of the metal by forming a couple with it, but does not itself dissolve. 10 cc of 3 *N* hydrochloric acid are placed in the apparatus, and enough water at room temperature is placed in the jacket around the bulb to keep the temperature constant during the reaction. A thermometer should stand in this water. After allowing time for the temperature of the apparatus to reach that of the bath the sample is allowed to drop into the acid and the cock is immediately closed. Danger of losing hydrogen here may be prevented by placing a finger over the end of the stopcock tube at the moment of opening and closing. After solution of the metal is complete the pressure is carefully read off as described under the previous method.

The method of calculation hardly needs mention. In taking the volume, however, allowance must be made for the 10 cc occupied by the acid. The total capacity of the apparatus will be practically the same as before. The volume of hydrogen under standard conditions is calculated as usual. No allowance is made for aqueous tension or HCl gas, since both had come into equilibrium before the apparatus was closed.

Sodium and Calcium.—The apparatus is arranged as for molecular weights. If sodium is used 10 cc of absolute alcohol are placed in the apparatus and time allowed for the vapor tension to reach its maximum. This time is much shortened if the alcohol is allowed to run down the inside of the flask. It should not exceed 6 minutes. In the meantime the metal is quickly cut in a single clean piece as large as can be slipped into a No. 3 gelatine capsule (previously weighed), and when covered is weighed at leisure. When all is ready the capsule is uncovered and is then dropped into the T-tube as in molecular weights. The rest of the procedure and the calculation need no description.

The reaction between the sodium and the alcohol is quiet and without danger. Water must *not* be used, as dangerous explosions will almost certainly occur.

If calcium is used normal hydrochloric acid should be used in the apparatus. The metal is cleaned by filing, and is weighed in the capsule.

Magnesium.—This metal is best used in the form of wire of about 2 mm diameter. It is cleaned with emery cloth and cut into lengths weighing about 0.075 g. ($^1/_2$ inch). The apparatus has the form used with sodium and calcium. I find it difficult to obtain pure magnesium; hence the values obtained are rather wide of the mark. One sample examined contained aluminum, and all contained some carbonate and silicide.

Results:

	Zn	Al	Na	Ca	Mg
	32.63	9.02	23.12	20.29	11.9
	32.80	9.09	23.07	20.05	11.5
	32.33	9.08	23.37	20.01	11.6
	32.80	9.02	22.63	19.93	11.6
Accepted values	32.68	9.03	23.00	20.03	12.16

Oberlin, Ohio

ADSORPTION IN VACUUM TUBES

BY WILDER D. BANCROFT

It is a little hard to tell whether the change in the vacuum of a Crookes' tube can be said to be due to the adsorption of the gas by the glass or not. There are some rather interesting phenomena which have been studied by Swinton,[1] who examined some tubes which had been in operation, nearly ten years before, for many hours "under extremely severe conditions, the alternating current employed having a volume of some 20 milli-amperes at about 8000 volts pressure.

"The condition of the glass walls of these tubes is now found to be as follows: When cleaned by rubbing they are quite transparent to casual inspection, though careful examination with the microscope shows that the inner surfaces of those portions that had been subjected to cathode ray bombardment are materially roughened. When these portions of the glass are heated strongly in a blow pipe, they immediately become clouded, the effect being due to quantities of minute spherical bubbles in the glass, which may clearly be seen with a microscope. The bubbles vary to some extent in size, but on the average are about 0.01 mm in diameter. They are usually packed closely together in a single layer and are always very near the side of the glass that formed the inner surface of the tube. On measuring the thickness of the glass with a micrometer gauge, dissolving the inner surface with hydrofluoric acid until the bubbles had just disappeared and then again measuring the thickness, it is found that, after making allowance for the size of the bubbles, the centres of these bubbles were about 0.122 mm from the inner surface of the glass. A similar estimate was obtained by grinding the inner surface of the glass until the bubbles just disappear and making micrometer measurements as before. It would, therefore, appear that the particles of gas must have been shot into the glass to about the depth stated.

"In a typical piece of glass the number of bubbles per

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[1] Proc. Roy. Soc., 79A, 134 (1907).

square centimeter of glass was found to be about 625,000, so that, allowing for the expansion of the gas on heating the glass up to redness, there was occluded about 0.000113 cc of gas at atmospheric pressure per square centimeter of glass, and as the amount of glass surface that was bombarded in each tube was about 400 cm^2 the total amount of gas at atmospheric pressure occluded in each tube is nearly 0.05 cc. apart from any further amount that may have escaped from the glass in the heating of the latter. An interesting question arises as to whether the gas is merely mechanically mixed with the glass or whether there has been any chemical combination between the two. In the latter case, it seemed unlikely that mere powdering of the glass would cause the gas to come out, while in the former case it seemed probable that powdering the glass would have this effect."

The experiment was tried of powdering the glass inside a vacuum tube and gas was given off which was found to be mainly hydrogen. 'It would appear, therefore, that the gas occluded in soda-glass vacuum tubes exhausted in the ordinary manner from air is almost entirely hydrogen, no doubt due to electrolysis of water vapor condensed on the walls of the tube prior to exhaustion, the oxygen of which is adsorbed by oxidation of the aluminum electrodes."

As a further test the experiment was repeated with helium in the tube. On heating the glass, bubbles were obtained as before and helium was given off when the glass was crushed. "Seeing that helium does not combine with anything at ordinary temperatures, and seeing further that it could be extracted from the glass by the mere mechanical powdering of the latter, it would appear that the occlusion is due to the mechanical driving of the gas into the glass and not to any chemical combination."

The weak points in this argument are that the author does not consider the possibility of adsorption as something different from "mechanical entanglement," and that it does not appear definitely whether the glass which was pulverized had previously been heated so as to cause the formation of visible bubbles. If it had been heated, the experiments prove nothing as to adsorption. In case the glass was not heated, as seems probable, we must consider what the author means by mechanical entanglement. It may be that the bubbles of gas were driven into the glass and that the glass flowed round behind them enclosing the bubbles. This would certainly be mechanical entanglement and it certainly would not be adsorption any more than one would speak of the air inside a sealed tube as being adsorbed. On this assumption the gas would be retained until the glass was heated or pulverized. On the other hand, it seems rather improbable that the glass would flow round the bubble in this way. If not, we must assume that the gas was shot into the glass, forming bubbles which still communicated with the inner part of the tube by fine pores. On this assumption the gas would actually be adsorbed in the pores. Since a capillary pore will adsorb more gas than an exposed surface, it is not surprising that the gas escaped when the glass was pulverized, quite apart from any question of heating or electrification which may occur while the glass is being pulverized. Until it is known whether or not the glass flowed round the bubbles and enclosed them, it is impossible to say whether this is a case of mechanical entanglement or of adsorption. Unfortunately this did not occur to Swinton and will have to be decided by somebody else.

The general results of this paper are as follows:

1. In a Crookes tube gas bubbles may be driven into the glass for a distance of about 0.1 mm.
2. This gas is set free when the glass is pulverized.
3. It is not known whether the glass flows round behind the bubbles cutting them off completely from the inner portion of the tube, or whether the holes made by the bubbles in passing into the glass do not close completely.
4. If the bubbles are sealed in the glass, this is merely a case of mechanical entanglement; but if the bubbles are connected with the inner portion of the tube by fine pores, it is a case of adsorption.
5. Hydrogen and helium tubes behave alike.

Cornell University

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ON THE APPLICATION OF THE MASS LAW TO THE PROCESS OF DISINFECTION—BEING A CONTRIBUTION TO THE "MECHANISTIC THEORY" AS OPPOSED TO THE "VITALISTIC THEORY"

BY RICHARD EDWIN LEE AND C. A. GILBERT[1]

1. Introduction

This paper is a report of an inquiry into the mechanism or process of disinfection with a view to ascertaining if it is analogous to chemical reaction and like the latter may be interpreted in terms of the Mass Law.

Ever since Lister, in England, and Pasteur, in France, laid the foundation for the study of disinfection by demonstrating the action of certain substances in destroying putrefactive and disease-producing micro-organisms, the general subject of "antiseptics and disinfectants" has received much attention and deservedly so. The literature records, however, that a number of years elapsed before the general principles established by these master workers in the field of preventive medicine were accorded the recognition to which their present-day usefulness indicates that they were entitled.

It is doubtful whether the history of science can supply a more marked example of the baleful influence of prejudice and jealousy in preventing the development and application of principles of inestimable value to society than is afforded by the experiences of Lister and Pasteur in blazing the way for the new science of preventive medicine.

The credit probably belongs to Robert Koch for being the first to formulate procedures from which our present methods for estimating the relative efficiency of disinfectants have been developed. In 1886, this German investigator made a comparative study of practically all of the then known substances of this class. For years this seems to have remained

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[1] Contribution from the Carnegie Hall of Chemistry, Allegheny College.

the most attractive phase of the problem. And a survey of the current literature will show that interest in this field of inquiry has not greatly diminished, as much work is still being done with a view to perfecting such methods as the "Rideal-Walker" and the "Hygienic Laboratory," for determining the so-called "phenol coefficients" of these substances. There is, however, another phase of the subject, namely, the *mechanism* of the *process* of disinfection which has enlisted the attention of only a comparatively small number of investigators. It is probably true that results obtained from an investigation of this kind will have less practical value than those resulting from work along the lines to which reference has been made. Nevertheless, data secured in this field must eventually possess much contributory value in the solution of other problems in this field of inquiry.

As noted previously, the literature relating to the subject does not show a large number of workers concerned with this special problem. Those who have contributed in the effort to solve this phase of the problem, however, may be conveniently separated into two groups accordingly as they have supported what may be termed the "vitalistic" conception and the "mechanistic" conception of the process of disinfection.

2. The "Vitalistic" Conception of the Process of Disinfection

The "vitalistic" conception of the disinfection process has received the support of many of the most prominent bacteriologists who have given consideration to the problem. And if viewed from the standpoint of the number of adherents to the respective theories, the "vitalistic" conception would in all probability be adjudged the more popular. In the list of contributors to the "vitalistic" explanation of the process are found the names of such authorities as Bellei,[1] Eijkman,[2] Hewlett,[3] Reichel[4] and Reichenbach.[5]

This group of investigators contend that the disinfection process is not analogous to chemical action, and have proposed several different explanations of the process, the essential principle of each being, however, what may be designated here as "the theory of grade resistances."

The Theory of Variable Permanent Resistance.—For a number of years it has been a sort of a working hypothesis or principle in certain fields of investigation that many biological characteristics are not distributed as a rule in the same degree to different individuals in a collection or group of apparently similar forms. By a special application of this principle those in support of the vitalistic conception have been led to conclude that the *progressive* nature of disinfection is best accounted for by assuming that *different degrees of resistance* to disinfection are possessed by the different individuals in a "culture" of apparently similar micro-organisms. This conclusion seems to be justified when it is correlated with that which has been regarded as an experimentally established fact, namely, that all of the individuals of a given "culture," say of B. typhosus, are not destroyed with equal ease by the disinfectant, and that more time is required for the destruction of certain ones in the group, than for others.

To briefly summarize the "vitalistic" conception—the progressive nature of the disinfection process is accounted for as being due to a type of biological variation, namely, *permanent differences* in the degree of resistance possessed by the various individual micro-organisms of a "pure culture." This is commonly known as the "theory of variable permanent resistance."

3. The "Mechanistic" Conception of the Process of Disinfection

According to the "mechanistic" conception the process of disinfection "is an orderly time-process presenting a close analogy to a chemical reaction, the micro-organism and the disinfectant being regarded as the respective reagents." Those who have been responsible for the development and formulation of this conception assert the improbability of the frequent occurrence of any type of biological variation which will account for the progressive nature of the disinfection process. In other words, the "vitalistic" conception is declared to be inadequate if all of the phenomena attendant upon disinfection are to be explained. In supporting this criticism it is pointed out that if the *progressive* nature is to be attributed to *permanent* differences in degrees of resistance occurring among the various individuals of micro-organisms then disinfection would indeed be gradual, but the *rate* at any time would be proportional to the concentration of the surviving individuals—a condition required by the progressive nature of the process. But this could occur only when the "variable permanent resistances" were distributed according to one definite arrangement—an arrangement which obviously would not always be present. Nevertheless, it should be noted that such a definite arrangement would always have to be present to account for the observed facts. Furthermore, it is urged in this connection by the opponents of the "vitalistic" theory that the biological characteristic, resistance in this case, subject to variation *is as a rule distributed in a manner quite different from that which had been assumed in accounting for the progressive nature of the disinfection process*. Usually those individuals, of a group, possessing the *average* degree of a varying characteristic are found in the majority; while those possessing it in a maximum or minimum degree are found in the minority. An interpretation of observed relations of the disinfection process in terms of biological variation, however, would lead to the contrary conclusion, namely, that those individuals of a group possessing the characteristic in a *minimum* degree are invariably present in the greatest number.

The fairness of this argument has been admitted by many who have supported the theory which it attacks; in this group, however, there have been a number who contend that this apparent discrepancy is satisfactorily accounted for if the theory of "graded resistances" be accepted.

According to this theory multiplication among the individuals of a group is general at first, but as time elapses the process is maintained by a constantly decreasing proportion of the individuals with the result that a definite grading of resistances would be established in the group. It has been well pointed out by Chick,[6] however, that "two assumptions are made in this theory," "first that the age of the bacterium and its resistance are bound up with one another and, secondly, that the number remaining undivided in each successive generation increases with mathematical regularity."

Probably a sufficiently large number of facts relating to the two conflicting conceptions of the disinfection process have now been presented to make it obvious that more data must become available before a conclusion as to the exact mechanism of the process can be justified.

For a number of years it has been a matter of frequent suggestion that the process of disinfection probably conforms to the laws relating to chemical action. The possibility of the existence of such a relationship was suggested not only by the literature but by observations of routine work of students in this laboratory in determining "phenol coefficients." Finally, with a view of securing data at first hand, the authors undertook the task of making an examination of available results obtained by other workers and of supplying new experimental data.

4. Analysis of Problem

It was clearly seen at the beginning of the work that if the disinfection process is proven to be strictly analogous to a chemical reaction it would be necessary to establish the following:

That the reaction, disinfection process, is a progressive and orderly time process proceeding according to a rule which is similar to the Mass Law; that is, there must be found a logarithmic relation between the two variables, namely, the concentration of surviving individuals in the system and time. In other words, the process must be found to conform to the formulation

$$\frac{dC}{dt} = KC, \text{ or } \frac{1}{t_2 - t_1} \log \frac{C_1}{C_2} = K$$

in which C_1 and C_2 represent the number of surviving microorganisms after times t_1 and t_2, respectively; or to some formulation of the law for the reactions of a "higher order."

In presenting the data which has been accumulated during the investigation, the report has been divided into three parts. In the first part there has been given the data obtained by examination and calculation of the numerical results obtained by other workers. In many cases the results that the authors of this paper have used were obtained by contributors who had no thought of the bearing of their work on the establishment of a possible analogy between the disinfection process and chemical reaction. The second part is devoted to a statement of the experimental work conducted in this laboratory. Finally, in the third part there has been submitted a discussion and interpretation of results and a summary.

5. Historical

Probably the first to undertake work which was of value to the authors were Krönig and Paul. In addition to being among the first to call attention to the relationship apparently existing between the disinfectant action and the electrolytic dissociation of certain inorganic substances, they outlined a method for determining their relative efficiencies by a comparison of the *rates* of disinfection. In their published results in 1897 they pointed out that time and temperature and concentration are factors in the process of disinfection; but no attempt was made by the authors of the paper to formulate a theory of disinfection on the basis of results obtained. Nor have the authors of this paper been able to find that this was attempted by any investigator until comparatively recently, and then, by only a very few.

In this connection particular reference should be made to the published works of Madsen and Nyman[7] in 1907 and Chick and Martin[8] in 1908. Their work is of great significance and value in accounting for the phenomena attendant upon the process of disinfection. The results obtained by these individuals and their associates in the work constitute probably the best evidence for the "mechanistic" conception. Working simultaneously but independently on the results obtained by Krönig and Paul, they were led to the same conclusion, that "disinfection is an orderly time process," for if the concentrations, *i. e.*, numbers, of micro-organisms escaping the action of the disinfectant at the end of the different periods of time be plotted as ordinates against time periods as abscissas these experimentally established points locate fairly smooth curves. And furthermore, if the *logarithm* of the concentration, numbers of surviving micro-organisms, be plotted as ordinates against time as abscissas experimentally established curves are obtained, when an excess of the disinfectant is used, which are very similar to curves indicating the progress of a "reaction of the first order," the formulation of which gives the well known equation,

$$K = \frac{1}{t} \log \frac{C}{C - X}, \text{ or } K = \frac{1}{t_n - t_0} \log \frac{N_0}{N_n},$$

where N_0 and N_n are the numbers of micro-organisms surviving after times t_0 and t_n, respectively.

The following tables, prepared from the results obtained by Krönig and Paul, 1897, and Chick, 1910, show in tabulated form the relationships just pointed out.

Table I

Disinfection of Anthrax Spores with Mercuric Chloride[1]
Concentration of Disinfectant, 0.11%. Temperature, 18° C.

Time in Minutes $= t$	Mean Number of Micro-organisms Surviving $= N$	Log. of Concentration $= \text{Log}_{10} N$	$K = \frac{1}{t_n - t_0} \log \frac{N_0}{N_n}$
$10 = t_0$	$2027 = N_0$	3.307	—
15	672	2.827	0.096
20	564	2.751	0.056
25	382	2.582	0.048
30	251	2.400	0.045
35	179	2.253	0.042
40	138	2.140	0.039
45	101	2.004	0.037
50	80	1.903	0.035
60	39	1.591	0.034
70	6	0.778	0.042
80	3	0.477	0.040

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[1] Calculated from Krönig and Paul's data, Zeit. Hyg., 25, 26 (1897).

TABLE II

Disinfection of B. typhosus with Phenol[1]
Concentration of Disinfectant, 0.6%. Temperature, 20° C.

Time in Minutes $= t$	Mean Number of Micro-organisms Surviving $= N$	Log. of Concentration $= \log_{10} N$	$K = \frac{1}{t_n - t_0} \log \frac{N_0}{N_n}$
0.5 $= t_0$	231.3	2.364	—
1.5	190.0	2.279	0.085
2.6	167.0	2.223	0.067
4.6	114.2	2.058	0.075
6.6	77.8	1.891	0.077
10.5	31.6	1.500	0.086
15.0	11.3	1.053	0.090
20.0	2.4	0.380	0.102
30.0	0.35	—0.456	0.096

TABLE III

Disinfection of Staphylococcus Pyogenes Aureus with Phenol
Concentration of Disinfectant, 0.6%. Temperature, 20° C.

Time in Minutes $= t$	Mean Number of Micro-organisms Surviving $= N$	Log. of Concentration $= \log_{10} N$	$K = \frac{1}{t_n - t_0} \log \frac{N_0}{N_n}$
Control	1293	3.112	—
1	1141	3.057	—
3	1044	3.019	—
4 t_0	952 N_0	2.979	—
5	708	2.850	0.129
6	543	2.735	0.122
7	401	2.603	0.125
8	243.2	2.386	0.148
9	202.5	2.306	0.135
10	156.1	2.193	0.131
12	45.4	1.657	0.165
15	21.8	1.338	0.149

If the logarithmic relationships shown in the foregoing tables are expressed graphically, the experimentally established points are seen to lie along straight lines. (See Fig. I.)

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[1] Arranged from Chick's data: Jour. Hyg., 10, 237 (1910).

It will be observed in the case of the action of 0.6 percent phenol on the Staphylococcus pyogenes aureus at 20° C., that at the beginning of the disinfection there was a short period, about four minutes, before the process proceeded as a "reaction of the first order." The authors are unable to account for this at the present time, although the researches of Reichel and Copper[9] suggest that the first stage of the disinfection of micro-organisms, in the presence of water, by phenol and other coal-tar derivatives, consists of a distribution of the disinfectant between the water and the bacteria. It is probably unnecessary to point out that this behavior of the disinfectant does not affect the conclusions to be deduced as regards the nature of the process of disinfection.

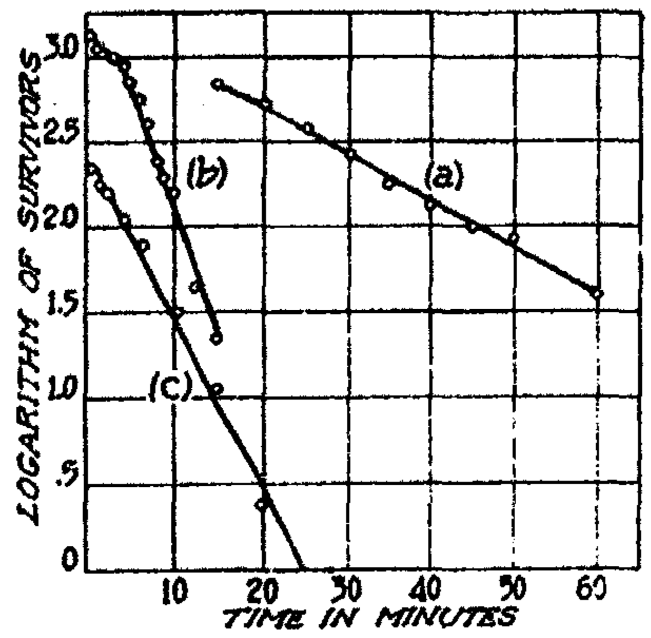

Fig. 1

(*a*) Disinfection of anthrax spores with 0.11% mercuric chloride at 18° C. (See Table I)

(*b*) Disinfection of staphylococcus pyogenes aureus with 0.6% phenol at 20° C. (See Table III)

(*c*) Disinfection of B. typhosus with 0.6% phenol

Although the data pointing to the conclusions indicated is rather limited the "mechanistic" conception apparently offers the best explanation of observed relations of any of the proposed theories. Reichenbach insists, however, that it is a violation of the laws of rigorous reasoning to attempt to account, on the basis of a chemical analogy, for the logarithmic death-rate of the micro-organisms from "a conceivable logarithmic destruction of the constituent molecules of the bacterial cell." Although it must be admitted in replying to this argument that the molecule is exceedingly small in comparison with the bacterium, and, furthermore, if it is conceded that the death of the latter occurs only after a large number of its constituent molecules have interacted with the disinfectant, yet it is possible to account for the progressive nature of the process by regarding each micro-organism as a receptacle in which a reaction is progressing by stages to completion or the death point of the individual. Again, it is no more probable that juxtapositions of bacteria and molecules of disinfectant necessary to establish this point would occur simultaneously, for all the individuals requiring, say three units of disinfectant to produce death than there would be in the case of individuals requiring but one unit of disinfectant to produce the same effect.

The nitration of toluol with the ultimate formation of *tri*-nitro toluol, $C_7H_5(NO_2)_3$, is an analogous process if the NO_2 particles are kept in excess as is conditioned in the case of the disinfectant.

If the argument is urged that this conception involves reactions of a higher order than that indicated by the formula

$$K = \frac{1}{t_n - t_o} \log \frac{N_o}{N_n}$$

attention may be directed to the well known rule of chemical kinetics that reactions of a higher order for which it is necessary to formulate more complicate equations are found to run according to formulations for reactions of much lower order. Nernst has suggested that reactions of "higher order" doubtless occur in steps or stages and that they run to completion by a series of unimolecular or bimolecular reactions and the experimental results fit into the simpler formulations. It thus appears that if the contentions of Reichenbach be granted the argument for the chemical analogy is not weakened. On the contrary, by assuming that disinfection is analogous to chemical reaction of a "higher order," rather than a reaction of the first order, as is necessitated by admitting his arguments, we are able to account for a comparative *slowness* with which the disinfection process occurs. For as the number of individuals which meet in one point before a given reaction can occur increases, the chances for juxtapositions become rapidly less. Consequently any reaction of an order higher than the second or third must be very slow indeed.

Further discussion, however, will be delayed until after the experimental data have been presented.

In undertaking this part of the work the author has attempted to follow the procedure that is ordinarily used in determining the order of a chemical reaction with a view to ascertaining whether the velocity constants obtained by observation of different disinfection processes can be calculated according to any of the formulations for the different orders of chemical reactions, the conclusion being, as has been pointed out, that if this can be done the disinfection process is probably analogous to chemical reaction.

6. Experimental

In presenting the experimental data the author has divided it into two parts:

First, that which is directly related to the establishing of disinfection as an *orderly time process*, and

Second, that which is introduced by way of further confirmation of the chemical analogy by showing the influence of variation in concentration and time on the velocity of disinfection.

(A) To Show the Progress of a Disinfection Process

General Theory.—The procedure followed in the following series of experiments undertaken to ascertain if disinfection proceeds as an orderly time-process was strictly analogous to the methods frequently used in determining the speed of a chemical reaction of the "first order"—or more accurately, a "bimolecular" reaction with one reagent in excess. In this work the reagent in excess is always, of course, the disinfectant.

Procedure.—The technique employed was a modification of the "Rideal-Walker drop method" used in standardizing disinfectants. A suitably small quantity of the diluted broth culture of the micro-organism under examination was put into a test tube containing a quantity of disinfectant solution of known concentration and then placed in an incubator regulated to any constant temperature desired. After successive definite time intervals accurately measured portions were transferred by means of a special capillary pipette from these tubes to Petri dishes and "plated" on a suitable media and incubated for two to four days, after which the colonies, representing of course the surviving micro-organisms, were counted.

In order to eliminate the possibility of introducing errors due to a fluctuating temperature caused by opening the door of the incubator the tube containing the "culture" and the disinfectant solution was sealed into a large dark-colored glass vessel. This annular air-jacket provided the insulation desired. The time to which the micro-organisms were subjected to the action of the disinfectant was determined with accuracy by transferring the measured portions to a cubic centimeter of distilled water previously placed in each Petri dish. Usually about 10,000,000 organisms were found to be present in the first portion transferred. "Cultures" six to twelve hours old were used.

In the last column of each table are given the values of the *velocity constant.* In calculating this constant it was assumed, of course, that the *rate* of disinfection is always proportional to the concentration of surviving micro-organisms.

TABLE IV

Disinfection of B. typhosus with Phenol
Concentration of Disinfectant, 0.2%. Temperature 37.5° C.
(First Series)

Time in Minutes $= t$	Mean Number[1] of Micro-organisms Surviving $= N$	Log. of Concentration $= \log_{10} N$	$K = \frac{1}{t_n - t_0} \log \frac{N_0}{N_n}$
Control $= t_0$	20400 $= N_0$	4.30	—
2	18000	4.25	—
4	11600	4.06	0.060
6	8000	3.90	0.067
8	6400	3.80	0.062
10	5200	3.71	0.059
15	2800	3.44	0.057
20	1500	3.17	0.057
25	750	2.87	0.058
30	400	2.60	0.057
35	250	2.39	0.055
40	120	2.07	0.056
45	64	1.80	0.056

TABLE V

Disinfection of B. typhosus with Phenol
Concentration of Disinfectant, 0.2%. Temperature 37.5° C.
(Second Series)

Time in Minutes $= t$	Mean Number of Micro-organisms Surviving $= N$	Log. of Concentration $= \log_{10} N$	$K = \frac{1}{t_n - t_0} \log \frac{N_0}{N_n}$
0	5800	3.76	—
2 $= t_0$	1800 $= N_0$	3.25	—
4	1360	3.13	0.060
6	1075	3.02	0.056
8	800	2.90	0.058
10	670	2.82	0.053
15	400	2.60	0.050
20	290	2.46	0.044
25	180	2.15	0.043
30	110	2.04	0.044
35	60	1.77	0.044
40	30	1.47	0.046

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[1] The "mean number" as used in this and all other tables in this paper represents the "mean" of the "count" given by three "plates."

TABLE VI

Disinfection of Anthrax Spores with Mercuric Chloride
Concentration of Disinfection, 0.1%. Temperature, 20° C.

Time in Minutes $= t$	Mean Number of Micro-organisms Surviving $= N$	Log. of Concentration $= \log_{10} N$	$K = \frac{1}{t_n - t^{o}} \log \frac{N_0}{N_n}$
Control $= t_0$	15500 $= N_0$	4.19	—
5	7200	3.85	—
10	4100	3.61	0.057
15	2200	3.34	0.056
20	1500	3.17	0.050
25	925	2.96	0.049
30	700	2.84	0.045
40	250	2.39	0.045
50	80	1.90	0.045
60	41	1.61	0.043

TABLE VII

Disinfection of Staphylococcus Pyogenes Aureus with Phenol
Concentration of Disinfectant, 0.2%. Temperature, 20° C

Time in Minutes $= t$	Mean Number of Micro-organisms Surviving $= N$	Log. of Concentration $= \log_{10} N$	$K = \frac{1}{t_n - t_o} \log \frac{N_c}{N_n}$
Control	1250	3.09	—
2	1160	3.06	0.0146
4	1090	3.03	0.0142
6	1010	3.00	0.014
8	950	2.97	0.014
10	890	2.94	0.014
15	790	2.89	0.013
20	685	2.83	0.013
25	605	2.78	0.013
30	525	2.72	0.0125
35	450	2.65	0.013
40	355	2.55	0.0136
45	325	2.51	0.0129
50	275	2.43	0.0142
55	205	2.31	0.0132

Discussion

An examination of the foregoing tables of experimental data will show that the disinfection processes are not sudden, but gradual; and that they proceed in a manner which makes possible their formulation in terms of the well-defined logarithmic law, known as the Mass Law, in terms of which chemical reactions are formulated.

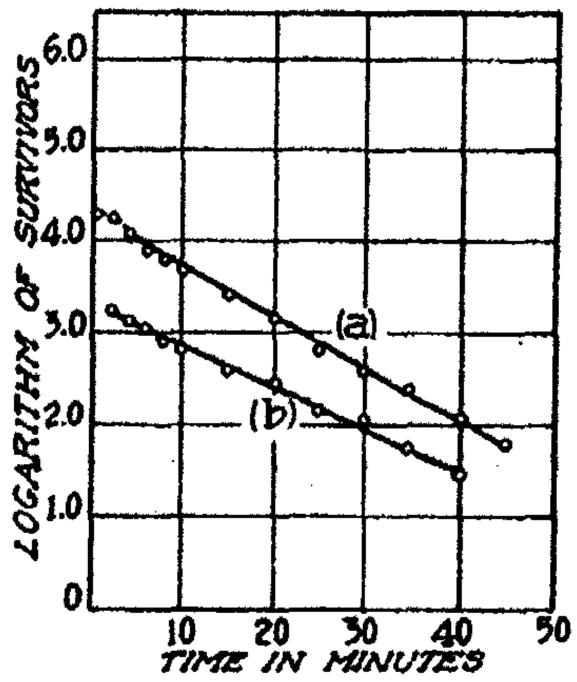

Fig. 2

Disinfection of B. typhosus with 0.2% phenol:
(*a*) First series
(*b*) Second series

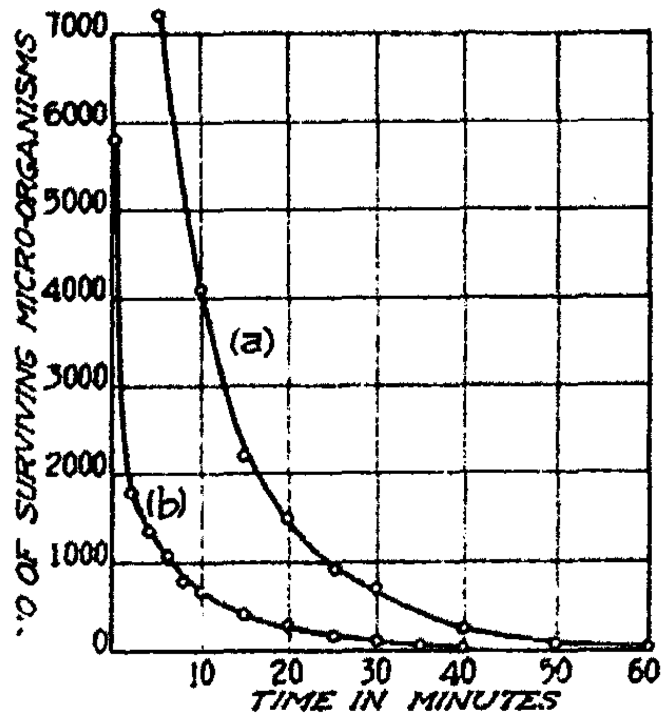

Fig. 3

Rate of disinfection of:
(*a*) Anthrax spores with 0.1% mercuric chloride at 20°C. (See Table VI)
(*b*) B. typhosus with 0.2% phenol at 37.5° C. (See Table V)

It will be noted, furthermore, that regardless of the difficulty of controlling variables peculiar to the problem owing to its nature, the velocity constants, K, are in close agreement. It is scarcely probable that such results would be reproducible if there were not an analogy between disinfection processes and chemical actions of a given "order."

The slight falling off of the rate of disinfection as the reaction progresses as observed in a few cases is rather to be expected in the case of certain "cultures" if the effects of variation in age and nature of environment are to be evaluated. The researches of Lane-Claypon[12] may be cited in support of this conclusion.

A comparison of the following graphs showing the rates of disinfection of typical examples chosen at random, with graphs of chemical reactions of the "first order" will show the marked similarity which has been predicted.

The logarithmic relationships shown in Tables IV and V are expressed graphically in Fig. 2. It will be seen that the experimentally established points lie along straight lines as would be required if the chemical analogy exists.

Disinfectant Action of Light Emitted by a 100 Watt Gas-Filled Lamp

In these experiments pure cultures of B. coli were exposed to the direct rays of light emitted by a "bulb" of the "concentrated filament" type. The "culture" was kept constantly stirred during the period of exposure by means of a stirring device. Care was exercised to locate the tube containing the "culture" at sufficient distance from the source of light to prevent any thermal effects.

The results obtained in five series of experiments were so concordant that it was a matter of indifference as to which series should be reported.

It will be seen that the concentration of survivors which was determined from time to time by means of plate cultures varies logarithmically with time; and that the velocity constant, K, remains fairly constant in value until sterilization is approximated. At this stage of the reaction a slight increase in the velocity was noted.

The authors have refrained from drawing any conclusions from this set of results until such time as it may be possible to report more fully on this type of action.

TABLE VIII

Disinfectant Action of Light Emitted from an "Electric Bulb" upon B. coli communis (Second Series)

Time in Minutes $= t$	Mean Number of Micro-organisms Surviving $= N$	Log. of Concentration $= \log_{10} N$	$K = \frac{1}{t_n - t_0} \log \frac{N_0}{N_n}$
Control	107	2.02	—
2	92	1.96	0.021
3	86	1.93	0.031
5	81	1.90	0.024
10	74	1.86	0.016
15	65	1.81	0.014
20	56	1.74	0.014
25	49	1.69	0.013
30	43	1.63	0.013
40	33	1.52	0.013
50	27	1.43	0.012
60	16	1.20	0.013

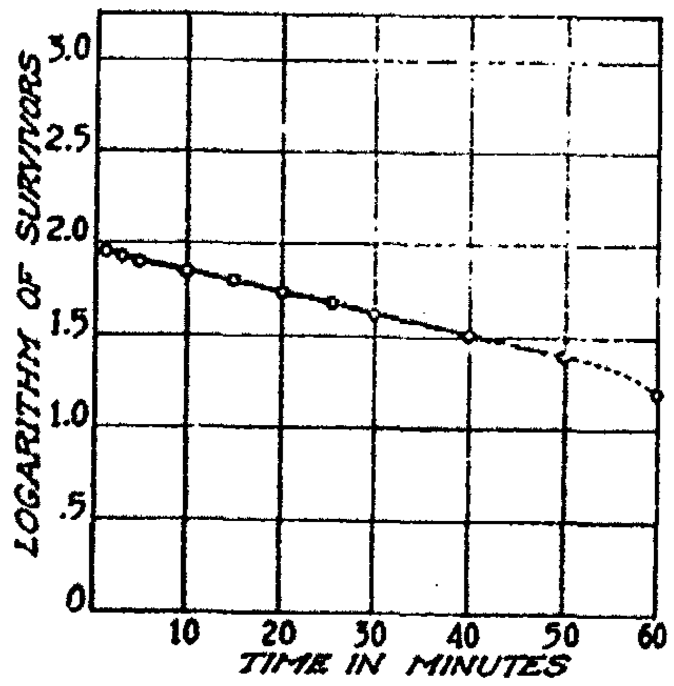

Fig. 4
Disinfection of B. coli communis by light. (See Table VIII)

(B) Effect of Variation in Temperature and Concentration upon the Rate of Disinfection

General Theory.—The periods of time necessary for the complete disinfection of a constant number of micro-organisms, of a pure culture, in various concentrations of the disinfectant at a constant temperature were measured. These periods of time were taken to be inversely proportional to the mean reaction velocities of the processes. These experiments were then repeated at other temperatures.

It is recognized that an "end-point" method is not regarded as an ideal method, but the only alternative—a comparison of the velocity constants with varying concentration of the disinfectant—would be extremely laborious owing to the very large number of experiments required.

Procedure.—In most cases about 10,000,000 micro-organisms were added to a disinfection mixture of known concentration; after definite time intervals accurately measured portions were removed and tested by the "plate" method for surviving micro-organisms. The disinfection time for a given concentration of the disinfectant was taken to be the "time of exposure" to the disinfectant mixture *of that portion* which first gave a negative or sterile plate.

TABLE IX

Effect of Variation in Concentration of the Disinfectant on the Speed of the Disinfection Process

Disinfectant, Phenol — Micro-organism, B. typhosus — Temperature, 37.5° C

(First Series)		(Second Series)	
Conc. of Phenol in Percent	Time Required for Disinfection = t Min.	Conc. of Phenol in Percent	Time Required for Disinfection = t Min.
1.5	4	1.5	4.5
1.3	9.5	1.2	10
1.0	25	1.0	26
0.9	50	0.8	75
0.7	155	0.7	155
0.6	360	0.6	360

TABLE IX—(*Continued*)

Disinfectant, Phenol　Micro-organism, Staph. pyogenes aureus　Temperature, 20° C

(First Series)		(Second Series)	
1.0	25	1.2	7
0.9	9	1.0	26
0.8	95	0.8	100
0.7	186	0.6	400
0.6	395	0.5	1200

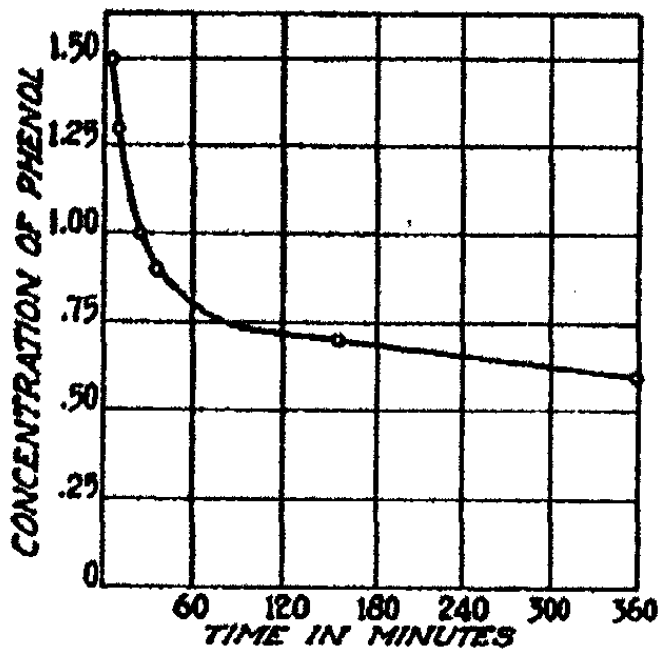

Fig. 5
Effect of the variation in concentration of phenol on the time required for the disinfection of B. typhosus. (See Table IX)

Discussion

The results obtained from this series of experiments, undertaken for the purpose of determining the influence of variation in *concentration* of the disinfectant on the reaction velocity, show a definite logarithmic relationship between the former and the latter. In all cases investigated equally concordant results pointed to the existence of this relationship, a rational interpretation of which may be rendered in terms of the chemical analogy proposed by the author.

In this connection the researches of Watson[14] are of particular significance. This worker, while engaged in a study of the effect of variation in concentration of the disinfectant on the time required for disinfection was led to the conclusion that this relationship which has been pointed out might be formulated in terms of the logarithms of the concentration of the disinfectant and the time required for disinfection. The formulation may be represented thus:

$$n \operatorname{Log} C + \log t = \text{constant}$$

in which n represents the numerical ratio of the molecules of the disinfectant to the micro-organisms, of a pure culture, which are interacting at any instant, assuming the former to be present in the system in large excess. Substituting the experimental data obtained by the disinfection of Staphylococcus pyogenes aureus with phenol, Watson found that the equation would have the form,

$$5.5 \log C + \log t = \text{constant},$$

from which he concluded that the logarithmic relationship

TABLE X

Effect of Variation in Temperature on the Speed of the Disinfection Process

Disinfectant, 0.01% $HgCl_2$ solution — Micro-organism, B. paratyphosus

Temp. of Disinfection $= T_1$	Time Required for Disinfection in Minutes	$A = \log \frac{t_2}{t_1} \cdot \frac{T_1 T_2}{T_1 - T_2}$	Temp. Coeff. for Rise of 10° C
$314.6 = T_1$	$0.75 = t_1$	—	—
303.7	2.5	4580	—
292.8	11.5	5010	—
286.9	36.0	5480	—
279.8	50.0	4610	—
273.0	101.0	4390	—
		Mean, 4810	3.0
Disinfection of B. paratyphosus with 0.6% phenol			
$308.7 = T_0$	$9.0 = t_0$	—	—
303.5	27.5	8650	—
301.0	47.5	8660	—
298.0	95.0	8750	—
294.0	251.0	8890	—
289.0	350.0	7180	—
279.0	600.0	—	—
		Mean 8430	7.5

will not be maintained unless the *interacting* particles of phenol and Staphylococcus pyogenes aureus are in the ratio of 5.5 to 1.

The values for *n* were found to be 4.9 and 3.8 for the disinfection by mercuric chloride (Hg ions) of anthrax spores and B. paratyphosus, respectively.

On substituting the data presented in Table X,—disinfection of B. paratyphosus with phenol, the author found that by giving *n* a value of 6 that the constants so calculated were in close agreement.

In concluding this discussion the authors would call attention to the fact that this equation of Watson has not been introduced with the thought that it should be accepted without further application, although it does hold fairly well for that type of chemical reaction in which one molecule of one factor is interacting with *n* molecules of the other factor, the latter being present in considerable excess.

Discussion

In undertaking the work to determine whether the influence of variation in temperature on the velocity of the disinfection process is similar to that on the velocity constants of certain types of chemical reactions, it was finally decided to subject the results to the tests of the empirical formulation for "*irreversible*" reactions at different temperatures, known as the "law of Arrhenius,"[13] which may be formulated as follows:

$$\log \frac{Kt_2}{Kt_1} = A\left(\frac{1}{T_1} - \frac{1}{T_2}\right).$$

On adapting it to the process of disinfection it becomes

$$\log \frac{t_2}{t_1} \cdot \frac{T_1T_2}{T_1 - T_2} = A$$

in which T_1 and t_1 represent the initial (maximum) absolute temperature at which the disinfection is originally run, and t_1 the time required for disinfection at that temperature, respectively; T_2 and t_2 represent the latter (also lower) absolute temperatures of disinfection, and times required for disinfection at these temperatures, respectively.

The experimental data reported in the preceding tables indicate that the speed of the disinfection process is influenced by temperature in a manner which seems to be in close accord with this law.

Furthermore, the disinfectant processes show a marked similarity to chemical action in that they may be divided into groups according as their velocity constants are influenced in a relatively slight or marked degree by variation in temperature. This is particularly true of the inorganic disinfectants, like mercuric chloride and silver nitrate, which have temperature coefficients varying from 2 to 4 for 10° C. change of temperature over the range from 20° C. to 40° C.

In the case of the organic disinfectants like phenol and other coal-tar derivatives the temperature coefficients are much larger as a rule, ranging from 7 to 15 for a rise of 10° C. It is worthy of note that the temperature coefficients of these disinfectants vary with the concentration.

Summary and Conclusions

1. An effort has been made to present a brief outline of the historical development of the existent theories of disinfection.

2. It has been proposed to group all these theories into two classes,—namely, "vitalistic theories" and "mechanistic theories."

3. The various theories have been subjected to analysis and criticism in the light of data obtained by calculation of results obtained by a number of investigators working independently of one another, and from investigations conducted in this laboratory.

4. In view of the experimental evidence which has been presented, disinfection, in the opinion of the authors, must be regarded as *an orderly time-process which is closely analogous to chemical reaction,*—the micro-organisms and the disinfectant being regarded as the respective reagents.

5. A definite logarithmic relationship between velocity of disinfection and concentration has been found to exist in all cases investigated. Likewise, the values for K, the velocity constant, have been in close agreement in each case.

6. Further confirmation of the foregoing conclusions has been presented by showing that the reaction velocity of disinfection is influenced by variations in temperature and concentration in an orderly manner in accordance with the Mass Law.

7. The explanation why disinfection is not sudden, but gradual, and proceeds in close agreement with the well defined logarithmic law, known as the Mass Law, is best found in those chemical processes which proceed as "uni-molecular" reactions. The explanation offered by the chemist in the case of this type of reactions is that at any given time only a proportion of the molecules of the intereacting substances are in a position or condition to participate in the reaction. This *proportion* of molecules, however, capable of interacting at any moment is a *constant.*

The process of disinfection may be explained according to a similar hypothesis. Owing to changes in bacterial constituents only a certain number of individuals are in a condition to be attacked by the disinfectant at a given time, but the total number of individuals in such a condition at any moment represent *a constant proportion* of the surviving micro-organisms.

8. The objections of Reichenbach to the "mechanistic" conception have been considered and it has been pointed out in reply that it is not necessary to regard the disinfection process as a reaction of the "first order" but as a reaction of "higher order" viewed as Nernst has suggested, in which case the foregoing objections as stated are at least polemically eliminated. Likewise the "theory of graded resistance" as advanced by Eijkman, Hewlett and Reichel has been reviewed and attention has been directed to the fact that biological characteristics are distributed as a rule in a manner quite different from that which they have assumed in formulating their theory.

9. In view of these observations, the authors are led to the conclusion that the *logarithmic nature* of the disinfection process is due to a *general similarity* of the individuals in a *given pure culture* of micro-organisms rather than to a *dissimilarity* of the individuals as postulated in the theories of graded resistances by the supporters of the "vitalistic theory." There is some evidence at hand, however, which indicates, there may be a difference in the degree of resistance possessed by the individuals of different pure cultures depending perhaps on their respective ages, temperatures of incubation, etc.

10. Finally, the authors would point out that whereas the work of Chick and Martin, Browning and Gilmour,[26] and Churchman[27] indicates the *specificity* of disinfectants, *i. e.*, that certain disinfectants possess specific bactericidal action toward different species of bacteria, this behavior is to be expected if the disinfection process is analogous to chemical action. For in the application of the principle as well as in the general formulation of the Mass Law the influence of the "affinity factor" is always taken into account by the chemist. For example, "Interactions of substances depend not only upon the *affinities* involved but also upon the active mass of the substance in a unit volume"—represents one of the familiar forms of stating this law.

Churchman's experiments, in particular, showing the selective affinity of gentian violet for only one of five strains of B. enteritidis possess added significance in this connection as indicating the degree in which current ideas of the action of disinfectants and the methods for their standardization may be modified by the introduction of the conception of *chemical affinity*.

Therefore, if the disinfection process be considered from the viewpoint of either one or all of the factors determining *chemical action*, namely chemical affinity, temperature, and concentration effect, there seems to be much data at hand to support the "mechanistic theory."

Further work in this field is contemplated.

REFERENCES

1. Bellei: Münch. med. Woch., No. 7 (1904).
2. Eijkman: Biochem. Zeit., **11**, 12 (1908).
3. Hewlett: Lancet (March 13, 20, 27, (1909)).
4. Reichel: Biochem. Zeit., **22**, 149 (1909).
5. Reichenbach: Zeit. Hyg., **69**, 171 (1911).
6. Chick: Jour. Hyg., **10**, 237 (1910).
7. Madsen and Nyman: Zeit. Hyg., **57**, 388 (1907).
8. Chick: Jour. Hyg., **8**, 92 (1908).
9. Cooper: Biochem. Jour. (1912).
10. Krönig and Paul: Zeit. Hyg., **25**, 1 (1897).
11. Rideal and Walker: Jour. Roy. San. Inst., **24**, 424 (1903).
12. Lane-Claypon: Jour. Hyg., **9**, 239 (1909).
13. Arrhenius: Zeit. phys. Chem., **4**, 226 (1889).
14. Watson: Jour. Hyg., **8**, 536 (1908).
15. Rideal: "Disinfection and Disinfectants."
16. Am. Jour. Pub. Health, **2**, (1912); **3**, (1913), 4 (1914).
17. Bull. Hyg. Lab., No. 82 (1912).
18. Pub. Health Bull., No. 42 (1910).
19. Abbott: "Principles of Bacteriology" (1910).
20. Marshall: "Microbiology" (1917).
21. Arrhenius: "Immuno-Chemistry" (1913).
22. Fowler: "Bacteriological and Enzyme Chemistry" (1911).
23. Koch: "Ueber Desinfection, Mitt. Kaiserl. Gesundheitsamte, 1."
24. Rosenau: "Disinfection and Disinfectants."
25. Jour. Infectious Diseases, **8**, No. 1 (1911).
26. Browning and Gilmour: Jour. Path. and Bact., **18**, 144 (1913).
27. Churchman: Jour. Exper. Med., **16**, 221, 822 (1913).

Meadville, Penna.

THE SIGN OF THE ZINC ELECTRODE

BY WILDER D. BANCROFT

The German physical chemists have changed their position several times as to the sign to be applied to the zinc electrode. In 1887, Ostwald[1] used the minus sign. "Zinc and cadmium are negative in all the acids tried and copper, antimony, bismuth, mercury, and silver are positive in all, while tin, lead, and iron show positive and negative values of 0.1–0.2 volt. The average potential for zinc is —0.7 volt, for cadmium —0.3, for tin, lead, and iron ±0, for copper +0.3–0.4, for bismuth +0.4, for antimony +0.3, for silver +0.5, and for mercury +0.8." Ostwald takes the potential of the solution as zero, p. 600.

In 1893, Ostwald[2] uses the plus sign with zinc, probably because Nernst had developed the idea of solution pressure and zinc had a positive solution pressure. "The values in volts for the single potentials of a number of the more important metals in solutions containing one gram-atom of the metal per liter are: Mg +1.22, Zn +0.51, Al +0.22, Cd +0.19, Fe +0.06, Pb —0.10, Cu —0.60, Hg —0.99, Ag —1.01. The values are given from the metal to the electrolyte, the potential of the metal being called zero. The plus sign with zinc denotes that the electrolyte is charged positively with respect to zinc. If one counted from the electrolyte to the metal, one would call the zinc potential negative."

LeBlanc[3] adopts the same point of view in 1896. "We will call the potential of the metal or the electrode zero, in which case the plus or minus sign shows whether the electrolyte is positive or negative with respect to the electrode. We must, therefore, say Hg | Hg_2Cl_2 in *N*/1 KCl = 0.56 volt .... and Zn | *N*/1 $ZnSO_4$ = +0.52 volt." In 1900,

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[1] Zeit. phys. Chem., 1, 604 (1887).

[2] Lehrbuch allgem. Chemie, 2 II, 946 (1893).

[3] Lehrbuch der Elektrochemie, 177 (1896).

Nernst,[1] Wilsmore[2] and Ostwald[3] all use a plus sign with the zinc electrode and a minus one with the calomel electrode. Another change was foreshadowed in 1905 when Luther[4] wrote: "I consider it very advisable to put a plus sign before the potential difference when the electrode in question is positive to the zero electrode, whether that be the calomel electrode, the hypothetical flowing electrode, or the extrapolated hydrogen electrode."

None of the books now accessible show when the Bunsen Society adopted this suggestion; but in 1915, Foerster[5] writes: "To show the direction of the electrical polarity between metal and solution we place before the value of the difference of the two potentials, the so-called potential of the metal, the sign of the charge on the metal. When dipped in solutions of their own simple salts or of acids, the readily oxidizable metals such as Al, Mg, Mn, Zn, Cd, Tl, Fe, acquire a negative potential, while the less readily oxidized, or noble metals such as Cu, Hg, Ag, acquire a positive charge.[6] Volta arranged his first cell, Cu, Zn, H_2SO_4, Cu, Zn, and consequently the copper carried off the negative charges and the zinc the positive charges. Because of this, Berzelius called the readily oxidized metals electropositive. This nomenclature remained unchanged even though the error of Volta's arrangement was soon corrected. In consequence, for a long time—and also in the first edition of this book—the sign of the potential of the solution was made the same as the charge on the solution and the potential of the zinc was, therefore, called positive.[7] Especially for students, the difficulties were so great in a point of view whereby the negative current flowed from a positive electrode, that it became necessary to adopt the recommenda-

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[1] Zeit. Elektrochemie, 7, 254 (1900).

[2] Zeit. phys. Chem., 35, 291 (1900).

[3] Ibid., 35, 333 (1900).

[4] Zeit. Elektrochemie, 11, 780 (1905).

[5] Elektrochemie der wässerigen Lösungen, 125 (1915).

[6] [The rest of this paragraph is a foot-note in the original, but that seems unnecessary here.—W. D. B.]

[7] [Foerster has overlooked Ostwald's position in 1887.—W. D. B.]

tion of the Bunsen Society to denote the potential in accordance with the charge on the electrode."

All the Germans now use the minus sign for the potential of zinc in zinc sulphate solution, and so do the English. In this country the practice is by no means uniform as may be seen from the rather acrimonious discussion at Detroit.[1]

Lewis[2] came out strongly some years ago in favor of using the plus sign for the zinc electrode. "On account of the importance in free energy calculations of those chemical reactions which occur in a voltaic cell during the passage of a current, it is very desirable that suitable conventions be adopted for the sign of an electromotive force, or of a single potential difference. It is not sufficient to state that a cell composed of cadmium amalgam, saturated cadmium sulphate solution, mercurous sulphate, and mercury gives an electromotive force of 1.0183 volts at 20°; for a person unacquainted with the cadmium cell would not know whether the cell would do work through the consumption of cadmium and the deposition of mercury or *vice versa.* We may, however, in this as in other cases, eliminate any ambiguity by writing the chemical equation,

$$\mathrm{Cd}(12.5\%\ \text{amalg.}) + \mathrm{Hg_2SO_4}(s) + 8/3\mathrm{H_2O}\ (\text{saturated with}\ \mathrm{CdSO_4}\ 8/3\mathrm{H_2O}) = \mathrm{CdSO_4}\ 8/3\mathrm{H_2O}\ (s) + 2\mathrm{Hg}\ (l)$$

and now if we say that at 20° the E. M. F. is 1.0183 volts, the positive sign will indicate that the cell is capable of doing work when the reaction runs from left to right. So also we write for the reaction

$$^1/_2\mathrm{Hg}(g) + {}^1/_2\mathrm{Cl_2}(g) = \mathrm{HCl}\ (0.1\ M);\ E = +1.4881\ \text{at}\ 25°$$

meaning that work is done by a cell in which hydrogen and chlorine combine to form hydrochloric acid in 0.1 M solution. Instead of writing the chemical reaction in such a case, we may express the same facts in another way, which shows better the actual construction of the cell in question. The form

$$\mathrm{H_2}(g),\ \mathrm{HCl}(0.1\ M),\ \mathrm{Cl_2}(g);\ E = +1.4881$$

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[1] Trans. Am. Electrochem. Soc., 31, 249–255 (1917).

[2] Jour. Am. Chem. Soc., 35, 1, 25 (1913).

expresses the same facts. In such an expression *the positive E. M. F. indicates the tendency of the positive current to run through the given cell from left to right.......*

"The committee of the Bunsen Gesellschaft has adopted two symbols E_c and E_h for electrode potentials measured against the two standards, the normal calomel electrode and the normal hydrogen electrode. The potentials, as given in the following papers, based upon the standard above defined, are approximately equal to E_h except for sign. The Bunsen Gesellschaft makes the potential of sodium negative, and that of chlorine positive. I have adopted the opposite sign in conformity with the older and more common usage. Exactly what the committee means by the normal hydrogen electrode they have not stated. The potential of hydrogen against a normal solution of hydrochloric or of sulphuric acid is a perfectly definite thing, but the potential of hydrogen against a solution normal in hydrogen ion must depend upon some assumption regarding the degree of dissociation, and different views will lead to values differing by 5 or 10 millivolts."

We are all agreed that electricity tends to flow from a place of higher potential to a place of lower potential, but that is not sufficient to enable us to settle the problem. In the Daniell cell the so-called positive current flows from the copper to the zinc outside the cell, from which we may deduce that the potential of copper is higher than zinc. On the other hand, the positive current flows from zinc to copper inside the cell, from which we may deduce that the potential of zinc is higher than that of copper, and we are no further ahead than before. The physicists have been interested in the current outside the cell and consequently they call the copper pole the positive one. The engineers have followed the lead of the physicists and call the positive pole of the dynamo the one where the positive current comes out of the machine. This brings the dynamo and the primary cell into line when considered as sources of electrical energy. It is also the point of view adopted officially by the Bunsen Society, and unofficially by the English electrochemists. It is apparently the only point of view which can possibly be adopted universally. On the other hand, it is one that is repugnant to chemists at first sight. Zinc precipitates copper from a copper sulphate solution, and, therefore, has a higher potential than copper. This is the side of the problem which appeals to Lewis, for instance. He knows that the free energy of zinc is greater than that of copper. I sympathize fully with Lewis' point of view and if there were no way out of the dilemma, I should be inclined to break with the physicists rather than to sacrifice a fundamental tenet of chemistry.

As I see it now the difficulty is not a real one. We know that the electromotive force of a reversible cell is a measure of the chemical potential, or chemical affinity, and I have made the mistake in the past of assuming that since the values were the same the signs must also be. The whole difficulty disappears if we say that the chemical potential of zinc in the Daniell cell is higher than that of copper while the electrical potential of copper is higher than that of zinc. When a piece of zinc is dipped into a zinc sulphate solution, some of the zinc goes into solution as ion, charging the solution positively and leaving the zinc charged negatively. A positive current tends to flow from the solution, the place of higher electrical potential, to the zinc, the place of lower electrical potential; but no current does flow because the electrical potential from the solution to the metal is balanced by the chemical potential from the metal to the solution. If we dip a piece of copper into a copper sulphate solution, we usually consider that some copper ions are precipitated on the copper charging the copper positively, and leaving the solution charged negatively. No current flows after the charging current because, by hypothesis, the positive electrical potential difference from metal to solution is balanced by the chemical potential difference from the copper sulphate to the copper. When the zinc and copper electrodes are joined metallically, a current flows from the copper to the zinc and the chemical reaction regenerates the electrical potential difference continually. Neglecting a possible potential difference between the zinc sulphate and copper sulphate solutions, the electrical potential in a Daniell cell on closed circuit drops from the zinc sulphate solution next the zinc electrode to the copper sulphate solution at the copper electrode. Here it is pumped up by the chemical energy if the copper is positive to the solution on open circuit. From the copper electrode the electrical potential drops through the metallic circuit to the zinc electrode which is the place of lowest electrical potential in the whole circuit. Here the chemical energy of the zinc pumps up the electrical potential to the old level and so forth. While the zinc electrode is always the place of lowest electrical potential in the circuit, the place of highest electrical potential will vary with the conditions under which the cell is operating. If the internal resistance is low and the external resistance is high, the drop of electrical potential through the solutions will be less than the rise of potential at the copper electrode and consequently the copper electrode will be the point of highest electrical potential in the system. The limiting case is, of course, when the cell is on open circuit. If the internal resistance is very large and the external resistance practically negligible, the place of highest electrical potential will be the zinc sulphate solution in immediate contact with the zinc electrode, because the drop of potential through the solution is greater than the rise of potential at the copper electrode. If we have a cell of the Daniell type, Zn | $ZnSO_4$ | $CdSO_4$ | Cd, where cadmium is also charged negatively and the solution positively by definition there will be a fall of electrical potential when passing from the cadmium sulphate solution to the cadmium electrode, and consequently the place of highest electrical potential will always be in the zinc sulphate solution right next the zinc electrode, though the drop of potential from here to the cadmium sulphate solution in contact with the cadmium electrode will be practically zero when the cell is on open circuit.

When the electrodes form positive ions, the metal with the higher chemical potential, or the greater free energy, becomes the anode. With electrodes which form anions, the reverse will, of course, be true and the substance with the greater free energy will form the cathode. Bromine sets free iodine from iodide solutions and, therefore, has the greater free energy. In a cell with iodine and bromine electrodes, the bromine electrode is the cathode. It is interesting to note that this whole argument was given in a very condensed form by Gibbs.[1] "When all the conditions of equilibrium are fulfilled in a galvanic or electrolytic cell, the electromotive force is equal to the difference in the values of the [chemical] potential of any ion or apparent ion at the surface of the electrodes multiplied by the electrochemical equivalent of that ion, the greater [chemical] potential of an anion being at the same electrode as the greater electrical potential, and the reverse being true of a cation."

The general results of this paper are as follows:

1. The chemical potential of the zinc in the Daniell cell is greater than the chemical potential of the copper, but the electrical potential is less.

2. With electrodes which form cations the electromotive force is a measure of the difference of the chemical potentials, but has the opposite sign; with electrodes which form anions the two potentials have the same sign.

3. Since the electrical potential of the copper in the Daniell cell is higher than that of the zinc, and since the zinc electrode is the place of lowest electrical potential, though highest chemical potential, we ought to use the minus sign when speaking of the electrical potential difference Zn | $ZnSO_4$.

4. Calling the zinc potential minus is in line with the practice of all physicists, of the Bunsen Society, and of the Faraday Society.

5. The distinction between chemical potential and electrical potential was stated concisely by Gibbs.

Cornell University

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[1] Scientific Papers, 1, 333 (1906).

NEW BOOKS

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Theoretical and Applied Colloid Chemistry. *By Wolfgang Ostwald. Translated by M. H. Fischer. 23 × 16 cm; pp. xvi + 232. New York: John Wiley and Sons, Inc., 1917. Price: $2.50.*—This book is based on lectures given by the author in America during the winter of 1913–1914. In the preface the author says: "There already exist a number of strictly scientific text-books treating of colloid chemistry and a number of more or less valuable introductions to colloid chemistry of a popular or semi-popular nature. So far as I know, however, none of these has tried to establish the right of modern colloid chemistry to existence as a separate and independent science while emphasizing at the same time its great possibilities of scientific and technological application. The attempt to give a general survey of modern colloid chemistry as a pure and as an applied science and in a form readily intelligible to the general reader seems to be new."

The first lecture deals with: fundamental properties of the colloid state; colloids as examples of dispersed systems; methods of preparing colloid solutions. The subjects treated in the second lecture are: classification of the colloids; the physico-chemical properties of the colloids and their dependence upon the degree of dispersion. The third lecture is devoted to the changes in state of colloids and the fourth lecture to some scientific applications of colloid chemistry, while some technical applications of colloid chemistry are discussed in the fifth lecture.

The lectures must have been very interesting ones to attend because of the large number of surprisingly good experiments which were shown. Since these lectures were primarily popular ones, their first mission was to be interesting. How successful they were in this respect may be judged from the following quotations, pp. 179, 187:

"The clothes you wear are plant gels, be they wool, cotton, or silk. They are dyed with colors which are often colloid in type, as the indigos and the blacks for instance. In the process of dyeing, adsorption and other colloid-chemical reactions take place between the colloid substrates of the fabrics and the colloid dyes which color them. The leather of your shoes is an animal gel, closely related in its general properties to that prototype of the colloids, gelatine. Leather is tanned with substances of which the majority are colloids, and the whole process of tanning is punctuated with the colloid phenomena of hydration, dehydration and adsorption. The wood of the chairs in which you rest is made of cellulose, which in all its various forms is colloid in nature. The colloid swelling of wood, as I emphasized earlier, was used by the old Egyptians to aid their quarrying of stone. The woods of your chairs are held together by glue or with metals. You already know glue to be a colloid; but it may surprise you to learn that colloid chemistry has much to say in metallurgy and that steel, for instance, is a colloid solid solution. The paper upon which you write is essentially cellulose, in other words, again colloid. It has been given a body by being mixed with water-glass, with rosin or some similar material, in other words with various colloids. The ink in your fountain pens is probably also colloid if it is the ordinary iron tannate, and colloid, too, is the hard rubber of your penholders, prepared from that notoriously colloid mother-substance, soft rubber.

"I could continue this list indefinitely, pointing in this manner to one colloid after another in your immediate surroundings and belonging to the things of your every-day life. Perhaps you think—perhaps since yesterday's lecture you think you know—that I am possessed of a colloid mania because I see colloids everywhere. Let me admit that I do see colloids everywhere, only I do not believe that because of this I must be adjudged insane. It is simply a fact that *colloids constitute the most universal and the commonest of all things we know*. We need only to look at the sky, at the earth, or at ourselves to discover colloids or substances closely allied to them. We begin the day with a colloid practice—that of washing—and we may end it with one in a bedtime drink of colloid tea or coffee. Even if you make it beer, you still consume colloid.....

"An interesting illustration of color due to a colloid element is seen in the case of *ultramarine*. There still rages an old debate concerning the causes for the color in this mixture of different silicates, borates, etc., with sulphur or sulphur compounds. Even recently, nothing short of desperate efforts have been made to explain the color of this dye substance on the basis of its 'chemical constitution.' I say desperate because not only are the quantitative relationships found in the different ultramarines totally different; but uncolored, gray, yellow, red, blue, and even green ultramarines can be produced by heating the normal ultramarine. On the basis of differences in chemical constitution we would have to assume that each of these different colors represented a different chemical compound.

"What we observe is entirely analogous to what we discussed previously when dealing with the photohalides. We can produce blue and green solutions of sulphur by simply introducing this element into molten sodium chloride, into a borax bead, into liquid ammonia, or into hot organic liquids like glycerine. These facts render it most improbable that ultramarine is blue because of the existence in it of a specific blue sulphur compound. We have therefore come to the conclusion that ultramarine represents a solid solution of highly dispersed sulphur. The degree of dispersion may oscillate between molecular and colloid dimensions, and as this happens there are produced the different colors discussed above, which represent different degrees in the dispersion of the element sulphur.

"Of the many facts which confirm this view, I would like to emphasize the analogy between the production of ultramarine and the production of ruby glass, of blue rock salt, etc. In making ultramarine the necessary salts and the sulphur are melted together at a high temperature. This yields the grayish white or yellowish 'mother of ultramarine.' This product is then reheated, cooled, and reheated again, just as in the case of ruby glass, until the requisite color is obtained. The original product is obviously a molecularly dispersed solution, the particles of which, through reheating, are permitted to condense to colloid dimensions. Support for the correctness of this view may be found in mineralogy. Mineralogists are familiar with a complex, sulphur-rich, silicate compound known as haüynite, which appears in different colors ranging from colorless to green and blue. It has been shown that the colorless varieties may be colored blue or green by heating them with sulphur in a closed tube, an experiment entirely analogous to the production of blue rock salt by heating this with metallic sodium. There exist reasons for believing that with many of the so-called sulphur dyestuffs (dyes produced by melting together sulphur and different organic compounds in the presence of alkali) we have also to do with similar solid solutions of highly dispersed sulphur. There certainly exists little hope of explaining their colors on the basis of chemical constitution. Let me, in passing, emphasize that the alkali used in the preparation of either the inorganic or the organic sulphur systems tends to increase their degrees of dispersion. In other words, it has a peptizing or stabilizing influence." *Wilder D. Bancroft*

6 **Laboratory Manual of General Chemistry.** *By William J. Hale. 19 × 13 cm; pp. xii + 474. New York: The Macmillan Company, 1917. Price: $1.50.*—In the preface the author says: "In experimental general chemistry we find but few laboratory manuals which make any pretense to a general systematic study of the elements. Whatever criticism they may have received must lie primarily in the lack of correlation of the experimental work, for the fact remains that modern chemistry demands a thorough and rigorous training in experimental general chemistry as a prerequisite for all other courses in the science."

It is evident to anybody who does not teach general chemistry that one should emphasize somewhat the reactions which are to be used later in qualitative analysis. It is one of the good features of this manual that this point is kept in mind throughout. The author has a strong prejudice against note-books and has arranged this manual so that each question must be answered in a small blank space on the opposite page. This ingenious method does not appeal to the reviewer at all. The student will never use it in later life because his problems do not ordinarily appear in the form of printed questions. The only advantage of the form adopted by the author seems to be a financial one, because the manual cannot be resold to a subsequent freshman. Another idiosyncrasy is the use of the word ionogen instead of electrolyte.

The reviewer has noted but few actual errors. Copper is not obtained when a cupric chloride solution is electrolyzed, p. 172, and nickel does not ordinarily precipitate copper from solutions of copper salts, p. 468. It hardly seems a good illustration of filtration to boil a solution of litmus with powdered charcoal and then filter, p. 46. The showy part of the experiment illustrates something else. It is true but obscure to say that an increase in the volume of the solvent reduces the concentration of the ionic substances and, therefore, increases the dissociation, p. 156. The reviewer is unable to answer Question 3 about distillation, p. 45; but perhaps the student can. *Wilder D. Bancroft*

10 **Standard Table of Electrochemical Equivalents and Their Derivatives.** *By Carl Hering and Frederick H. Getman. 19 × 12 cm; pp. vii + 130. New York: D. Van Nostrand Co., 1917. Price: $2.00.*—In the preface the authors say: "The chief purpose of this publication is to serve as a reference book on account of the tables and other data given in it, and not as a treatise on electrochemistry in general; sufficient explanatory text has, however, been added to enable the data to be used for most purposes without the need of further treatise on the subject. To make the data available also to the student, electroplater, engineer, and others who may not have made a special study of chemistry and electrochemistry, the descriptive text has been given in elementary and easily understood terms."

The subject is presented under the following headings: fundamental laws; fundamental data and description of the tables; electrochemical equivalents by weight; grams per ampere hour in the order of magnitude; electrophysical equivalents by volume; valences of the elements in their combinations; calculations involving electrochemical equivalents; electrolysis; the electronic theory; valence; elementary principles of chemical reactions and calculations; conversion factors used in electrochemical calculations; glossary of terms.

The tables are admirable and the chapter on the electronic theory is good, though incomplete. The rest of the text is interesting chiefly as showing what the senior author considers a simple and helpful way of presenting things. The reviewer is quite unable to do justice to the eccentricities of the text otherwise than by quoting a few passages, pp. 1, 5, 103, without comment.

"The simplest and most basic law of electrolysis refers to the elements when they are in their gaseous state, or in the state of vapor. When in this state it is true alike for every element that to set free a liter of this gas or vapor requires the same constant amount of electricity in coulombs or ampere-hours when there is one atom to the molecule and when the change of valence is unity. For those elements in which there are two or more atoms to the molecule it will require two or more times this constant quantity of electricity, in direct proportion; and for any other change of valence the constant must also be increased in direct proportion......

"The valence of any element in its free, uncombined state must be considered to be zero, because the term valence, in Faraday's law at least, must be interpreted to mean the number of bonds per atom which hold it in combination with another element; hence, when the element is no longer combined, these bonds, of course, no longer exist. Therefore, when an element has been set free by electrolysis it means that it has changed its valence from what it had in that compound to zero; in that specific case, therefore, and only in that case, is the valence numerically equal to the change of valence and it is only this particular case and not the more general one, that the text-books can refer to when they give Faraday's law in terms of valence instead of more broadly and more correctly in terms of the change of valence.......

"According to the more modern electronic theory, however, it is the negative electricity which is conceived to flow in the opposite direction, a positive charge being then the result of a loss of negative electrons; a loss of a charge, therefore, means that it was a negative charge. And according to the modern dissociation theory, before any current is applied and before they reach the electrodes the ions have already been dissociated or ionized, whereby they have received their charges; dissociation means decomposition, hence a reduction of the cation. The true chemical reduction of the cations, therefore, really took place during this process of dissociation, and as they are then left with a positive charge there has been a reduction or *loss* of *negative* electrons during the actual chemical reduction. The final freeing of an element is not an essential part of reduction; ferric salts are correctly said to be reduced to ferrous, yet nothing is set free thereby. The final freeing of the dissociated ions is a different and subsequent process, and is not the real reduction." *Wilder D. Bancroft*

An Elementary Study of Chemistry. *By William McPherson and W. E. Henderson. Second revised edition. 19 × 14 cm; pp. xii + 576. Boston: Ginn & Company, 1917. Price: $1.00.*—Some alterations have been made in the presentation. "Carbon and carbon dioxide are presented at an earlier point; the chapter on neutralization is preceded by a brief chapter devoted to a metal (sodium) and a base (sodium hydroxide), and one devoted to a non-metal (chlorine) and an acid (hydrochloric acid); the space given to the compounds of carbon has been extended a little, and the material has been brought forward into its appropriate place in the text."

In the chapter on the colloidal state, the authors mention sols and gels, coagulation of colloids, preparation of colloidal sols, colloids and hydrolysis, nature of colloids, colloids and the industries, emulsions, and fogs. On p. 386 the authors say: "It is probable that each particle of a typical colloid consists of thousands of molecules, but that these are clumped together without any special order. When the particles assume an orderly arrangement, they constitute *crystals*, and crystalline particles continue to grow in size, precipitating from the solution in definite solid form. On the other hand, the colloid clumps tend to form networks or sponge-like forms that enclose water and constitute jellies." *Wilder D. Bancroft*

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Practical Pyrometry. *By E. S. Ferry, G. A. Shook, and J. R. Collins. 20 × 15 cm; pp. vii + 147. New York: John Wiley and Sons, Inc., 1917. Price: $1.50.*—This book is primarily a text-book for a course in high temperature measurements required of students of chemical engineering at Purdue University. The preface states also that it is designed to meet the needs of technically trained men dealing with processes requiring such measurements, and for less-trained observers who may make the measurements.

The physical principles underlying the measurement of temperatures by resistance pyrometers, thermocouples, radiation and optical pyrometers are described in the standard manner of a text-book in physics. The likeness to a text-book of physics is further manifest by the rigid exclusion of any discussion of how to apply a pyrometer to any sort of industrial furnace. There is a page and a half of generalities on "the selection of pyrometers for particular uses." After assimilating this book one could write a good report on the subject in a college course in physics; but he would have to look farther for useful information on how to install and protect his apparatus in order to get correct readings and reasonable life in industrial work. Evidently the student is not supposed to desire any further information on any point covered by the book, for there is an entire absence of references to the literature.

The subject is neither so fully, practically, nor interestingly covered as is done by Burgess. The book might satisfy a pure physicist, but the chemist who needs it at all needs a lot that is not included which is just as important to him as what has been set forth. A book that would live up to the title "Practical Pyrometry" would be a distinct acquisition, but in this case the title is camouflage. *H. W. Gillett*

HAIL AND DUST

BY WILDER D. BANCROFT

Under the heading solid and gas, the behavior of suspended dust is the most important item. As an intermediate step between fog and smoke we have the precipitation of water vapor in a solid form as snow, sleet, or hail. Moore[1] points out that "when the dew point is decidedly below freezing, the particles of water vapor condense directly as crystals of ice, ice needles, or snow flakes. When the spherules are warm and rise into colder air they may cool to 32° F. and change to crystals of ice, or, more frequently, they cool too far below the freezing point without turning to ice. These subcooled water spherules will, however, suddenly turn into ice as soon as they touch one another or any cold solid or liquid surface. When subcooled raindrops strike solid substances they cover these with a coating of transparent ice, but when ordinary rain falls through great depths of ice-cold air it freezes to solid ice spheres or 'sleet' and accumulates on the ground without forming icy coatings."

It is generally recognized that the production of hail requires the occurrence of ascending air currents of considerable velocity.[2] "Hail is a frequent accompaniment of thunderstorms. It is generally recognized that, with the exception of fine-grained watery hail, hail falls only during thunderstorms. The electrical discharges are distinctly characteristic; lightning flashes are very frequent, almost incessant, while the thunder is not loud, merely a continuous grumble. The discharges appear to take place only between the clouds and to be of light intensity. In most cases hail falls at the beginning of the storm and the rain comes later. Although the hail begins with the storm, there is not always hail along the

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[1] "Descriptive Meteorology," 205 (1910).

[2] Muller-Pouillets Lehrbuch der Physik, 3 IV, 908 (1917); cf. Simpson: Phil. Trans., 209A, 406 (1909).

whole path of the storm; usually the path of the thunderstorm is much broader than that of the hail storm.

"Any attempt to account for the formation of hail must deal chiefly with the answers to two questions. How is it that we get a formation of ice at the warmest season of the year and during the hottest hours of the day? What prevents the hailstones from falling until they have had time, in some cases, to grow to an enormous size?

"The first question is relatively easy to answer in view of our present knowledge in regard to the temperatures prevailing at different levels and to the changes taking place in ascending masses of moisture. From balloon ascensions we know that in summer (May to August) the following temperatures prevail at heights of 4 to 10 kilometers even in the hottest hours of the day:

Height in kilometers	4	5	6	7	8	9	10
Mean temperature	0°	—12°	—18.5°	—26°	—33°	—41°	—47°

"The daily heating extends from the earth only about 1.5 kilometers up into the air. The difference of temperature between the icy upper layers of the air and the heated lower layers therefore reaches a maximum in the hot summer afternoons. These observations answer the question as to the source of the cold which can form ice in the air on hot summer afternoons. These cold layers are also to be found at relatively short distances up and it is probable that these distances are even less before and during a hail storm. Barral and Bixis found a temperature of —39° in a rain cloud scarcely 7 kilometers above Paris in July, 1850. On May 13, 1897, the temperatures above Strassburg and Berlin were —21° at a height of 4 kilometers, —32° at 5 kilometers, and —40° at 6 kilometers. The upward sweep of ascending masses of warm air can therefore easily carry them into the icy regions. As a matter of fact, measurements show that cumulus clouds and thunder clouds often rise to heights of 8–10 kilometers or even higher. The precipitated water vapor formed at or carried to those heights can therefore consist only of supercooled water or of ice crystals mixed with sleet. It is now easy to see why we get hail chiefly in summer, *i. e.*, in warm air. We have to have heat to carry the air up to the cold regions by giving it the necessary upward sweep, and we have to have a high content of water vapor to furnish the material for a large formation of ice. In winter the vertical temperature gradient is too slight and the air contains too little water vapor; consequently we get no real hail, especially far from the sea.

"There is no especial difficulty in forming a fairly good picture of the way a hailstone is formed. The structure of the hailstone gives us some clues. Round a cloudy opaque center, something like sleet, there are transparent shells of ice arranged more or less like the coating of an onion. These are often full of air bubbles and appear partly white. Trabert has pointed out that a hailstone seems to contain three kinds of ice: the center of frozen snow; the concentric sheaths of ice; and occasionally clear, even crystalline, ice on the outside, though in very many cases this last form cannot be detected.

"L. Dufour has shown that highly supercooled drops of water are fairly stable; these appear to play an important part in the formation of hail. As soon as they come in contact with needles of ice, they freeze at once. the temperature rising to the freezing point and a small part of the water remaining liquid in consequence of the heat evolved. Grains of sleet form the nuclei on which the ice sheaths are formed from the supercooled drops. Sleet is formed at those levels where the temperature is close to the freezing point and the weather is stormy, as at the surface of the earth in very early spring. Sometimes the frozen masses are covered with ice even then. In summer the isotherm for 0° is higher up and as a matter of fact the precipitation on high mountains during thunderstorms consists chiefly of sleet. The clouds are then much larger and contain more water. Trabert is right in saying that we must look for the formation of sleet where snow crystals and supercooled drops come together, as the structure itself shows. Sleet consists of snow crystals welded together by supercooled drops. Sleet changes to hail when the supercooled drops precipitate in the form of sheaths of ice.[1]

"What takes place in the hailstone from the inside to the outside takes place also in the clouds from above to below. In the uppermost portions of the clouds we have snow crystals and supercooled drops; in the lowest portions only the ordinary mist at a temperature not much above the freezing point. The upper region furnishes the center of the hailstone; the middle one the concentric sheaths of ice; and the third the material of the more or less crystalline deposits gradually formed on the hailstone (Trabert). In fact the hailstones often reach the earth while their temperature is far below the freezing point. During the growth of the hailstones the extraordinarily electrical frequent discharges from the hail clouds doubtless play a part and cause a frequent, sudden, coalescing of the supercooled drops. Each such coalescing corresponds to a new layer of ice on the sleet nucleus or hailstone and thus explain the alternation of transparent and white layers in the sheaths of ice on the hailstone.

"The second question was how the hailstones could remain floating in the air long enough to reach the extraordinary size which they sometimes attain. The only possible explanation for this is that it is due to ascending eddies of air in the hail clouds. It is very probable that hail is formed in vertical, local eddies of air which move forward with the storm, chiefly along the edge of it. An argument in favor of this is the precipitation of hail over comparatively narrow belts. Such eddies are formed by the sudden uprushing of overheated

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[1] On Pike's Peak (4308 m, about 38° N) it has been noticed that the hailstones often consist of snow which has been partly melted and then frozen again, or which has been mixed with drops of water and the mass then frozen. This is evidence that the hailstones must have gone up and down several times and consequently may have passed several times through Hertz's stages of rain, hail, and snow.

moist masses of air into the high, very cold levels during thunderstorms, and also during the general disturbance of atmospheric equilibrium when a cold wind from above passes over the hotter lower layers of the atmosphere. Similar eddies often pass along the surface of contact between hot and cold layers of air, the phenomenon often being repeated a number of times.

"Ferrel considers that hailstones are formed in very violent uprushing eddies of air having small cross sections, and he assumes that the small hailstones are whirled upward repeatedly until their weight becomes so great that they fall to the earth. The velocities called for in the eddies are not improbable ones when we consider the effects produced by local eddies, such as cyclones and tornadoes, even at the earth's surface."

Simpson[1] says that "falls of hail are frequently associated with thunderstorms, and hailstones—as has already been pointed out—can only form if they are supported during formation by strong ascending currents. Further, the structure of a hailstone indicates that it is often carried up and down past the zero isothermal. Now a current of air sufficiently strong just to support a hailstone as big as a pea would be more than sufficient to carry up the water it condenses within itself; hence hailstones would always have a greater downward velocity relative to the ascending current than the water in the current, and there would be a large amount of splashing between the two. There could be, consequently, a much greater amount of separation of electricity than would have taken place without the hailstones, and this might very well account for the great violence of the electrical discharges in hail storms."

Unless subjected to special treatment, the air always contains dust. The air of large cities invariably shows hundreds of thousands of dust-motes per cubic centimeter,[2] that of the village or town thousands, and that of the open coun-

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[1] Phil. Trans., 209A, 412 (1909).

[2] Moore: "Descriptive Meteorology," 30 (1910).

try at least hundreds. The dust may be soil from the fields and roads, particles of animal or plant origin, including pollen, products of combustion, salt from the spray of the ocean, volcanic dust, or cosmic dust. The dust from the eruption of Krakatoa was shot high into the air and was carried entirely round the world, falling on the decks of ships and on various parts of the earth. Owing to the enormous distances to which volcanic dust may be carried, it is necessary to have some definite test before we can say that a given sample of dust is really cosmic dust coming from meteors which have burned up in passing through the earth's atmosphere. This matter has been studied by Hartley and Ramage.[1]

"Baron Nordenskjold has described three different kinds of dust which were collected by him.[2] Of two of these, one consisted of diatomaceae and another of a siliceous and apparently feldspathic sand; both were found on ice in the arctic regions. The third variety was quite different and appeared to be of a cosmic origin. He observed that some sand collected at the end of a five or six days' continuous fall was mingled with a large quantity of sooty-looking particles, consisting of a material rich in carbon. It appeared to be similar to the dust which fell, with a shower of meteorites, at Hessle near Upsala, in the beginning of the year 1869. As in this particular instance, it might be supposed that the railways and houses of Stockholm had contributed some of this matter to the atmosphere, and that the snow had carried it down, he requested his brother, who then resided in a desert district of Finland, to give his attention to the subject, with the results that he collected a similar powder. The snow gathered in the latitude of 80° N., in an expedition to Spitzbergen, and that collected from floating ice in the arctic regions, and on the glaciers of Greenland, leaves, after it has melted, a greyish residue, which consists largely of diatomaceae, but mixed with these organisms there were also particles of a carbonaceous dust of considerable size, which, on analysis,

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[1] Proc. Roy. Soc., 68, 97 (1901).

[2] Comptes rendus, 78, 236 (1874).

were found to contain metallic iron, cobalt, and nickel, also silicon, carbon and phosphorus. The origin of this mineral matter was at first doubtful. Two of its constituents, cobalt and nickel, were believed to be a very uncommon occurrence in terrestrial matter, while, on the other hand, they are elements invariably associated with the metallic iron of meteorites, the nickel being more particularly in large proportion. If we suppose that this dust is discharged from the mouth of a distant volcano, or that it may be sand carried up by a whirlwind, we have yet to explain the peculiarities in its composition which render it similar to that of meteorites.

"Nordenskjold arrived at the conclusion that it was meteoric matter which had descended upon the earth in a shower similar to that which occurred near Upsala. By the facts which he had collected, it appears to have been proved that cosmic dust is falling imperceptibly and continually. It seems that this view is either generally not accepted or that the facts are not commonly known."

Hartley and Ramage collected numerous samples of dust in the neighborhood of Dublin and examined them spectroscopically as well as other samples furnished by friends. "The specimens of soot required no preliminary treatment before being burnt, and the analysis of each is given in the tabular statement only; but the different kinds of volcanic dust and flue dust were dissolved and the silica removed, after which the bases were separated into groups, and the spectra of the groups photographed." The data for the bases are given in Table I, italics being used when only a trace of the metal is present. The relative strength of the lines, as seen by comparing the different spectra, is, in some instances, indicated in the table by suffixes, the Number 1 indicating the weakest line and 10 the strongest.

Hartley and Ramage make the following comments on these data: "The principal characteristics of dust which has fallen directly from the clouds or collected by hail, snow, sleet, or rain, is its regularity in composition—each specimen appears to contain the same proportions of iron, nickel, calcium,

TABLE I

	Na	K	Rb	Cu	Ag	Mg	Ca	Sr	Ga	In	Tl	Fe	Ni	Mn	Cr	Pb
Dust from sleet fell March 28, 1896	Na	K	Rb?	Cu	Ag		Ca		Ga		Tl	Fe	Ni	Mn		Pb
Dust from hail fell April 14, 1897	Na	K		Cu	Ag		Ca		Ga?			Fe	Ni	*Mn*		Pb
Dust from clouds fell Nov. 16, 1897	Na	K		Cu	Ag		Ca		Ga		Tl	Fe	Ni	Mn	*Cr*	Pb
Dust from rain fell Nov. 13–15, 1897	Na	K		Cu	Ag		Ca	*Sr*	*Ga*		Tl	Fe	Ni	*Mn*		Pb
Volcanic dust from New Zealand																
(1) Te Ariki	Na	K	Rb	Cu	*Ag*	MgO	Ca	Sr	*Ga*			Fe	*Ni*	Mn		Pb
(2) Tauranga	Na	K	Rb	Cu	*Ag*	MgO	Ca	Sr	*Ga*			Fe	*Ni*	Mn		Pb
(3) Te Hope-O-Toroa	Na	K	Rb	Cu	*Ag*	MgO	Ca	Sr	*Ga*			Fe	*Ni*	Mn		Pb
Pumice from Krakatoa	Na	K	Rb	Cu	Ag		Ca	Sr	Ga	In?		Fe	Ni	Mn		Pb
Lead chloride from crater of Vesuvius	Na	K	Rb	Cu							Tl	Fe				Pb
Soot from chimneys																
(1) Bedroom chimney	Na_9	K_4	Rb?	Cu_2			Ca_7	*Sr*	Ga_2		Tl_1	Fe_8	Ni_1	Mn_1		Pb_4
(2) Kitchen chimney	Na_3						Ca_3					Fe_2				
(3) Laundry chimney	Na_9	K_4	*Rb?*	Cu_4	*Ag*		Ca_7	Sr_1	Ga_2		Tl_2	Fe_9	Ni_3	Mn_3	Cr_1	Pb_5
(4) Assay laboratory, fusion furnace	Na_7	K_8	*Rb?*	Cu_4	Ag_4		Ca_2		Ga_2		Tl_3	Fe_7	Ni_3	Mn_1		Pb_9
(5) Assay laboratory, gas muffle	Na_7	K_3		Cu_3	Ag_2		Ca_3		*Ga?*		Tl_1	Fe_7		Mn_1		Pb_8
(6) Heating apparatus furnace	Na_9	K_4	Rb?	Cu_3			Ca_9	Sr_2	Ga?		Tl_1	Fe_9	Ni_1	Mn_6		Pb_3

TABLE I—(*Continued*)

Flue dust:[1]																
(1) Gas works, Crewe	Na	K	*Rb*	Cu	Ag		Ca	Sr	Ga			Fe	Ni	Mn		Pb
(2) Boyd's chemical works, Dublin	Na	K		Cu	Ag		Ca			In	Tl	Fe				Pb
(3) Nicholson's Copper Works, Leeds, 0.5 g	Na	K	Rb	Cu	Ag		Ca		Ga	In	Tl	Fe				Pb
Ditto, 20 g[2]	Na	K	Rb	Cu	Ag		Ca	Sr	Ga	In	Tl	Fe	Ni	Mn	*Cr*	Pb
(4) Ferromanganese furnace, Pittsburgh	Na	K	Rb	Cu			Ca				Tl	Fe	Ni	Mn		Pb
(5) Ferromanganese furnace[3]	Na	K	Rb	Cu	Ag		Ca		Ga	*In*	Tl	Fe		Mn		Pb
(6) Cleveland iron furnace, Samuelson, Middlesbrough	Na	K	Rb	*Cu*	*Ag*		Ca		*Ga*		Tl	Fe	*Ni*	Mn		Pb
(7) Cleveland iron furnace	Na	K	Rb	*Cu*	*Ag*		Ca		*Ga*	*In*	Tl	Fe	*Ni*	Mn		Pb
(8) Basic iron furnace[3]	Na	K	Rb	*Cu*	*Ag*		Ca	Sr	*Ga*	*In*	Tl	Fe	*Ni*	Mn		Pb
(9) South Wales iron furnace	Na	K	Rb	*Cu*	*Ag*		Ca		*Ga*	*In*		Fe				Pb
Meteoric stone, Alfianello	Na	K		Cu	Ag	MgO	Ca		*Ga*			Fe	Ni	Mn		Pb
Meteoric stone, Pultush	Na	K		Cu	Ag	MgO	Ca					Fe	Ni	Mn	Cr	Pb
Meteoric stone, Mocs	Na	K		Cu	Ag	MgO	Ca	*Sr*				Fe	Ni	Mn	Cr	Pb
Siderolite Atacama	Na	K		Cu	Ag	MgO	Ca					Fe	Ni	Mn	Cr	Pb

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[1] Lithium was found in all the flue dusts.

[2] Bi, Al, Zn, Cd, Sn, *Cs* and *Co* were found in this dust.

[3] *Cs* was found in this dust.

copper, potassium, and sodium. The proportion of carbonaceous matter must be small, otherwise a diminution in the proportion of the metals present would render the metallic lines weaker. There is a very considerable difference between the dust from sleet, snow, and hail suddenly precipitated, the difference being in the proportion of lead, which, in the dust from sleet, is much larger than in the other specimens, though dust from hail and one quantity collected from rain contain more than is found in any other specimen with such an origin. The only meteorite which contains as much lead as this is the Siderolite from Atacama. If we examine the spectra of specimens of volcanic dust, it is noticeable that the heavy metals are, without exception, in comparatively small proportions—lead and iron, for example—while lime, magnesia, and the alkalies are the chief basic constituents. . . .

"The nature of soot from different sources is characterized by the small proportion of iron in most specimens and of metals precipitated from hydroxides; its large proportion of lime and the greater variability in the proportions of its different constituents distinguished it from other kinds of dust collected from the clouds or in the open air. It was certainly unexpected when nickel, calcium, manganese, copper and silver were found to be constant constituents of soot from different chimneys and flues. The proportions of lead, silver, and copper are much larger in the soot from the assaying furnace and the laundry chimney. . . .

"In flue dust from different sources the chief characteristics are the presence of lead, silver, and copper in larger proportions than in other varieties of dust or of coal ashes which have also been examined. Nickel and manganese are in larger proportions. But the most striking feature is the quantity of rubidium, gallium, and thallium in all samples examined.

"It is evident that we can state with absolute certainty whether two kinds of dust have the same composition or in what constituents they differ substantially.

"When dust is collected in the open air it is liable to become mixed with other dust and soot, and we cannot be certain whether it comes from only one source or not, but soot, as a rule, can be separated by washing it away from the heavier matter. The occurrence of nickel in soot and flue dust was certainly unexpected. It is probably disseminated in extremely minute traces in coal, and its concentration in soot is owing to the conditions in a coal fire being favorable to the formation of nickel tetracarbonyl and its subsequent decomposition."

Hartley and Ramage drew the following conclusions:

1. The presence of nickel, as shown by the examination of soot, is not positive evidence that the dust from the clouds comes from other than a terrestrial source.

2. The dust which fell on the 16th and 17th of November, 1897, with its regularity in composition and its similarity to meteorites, being magnetic, also its comparative freedom from extraneous matter, exhibits properties which are quite in favor of its cosmic origin. However, its composition is totally unlike that of volcanic dust and flue dust from various chemical and metallurgical works. This dust for the most part fell on a perfectly calm fine night, and there was no rain for twenty-four hours or more afterwards.

"We beg to draw attention once more to the very wide distribution of gallium in minute proportions; it occurs in all aluminous minerals, flue dust of every kind, soot and atmospheric dust, also in a great variety of iron ores. Bauxite contains it in larger proportion than any other mineral, but the quantity even in this substance is very small. We have hopes of finding it concentrated in some mineral, as thallium, caesium, germanium, and indium are. Indium and thallium, the other members of the same group of elements, are found in blende and pyrites, and accordingly we might expect gallium to occur in a concentrated state in a sulphide, arsenite, or similar compound. Judging, however, from its analogy with aluminum, there does not seem to be much probability of this."

Unfortunately, Hartley and Ramage do not tell us exactly how to identify cosmic dust and it is not an easy matter to formulate a rule from the data. The first four samples of dust differ from the volcanic dust in not containing magnesia or strontium; they differ from the flue dust and the soot from chimneys in not containing rubidium and in containing more nickel. If we are to take only the dust which fell on Nov. 16 and 17, 1897, as of cosmic origin, the only difference is the trace of chromium. The situation is complicated farther by the fact that the meteoritic stones all contain magnesia and strontia. It is not clear at all why these should have disappeared in the alleged cosmic dust. So far as one can formulate a conclusion from this work, it seems to be that dust is of cosmic origin when it contains sodium, potassium, copper, silver, calcium, gallium, thallium, iron, nickel, and lead, but no rubidium, strontium or magnesia. The dust must also be magnetic, this last probably being the most important criterion of all though it does not appear in the table.

Preliminary work on the precipitation of smoke and dust was done by Nahrwold[1] and by Aitken[2] and then the matter was taken up more seriously by Lodge.[3] Owing to convection currents, dust and soot will settle more readily on cold surfaces than on hot ones. Thinking that this might be due in part to electrification of the air, Lodge tried the effect of electrification on a mass of smoke. With potentials of one hundred volts or so very little effect could be detected. When the potential rose to a few thousand volts and a brush discharge began to be possible, the smoke agglomerated and settled very rapidly. "To observe this new phenomenon is very easy. Fill a bell-jar with any kind of smoke: tobacco, camphor, turpentine, magnesia, ammonic chloride, ammonic sulphide, brown paper, steam, phosphoric oxide, lead fume, zinc fume, no matter what, and then discharge electricity into it from a point connected with a Voss or Wimshurst machine, the other pole of which is connected with the ground or with the base

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[1] Wied. Ann., **5**, 460 (1878).

[2] Nature, **29**, 322 (1884); Trans. Roy. Soc. Edin., **32**, 239 (1884).

[3] Phil. Mag., (3) **17**, 214 (1884); Jour. Soc. Chem. Ind., **5**, 572 (1886).

of the bell-jar. In a second or two, aggregation of the smoke particles sets in, they form in masses or flakes along the lines of force, and in another instant the jar is clear of smoke, or has all been condensed on the floor of the vessel."

The general principle of electrical precipitation of suspended particles was patented by A. C. Walker of the Dee Bank Lead Works. In 1885 an apparatus was installed consisting of a system of metallic points situated in the flue from the lead furnaces and excited from two Wimshurst machines with glass plates five feet in diameter, each machine being driven by a one horse power steam engine. The process seems not to have been a commercial success. It is only through the work of Cottrell[1] that the electrical precipitation of suspended particles has been put on a commercial basis. Cottrell believes that "in the case of the large volumes of rapidly moving gases in smelter flues the agglomerating and settling process is, however, too slow even when the flues are expanded into as large dust chambers as are commercially feasible. It is in such cases that direct current methods have been particularly important.

"If we bring a needle point connected to one side of a high-potential direct-current line opposite to a flat plate connected to the other side of the line we find that the air space between becomes highly charged with electricity of the same sign as the needle point, irrespective of whether this is positive or negative, and any insulated body brought into this sphere instantly receives a charge of the same sign. If this body is free to move, as in the case of a floating particle, it will be attracted to the plate of opposite charge and will move at a rate proportional to its charge and the potential between the point and the plate.

"Even if there are no suspended particles the gas molecules themselves undergo this same process, as is evidenced by a strong wind from the point to the plate even in perfectly transparent gases. The old familiar experiment of blowing

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[1] Jour. Ind. Eng. Chem., 3, 542 (1911).

out a candle flame by presenting to such a charged point is simply another illustration of the same phenomena."

When discussing the behavior of nuclei in the air, attention was drawn to the fact that ammonium chloride smoke can be bubbled through several wash bottles without being completely absorbed.[1] Schloesing[2] has put the thing more generally by saying that it is much easier to take a gas out of a gaseous mixture than suspended liquid or solid particles. Nobody knows to what extent the particles are carried through the liquid in the center of a gas bubble or to what extent a film of adsorbed air protects the particle. It is probably largely the latter because the sulphur trioxide from the contact process can be taken up readily by concentrated acid and not by water, though we do not at present know why these two liquids should behave so differently.

When studying the behavior of rain drops, we saw that drops become electrified positively when broken up by a current of air. Electrification is also to be noticed when dust is blown about by the wind.[3] "In the course of some work on the value of the atmospheric potential gradient in South Africa, the author has pointed out the important influence exerted by the clouds of dust raised by the wind. The normal fine weather charge possessed by the atmosphere is of course positive, and in Bloemfontein, at an elevation of 4500 ft. seldom exceeds a maximum value of 200 volts per meter. But during a dust storm the sign of the charge changes and gives rise to values exceeding 500 volts per meter. It is not necessary for the instrument used for measuring the potential to be actually in the dust itself, for a "dust devil," *i. e.*, a whirlwind which carries up a column of fine sand, sometimes two or three hundred feet in height, can produce a very perceptible effect at a distance of more than two miles, reversing the positive charge in the air and giving a large negative one.

"It is generally believed that as a consequence of the air-

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[1] Engler and Wild: Ber. deutsch. chem. Ges., **29**, 1933 (1896).

[2] Comptes rendus, **94**, 1187 (1882).

[3] Rudge: Phil. Mag., (6) **23**, 852 (1912); **25**, 481 (1913).

earth current flowing into the earth, the latter possesses a negative charge; and explanation of the negative potential caused by the dust storm appeared to lie in assuming that the particles of sand carried up by the wind, being themselves negatively charged, gave rise to the negative potential. But this is not the case, for, as will be shown, the dust particles are positively charged, and, at all events in the situation where the observations were carried out, the surface of the earth is also charged with positive electricity.

"The climate of South Africa is, on account of its dryness, eminently suitable for observations on atmospheric electricity, but it is quite possible that similar conditions may prevail elsewhere, and the following experiments may perhaps be successful in other places:....

"In order to collect the charge in the air, a plate coated with radium was attached to the electrometer. Various means were adopted by which a cloud of dust could be raised, such as throwing a handful of dust into the air; by directing a stream of air from a pair of bellows against a heap of fine dust; by shaking from the end of a pole a fine muslin bag filled with fine dry sandy earth; and lastly, and most efficaciously, by setting a team of mules to plough up the dry earth. In all these cases, an electroscope placed at some little distance from the cloud gave indications of a negative charge being present in the air. This could be detected by the normal positive charge indicated by the electroscope becoming smaller, or if the distance were less than 50 meters, the charge would be reversed and potentials up to 200 volts per meter registered.

"In the course of these experiments, it was noticed that if the dust fell on the electroscope, the effect was smaller, as though the dust had imparted a charge of a character different from that given by the air, and further investigation showed this to be the case. The charge upon the dust was always positive. This was easily shown by taking a conical net of fine wire gauze, drawing it rapidly through the cloud so as to catch some of the dust raised by the plough, and then putting it in communication with the electroscope, when a very strong charge of positive electricity was shown, and on some occasions small sparks were drawn from the net.

"The negative charge indicated by the electroscope during a dust storm must therefore reside in the air itself, and not in the dust particles caught up by the wind. By way of contrast, it may be noted that when steam suffers condensation in the open air, it gives to the air a positive charge which persists after the cloud has disappeared. The general electrification produced by raising dust composed of different materials has been investigated, and will form the subject of a future paper."

"The electrification developed during dust storms in South Africa is invariably negative, neutralizing and reversing the positive charge usually present in the air. In England, in places where the matter was tested, the clouds of dust raised by motor cars had the effect of *increasing the positive charge*. In South Africa the dust is usually of a siliceous character, whether it comes from the sea-shore, inland wastes, cultivated soils, or the mine-heaps in the neighborhood of Johannesburg. In England road dust is usually calcareous. It is quite easy to show the production of a charge of electricity by raising a cloud of dust. If a small quantity of flour is placed upon the plate of an electroscope and then suddenly blown away, the electroscope will indicate a charge whose magnitude will depend to some extent on the fineness of the flour. The experiment can be performed in a room, but the effect is very much greater if it is done out in the open air. By raising a cloud of flour dust in any way and catching the particles in a hollow insulated vessel, it is always possible to show the presence of a charge of electricity....

"When fine sand or dry earth was used, a strong positive charge was indicated as would have been expected....; but, on using other material, the charge was *positive* or *negative*, according to the nature of the material. Almost the only references to the electrification of dusts are those relating to the production of Lichtenberg's figures, by shaking a mixture of red lead and sulphur in a muslin bag, and allowing the powders to fall upon an irregularly electrified plate composed of some non-conducting material. A separation of the red lead and sulphur particles is effected because of the opposite charges acquired by these materials, the sulphur particles being stated to be negatively electrified while those of the red lead are positive. Now powdered sulphur, when blown into a cloud in the apparatus, acquires a positive charge, and red lead a negative one. This fact seemed sufficient to warrant an investigation into the kind of electrification accompanying the raising of clouds of dust from different materials."

From the experiments the author deduced four generalizations. Non-metallic elements give positively charged clouds when the finely-divided solid material is blown into a cloud by a current of air. Metallic elements give negatively charged clouds when the finely divided material is blown into a cloud by a current of air. Solid acid-forming oxides give positively charged clouds, and basic ones negatively charged clouds. In the case of salts the change apparently depends on the relative strength of the acid and basic ions.

The optical phenomena due to suspended solids are quite as interesting as those due to suspended drops of liquid. When a beam of sunlight passes into a dark room particles of dust can be seen dancing in the path of the beam. These scatter the sunlight so that the beam can be seen by an observer standing at one side. Tyndall[1] showed that when the air was so sifted as to remove entirely the visible floating matter, there is nothing to scatter the light; the space is optically empty and the path of the beam through the air cannot be seen. This scattering of a parallel or convergent beam of light by suspended particles is known as the Tyndall effect. When making experiments on the decomposition of vapors by light, Tyndall was struck by the appearance of the cloud which was formed. "It has hitherto been my aim to render the chemical action of light upon vapors visible. For this

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[1] Proc. Roy. Soc., 17, 92, 223 (1869); Phil. Trans., 160, 333 (1870).

purpose substances have been chosen, *one* at least of whose products of decomposition under light shall have a boiling point so high that as soon as the substance is formed it shall be *precipitated*. By graduating the quantity of the vapor, this precipitation may be rendered of any degree of fineness, forming particles distinguishable by the naked eye, or particles which are probably far beyond the reach of our highest microscopic powers. I have no reason to doubt that particles may be thus obtained whose diameters constitute but a very small fraction of the length of a wave of violet light.

"In all cases when the vapors of the liquids employed are sufficiently attenuated, no matter what the liquid may be, the visible action commences with the formation of a *blue cloud*. I would guard myself at the outset against all misconception as to the use of this term. The blue cloud to which I here refer is totally invisible in ordinary daylight. To be seen, it requires to be surrounded by darkness, *it only* being illuminated by a powerful beam of light. This blue cloud differs in many important particulars from the finest ordinary clouds, and might justly have assigned to it an intermediate position between these clouds and true cloudless vapor....

"Dry air was permitted to bubble through liquid nitrite of butyl until the experimental tube, which had been previously exhausted, was filled with the mixed air and vapor. The visible action of light upon the mixture after fifteen minutes' exposure was slight. The tube was afterwards filled with half an atmosphere of the mixed air and vapor, and another half atmosphere of air which had been permitted to bubble through fresh commercial hydrochloric acid. On sending the beam [of electric light] through this mixture, the action paused barely sufficiently long to show that at the moment of commencement the tube was optically empty. But the pause amounted only to a small fraction of a second, a dense cloud being immediately precipitated upon the beam which traversed the mixture. This cloud began *blue*, but the advance to whiteness was so rapid as almost to justify the application of the term instantaneous. The dense cloud, looked at perpendicularly to its axis, showed scarcely any signs of polarization. Looked at obliquely the polarization was strong.

"The experimental tube being again cleaned and exhausted, the mixed air and nitrite of butyl vapor was permitted to enter it until the associated mercury column was depressed $^1/_{10}$ of an inch. In other words, the air and vapor united, exercised a pressure not exceeding $^1/_{300}$ of an atmosphere. Air passed through a solution of hydrochloric acid was then added till the mercury column was depressed three inches. The condensed beam of the electric light passed for some time in darkness through this mixture. There was absolutely nothing within the tube competent to scatter the light. Soon, however, a superbly blue cloud was formed along the track of the beam, and it continued blue sufficiently long to permit of its thorough examination. The light discharged from the cloud at right angles to its own length was *perfectly* polarized. By degrees the cloud became of whitish blue, and for a time the selenite colors obtained by looking at it normally were exceedingly brilliant. The direction of maximum polarization was distinctly at right angles to the illuminating beam. This continued to be the case as long as the cloud maintained a decided blue color, and even for some time after the pure blue had changed to a whitish blue. But as the light continued to act, the cloud became coarser and whiter, particularly at its center, where it at length ceased to discharge polarized light in the direction of the perpendicular, while it continued to do so at both ends. But the cloud, which had thus ceased to polarize the light emitted normally, showed vivid selenite colors when looked at obliquely. The direction of maximum polarization changed with the texture of the cloud. . . .

"A blue, equally rich and more durable, was obtained by employing the nitrite of butyl vapor in a still more attenuated condition. Now the instance cited here is *representative*. In all cases, and with all substances, the cloud formed at the commencement, when the precipitated particles are sufficiently fine,' is *blue*, and it can be made to display a color rivalling that of the purest Italian sky. In all cases, moreover, this fine blue cloud polarizes *perfectly* the beam which illuminates it, the direction of polarization enclosing an angle of 90° with the axis of the illuminating beam.

"It is exceedingly interesting to observe both the perfection and the decay of this polarization, for ten or fifteen minutes after its first appearance the light from a vividly illuminated incipient cloud, looked at horizontally, is absolutely quenched by a Nicol's prism with its longer diagonal vertical. But as the sky-blue is gradually rendered impure by the introduction of particles of too large a size, in other words, as real clouds begin to be formed, the polarization begins to deteriorate, a portion of the light passing through the prism in all its positions. It is worthy of note that for some time after the cessation of perfect polarization, the *residual* light which passes, when the Nicol is in its position of minimum transmission, is of a gorgeous blue, the whiter light of the cloud being extinguished.[1] When the cloud texture had become sufficiently coarse to approximate to that of ordinary clouds, the rotation of the Nicol ceases to have any sensible effect on the quality of the light discharged normally."

"When the quantity of nitrite [of amyl] vapor is considerable and the light intense, the chemical action is exceedingly rapid, the particles precipitated being so large as to *whiten* the luminous beam. Not so, however, when a well-mixed and attenuated vapor fills the experimental tube. The effect now to be described was obtained in the greatest perfection when the vapor of the nitrite was derived from a residue of the moisture of its liquid which had been introduced accidentally into the passage through which the dry air flowed into the experimental tube. In this case the electric beam traversed the tube for several seconds before any action was visible. Decomposition then visibly commenced, and ad-

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[1] This seems to prove that particles, too large to polarize the blue, polarize perfectly light of lower refrangibility.

vanced slowly. The particles first precipitated were too small to be distinguished by an eye-glass; and when the light was very strong, the cloud appeared of a milky blue. When, on the contrary, the intensity was moderate, the blue was pure and deep. In Brücke's important experiments on the blue of the sky and the morning and evening red, pure mastic is dissolved in alcohol, and then dropped into water well stirred. When the proportion of mastic to alcohol is correct, the resin is precipitated so finely as to elude the highest microscopic power. By reflected light, such a medium appears bluish, by transmitted light yellowish, which latter color, by augmenting the quantity of the precipitate, can be caused to pass into orange or red.

"But the development of color in the attenuated nitrite of amyl vapor, though admitting of the same explanation, is doubtless more similar to what takes place in our atmosphere. The blue, moreover, is purer and more sky-like than that obtained from Brücke's turbid medium. There could scarcely be a more impressive illustration of Newton's mode of regarding the generation of the color of the firmament than that here exhibited; for never, even in the skies of the Alps, have I seen a richer or a purer blue than that attainable by a suitable disposition of the light falling upon the precipitated vapor. May not the aqueous vapor of our atmosphere act in a similar manner? And may we not fairly refer to liquid particles of infinitesimal size the hues observed by Principal Forbes over the safety valve of a locomotive, and so skilfully connected by him with the colors of the sky?"

The theory of the blue color has been studied by Rayleigh[1] who deduced the law that "when light is scattered by particles which are very small compared with any of the wave-lengths, the ratio of the amplitudes of vibrations of the scattered and incident light varies inversely as the square of the wave length, and the intensity of the lights themselves as the inversed fourth power."

"Before making out the theory, I had endeavored to as-

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[1] Phil. Mag., (4) 41, 107, 274, 447 (1871); (5) 12, 81 (1881).

certain by observation the actual prismatic composition of the blue of the sky and had obtained preliminary results. The experimental method (the description of which I must reserve for another opportunity) was fully adequate to the comparison of two given lights; but the difficulty was to find something to compare the blue light with. In the only complete set of observations that I have hitherto been able to make, the blue of the sky (apparently a very good one) taken from the neighborhood of the zenith was compared with sunlight, diffused through white paper. About thirty consistent comparisons were made, ranging over the spectrum from C to beyond F... The following numbers will give an idea of the results:

C	D	b_3	F
25	40	63	80 calc.
25	40	71	90 observed

"The upper line gives the theoretical intensities for the fixed lines C, D, b_3, F, while the lower gives the observed ratios between the lights (sky and diffused sunlight), the two sets of numbers being made to agree at C. Considering the difficulties and uncertainties of the case, the two curves agree very well; and it should be noticed that the sky compared with diffused light was even bluer than theory makes it, on the supposition that the diffused light through the paper may be taken as similar to that whose scattering illuminates the sky. It is possible that the paper was slightly yellow; or the cause may lie in the yellowness of sunlight as it reaches us compared with the color it possesses in the upper regions of the atmosphere. It would be a mistake to lay any great stress on the observations in their present incomplete form, but at any rate they show that a color more or less like that of the sky would result from taking the elements of white light in quantities proportional to λ^{-4}. I do not know how it may strike others, but individually I was not prepared for so great a difference as the observations show, the ratio for F being more than three times as great as for C."

Although Tyndall was quite clear that any sufficiently small particles would give rise to a blue color, he was of the opinion that the blue color of the sky was due to particles of liquid water[1] "That *water particles*, if they could be obtained in this exceedingly fine state of division, would produce the same effects does not admit of reasonable doubt. And that they must exist in this condition in the higher regions of the atmosphere is I think, certain. At all events, no other assumption than this is necessary to account completely for the firmamental blue and the polarization of the sky.[2] Suppose our atmosphere surrounded by an envelope impervious to light, but with an aperture on the sunward side through which a parallel beam of solar light could enter and tranverse the atmosphere. Surrounded on all sides by air not directly illuminated, the track of such a beam through the air would resemble that of the parallel beam of the electric lamp through an incipient cloud. The sunbeam would be *blue* and it would discharge laterally light in precisely the same condition as that discharged by the incipient cloud. In fact the azure revealed by such a beam would be to all intents and purposes that which I have called a blue cloud."

Lord Rayleigh[3] says in regard to this point that "all who have written on this subject seem to have taken it for granted that the foreign matter in the atmosphere is water or ice. Even Tyndall, who expressly says that any particles, if small enough, will do, still believes in the presence of water particles. But this view is encumbered with considerable difficulty, for even if, in virtue of its transparency to radiant heat, the air in the higher regions of our atmosphere is at a very low temperature, it would still be capable of absorbing the very small

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[1] Tyndall: Proc. Roy. Soc., 17, 227 (1869).

[2] Any particles, if small enough, will produce both the color and the polarization of the sky. But is the existence of small water particles on a hot summer's day *in the higher regions of our atmosphere* inconceivable? It is to be remembered that the oxygen and nitrogen of the air behave as a vacuum to radiant heat, the exceedingly attenuated vapor of the higher atmosphere being therefore in practical contact with the cold of space.

[3] Phil. Mag., (4) 41, 277 (1871).

quantity of water which is sufficient to explain the blue of the sky. At any rate it is difficult to imagine particles of water smaller than the wave-length of light endowed with any stability. These difficulties might perhaps be gotten over if there were any strong argument in favor of the water-particles, but of the existence of such I am not aware. Every one knows that a blue haze evidently akin to the azure of the sky obliterates the details and modifies the color of a distinct mountain; and this, when it occurs on a hot day, cannot possibly be attributed to aqueous particles. On the face of it, there is no reason for supposing that near the earth's surface the foreign matter is of one kind and at a great altitude another. If it were at all probable that the particles are all of one kind, it seems to me that a strong case might be made out for common salt. Be that as it may, the optical phenomena can give us no clue."

The blue of cigar smoke is unquestionably due to solid particles; the blue color of skimmed milk or of oil emulsions is due to liquid particles. In a later paper Rayleigh[1] claims that the molecules of oxygen and nitrogen are in themselves large enough to give rise to a blue sky even if the air contained no suspended matter in the ordinary sense of the word. In fact he deduces from his formula the value of the Avogadro constant, the number of molecules per gram molecule.[2]

There is, nevertheless, a serious question whether Rayleigh's theory accounts for all the facts.[3] "The phenomena of polarization indicate beyond any doubt the turbidity of the air as one source of the blueness of the sky. In the case of the ideal turbid medium of Rayleigh, in which all the particles are small as compared with the wave-length of light, the composition of the diffused light, as is well known, is such that the ratio of the intensity of the reflected ray to that of the incident ray varies inversely as the fourth power of the wave-length. This would give us a sky about twelve times as bright

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[1] Phil. Mag., (5) 47, 375 (1899).
[2] Cf. Perrin: "Die Atome," 129 (1914).
[3] Nichols: Phys. Rev., 26, 497 (1908).

in the extreme violet as in the red, as compared with sunlight. Rayleigh's analysis may be said to have found complete verification in the experimental study of artificial turbid media, particularly in the colors of the steam jet by Bock.[1] Spectrophotometric measurements of the sky itself have, however, led to widely varying results. Zettwuch,[2] who made many measurements of the sky at Rome, calls special attention to its extreme variability. Crova,[3] who has made more measurements of this sort than any other investigator with whose work I am acquainted, obtained, in the course of measurements at Montpellier, extending over more than two years, relations for the variation of intensity with wave-length in which the exponential constant varied from 1.61 to 6.44. Crova's measurements unfortunately extend only through the brighter parts of the spectrum from 0.635μ to 0.510μ; the extreme red and violet being omitted. If, however, we are to admit his exponential coefficients as even approximately correct, we shall have to admit other sources for the blue of the sky than that of turbidity."

Nichols cites some quantitative measurements of his own and draws the conclusions:

(*a*) That while there is good reason for regarding the sky as a turbid medium, the experimental study of the spectrum of skylight affords evidence of a distribution of intensities which can not be altogether accounted for by the assumption of an atmosphere conforming to Rayleigh's formula nor of a turbid medium containing coarser particles.

(*b*) That the illumination of the atmosphere by selectively reflected light from the surface of the earth and from cloud masses and mist modifies the character of the light from the sky to an extent which, while perhaps not readily discernible with the unaided eye is definite and unmistakable when the sky is studied with the spectrophotometer.

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[1] Wied. Ann., **68**, 674 (1899).

[2] Phil. Mag., (6) **4**, 199 (1902).

[3] Comptes rendus, **109**, 493 (1889); **112**, 1178 (1891); Ann. Chim. Phys., (6) **20**, 480 (1890).

(*c*) That the deviation of the observed distribution of intensities recorded by several investigators indicated a blue absorption color of the air or, since the preponderance in the violet appears to be variable in amount, the existence of fluorescence of some mistakable factor of the atmosphere such as ozone or both.

Bieber[1] points out that "ammonia may form from its components under the influence of ultra-violet light. Though this reaction may perhaps take place but to a very slight extent in the tropo-sphere, owing to the very small amount of water present, the conditions are favorable for the formation of ammonia in certain layers of the atmosphere where the water content increases. The yield of ammonia also becomes better with falling temperature and decreasing pressure[2] conditions which are certainly satisfied at these heights. Since an oxidation must also take place and since hydrogen, nitrogen, and oxygen occur to about the same extent in the stratosphere, there must be a formation of ammonium nitrite or nitrate through the action of sunlight on these three gases. If, however, these small solid particles are always present in the upper regions of the atmosphere, we do not need to account for the blue color of the sky by postulating diffraction by gas molecules as Rayleigh[3] has done, because these particles, which are small in comparison with the wave-length of the more refrangible rays will diffract the shorter wave-lengths more than the other, and so produce a blue sky. Changes in the hue are due chiefly to clouding in the lower layers. The number of particles does not increase indefinitely because a state of equilibrium occurs, depending on the formation of ammonia and of ammonium nitrite."[4]

It seems probable that Bieber cited Briner and Mettler's work without having read it. They placed a mixture of one volume of nitrogen and three of hydrogen in a glass vessel,

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[1] Drude's Ann., 39, 1313 (1912).

[2] Briner and Mettler: Comptes rendus, 144, 694 (1907).

[3] Wegener: "Thermodynamik der Atmosphäre," 249 (1911).

[4] D. Berthelot and Gaudechon: Comptes rendus, 162, 522 (1911).

plunged the vessel into liquid air, and passed sparks through the mixed gases. At a pressure of 100 mm the yield was 0.17 gram NH_3 per K. W. H., the yield dropping off both for lower and higher pressures, and becoming practically zero at 760 mm. Increasing pressure should increase the rate of reaction, but it decreases the conductivity of the gases and consequently the yield per unit electric energy expended passes through a maximum, which is quite different from what Bieber says.

Moore[1] says that "if it were not for dust-motes there would be a different and less brilliant twilight. The bending or refraction of light, as the sun's rays pass obliquely from the ether, at sunrise, or at sunset, into the optically denser medium of the air, displaces the apparent position of the sun, elevating it by an amount about equal to its apparent diameter, so that one may still see it and receive its light directly when geometrically it is entirely below the horizon. A little later in the evening and its rays fall upon the upper air too obliquely to be bent down to the earth by refraction, but darkness does not yet ensue, for the rays are scattered by the molecules of gases and the dust-motes and sent downward from particle to particle, resulting in a soft shimmering light that almost imperceptibly fades away, and which in higher latitudes, because of the obliqueness there of the sun's path to the horizon, may last for hours."

"When an observer is on the summit of a mountain or when he ascends in a balloon, the bluish tint becomes feebler in proportion as the mass of the air above him diminishes and the blue sky gradually becomes darker or blacker until the brighter stars begin to be visible and the zenithal portion of the sky has the color of late twilight, and, granting its possibility, if one should ascend to the upper limits of the atmosphere, where there is nothing to diffuse the light rays, he would find himself surrounded by total darkness."

"An observer inside of a bank of fog usually reports that the sky is cloudy and of a gray tint, since this is about the

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[1] "Descriptive Meteorology," 32, 244, 254, 245 (1910).

character of the light that penetrates the bank of fog, unless it be a very light fog or haze, or he be near the surface. There is quite a distinction between the tints seen inside a wet fog or cloud and those seen inside a dry fog or haze, such as is always associated with the harmattan on the west coast of Africa. In the latter case the sky has a chalky white tint and the air is very dry. We attribute the whitish tint not to any moisture, but to the presence of innumerable fragments of microscopic diatoms or siliceous shells. The whitish color or the haze must be attributed to the reflection of light from their surfaces. A similar white haze occurs in air that is full of grains of pollen, or fine crystals of snow, or almost any other kind of small particles."

"In addition to the sky colors due to aqueous vapors, there are tints due to the presence of floating dust particles. The sky tint is not the color of the dust proper, but is determined principally by the irregularity in the size of the particles and by their translucency. The air and the particles form a non-homogeneous mixture that in large measure cuts out the shorter waves, while transmitting the longer ones so that the residual color is reddish, yellowish or brownish. As the dust increases, the browns become ashy gray and darker, and eventually all light is lost as it is in the midst of dust-clouds, dust showers from volcanoes, and dense thunder and tornado clouds."

Tyndall[1] calls attention to the fact that even in the absence of definite clouds there are considerable variations in the hue of the firmament. "Everybody knows, moreover, that the purer blue is impaired as the sky bends toward the horizon. To measure the intensity of the color De Saussure invented a cyanometer, and Humboldt has given us a mathematical formula to express the diminution of the blue, in arcs drawn east and west from the zenith downward. This diminution is a natural consequence of the predominance of the coarser particles in the lower regions of the atmosphere. Were the particles which produce the purer celestial vault all swept

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[1] "Fragments of Science: The Sky" (1888).

away, we should, unless helped by what has been called 'cosmic dust,' look into the blackness of celestial space. And were the whole atmosphere abolished along with its suspended matter, we should have the 'blackness' spangled with steady stars; for the twinkling of the stars is caused by our atmosphere. Now, the higher we ascend, the more do we leave behind us the particles which scatter the light; the nearer, in fact, do we approach to that vision of celestial space mentioned a moment ago. Viewed, therefore, from the Alpine summits, the firmamental blue is darker than it is ever observed to be from the plains. . . ."

"Let us now complete our thesis by following the larger light waves, which have been able to pass among the aërial particles with comparatively little fractional loss. Without going beyond inferential considerations, we can state what must occur. The action of the particles upon the solar light increases with the atmospheric distances traversed by the sun's rays. The lower the sun, therefore, the greater the action. The shorter waves of the spectrum being more and more withdrawn, the tendency is to give the longer waves an enhanced predominance in the transmitted light. The tendency, in other words, of this light, as the rays traverse the ever-increasing distances is more and more toward red. This I say, might be stated as an inference, but it is borne out in the most impressive manner by facts. When the Alpine sun is setting, or better still, some time after he has set, leaving the limbs and shoulders of the mountains in shadow, while their snowy crests are bathed by the retreating light, the snow glows with a beauty and solemnity hardly equalled by any other natural phenomenon. So, also, when first illumined by the rays of the unrisen sun, the mountain heads, under favorable atmospheric conditions, shine like rubies. And all this splendor is evoked by the simple mechanism of minute particles, themselves without color, suspended in the air. Those who referred the extraordinary succession of atmospheric glows, witnessed some years ago, to a vast and violent discharge of volcanic ashes, were dealing with 'a true cause.' The fine floating residue of such ashes would, undoubtedly, be able to produce the effects ascribed to it. Still the mechanism necessary to produce the morning and the evening red, though of variable efficiency, is always present in the atmosphere. I have seen displays, equal in magnificence to the finest of those above referred to, when there was no special volcanic outburst to which they could be referred. It was the long-continued repetition of the glows which rendered the volcanic theory highly probable."

Beck[1] points out that in very clear air the shadows are harsh because there is no diffraction of light into them and that this must be kept in mind by the photographer. "The first time I set up my camera in Egypt I was startled at the way in which the picture looked on the focussing screen. Instead of a beautiful harmonious image it looked like a harsh photograph. There were crude, bright lights and immediately adjoining them, almost without intermediate steps, were deep, black shadows showing almost no details. It was clear to me at once that, in spite of all theory, a short exposure was out of the question. In fact, on account of the deep shadows, it would be necessary to give a longer exposure than would be customary under the same conditions at home in Vienna. After thinking the matter over for a while I saw clearly what was the cause of the great contrasts and especially of the heavy dark shadows. I perceived that the purer air of the South—just because of its clearness and permeability to light—did not scatter the rays so much as our own air does. Since the shadows were lighted so little by diffracted light, they are necessarily heavier and darker than they would have been in our latitudes.

"The phenomenon of the dark black shadows appeared in the most surprising way in the dry, crystal-clear, desert air of Upper Egypt. For three weeks, while I was partly on the Nile and partly in the desert, I had absolutely no chance to develop my plates; but I was nevertheless so convinced of the accuracy of my observations that in practically every case I

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[1] Jahrbuch der Photographie, 18, 159 (1904).

made longer exposures than were permissible theoretically. The results were an eminently satisfactory confirmation of my conclusions. In view of all this[1] and as a consequence of similar experiences in Africa, Spain, Greece, and elsewhere, I should sum up my experiences in regard to length of exposure in southern countries as follows: In southern countries a relatively brief exposure is permissible only when practically all of the parts of the subject to be photographed are well lighted. If large or important portions are in shadow, a shorter exposure will not do and one must expose at least as long, and in very clear air up to twice as long, as one would do at home under equally favorable conditions of light. Of course, this is after taking into account variations due to differences in the season, length of day, and height of sun, resulting from the difference between our latitude and that of the southern country."

Aitken[2] has shown that there is no evidence to indicate that water vapor has any hazing effect, and shows that "the haze is entirely due to dust, the density of the haze increasing with the increase in the number of dust particles in the air and also with the *relative* humidity. The humidity does not act as vapor, but by condensing on the dust and increasing the size of the particles, as it is not the amount of vapor present, but the degree of saturation that affects the result; the more saturated the air, the more vapor is condensed on the particles, so they become larger and their hazing effect increased. The relations of haze or transparency of the air to the number of dust particles was observed on five visits to the Rigi Kulm. The visibility of Hochgerrach, a mountain 70 miles distant from the Rigi, was used for estimating the amount of haze when the air was clear. During the visits this mountain was visible thirteen times, and it was never seen except when the number of particles was low. On eight occasions the mountain was only one-half to one-fifth hazed, and on these days the number of particles was as low as from

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[1] Cf. Wiener: Phot. Blätter, 1898, 267; Phot. Correspondenz, 1899, 45.

[2] Encyclopedia Britannica, 8, 715 (1910).

326 to 850 per cc. It was seen five times when the number was from 950 to 2000 per cc; but the mountain was only just visible on these occasions, and it was never seen when the number was a little over 2000 per cc.

"It has been pointed out that the relative humidity has an effect on the dust by increasing the size of the particles and so increasing the haze. It was therefore necessary in working out the dust and haze observations at the different places to arrange all the observations in tables according to the wet-bulb depressions at the time. All the observations taken when the wet-bulb depression was between 2° and 4° were put in one table, all those when it was between 4° and 7° in another, and all those when it was over 7° in a third. It should be noted here that when the dust particles were counted and the wet and dry bulb observations taken, an estimate of the amount of haze was also made. This was done by estimating the amount of haze on a mountain at a known distance. Suppose the mountain to be 25 miles distant; and at the time to be one-half hazed; then the limit of visibility of the mountain under the conditions would be 50 miles, and that was taken as the number representing the transparency of the atmosphere at the time. In the tables above referred to, along with the number of particles, was entered the limit of visibility at the time. When this was done, it was seen at once that as the number of particles increased the limit of visibility decreased, as will be seen from the following short table of the Rigi Kulm observations when the wet-bulb depression was between 2° and 4°, Table II:

TABLE II

Date	Mean number	Limit of visibility in miles	C
May 19, 1891	559	150	83850
May 22, 1889	642	100	64200
May 16, 1893	1912	40	77480

"When the number of particles is multiplied by the limit of visibility in the tables a fairly constant number C is obtained. All the observations taken at different places were treated in a similar manner and the mean of all the observations at the different humidities were obtained, and Table III gives the mean values of C at the different wet-bulb depressions of all the observations made at the different places.

TABLE III

Wet-bulb depressions	2° to 4°	4° to 7°	7° and over
Mean values of C	76058	105545	141148

"From Table III it will be seen that as the dryness of the air increased it required a larger number of particles of produce a complete haze, nearly double the number being required when the wet-bulb depression was over 7° than when it was only 2° to 4°. To find the number of particles required to produce a complete haze, that is, to render a mountain just invisible, all that is necessary is to multiply the above constant C by 160930, the number of centimeters in a mile. When this is done with the observations made in the West Highlands we get the numbers given in Table IV.

TABLE IV

Wet-bulb depressions	Number of particles to produce a complete haze
2° to 4°	12,500,000,000
4° to 7°	17,100,000,000
7° to 10°	22,600,000,000

"This table gives the number of particles of atmospheric dust in a column of air having a section of one centimeter square, required to produce a complete haze, at the different humidities, that is to make a distant object invisible, and is of course quite independent of the length of the column.

"In making these dust and transparency observations three things were noted: the number of particles; the humidity; and the limit of visibility. From the results above given, it is evident that if we know any two of these we can calculate the third. Suppose we know the limit of visibility and the humidity, then the number of particles can be calculated by the aid of the above tables.

"To show the hazing effects of dust it is not, however, necessary to use a dust counter. Aitken for some years made observations on the haze in the air at Falkirk by simply noting the direction of the wind, the wet-bulb depression at the time, and the transparency of the air. Falkirk is favorably situated for such observations owing to the peculiar distribution of the population surrounding it. The whole area from west, northwest, to north, is very thinly populated, while in all other directions it is densely populated. It was found that the air from the thinly inhabited parts, that is the northwest quadrant, was nine times clearer than the air from the other directions with the same wet-bulb depression, and that the density of the haze was directly proportional to the density of the population of the area from which the wind blew. These observations also showed that the transparency of the air increases with the dryness, being 3.7 times clearer when the wet-bulb depression is 8° than when it is only 2°, and that the air coming from the densely inhabited parts is about 10 times more hazed than if there were no inhabitants in the country."

De Lury[1] points out that "spectrum of haze, probably altogether terrestrial in its origin, accounts for much of the variation in the values of the solar rotation obtained by various observers at different times. Variations hitherto ascribed to the sun appear to be due to variations in scattered light. Spectrum of haze, being different in character to spectrum of limb depending in general on the intensity of the line, blends with spectrum of limb in such a way as to make it appear that different spectral lines yield different values for the velocity of rotation of the sun. Such differences found in measures of the solar rotation at Mount Wilson and at Ottawa are explained satisfactorily in this manner, and it seems possible to dispense with Adams' level hypothesis."

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[1] Astrophys. Jour., 44, 177 (1916).

"It has been shown[1] that a variable haze between the observer and the sun, causing to be blended on the spectrum of the limb a spectrum of variable intensity and of character somewhat similar to that of the center of the solar disk in regard to intensity and wave-length of the spectral line causes: (*a*) The spectroscopic determinations of the solar rotation to vary; and (*b*) the velocities of the rotation from the different lines to decrease in general with decrease in intensity of the lines, the amount of decrease in velocity for a given line depending on the strength of the continuous spectrum due to the haze relative to the continuous spectrum of the limb and on the ratio of the intensities of the line in the spectrum of the haze and in the spectrum of the limb. Observations already made make it seem probable that the variable terrestrial atmosphere and its clouds and hazes are sufficient to account for differences (*a*) and (*b*) after eliminating the systematic and accidental errors mentioned above. But if in any series of observations the spectrum of terrestrial haze can be proved of insufficient strength, then we may introduce the idea of haze existing between the earth and sun, near the sun, or even in the solar atmosphere (such as produced by matter falling in variable amounts into the sun and requiring an interval of time before being swept along into the general rotation). Such variable haze could possibly account for the differences in the solar radiation observed by Abbot and others; it would be interesting to make simultaneous observations of solar rotation and radiation to see whether the changes in their values synchronize."

With ice crystals in the air, we sometimes get halos and mock suns.[2] "The reflection and refraction of the sunlight by small ice crystals in the air give rise to a very complicated series of phenomena, which unlike the rainbow, can be seen at all altitudes of the sun. The ice crystals are all hexagonal, either flat plates or needles (spiculae). In still air these crys-

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[1] De Lury: Jour. Roy. Astronom. Soc. Canada, 10, 201 (1916).

[2] Wood: "Physical Optics," 347 (1911); Moore: "Descriptive Meteorology," 250 (1910).

tals will fall slowly with the principal axis vertical in the case of the flat plates or with the principal axis horizontal in the case of spiculae because bodies moving through a resisting medium set themselves in the position of greatest resistance.

"It is possible to show that the observer, looking through a filmy cloud of such crystals, would see in one part of the sky a halo, in another part an arc of light, and in other directions bright spots like the sun, all of them arranged symmetrically with regard to the sun and the observer's zenith. This resulting complex arrangement of circles and spots is known as a complete halo. It is rare that all possible combinations are seen at any one time, but on several occasions solar halos have been recorded that corresponded very nearly to this ideal. Three of these have become classic—namely, that observed by Scheiner at Rome in 1630, that observed by Havelius at Dantzig on February 20, 1861, and that observed by Löwitz at St. Petersburgh on June 18, 1790....

"In general, halos do not appear at their best in very cloudy or thick, hazy weather, but when the atmosphere is clear, with only a thin veil of falling crystals spread between the observer and the sun. Although the halo phenomena appear to belong to some very distant upper layer of air, yet practically they often originate in the very lowest layer. They depend simply upon the fact that there is a myriad of ice crystals, some in a position to make one part of the halo and some in a position to make another part, with plenty of particles substituting for others as fast as they fall out of place.

"The most common of the halos is the one of 22° radius, or a small ring around the sun or moon; this circle has a red border on the inside edge, or next to the sun, followed by a little yellow or green, and with bluish white on the outside. The measured angular radius is not always 22°, but varies between 21° 40′, the average being slightly less than 22°.

"Adjoining the halo of 22°, tangent to it at the upper and lower edges, but, in general, outside of it, there appears an elliptical halo whose longer radius is about 25°.

"Entirely outside of these is a great ring, or halo, of 25°

radius and outside of that a halo of 90°, both of which are rarer, and the last especially rare. The latter is supposed to be colorless, while the former has the interior ring red, and the exterior possibly blue; but it is more common that the red merges into the yellow and that no outer colors are visible.

"We come now to several tangential arcs or bows, and the first is that which is tangent to the upper halo of 22°; this is usually of the most brilliant rainbow colors. There is another similar or tangential bow at the lower edge, but not so often visible, since the sun is too near the horizon. Then again, there is a tangential arc at the lower edge of the circle of 46° radius, but this can be seen only when the sun is 46° above the horizon. It, also, is a colored bow, with the red on the side next to the sun, and seems to be parallel to the horizon. Again, there is a circular arc that sometimes appears near and surrounding the zenith, and also sometimes intersecting the halos of 22° and 46°. Besides these halo circles, there are bright spots, or sundogs, which belong, respectively, to the circles already described.

"The intersection of any two features is sometimes spoken of as a mock-sun, and these may be on either side of the true sun or on either side of the anti-sun. The latter is on a horizontal circle, passing through the primary mock-sun, but is distant from it 180° in azimuth. There are usually two mock suns, one on each side of the true sun, and two also where the halo of 22° intersects the horizontal circle. It may happen that only the mock-sun, or the horizontal circle, or the halo ring of 22° shall be present. In general, these mock suns are the most highly colored of the halo phenomenon.

"The first to explain these halo phenomena was Descartes, who suggested that they might be produced by star-shaped crystals of ice thicker in the middle than at the edges, and therefore producing rings that are larger in diameter in proportion to the thickness of the ice. Huyghens came much nearer to the truth, but Mariotte was the first to perceive that crystals of ice were involved in their production. The greatest success attended the labors of Bravais, who prepared artificial models of crystals and studied them by giving them rapid rotation round their axes."

The whole effect of light on fog and haze may change in a remarkable way if one varies the ratio between polarized and unpolarized light. This has been brought out clearly by Tyndall.[1] "The vision of an object always implies a differential action on the retina of the observer. The object is distinguished from surrounding space by its excess or defect of light in relation to that space. By altering the illumination, either of the object itself or of its environment, we alter the appearance of the object. Take the case of clouds floating in the atmosphere with patches of blue between them. Anything that changes the illumination of either alters the appearance of both, that appearance depending, as stated, upon differential action. Now the light of the sky, being polarized, may, as the reader knows, be in great part quenched by a Nicol's prism, while the light of a common cloud, being unpolarized, cannot be thus extinguished. Hence the possibility of very remarkable variations, not only in the aspect of the firmament, which is really changed, but also in the aspect of the clouds, which have that firmament as a background. It is possible, for example, to choose clouds of such a depth of shade that when the Nicol quenches the light behind them, they shall vanish, being indistinguishable from the residual dull tint which outlives the extinction of the brilliancy of the sky. A cloud less deeply shaded, but still deep enough, when viewed with the naked eye, to appear dark on a bright ground, is suddenly changed to a white cloud on a dark ground, by the quenching of the light behind it. When a reddish cloud at sunset changes to float in the region of maximum polarization, the quenching of the surrounding light causes it to flash with a brighter crimson. Last Easter eve the Dartmoor sky, which had just been cleansed by a snowstorm, wore a very wild appearance. Round the horizon it was of steely brilliancy, while reddish cumuli and cirri floated southward. When the sky was quenched behind them these float-

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[1] "Fragments of Science: The Sky of the Alps."

ing masses seemed like dull embers suddenly blown upon; they brightened like a fire.

"In the Alps we have the most magnificent examples of crimson clouds and snows, so that the effects just referred to may be here studied under the best possible conditions. On August 23, 1869, the evening Alpen-glow was very fine, though it did not reach its maximum depth and splendor. The side of the Weisshorn seen from the Bel Alp, being turned from the sun, was tinted *mauve;* but I wished to observe one of the rose-colored buttresses of the mountain. Such a one was visible from a point a few hundred feet above the hotel. The Matterhorn also, though for the most part in shade, had a crimson projection, while a deep ruddy red lingered along its western shoulder. Four distinct peaks and buttresses of the Dom, in addition to its dominant head—all covered with pure snow—were reddened by the light of sunset. The shoulder of the Alphubel was similarly colored, while the great mass of the Fletschhorn was all aglow, and so was the snowy spine of the Monte Leone.

"Looking at the Weisshorn through the Nicol, the glow of its protuberance was strong or weak according to the position of the prism. The summit also underwent striking changes. In one position of the prism it exhibited a pale white against a dark background; in the rectangular position it was a dark mauve against a light background. The red of the Matterhorn changed in a similar manner; but the whole mountain also passed through wonderful changes of definition. The air at the time was filled with a silvery haze, in which the Matterhorn almost disappeared. This could be wholly quenched by the Nicol, and then the mountain sprang forth with astonishing solidity and detachment from the surrounding air. The changes of the Dom were still more wonderful. A vast amount of light could be removed from the sky behind it, for it occupied the position of maximum polarization. By a little practice with the Nicol it was easy to render the extinction of the light, or its restoration, almost instantaneous. When the sky was quenched, the four minor peaks and buttresses, and the summit of the Dom, together with the shoulder of the Alphubel, glowed as if set suddenly on fire. This was immediately dimmed by turning the Nicol through an angle of 90°. It was not the stoppage of the light of the sky behind the mountains alone which produced this startling effect; the air between them and me was highly opalescent, and the quenching of this intermediate glare augmented remarkably the distinctness of the mountains.

"On the morning of August 24, similar effects were finely shown. At 10 A.M. all three mountains, the Dom, the Matterhorn, and the Weisshorn, were powerfully affected by the Nicol. But in this instance also, the line drawn to the Dom being very nearly perpendicular to the solar beams, the effects on this mountain were most striking. The gray summit of the Matterhorn, at the same time, could scarcely be distinguished from the opalescent haze around it; but when the Nicol quenched the haze, the summit became instantly isolated, and stood out in bold definition. It is to be remembered that in the production of these effects the only things changed are the sky behind, and the luminous haze in front of the mountains; that these are changed because the light emitted from the sky and from the haze is plane polarized light, and that the light from the snows and from the mountains, being sensibly unpolarized, is not directly affected by the Nicol. It will also be understood that it is not the interposition of the haze *as an opaque body* that renders the mountains indistinct, but that it is the *light* of the haze which dims and bewilders the eye, and thus weakens the definition of objects seen through it.

"These results have a direct bearing upon what artists call 'aerial perspective.' As we look from the summit of Mont Blanc, or from a lower elevation, at the serried crowd of peaks, especially if the mountains be darkly colored—covered with pines, for example—every peak and ridge is separated from the mountains behind it by a thin blue haze which renders the relations of the mountains as to distance unmistakable. When this haze is regarded through the Nicol perpendicular to the sun's rays, it is in many cases wholly quenched, because the light which it emits in this direction is wholly polarized. When this happens, aerial perspective is abolished, and mountains very differently distant appear to rise in the same vertical plane. Close to the Bel Alp, for instance, is the gorge of the Massa, and beyond the gorge is a high ridge darkened by pines. This ridge may be projected upon the dark slopes at the opposite side of the Rhone valley, and between both we have the blue haze referred to, throwing the distant mountains far away. But at certain hours of the day the haze may be quenched, and then the Massa ridge and the mountains beyond the Rhone seem almost equally distant from the eye. The one appears, as it were, a vertical continuation of the other. The haze varies with the temperature and humidity of the atmosphere. At certain times and places it is almost as blue as the sky itself; but to see its color, the attention must be withdrawn from the mountains and from the trees which cover them. In point of fact, the haze is a piece of more or less perfect sky; it is produced in the same manner, and is subject to the same laws, as the firmament itself. We live *in* the sky, not *under* it.

"These points were further elucidated by the deportment of the selenite plate, with which the readers of the foregoing pages are so well acquainted. On some of the sunny days of August the haze in the valley of the Rhone, as looked at from the Bel Alp, was very remarkable. Toward evening the sky above the mountains opposite to my place of observation yielded a series of the most splendidly colored iris rings; but on lowering the selenite until it had the darkness of the pines at the opposite side of the Rhone valley, instead of the darkness of space, as a background, the colors were not much diminished in brilliancy. I should estimate the distance across the valley, as the crow flies, to the opposite mountain, at nine miles; so that a body of air of this thickness can, under favorable circumstances, produce chromatic effects of polarization almost as vivid as those produced by the sky itself.

"Again: the light of a landscape, as of most other things, consists of two parts; the one, coming purely from superficial reflection, is always of the same color as the light which falls under the landscape, the other part reaches us from a certain depth within the objects which compose the landscape, and it is this portion of the total light which gives these objects their distinctive colors. The white light of the sun enters all substances to a certain depth, and is partly ejected by internal reflection, each distinct substance absorbing and reflecting the light, in accordance with the laws of its own molecular constitution. Thus the solar light is *sifted* by the landscape, which appears in such colors and variations of color as, after the sifting process, reach the observer's eye. Thus the bright green of grass, or the darker color of the pine, never comes to us alone, but is always mingled with an amount of light derived from superficial reflection. A certain hard brilliancy is conferred upon the woods and meadows by this superficially-reflected light. Under certain circumstances, it may be quenched by a Nicol's prism, and we then obtain the true color of the grass and foliage. Trees and meadows thus regarded, exhibit a richness and softness of tint which they never show as long as the superficial light is permitted to mingle with the true interior emission. The needles of the pines show this effect very well, large-leaved trees still better, while a glimmering field of maize exhibits the most extraordinary variations when looked at through the rotating Nicol.

"Thoughts and questions like those here referred to took me, in August, 1869, to the top of the Aletschhorn. The effects described in the foregoing paragraphs were, for the most part, reproduced on the summit of the mountains. I scanned the whole of the sky with my Nicol. Both alone, and in conjunction with the selenite, it pronounced the perpendicular to the solar beans to be the directiom of maximum polarization. But at no portion of the firmament was the polarization complete..... All along the arc, from the Matterhorn to Mont Blanc, the light of the sky immediately above the mountains, was powerfully acted upon by the Nicol. In some cases the variations of intensity were astonishing. I have already said that a little practice enables the observer to shift the Nicol from one position to another so rapidly as to render the alternative extinction and restoration of the light immediate. When this was done along the arc to which I have referred, the alternations of light and darkness resembled the play of sheet lightning behind the mountains. There was an element of awe connected with the suddenness with which the mighty masses, ranged along the line referred to, changed their aspect and definition under the operation of the prism."

The removal of dust from the air is an important matter in some industries. In photographic work dust particles in the film mean clear spots on the negative and black ones on the positive. In the manufacture of gas mantles, contamination by dust may cause pinholes in the product. It is pointed out by the Spray Engineering Company that in the ventilation of electric generators, an "important feature is that of the cleanliness of the ventilating air, and, unless proper equipment is provided to eliminate the dust or soot from the air, an accumulation of dirt is soon deposited within the machine, greatly reducing the cooling effect. Oily vapors that exist in air taken from the inside of power plants make such accumulations in the air passages particularly rapid. Dirty air, therefore, means excessive heat, which not only increases the ohmic resistance of the various windings, but shortens the life of the insulation, causing field-grounds and even burn-outs unless the generator is taken apart and cleaned often.....

"Few people realize the enormous quantity of air required for ventilating large turbo-generators. Assume, for instance, a moderately large generator using 65,000 cubic feet of air per minute. This amount of air weighs approximately 2.5 tons, so that within one-half to three-quarters of an hour a modern turbo-generator handles an amount of air equal in weight to its own total weight. With 65,000 cubic feet of air per minute passing through the machine, a total of

93,600,000 cubic feet will be handled in twenty-four hours. As a rough approximation, it may be assumed that one hundred-millionth of the volume of the air in the vicinity of power plants consists of dust, dirt, and other foreign particles. This would mean that 0.936 cubic feet of dirt would pass through the machine in twenty-four hours, or 86 cubic feet in three months. A portion will be deposited, due to the air swirls and eddies, in the air passages. As already pointed out, such deposits of dirt become a considerable handicap to the ventilation as the quantity of air is decreased, due to the partial closing of the ventilating passages, and the cooling effect of the air is greatly diminished, owing to the fact that the air cannot come directly in contact with the heat-radiating surfaces."

There are a number of firms which make apparatus for washing and cooling air. All of them remove the dust by spraying drops of water through the air instead of bubbling the air through water. Hill[1] states that a considerable number of the minute dust particles that are always present in air "are not caught in the liquid when dust is collected by bubbling through water, but pass through with the bubbles, the amount retained increasing as the size of the bubbles and velocity of air passing through the liquid decreases. We have repeatedly drawn room air through a Drechsel bottle with a three-inch water seal and have counted as high as 7000 small particles per cubic foot that were not retained in the water. Air passed through four wash bottles in series still gives a light beam with the diffractoscope."

Hill also made some tests with a commercial washer to show the percentages of various dusts removed. His data are given in Table V.

The percentage efficiency increases with increasing amount of dust entering the washer, for the figures in the third column are uniformly higher than the corresponding ones in the second column.

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[1] Pamphlet issued by Braemer Air Conditioning Corporation.

TABLE V

Percentage removal of dust by an air washer

Kind of dust used in test	Concentration of dust	
	Medium % Removal	High % Removal
Lamp black	89.4	91.2
Rubber dust	90.0	92.3
Street dust	96.2	98.2
Wood dust	96.5	99.2
Grain dust	98.5	99.2
Rattler dust	99.5	99.7

We know how effectively a rain clears the air and it is interesting to note that man has not succeeded in inventing a successful commercial type which differs from the natural one.

Cornell University

FLAME REACTIONS

BY JACOB PAPISH

In an attempt to explain the chemistry of some flames, Smithells[1] proved that carbon is set free in a hydrocarbon flame. He also showed[2] that metallic copper can be made to precipitate from the flame of a Bunsen burner which had been charged with a copper salt.

Bancroft and Weiser,[3] independently of the work of Smithells, have arrived at the conclusion that it is impossible to account for the flame spectra of copper salts without postulating the existence of free copper in some flames. Experiments with copper chloride confirmed the soundness of this conclusion. Extending their experimental work to other metallic salts, Bancroft and Weiser[4] proved that many of these salts dissociate at the temperature of the Bunsen flame, of the hydrogen-air flame, or of the oxyhydrogen flame, the metals being set free. The authors obtained metallic mirrors from the following compounds: Copper chloride, cadmium chloride, stannous chloride, silver nitrate, bismuth nitrate, lead nitrate, zinc chloride, arsenious oxide, antimony trichloride, molybdenum oxide and tungsten oxide. Mercuric oxide, when subjected to similar treatment, yielded drops of mercury. Dull red phosphorus was precipitated from phosphorus trichloride in a hydrogen flame, while yellow flowers of sulphur were obtained from sulphur dioxide in a hydrogen flame.

Hodgkinson[5] succeeded in precipitating sulphur on a cold object from a moderate-sized sulphur flame. He concluded that this sulphur precipitated because it escaped combustion: it vaporized and condensed on the cold object before ig-

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[1] Jour. Chem. Soc., **61**, 223 (1892).

[2] Phil. Mag., (5) **39**, 127 (1895).

[3] Jour. Phys. Chem., **18**, 252 (1914).

[4] Ibid., p. 261.

[5] Chem. News, **61**, 96 (1890).

niting. Hodgkinson "does not consider the possibility of free sulphur coming from sulphur dioxide."[1]

Sulphur, selenium and tellurium, in addition to their numerous properties in common, each imparts to the Bunsen flame a characteristic color. The precipitation of sulphur from a sulphur flame, and from a flame charged with sulphur dioxide, suggests the extension of the experiment to selenium and tellurium. For this purpose the materials were prepared as follows:

Selenium Dioxide.—Commercial selenium was dissolved in nitric acid with the aid of hydrochloric acid, and the solution was evaporated to dryness. The residue was sublimed, and the sublimate was dissolved in water. The filtered solution was strongly acidified with hydrochloric acid and saturated with sulphur dioxide gas. The precipitated selenium was removed, washed with water, fused and cast in blocks. Selenium dioxide was prepared by dissolving these blocks, previously pulverized, in nitric acid with the aid of heat. Careful evaporation with repeated portions of water, and heating to dryness, yielded a product free from nirtic acid.

Tellurium Dioxide.—Pulverized commercial tellurium was dissolved in aqua regia with the aid of heat. The white mass was heated to dryness, fused in a porcelain crucible and poured in water. The granular mass was collected, dissolved in the least amount of hot strong hydrochloric acid, and this solution was diluted with a large excess of cold water. The white precipitate was filtered and washed with cold water with the aid of a suction pump. The washed product was fused in a porcelain crucible and allowed to solidify.

The oxides of selenium and tellurium thus obtained were considered pure enough for the experimental work undertaken. These oxides were introduced in the Bunsen flame in a manner similar to the one employed by Bancroft and Weiser:[2] "A small hole was bored in the tube of the Bunsen burner about two inches from the top. A hard glass tube

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[1] Bancroft and Weiser: Jour. Phys. Chem., 18, 248 (1914).

[2] Ibid., p. 253.

of small diameter was drawn out to a jet that would fit this hole. Some of the dry salt (in this case, oxide) was placed in the glass tube. The tube was then heated, and a very slow current of air passed through it. The fumes of the volatilized salt (oxide) were thus carried into the burner and up into the flame. This secures a fairly uniform distribution of the salt (oxide) throughout the flame." A four-inch porcelain evaporating dish containing cold water was used as the cold object, and it gave satisfactory results.

Selenium Dioxide.—This substance volatilizes very readily, coloring the flame intensely blue. Elementary selenium was easily precipitated on the cold object in the form of a dark red stain surrounded by an area of brighter red, which terminated in yellow.

Tellurium Dioxide.—The vapors from tellurium dioxide imparted to the flame a blue color slightly modified by green. The uppermost part of the flame was distinctly green. A bright metallic mirror was easily produced on the cold object when the latter was held in the hottest portion of the flame.

Conclusions

It was proved by different experimenters that metallic salts and other compounds are dissociated or reduced in the flame, and that this dissociation or reduction is the cause of a characteristic luminescence or spectrum. To this list of compounds the oxides of selenium and tellurium should be added, since elementary selenium and tellurium can be easily precipitated from a Bunsen flame charged with their oxides. Selenium precipitates as the red variety, while tellurium yields a bright metallic mirror.

Indiana University

NOTE ON CONTACT CATALYSIS

BY WILDER D. BANCROFT

In a previous paper[1] I tried to show that it was not a theoretical impossibility for a solid catalytic agent to cause a displacement of equilibrium. Since writing that paper, I have come across a passage[2] to the effect that J. J. Thomson[3] had shown that both the velocity and the equilibrium relations could be changed markedly in surface films. This proves to be the case and Thomson's reasoning is so interesting that I reproduce selected portions of it.

"The first effect we shall consider is that due to the surface tension of the solution. We know that the surface tension depends on the strength and nature of the solution, so that since the composition changes as chemical action goes on the surface tension of the solvent and therefore its mean Lagrangian function will change; and therefore, by the principle we have just stated, the conditions for equilibrium will be altered by the surface tension.... If the solution be spread out in a film of thickness t, $\delta k/k$ is of the order $6/10\,t$ where k is the coefficient of chemical combination, as Thomson calls it. Thus, if the thickness of the film is $^1/_{10000}$ of a centimeter [$1\,\mu$] the value of k is altered by about 0.6 percent. If the thickness of the layer is comparable with molecular distance, say about 10^{-7} [$1\,\mu\mu$] then $\delta k/k$ might be as large as 6. This of course implies that the conditions of equilibrium would be altered completely. Thus in very thin films the influence of capillarity might be sufficient to modify completely the nature of chemical equilibrium, though we should not expect it to do much in the body of a fluid.

"If the surface tension increases as the chemical action goes on, the capillarity will tend to stop the action, while if the surface tension diminishes as the action goes on, the capil-

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[1] Bancroft: Jour. Phys. Chem., 21, 580 (1917).

[2] Ehrenberg: "Die Bodenkolloide," 252 (1915).

[3] "Applications of Dynamics to Physics and Chemistry," 203, 234 (1888).

larity will tend to increase the action. Thus the chemical action in a space such as a thin film, throughout which the forces producing the capillary phenomenon are active, might be very different from the chemical action in the same substance in bulk when most of it would be free from the action of such forces."

These remarks refer to solutions, but Thomson has also considered the case of gases. "Though the effects of surface tension are not nearly so prominent in gases as in liquids, still since there is perfect continuity from the liquid to the gaseous state, we should expect that the outer layer of molecules of a gas which was not in the perfect condition would, like the outer layer in a liquid, be under different conditions from the other molecules, and would therefore not possess the same amount of energy as the same number of molecules in the midst of the gas. In van der Waals' theory of the relation between the pressure and volume in an imperfect gas, the result of which is expressed by the relation

$$\left(p - \frac{a}{v^2}\right)(v - b) = R\theta,$$

the term a/v^2 is due to the action of the surface tension of the gas.[1]

"Though it is much more difficult to detect that existence of the action of surface tension experimentally in gases than in liquids, there is still some evidence of its existence from experiments such as those of Bosscha on the forms of clouds of fog and tobacco smoke. If the surface tension diminishes as dissociation goes on, in which case $\alpha T/\alpha\xi$ is positive, the dissociation will be greater the larger the surface of the gas.[2] We should expect *a priori* that the surface tension of the surface tension of the dissociated gas would be smaller than that of the undissociated, for in most cases the dissociated gas approaches more nearly than the other to the

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[1] Van der Waals': "Die Continuität des gasförmigen und flüssigen Zustands," 34.

[2] T is the quantity corresponding to the surface tension of the gas. For ether Thomson calculates $T = 3.24 \times 10^{-4}\xi$ is the mass of the substance.

state of a perfect gas: thus in most cases $\delta T/\delta \xi$ will be positive, so that dissociation will be facilitated by increasing the surface of the gas.

"If the gas be supposed to be a film of thickness t, then $\frac{\delta\lambda}{\lambda} = \frac{1.2}{t \times 10^8}$ [where λ is a measure of the dissociation], so that if the thickness of the film were comparable with molecular dimensions, say $t = 10^{-7}$ [1 $\mu\mu$] then the surface tension would produce very large effects. This example may be sufficient to show that, if we have the gas in thin films, surface tension may produce a very considerable effect; such films occur adhering to glass fibers or to matter in a fine state of division, such as spongy platinum or charcoal. The value of T given above is only part of the surface tension of the surface of contact of the gas and the solid. The surface tension of the surfaces separating A and B [gas and solid] is due to the energy of thin layers of A and B next their junction differing by a finite amount from the energy possessed by equally thin layers in their interior. The abnormal energy of these layers is due to the want of symmetry of the action on the two sides. In the preceding investigation we have calculated the part of the energy of the layer of one of these substances arising from the effects produced by its own molecules; in addition to this there is the energy arising from the action of the glass on the gas as well as the energy in the thin film of glass. Thus the value of the surface tension may be much greater than that given above and the effects due to it may therefore be greater than our estimate.

"The value of T may depend upon the substance to which the film adheres, and thus the nature of the walls of vessels used for chemical experiments may affect the chemical combination which goes on inside of them. Van't Hoff[1] has described some experiments which seem to show that effects of this kind do exist. He shows that the rate at which the polymerization of cyanic acid goes on is increased by increasing the area of the walls of the vessel in which it is contained, the

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[1] "Études de Dynamique Chimique," 56.

volume being kept constant. Thus when the area of the walls was increased six times, the rate of polymerization was increased in the ratio of 4 to 3. He also found that when the walls of the vessel were covered with a deposit of cyamelide the rate of polymerization of cyanic acid was increased three-fold. Victor Meyer too found that the decomposition of carbonic acid takes place in a porcelain vessel at a temperature several hundred degrees lower than in a platinum vessel. When the effects produced are of this magnitude, it is doubtful whether they can be due to the effect of surface tension; but it is probable that in the case of many catalytic actions, where we have thin films of gas, the effects observed might be explained by considerations of this kind."

Thomson[1] also discusses the effect of a neutral gas. "If the properties of the neutral gas are not affected in any way by the presence of the gas which is dissociating, the value of the mean Lagrangian function of the neutral gas will not change as dissociation goes on. The presence of this gas will therefore not affect the maximum amount of dissociation. The presence of a foreign gas certainly alters the rate of dissociation, and in some cases the experiments seem to show that it does alter the maximum amount of dissociation. This is contrary to the result we have just arrived at, and the only way of reconciling the two is to suppose that the gas is not perfectly neutral but has its properties affected to some extent by the presence of the other gases. If the dissociation were at all catalytic, we might explain the action of the neutral gas by supposing that by itself forming a film on the surface of the vessel it prevented to some extent the dissociating gas from doing so."

J. J. Thomson has brought out clearly the fact that there is nothing thermodynamically impossible about the displacement of equilibrium at the surface of a solid which acts as a catalytic agent. If he had put in the further assumption that the reaction took place with appreciable velocity only at the surface of the solid catalytic agent, his argument would

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[1] "Application of Dynamics to Physics and Chemistry," 207 (1888).

have been the same as mine in substance[1] though not in form. Thomson considers that the reaction will proceed so as to lower the surface tension. That is not an especially helpful way of putting it when we are dealing with a solid. If we adopt Freundlich's generalization that adsorption is always accompanied by lowering of surface tension, then the greatest decrease in surface tension will be caused by the substance which is adsorbed the most, provided other things are equal, Under these circumstances Thomson's criterion becomes essentially the same as the one adopted in the paper referred to.

Gibbs[2] has said the same thing in regard to liquid films, though not quite so clearly. "If the tension of the film is less than that of any other film of the same components which can exist between the same homogeneous masses (which has therefore the same values of t, μ_a, μ_b, etc.) and which, moreover, has the same values of the potentials μ_g, γ_h, etc., so far as it contains the substances to which these relate, then the first film will be stable. But the film will be practically unstable if any other such film has a less tension. It is, however, evidently necessary for the stability of the surface of discontinuity with respect to *deformation*, that the value of the superficial tension should be positive."

It is interesting also to note that Thomson had formulated clearly in 1888 the statement that an apparently neutral gas must cut down the adsorption of a reacting gas by the solid catalytic agent, if the first gas is to affect the equilibrium relations of the second. It is not quite clear why J. J. Thomson considered that the experiments of van't Hoff and of V. Meyer probably involved other factors. In the first place thermodynamics tells us nothing about reaction velocities which is what these men were studying. In the second place, the relative effect of walls may be almost anything if the reaction in the mass of the gas takes place sufficiently slowly. While J. J. Thomson has obtained the same results from a con-

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[1] Bancroft: Jour. Phys. Chem., 21, 580 (1917).

[2] Scientific Papers, 1, 240 (1906).

sideration of surface tension which have been obtained by a study of adsorption, it does not follow that the two methods of attack are equally good. Adsorption can be measured, while the surface tension of a solid cannot. It seems to me, therefore, that the consideration of adsorption relations is the safest and best way of attacking these problems even though it gives only qualitative results for the present.

The general results of this paper are as follows:

1. The statement that it was thermodynamically impossible for a solid catalytic agent to displace an equilibrium was disproved years before it was formulated.

2. Back in 1888 J. J. Thomson showed that a solid catalytic reagent would displace an equilibrium, and pointed out one criterion for determining the sign of the change.

Cornell University

COLOR DETERMINATION OF FAINT LUMINESCENCE

BY HARRY B. WEISER

In connection with the study of the faint crystalloluminescence of certain salts the author was confronted with the problem of determining the color of the emitted light. The difficulty arises from the fact that the intensity and duration of the light is such that it does not admit of spectroscopic investigation. The same is true of many chemiluminescent reactions and particularly of those that take place when the reacting substances are brought together in solution. In these cases spectrographs can not be obtained even by long-continued exposure. "Spectrographs of the strongest phenomena of crystalloluminescence and chemiluminescence could not be obtained even by repeated exposures for eight hours, using a large spectroscope with camera attachment."[1] Color photography of the luminescence[2] is likewise manifestly impossible. In consequence observers of faintly luminescent reactions have had to rely on the color sensitiveness of the eye to determine the color of the emitted light. For many reasons this is very unsatisfactory at the best.

In the first place the glow of faint luminescence appears white, and it is obviously very difficult to determine whether this whitish glow has its maximum in the red, yellow, green or blue. In speaking of the color of crystalloluminescence, Trautz says:[3] "The color of the light is white, sometimes greenish; only in one case, that of sodium fluoride, is it yellowish. Usually the effect is very delusive. To all outward appearances the quality of the light is similar in all cases." It is interesting to note that the single case of yellow crystalloluminescence referred to above was not observed by Trautz as he was unable to detect light during the crystallization of

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[1] Trautz: Zeit. phys. Chem., 53, 101 (1905).

[2] Lohr: Jour. Phys. Chem., 17, 675 (1913).

[3] Trautz: Zeit. Elektrochemie, 10, 593 (1904).

sodium fluoride. Berzelius[1] and Rose[2] each claim to have observed the luminescence but once.

As might be expected, there is a difference of opinion as to the actual color of the light emitted by certain reactions. Thus Bandrowski[3] describes the light emitted when a saturated solution of sodium chloride is precipitated with hydrochloric acid as bluish green. Farnau[4] takes it to be bluish white. When the light is very faint the color seems to me to be bluish; but at the point of maximum brightness which I have been able to obtain by a careful adjustment of the conditions of precipitation, the color appears decidedly yellowish. This is likewise the consensus of opinion of a score or more of people to whom I have exhibited the phenomenon.

A common source of error in the determination of the color of luminescence by the unaided eye is introduced by the "Purkinje Phenomenon." "When spectral colors are examined, it is obvious that some of the colors are brighter than others, the extreme red and extreme violet for instance, possessing little luminosity as compared with the yellow. The relative brightness of the different spectral colors is found to vary with the amount of illumination. With a brilliant spectrum the maximum brightness is in the yellow, but with a feeble illumination it shifts to the green. This accords with what is known as the Purkinje phenomenon, namely, the changing luminosity and color value of colors in dim lights. As the light becomes more feeble the colors toward the red end of the spectrum lose their quality, the blue colors being perceived last of all, just as in late twilight the sky remains distinctly blue after the colors of the landscape become indistinguishable."[5] On this account we should expect a very faint luminescence to *appear* blue to the eye even if the maximum color actually were in another portion of the spectrum.

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[1] Jahresbericht, 1823, 400.

[2] Pogg. Ann., 52, 443, 585 (1841).

[3] Zeit. phys. Chem., 15, 323 (1894).

[4] Eighth Internat. Congress Applied Chemistry, 20, 133 (1912).

[5] Howell: "Textbook of Physiology," 339 (1910).

The color of light by which luminescence is observed likewise has an effect. "It is striking," says Trautz,[1] "that just those liquids which show the clearest luminescence appear to undergo a decided change in color toward the blue if they are viewed by red light (ruby glass light). As an example I should like to call attention especially to the above mentioned pyrogallol luminescence. In the second stage of this reaction, after the first foaming has subsided, the liquid glows white in the dark and blue like petroleum in red light. The luminescence is too weak for spectroscopic investigation. . . . Glowing amarine behaves similarly. When treated with bromine water, the color of the light appears yellow-green in the dark and more of a blue-green in red light." In this connection I have noted that there is an apparent difference in the color of luminescence depending on whether I remained in total darkness while my eyes became sensitive enough to make the observations or whether the dark room was lighted faintly with a red light to facilitate the preparation for the experiments.

Trautz[2] claims that the addition of substances which change the color of the reacting mixture does not greatly change the color of the luminescence, but that such additions may diminish the intensity to such an extent that it is impossible to judge the color. He has found, for example, that the addition of potassium dichromate, fluorescein, iodine in potassium iodide, or alizarine blue does not change the glowing reddish color of light emitted during the oxidation of pyrogallol, but that addition of the colored substances diminishes the intensity. Thus, strong coloration with alizarine blue renders the light almost invisible. It should be mentioned at this point that Trautz considers the pyrogallol oxidation with hydrogen peroxide to take place in two stages: the first stage glowing with a relatively bright reddish light, and the second (after the foaming subsides), glowing much fainter and white. As it seems to me, the apparent change in color

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[1] Zeit. phys. Chem., **53**, 102 (1905).

[2] Ibid., p. 101.

is brought about by two things: first, the diminished intensity which is largely the result of the diminished reaction velocity; and second, the effect in increasing amount of the presence of the very highly colored reaction product. For the color of the solution doubtless has an effect, particularly in view of recent work on the modifying influence on flame spectra of the presence of colored substances in the flame.[1]

Considering all the possible sources of error it is evident that the determination of the color of faint luminescence with the unaided eye is most unsatisfactory. A method has been devised, however, whereby the color may be determined with a considerable degree of accuracy. The method consists essentially of photographing the luminescence on a panchromatic plate, interposing a series of different colored color screens between the source of light and the plate. Obviously the plate will be fogged only behind those color screens that transmit the light and in direct proportion to the amount each transmits. By comparing the photograph so obtained with a photograph of white light, using the same color screens, the color of the luminescence is readily determined. The method is applicable in all cases where the glow is uniform and sufficiently strong to fog the most sensitive photographic plate brought very close to it. For the purpose of demonstrating the usefulness and applicability of the method, I will describe in detail the results obtained with reactions varying in intensity from the relatively bright oxidation of alkaline pyrogallol to the faint crystalloluminescence of sodium chloride.

Experimental

The reactions were carried out in the mixing apparatus described at length in a previous communication.[2] This consists essentially of two concentric glass tubes: the outer one approximately 3.5 cm in diameter and the inner one 2 cm in diameter. With this apparatus practically instantaneous

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[1] Bancroft and Weiser: Jour. Phys. Chem., 18, 281 (1914).

[2] Weiser: Ibid., 20, 314 (1916).

and uniform mixing can be obtained and when necessary, the solution can be stirred by moving the inner tube up and down.

The exposure of the plate was conveniently accomplished in an apparatus especially designed for the purpose: A vertical slit 7 cm long and 0.9 cm wide was cut in a board 28 cm by 28 cm and 1 cm thick. On one side of this board were fastened two parallel horizontal strips so grooved that they held a photographic plate holder flush against the board and yet allowed the holder to slide back and forth in front of the slit. By this provision a number of exposures could be made on one plate. On the opposite side of the board two vertical cleats 3 cm by 3 cm were fastened on either side of the slit at such a distance apart that the mixer fit snugly between them. A groove was cut in the board to fit the curved surface of the mixer. Two buttons attached to one of the cleats could be so turned as to hold the mixer firmly in place during an exposure. To support the apparatus in a vertical position it was fastened to a strip of wood 4 cm by 9 cm by 28 cm. The apparatus was painted a dull black. In this "camera" the reacting vessel was held about 1 cm from the plate.

The highly recommended[1] panchromatic plates manufactured by Wratten and Wainwright were used when necessary to have a plate sensitive to red light. When this was not necessary the faster Hammer "red label" plates were substituted. A collection of 35 gelatine color screens manufactured by Wratten and Wainwright were obtained from the Eastman Kodak Company. The color of light which each would allow through was determined by interposing each in turn between a source of white light and the slit of a spectroscope. From the assortment of calibrated screens a number were chosen varying in color from deep red to deep violet. Strips of suitable width were cut from each and pasted close together over the slit of the "camera" so that they were next to the plate during exposure.

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[1] Baly: "Spectroscopy," 372 (1912).

The Oxidation of Pyrogallol.—Fifteen cubic centimeters each of 50 percent potassium carbonate solution, 10 percent pyragallol solution and formalin were placed in the outer compartment of the mixer and 40 cc of 40 percent hydrogen peroxide in the inner compartment.[1] This was set in the "camera" previously loaded with a panchromatic plate and the reaction started by mixing the contents of the two compartments. After several seconds' exposure to the light of the reaction, another portion of the plate was moved over the slit and a photograph of white light taken by exposing to daylight for an instant. The development and fixing of the plates were carried out in absolute darkness. A description of the filters used is given in Table I. Statements of the color of

TABLE I

Number	Color of filter	Light that passes through filter
1	Deep red	Red only
2	Red	Red to lithium beta line
3	Reddish orange	Red to the left of calcium beta line
4	Yellow	Red to the thallium line
5	Green	From lithium beta line to barium delta line. Small band in red
6	Green	From lithium beta line to barium alpha line. Small band in red
7	Dark green	From calcium beta line to barium beta band
8	Blue (purplish)	From barium beta band to midway between strontium delta line and rubidium alpha line. Little band in orange
9	Purple	From strontium delta line through the extreme violet. Red to lithium alpha line
10	Blue	From right of barium alpha line to right of indium alpha. Little band in orange
11	Blue	From left of barium beta band to indium alpha line
12	Deep blue	Blue only
13	Violet	Mercury violet filter

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[1] This recipe is recommended by P. Schorigen: Zeit. phys. Chem., 53, 596 (1904).

light that passes through the filters are of course only approximate as the absorption bands are not always sharply defined. The photographs which have been taken and which are referred to in the text have not been reproduced owing to the rather unsatisfactory effect of such half-tones.

It is evident from the photographs obtained that the color of the light emitted during the oxidation of pyrogallol lies almost entirely in the red and yellow portions of the spectrum. There is practically no green or blue as but little light passes through the filters 5 to 13, inclusive. The plate was fogged very slightly behind filters 5, 6, 9 and 10, but this hardly shows in the print. By reference to the table it will be seen that these filters allow either a little red or orange light to pass through. The plate was affected behind filters three and four almost equally, although when exposed to white light it is affected distinctly more behind Number 4. This indicates that the luminescence is made up of a band that extends from the red through the yellow with the maximum in the orange-red.

Oxidation of Phosphorus.—When a solution of phosphorus in glacial acetic acid is treated with a solution of hydrogen peroxide a luminescence is produced that appears to be colored greenish yellow to white, depending on the intensity of the light. This glow was photographed in the same way as the pyrogallol luminescence, using the same color screens.

Examination of the photograph shows that there is practically no red, orange or yellow in the luminescence, since no light passed through filters 1, 2 and 3. A little passed through Number 4, which allows some green through in addition to the red and yellow. It will be noted that the remainder of the plate was affected almost in the same way by the luminescence as by white light. Photographs taken with the series of filters described in Table II lead to the same conclusion, namely, that the luminescence is the same in quality as white light from the yellowish green through the violet.

Oxidation of Amarine with Chlorine and Bromine.—It was discovered by Radziszewski[1] that the oxidation with air or oxygen of a solution of amarine in alcoholic potassium hydroxide is a luminescent reaction. Trautz[2] found that the intensity of the luminescence is greatly increased by increasing the velocity of the reaction by the addition of 30 percent hydrogen peroxide or one of the halogens. With chlorine the color of the light is described by Trautz as blue-green, with bromine, yellow-green and with iodine, white.

Amarine, which is an isomer of hydrobenzamide, was prepared by heating the latter for several hours at a temperature of 125 degrees. 1.5 gram of the product were dissolved in 40 cc of an alcoholic solution of sodium hydroxide saturated at room temperature. This solution was heated to boiling and placed in the outer compartment of the mixing vessel and an equal amount of saturated chlorine water or bromine water in the inner compartment. The mixture was stirred continuously during the exposure of the plate. It was found that the luminescence with chlorine was fainter than with bromine but that it lasted longer and was more readily photographed. Better results were secured with bromine by adding a little of the liquid along with the water solution. Experiment showed that it was unnecessary to use a plate sensitive to the red as the emitted light contained no red. The filters used are described in Table II.

As before stated, there is no red in the amarine luminescence. Examination of the photographs shows that white light affects the plate most behind filter Number 7, whereas it is almost entirely unaffected at this point by the luminescence. This eliminates all the color from the strontium blue line through the violet. Further examination reveals that the plate is fogged the most behind those screens which transmit the most green light. Filter Number 5 definitely fixes the maximum color of the luminescence in the green and Number 6 shows it to be in the immediate region of the thallium green line.

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[1] Ber. deutsch. chem. Ges., 10, 70 (1877).

[2] Zeit. phys. Chem., 53, 86 (1905).

TABLE II

Number	Color of filter	Light that passes through filter
1	Yellow	Red to the thallium line
2	Green	From lithium beta line to barium delta line. Small band in the red
3	Green	From lithium beta line to barium alpha line. Small band in the red
4	Dark green	From calcium beta line to barium beta line
5	Light green	From lithium beta line to left of barium beta band. Red to lithium alpha line
6	Dark green	From calcium beta line to right of barium beta band. Maximum at thallium alpha line
7	Purple	From strontium delta line through the extreme violet. Red to lithium alpha line
8	Greenish blue	From left of thallium line to indium alpha line
9	Blue	From right of barium alpha line to right of indium alpha line. Little band in orange
10	Blue (purplish)	From barium beta band to midway between strontium delta line and rubidium alpha line. Little band in orange
11	Blue	From left of barium beta band to indium alpha line
12	Deep blue	Blue only

Filter Number 12 shows that there is relatively little blue in the light as the fogging behind this screen is almost imperceptible. It is interesting to note that the photographs using chlorine and bromine as oxidizing agents indicate that the color of the luminescence is the same in both cases even though they may not appear so to the unaided eye.

The Crystalloluminescence of Sodium Chloride.—When a saturated solution of sodium chloride is mixed with alcohol or hydrochloric acid, precipitation takes place with emission of light, the color of which is impossible to determine with any degree of certainty with the unaided eye. However, it readily lends itself to determination by the method under consideration.

Forty cubic centimeters of a sodium chloride solution saturated at room temperature were placed in the outer compartment of the mixing vessel and a like amount of hydrochloric acid, specific gravity 1.12, in the inner compartment. The precipitation was effected and the luminescence photographed as in the previous cases. To get a good negative it was necessary to expose the plate to the luminescence three times at the same place. The filters listed in Table I were used.

The photograph shows that there is no red, orange, yellow or green in the luminescence since the plate is unaffected behind filters 1 to 7, inclusive. Filters Numbers 8 and 9 show conclusively that practically all the color is beyond the strontium blue line. There is very little color in the blue to the left of the indium blue line since the plate is affected but slightly behind filters 10 to 12, inclusive. The color of the luminescence is therefore bluish violet.

The above series of experiments is sufficient to show that by the method described, it is possible to determine the color of luminescence with a degree of accuracy that is limited only by the number and choice of the ray filters employed.

The results of this investigation may be summarized as follows:

1. Spectroscopic investigation of faint luminescence is impossible.

2. The color of faint luminescence cannot be determined even with approximate accuracy with the unaided eye.

3. A method has been devised for determining the color of faint luminescence that is applicable whenever the glow is uniform and sufficiently strong to affect the most sensitive photographic plate brought very close to it. The method consists essentially of photographing the luminescence on a panchromatic plate interposing a series of color screens between the source of light and the plate.

4. An apparatus has been described for photographing the luminescence of reactions that take place in solution.

5. The applicability and usefulness of the method has been tested with a number of reactions that vary widely in the quality and intensity of the luminescence.

Department of Chemistry,
The Rice Institute,
Houston, Texas

NEW BOOKS

Manual of Milk Products. *By William A. Stocking. 20 × 14 cm; pp. xxvii + 578. New York: The Macmillan Company, 1917. Price: $2.00.*—The chapters are entitled: milk secretion; the chemical composition of milk; factors that affect the composition of milk; physical properties of milk; the testing of milk and cream; market milk; certified milk; butter-making; cheddar cheese; fancy cheeses; farm dairying; condensed and powdered milk; fermented milk; ice-cream making; the relation of bacteria to cheese.

Milk is an emulsion and its behavior is of distinct theoretical interest to the colloid chemist. There is a great deal that we do not yet know about casein. Creaming is a special case of a cracked emulsion. Butter-making involves agglomeration. The action of rennet in cheese-making calls for a great deal more study than has yet been given to it. Renovated butter, p. 281, is the formation anew of an emulsion. So it goes all the way down the list. Of course the author has not written his book with reference to the colloid chemist, but the latter can get a great deal of useful information out of it nevertheless.

On p. 91 there is a discussion of the viscosity of milk. "The consistency of milk or cream is made up of two factors, one dependent on the inherent characteristics of the solution (the milk-serum) and the other belonging to the matter suspended in this solution (fat, casein, and so on). The effect of the first factor we term viscosity in order to discriminate between substances in solution and in suspension. The combined effect of these two factors is what makes the body or consistency of milk or cream. The consistency of the milk-serum is due to the viscosity imparted by substances such as the sugar and the ash constituents which are in a state of perfect solution and also by the physical state of the casein and insoluble phosphates which are doubtless suspended in a semi-colloidal condition. These substances differ in their ability to impart consistency to milk-serum, the nitrogenous matter having about three times the influence of the milk-sugar in normal milk.

"The influence of the fat on the consistency is purely mechanical, it being wholly in suspension. In part, this is undoubtedly due to the inherent characteristics of the fat globule itself, such as size and its relation to surface tension, and so on, but to a much larger extent to the aggregation of the fat globules into small groups or clots, a condition which is always found to a greater or less extent in normal milk. The effect of these factors is greatly modified in a variety of ways. For example, centrifugal force in separating cream diminishes its consistency to a marked degree; on the other hand, the development of acid in spontaneous souring materially increases the body. The thickening of cream observed in the churn is a phenomenon likewise dependent on these conditions. Temperature also has a marked effect, the consistency being increased or diminished as it is lowered, or raised.

"It has previously been stated that variations in temperature have a marked effect on the consistency of milk and cream; that within moderate limits the effect is the same as with most viscous substances, it being made thinner when warmed, and the original consistency returning when cooled to the initial temperature. Pasteurized milk and cream show an apparent exception to this rule, inasmuch as the original consistency does not return after the milk or cream is thoroughly chilled. This condition is a serious objection to the use of these products on the part of the consumer, as he invariably refers this relative thinness to a lack of butter-fat. So serious has this complaint become that it has greatly militated against the general introduction of these products. As this is the only objection, and as these products have every advantage from a sanitary and economic standpoint in comparison with ordinary milk and cream, this has been the chief incentive from the practical standpoint for undertaking this study.

"Before attempting to find a remedy for this difficulty, it became necessary to study the general question of the conditions affecting the consistency of natural milk and cream when subjected to high temperatures such as are used in the pasteurizing and sterilizing processes. Here the microscope gave us an important clue to the physical constitution of milk and cream that had been submitted to the action of heat. A microscopic examination of pasteurized milk or diluted pasteurized cream presents a very different picture from that of normal milk or cream. In the case of the normal milk the fat globules, in place of being homogeneously distributed throughout the microscopic field, are grouped in part in irregular but well-defined masses. But not all of the fat globules are included in these fat aggregations. Some of the globules remain isolated and distinct, although there is a marked tendency in cover-glass preparations, owing to capillary currents, for these individual globules to be caught in these irregular groupings. The matrix that holds these fat globules together is under the microscope practically transparent, but by watching these currents with their floating fat globules, the irregular outline of the fat clots can be perceived. In these clots it will be observed that the individual fat globules retain their spherical form and do not coalesce, as is the case in incipient churning.

"The microscopic appearance of milk or cream that has been heated above 65° C (149° F) is totally different. Not only is this true with pasteurized milk, but sterilized or boiled milk as well as condensed milk likewise present a similar microscopic appearance. In these cases the fat globules are homogeneously distributed throughout the microscopic field. The fat aggregations that are so characteristic of the preparations of normal milk and cream are here entirely lacking. Hundreds of preparations have been made of both pasteurized milk and cream from individual and mixed milks, and in no case have we found any exception to this condition. This phenomenon is certainly coincident with the change in consistency, and we may reasonably expect that it is causally connected in some way with this microscopic appearance. To prove this point more conclusively, it is necessary to study simultaneously, both from a microscopical and a viscometrical standpoint, milks that have been heated at different temperatures. Experiments on this point were made, showing that the change in consistency did occur at practically the same temperature at which the microscopic clots in the milk broke down. This relation seems to show that the greater consistency of natural cream is very intimately connected with the presence of these fat aggregations. In milk this is less pronounced, owing to the greater effect that the serum solids have upon the total consistency of the fluid."

On p. 225 the question of creaming is taken up. "For butter-making the milk-fat is removed from the milk in the form of cream which should contain from about 30 percent to about 45 or possibly 50 percent of fat. This separation of the fat in the form of cream is possible, because of the difference in the specific gravity between the fat globules and the other constituents of the milk. If milk is allowed to stand undisturbed, the fat globules will rise slowly to the surface and can then be skimmed off in the form of cream, the rapidity and completeness with which the fat globules rise to the surface depending on the difference in specific gravity between the fat globules and the other elements in the milk, and on the viscosity of the milk-serum. Anything which affects either of these factors will affect the creaming process. The conditions which most commonly affect the creaming process are: the size of the fat globules, the percentage of solids not fat, and the viscosity of the serum. The larger the fat globules, the more easily they rise to the surface, because of the greater mass in proportion to the surface. For this reason, the milk from certain breeds, as the Jersey and Guernsey, creams more easily than that of others, as the Ayrshire and Holsteins. Since the fat globules decrease in size as the lactation period advances, the milk from new milch cows will cream more easily than that of cows far advanced in the period of lactation.

"Since the solids not fat are all heavier than water, their increase will increase the specific gravity of the milk-serum and increase the difference in specific gravity of the fat globules and the serum, thus making it easier from the cream to rise. However, an increase in solids increases the viscosity of the serum and retards the rising of the cream. The presence of fibrin in the milk may also interfere with the creaming process. Regarding the influence of fibrin upon the creaming process, Babcock (Wis. Report, 1893, p. 145) says: As the clots of fibrin are heavier than the milk-serum and become attached not only to the fat globules, but to other solid particles in the milk, often to the sides of the vessel in which the milk is set, it is evident that even the small amount of fibrin in milk may be a great hindrance to thorough creaming. If this is true, the most efficient creaming should be obtained when the conditions are such as to oppose the coagulation of fibrin. This is believed to be true in all gravity systems of creaming, at least all improvements which have been made in these systems have been in this direction. The centrifugal separator accomplishes the same end by making the effective difference between the weight of fat and the fibrin clots so great that the disadvantage is overcome, the fibrin being to a considerable extent separated. The fibrin clots, being heavy, accumulate upon the bowl of the separator and make up a large part of the slime which is found after large quantities of milk have been run through."

One would have liked to know more about the Cornell butter test, p. 274. "When butter is heated, a covering of casein will collect over the surface of the sample. When the sample becomes quite hot, this covering is of snow-white color. After heating the sample for a time, the foam begins to subside and loses its snow-white color, changing to a dirty brown. By comparison with the chemical method, it was found that when the foam had lost its snow-white color the sample had given up all of its moisture. The appearance of the dirty brown color was a sure indication that all of the moisture had passed off, and if the sample was not removed from the flame at this point, some of the butter would volatilize."

There is a very clear account on p. 296 of the way in which fat is lost in the whey when making cheese. "Fat is present in milk in the form of very minute globules. So small are these fat globules of milk that 5,000 of them of average size, laid side by side, would reach only one inch. These are all scattered through the milk in enormous numbers. Now, when the rennet causes the casein throughout the whole mass of milk to solidify or coagulate, the fat globules are retained or imprisoned in the solidified mass just where they were at the instant that coagulation took place. When the curd-knife passes through the mass, immense numbers of the minute fat globules are exposed on every cut surface and numbers of these fall into the whey and are not retained in the cheese. The more finely we cut the curd and the more violently we handle the cut pieces of curd, the larger will be the number of fat globules that go into the whey.

"In regard to the loss of casein, the larger portion of loss appears to be in the form of fine particles of coagulated casein, which pass through the strainer, when the whey is drawn from the curd. These minute particles can readily be seen by letting a pail of freshly-drawn whey stand until the casein settles, and then pouring off the whey, when a noticeable quantity of finely-divided casein can be seen at the bottom of the pail. This passage of casein into the whey is not entirely avoidable, but is needlessly made greater by carelessness or violence in cutting the curd and in subsequent handling, by agitation while drawing off the whey, and by imperfect strainers. The amount of casein that thus passes into the whey averages about 0.10 lb. for 100 lbs. of milk."

The question of fermented milk is taken up on p. 478. "Within recent years there has been a rapidly growing interest in the therapeutic value of buttermilk and other fermented milks, such as kefir, kumiss, and yoghurt. This is seen in the increasing sale of buttermilk, in the large number of special preparations now offered for sale, and in the frequent discussion of this subject in popular and scientific publications. Buttermilk is not only consumed in large quantities as a beverage, but is recommended by physicians as a therapeutic agent in the treatment of intestinal disorders, and is in constant use in many hospitals. All the more familiar fermented milks are the result of an acid fermentation in which the sugar of the milk is split up into lactic acid. This may be brought about by the presence in the milk of varieties of the common lactic acid group of bacteria, or, as in the case of yoghurt, by special organisms; or a yeast may be present, adding an alcoholic to the ordinary acid fermentation. In many large cities special fermented milk preparations can be obtained under various trade names, such as zoulak, vitallac, yoghurt, matzoon, bacillac, kefir, kumiss, and lactobaciline. These are all soured milks which have been introduced from southern Russia, Turkey, and neighboring countries. They are sold as freshly prepared milk, or in the form of tablets or powders in capsules which may be taken as such or used to ferment milk. These preparations have been widely advertised and are the subject of very positive statements in regard to the benefits derived from their use.

"Fermented milks have been used ever since very early times, but it is only within very recent years that physicians have become interested in the possibilities of their use for therapeutic purposes. Within the past twenty years there has been an increasing number of papers in the medical journals on this subject, and at one time the widespread popular interest in fermented-milk therapy was reflected by the numerous magazine and newspaper articles on various phases of the subject. This interest was stimulated in a large measure by the work of Metchnikoff and his associates. His views, which are set forth in some detail in Chapter V, "Lactic acid as inhibiting intestinal putrefactions," of his book entitled "The Prolongation of Life," are looked upon by the more conservative investigators of this country as overdrawn and as unsupported by experimental evidence. In this book great stress is laid on the longevity of the people of certain countries in which fermented milks are an important part of the diet. In considering evidence of this kind it should be remembered that many other things may contribute to the general health and vigor of the people, and that these factors cannot be excluded in drawing the conclusions. The people who habitually consume large quantities of fermented milk usually live a simple life, largely in the open air, and we have no means of knowing how much this may have contributed to the vigorous old age frequently observed among them.

After a discussion of the theory of auto-intoxication, the author concludes, p. 485, that "the bacteria of the high-acid type, which are apparently normally present in the intestines, are stimulated by the unusual amount of milk-sugar furnished by the milk diet and multiply to such an extent that the ordinary mixed flora is suppressed. The beneficial effect of a sour-milk diet is, perhaps, attributable not so much to the bacteria contained in the milk as to the milk itself, which provides material for an acid fermentation in the intestines."

Wilder D. Bancroft

American Lubricants. *By L. B. Lockhart. 23 × 16 cm; pp. x + 236. Easton: The Chemical Publishing Company, 1918. Price: $2.00.*—"The purpose of this book is to aid the user and the buyer of lubricants in a more intelligent selection of oils and greases. The point of view throughout is that of the user rather than that of the refiner. An effort has been made to include such facts, and figures in regard to lubricants as will serve best to bridge the gap between the refiner or manufacturer and the consumer. Of almost equal importance, a conscientious effort has been made also to *exclude* irrelevant matter so as not to obscure the main facts."

The subject is treated under the general heads: crude petroleum; the refining of petroleum; the refined products; friction and lubrication; lubrication of internal combustion engines; automobile lubrication; the lubrication of electrical machinery; the lubrication of steam cylinders and steam engines; the lubrication of steam railways; the lubrication of cotton mills and other textile mills; the lubrication of miscellaneous plants and machines; physical methods of testing lubricating oils; chemical methods of testing lubricating oils; lubricating greases; methods for testing and analysis of greases; animal and vegetable oils; methods of testing fatty oils; specifications for fatty oils; specifications for cylinder oils; specifications for special engine and machine oils and car oils; specifications for cutting oils; specifications for greases, graphite boiler compound, and cotton waste; specifications for burning oils; specifications for gasoline and fuel oils; gasolines; kerosene; tables.

The following quotations, pp. 43, 50, 78, 108, 128, will give some idea of the quality of the book so far as it appeals to the lay reader. The strictly technical man will probably be more interested in the chapters on specifications.

"While exactly the same amount of heat is developed in burning a given amount of the same gasoline completely, irrespective of the motor used, yet the temperature attained may be very different with different motors. Small cylinders have more cooling surfaces in proportion to their capacity than large cylinders, consequently the temperature of the cylinder walls is usually lower for small cylinders. Thus, the temperature of the cylinder walls of a twelve-cylinder motor will ordinarily be lower than the temperature of the cylinder walls of a four-cylinder motor of the same power.

"The following figures will give some idea of the temperature conditions in a water-cooled motor:

	Degrees F
Oil in crank case	100–225
Explosion temperatures	2,000–2,800
Temperature of piston	200–400
Temperature of piston head	300–900
Temperature of cylinder walls	200–350

"It can be readily seen that the temperatures to which the oil on the cylinder walls and piston head is exposed will not only greatly reduce its viscosity but will rapidly vaporize and burn the oil. Fortunately, the larger cylinders are always installed in a vertical position so that the weight of the piston does not come directly on the cylinder wall, otherwise much heavier oils would have to be used."

"Most motorists waste their cylinder oil. With an oil of proper viscosity and with proper piston clearance as in new cars; the oil consumption can be cut to 25 percent of the average per mile consumption. Cars which normally require a gallon of oil for each 150 to 200. miles can be run with proper motor conditions for 600 to 800 miles on the same amount of a suitable oil. With proper oil-feed, carbon troubles would be a thing of the past. The blue smoke from the exhaust is not always due to a low-grade gasoline; it is often due to an excess of cylinder oil.

"With loose, 'leaky' piston rings a heavier oil is needed and more of it. More gasoline is also required and the results are in general less satisfactory. The proper clearance of piston is not over 0.002 inch per inch of cylinder diameter. The crank-case reservoir should be cleaned out at frequent intervals. This becomes more necessary if there is leakage of contaminated and sooty oil past the piston head. A proper oil seal on the piston rings is as important as actual lubrication in saving power and in protecting the oil in the reservoir from contamination by hot gases and wastes from the cylinder.

"The secret of successful motor lubrication is to keep the motor in good mechanical conditions and use an oil of good (high) viscosity somewhat sparingly. It is not necessary to have an oil of quite as high viscosity for winter use as for summer use.

"The two most important and necessary characteristics of motor oils are proper viscosity at the working temperatures and low carbon formation. The excessive high engine speeds, 2,600 to 3,400 revolutions per minute in some modern automobile engines, and the attendant high rubbing speeds in the cylinders, make an oil of just the right viscosity absolutely necessary, otherwise the oil film will not have time to form and the power output of the engine will also be reduced."

"The great difficulty in the lubrication of car journals is not in getting an oil thick enough, but in getting an oil that will feed to the journal properly under the working conditions. In an ordinary bearing the pressure is on the lower side of the journal and so oil will feed by gravity to the point where it is needed. With car journals, the friction and pressure surface is on top of the axle, and the journal is equipped with a box to be packed with oil-soaked waste. This waste should be frequently inspected, and loosened up or repacked, so that it presses aginst the moving axle, else there is no way for the oil to get to the friction surface of the journal. Many journals are cut with suitable grooves to hold some oil, but this does not take the place of careful packing and regular inspection. One journal not properly lubricated may heat sufficiently to do serious damage to the car and its content, or to delay the whole train. The present high state of railway car lubrication has only been attained by rigid inspection of all cars before and at frequent intervals during the run. Well-fitted journals are also the rule which has made possible exceedingly low lubricating costs per car mile.

"In preparing waste for use in the journal boxes, it should be soaked for several days and then squeezed slightly so as not to drip, or allowed to drain well. It is then packed into the box loosely, except the part next to the inner end of the box, which is well packed. The waste should come up against the lower half of the journal. The waste acts as a wick to feed the oil to the moving axle, which carries it to the bearing. Car journals are also equipped with lubricating pads instead of waste, or even with mechanical force-feed lubricators. A thinner oil can be fed with these devices."

"The gravity test has been accorded too much weight in judging the lubricating value of oils, consequently oils have often been found unsuitable because some more vital test, such as viscosity, has been sacrificed to meet an impracticable gravity requirement. It has great value in the refinery as a quick method of judging when to make the 'cuts' or changes in distillation. So long as Pennsylvania crude was the only oil used, the gravity was an index to the viscosity and was, therefore, of real value to the user. With the production of lubricating oils from other crudes, the gravity test has lost much of its value unless taken in conjunction with other tests. The gravity is of value in judging the type of crude from which the oil was refined. This high viscosity oils(viscous neutrals) do not run over 30° Bé. unless from Pennsylvania or similar crude. For a given crude the viscosity is generally proportional to the gravity, but this is not necessarily true for oils of the same type from different crudes. All mineral oils contain about 85 percent actual carbon, so a possible variation of 1 or 2 percent in the carbon content of an oil as evidenced by a lower gravity can hardly be of any practical significance."

"Greases are used for lubricating bearings where the pressures are too great for successful oil lubrication; for lubricating difficultly accessible parts of machines; for preventing undesirable splashing as in certain greases for cotton mills; for preventing waste of lubricant from poorly housed bearings; and for reducing the cost of lubrication by reducing the attention required and the amount of lubricant fed to the bearings. Greases are made in varying consistencies, or in varying degrees of hardness, to suit different purposes, from the soft compression cup or rod cup greases to the solid greases used for locomotive journals.

The most usual type of lubricating greases to-day is the soap-thickened mineral oil type. Practically all the greases met with in general lubricating practice are made by combining mineral oils of different grades with varying amounts of lime soaps, soda soaps, or other soaps. The texture of these greases is influenced by the character of the mineral oil, the kind of soap (as soda or lime), the amount of soap, the kind of fatty oil from which the soap was made (such as tallow, etc.), by the presence of free fatty oils, by the presence of water in the grease, and by the process of manufacture."

Wilder D. Bancroft

The Chemical Constitution of the Proteins. *Part I, Analysis. By R. H. Plimmer. Third Edition. 24 × 15 cm; pp. xii + 174. New York: Longmans, Green & Company, 1917. Price: $1.80.*—On p. 9 the author says: "The complex problem of the constitution of the protein molecule has been solved by the method of hydrolysis, though other methods such as fusion with alkali, oxidation with permanganate, chromic acid, etc., action of halogens, have been employed. Hydrolysis has been effected by (*a*) boiling with acids, (*b*) boiling with alkalies, (*c*) the action of the various proteoclastic enzymes which occur in animals and plants."

The units composing the protein molecule (p. 15) belong the four different classes of organic compounds, but are divided into two main groups for the purpose of isolation and estimation:

A. The mono-amino acids, including proline and oxyproline. Tyrosine and cystine differ from the other mono-amino acids by their extremely slight solubility in neutral aqueous solutions. They are therefore easily obtained after hydrolysis by acids by neutralizing and concentrating the solution, when they crystallize.

B. The di-amino acids, including histidine. The three compounds in this groups were formerly called the hexone bases on account of their basic properties and the fact that each of them contains six carbon atoms. The remaining unit, tryptophan, is almost completely destroyed by hydrolysis by acid; it is usually isolated after hydrolysis by tryptin.

There is an interesting paragraph on p. 71. "As to the origin of the di-amino acids in the protamine of fish sperm the observations of Miescher suggested their formation from the muscular tissue of the fish. The salmon does not feed during its life in the river and loses weight at the expense of the increase in size of its roe. Kossel [1905] made calculations as to this possibility: the roe of a salmon contains 27 grams of protamine with 22.8 grams of arginine; if the muscular tissue contain 7.1 percent of arginine, 321 grams of it would be required: more than this quantity of muscle is decomposed during the life of the salmon in the river, so that, as there is no evidence for its synthesis, its origin is by transference from the muscular tissue. Actual analyses of the protein of salmon muscle and salmon tissue have been made by Weiss [1907] and they confirm the calculations. In the transference of the arginine from the muscle to the roe it seems that it is rendered stable by combination with nucleic acid or some other grouping and thus transported, for under the ordinary decomposition of tissues arginine is itself decomposed. The transfer appears to occur not as the transfer of a single unit, but as the transfer of a complex containing several units. Such a complex is a histone which contains more mono-amino acid units than a protamine."

Colloid chemists are interested in some of the statements about silk, p. 77. "Silk-fibroin is composed practically of only three amino acids, glycine, alanine, and tyrosine, and is probably the simplest protein known. It contains more tyrosine than any other protein except that of the carapace of the tortoise and is the best source of tyrosine. Silk-fibroin differs very markedly in composition from silk-gelatin; this substance contains more serine than any other protein.

"The composition of silk-fibroin and silk-gelatin from different sources is under investigation by Abderhalden and his pupils. The present data show that the composition of the various silk-fibroin is fairly similar, although many differences can be noted. The New Chwang, Shantung and Chefoo varieties are rather peculiar in leaving a somewhat large residue after hydrolysis, which seems to be connected with the food-stuff of the silk worms. The New Chwang and Schantung worms are fed on oak leaves. The Canton and Bengal silks are most like the Italian; Indian Tussore silk contains a considerable smaller amount of glycine. African Tussore silk is like other Tussore silks and the silk of *Bombyx mori* from Africa resembles that of *Bombyx mori* from other countries. The silk of *Anaphe* has also a similar composition. In fact, the silk of caterpillars, spiders, and of *Pinna nobilis* have an almost identical composition, with tyrosine, glycine, alanine as the chief constituents [Abderhalden, 1911]. No striking differences are to be noted in the various silk-gelatins.

"The silk of other arthropods has also been examined. The silk fibroin from spider's silk, except for its high content in glutamic acid, closely resembles that of the silk-worm. The silk examined by Suzuki, Yoshimura, and Inouye [1909] were distinctly different. The material spun by *Oeceticus* of the family *Psychidae* in order to unite the bits of wood together with which it builds its house contained no tyrosine, but otherwise resembled silk fibroin. The absence of tyrosine brings out a resemblance of ovokeratin."

Wilder D. Bancroft

Problems in General Physics for College Courses. *By Morton Masius. 21 × 14 cm; pp. vi + 90. Philadelphia: P. Blakiston's Sons & Co., 1917. Price: 90 Cents.* These problems are based upon Duff's Text-Book of Physics. In the introduction the author says: "It is believed that in most courses in general physics in engineering colleges about 200 or 250 problems are assigned. The problems in this book have been grouped so as to make four complete courses of 250 problems each, each course covering the whole ground, and all four courses being of about the same difficulty. Under the main heading of mechanics and properties of matter, the subheadings are: velocity and acceleration; force and mass; work, energy, and power; rotation; center of mass; moments of force and moments of inertia; parallel forces; equilibrium; friction; machines; gravitation;

elasticity; properties of liquids; properties of gases. Under wave motion the experiments are classified as simple harmonic motion and as waves. The third general heading is heat with the subdivisions of temperature, expansion, calorimetry, mechanical equivalent of heat, change of state, heat conduction, radiation, and thermodynamics. Under electricity and magnetism we find: magnetism; electrostatics; magnetic fields of currents; resistance and Ohm's law, Kirchhoff's laws; power and Joule's law; electrolysis; thermoelectricity; magnetic induction; electromagnetic induction; dimensions of electrical units. The fifth general heading is sound and under the sixth, which is light, the sub-divisions are: reflection; refraction; prisms; lenses; photometry; total reflection; interference; diffraction; spectrum.

In general, the experiments are very well selected. The reviewer was stumped for a while by Exp. 22. A freight train passes through a station at a speed of 12 miles per hour. At the same time a passenger train starts from rest and moves on a parallel track with a constant acceleration. What will be its speed when passing the freight train?" This problem seems at first to be indeterminate, but it is really quite simple. *Wilder D. Bancroft*

The Chemistry of Colloids. *By Richard Zsigmondy. Translated by Ellwood B. Spear. 23 × 16 cm; pp. vii + 288. New York: John Wiley and Sons, Inc., 1917. Price: $3.00.*—The book is in two parts, the first being a translation of Zsigmondy's book, while the second part is written by Spear and deals with some of the technical applications of colloid chemistry. The German edition was reviewed when it appeared (17, 560). It was a good book and a translation is welcome. One would have liked to see some discussion of the relation between the cuts on pp. 65 and 142; but that is one of the things one does not get.

In the preface to the second part the author says, p. 240: "The chemistry of the colloidal state of matter has become of such great importance to the chemical industries that it has seemed wise to devote several chapters in this book to a side of the question that is particularly interesting to the technical chemist. As the subject is far too inexhaustible to be dealt with comprehensively in the space available it has been found necessary to omit any protracted discussion of the wide field of biological chemistry. It has also been found impossible to deal adequately with the colloidal chemistry of carbohydrates and organoplastics, owing to the fact that a great deal of the necessary information is unavailable in the literature."

The technical portion is discussed under the headings: introduction; smoke, flue fumes, liquid particles in gases; rubber; tanning; milk; colloidal graphite; clays; colloids in sanitation. This part would be better if Mr. Spear did not rely on polymerization so much. His general point of view is taken from Lewis and is formulated as follows, p. 241: "Colloidal particles may be conceived to be built up of a relatively small unit *U* associated with itself by polymerization, condensation, adsorption or otherwise, *n* times. A single particle would therefore be represented by the formula *Un*. It is not necessary at this point to make any assumption as to the nature of the association. It may be chemical or physical or both." *Wilder D. Bancroft*

Chemical French. *By Maurice L. Dolt. 23 × 16 cm; pp. viii + 398. Easton: The Chemical Publishing Company, 1918. Price: $3.00.*—"This book is intended for students of chemistry wishing to acquire a reading knowledge of French in that particular science. A reading knowledge of French is required of students of chemistry in most institutions, especially of candidates for advanced degrees. For those who have had one or two years of French, the reading of scientific French will still offer certain difficulties which an ordinary dictionary will not solve, and for those who have not had any French, the task will be enough to discourage them. Moreover, the only available material has been articles in French journals of chemistry, and these articles, not being written for students of French, are often too hard for them."

There are twenty-four exercises each with a vocabulary and then come selections for advanced readers, which include articles by Job, Moissan, Berthelot, Gautier, Grignard, Friedel and Crafts, Sabatier and Senderens, Effront. Raoult, Pasteur, Becquerel, and Mme. Curie. Incidentally the student will learn a good deal of chemistry in addition to perfecting himself in the French language. There is a table of irregular verbs at the end of the book, and also a satisfactory vocabulary, so that the volume is complete in itself and should prove very useful to the student.

In a book of this sort it is very difficult to avoid misprints, because one gets relatively little help from the printing office. It is not surprising that there are a number of slips. The reviewer has noticed typographical errors on pages 4, 6, 8, 11, 12, 20, 22, 30, 50, 58, 59, 60, 65, 66, 77, 86, 95, 98, 100, 108, 110, 113, 116, 117, 118, 119, 121, 130, 131, 146, 147, 150, 155, 180, 195, 196, 206, 218, 230, 234, 243. 264, 268, 279. The following words occur at least twice in the vocabularies connected with the exercises: inodore, 4, 24, 44; incolore, 4, 19; huileux, 4, 44; broyer, 10, 94; acide étendu, 44, 54; craie, 54, 87; billes de verre, 94, 118; amorcer, 102, 118; while déceler is given on p. 66 as "to reveal" and on p. 127 as "to detect." These are not serious slips but they should be corrected in the next edition. There is a distinct need for such a book as this and this book will prove very helpful to the student.

Wilder D. Bancroft

THE OSMOTIC ACTION OF SOLUTIONS OF CANE SUGAR, SILVER NITRATE, AND LITHIUM CHLORIDE IN PYRIDINE, WHEN SEPARATED FROM PYRIDINE BY A RUBBER MEMBRANE

BY ALFRED E. KOENIG

In Kahlenberg's[1] paper, "On the Nature of the Process of Osmosis and Osmotic Pressure," there are described a few quantitative measurements of the pressures obtained when solutions of cane sugar, silver nitrate, and lithium chloride in pyridine were separated from pyridine by means of a rubber membrane. Cohen and Commelin[2] repeated some of these measurements with an apparatus of a slightly different design. Their results agree substantially with those of Kahlenberg. However, measurements carried on with the same solutions and under as nearly as possible identical conditions vary a great deal among themselves, as will be seen in connection with certain remarks in this paper. In view of the fact that these results show considerable variation, it was thought worth while to obtain more satisfactory measurements of the osmotic pressures of the above named solutions. The results of this work have been set forth in this paper.

Materials Used

The pyridine used was all of one lot of Merck's best grade. After drying for several months over sticks of potassium hydroxide, it was boiled with potassium permanganate and freshly ignited barium oxide under a reflux condenser for eight to ten hours. After distillation, it was kept in glass-stoppered bottles. The outer and inner liquids, after measurements had been made, were poured into bottles containing sticks of potassium hydroxide and redistilled for further use. The pyridine boiled with a constant boiling point of 114 to 115° under 740 mm pressure.

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[1] Jour. Phys. Chem., 10, 141 (1906).

[2] Zeit. phys. Chem., 64, 1 (1908).

A fine grade of rock candy, which was found to contain no reducing sugars, was prepared for use in two ways. Some of it was ground in a mortar fine enough to go through an eighty mesh sieve. It was spread in thin layers on large watch crystals and dried in a vacuum over calcium chloride at 90° for twelve to fifteen hours. Some of the sugar was made into a thick syrup with distilled water and thrown out as a very finely divided precipitate by means of alcohol, with constant stirring of the solution while the alcohol was added. The precipitated sugar was washed on a suction filter with absolute alcohol and dried in a vacuum over calcium chloride at 90° as in the case of the other sample. The sugar, prepared by precipitation, dissolved more readily in pyridine, probably due to its finely divided condition, but otherwise gave no results that differed from those obtained with the sugar prepared in the other way. The dried sugar was kept in desiccators over fresh calcium chloride.

The lithium chloride and silver nitrate, which were of Merck's make, were ground to a fine powder and dried in the same manner as the sugar. In the case of the silver nitrate the temperature at which it was dried was about 20° lower to avoid decomposition. The work with the lithium chloride was carried on during the cold dry weather of January and February, when it could be weighed without taking up an appreciable amount of moisture from the air.

The solutions were prepared as follows: The required amount of solute was weighed, dissolved in pyridine, and diluted to one liter at 25°, the temperature at which all the measurements were made.

The rubber for the membranes was a fine grade of dental rubber, obtained from the Goodrich Rubber Company of Akron, Ohio. It was very uniform in texture, light brown in color, and three to four-tenths of a millimeter in thickness when not stretched.

Apparatus and Method of Making Measurements

The arrangement of one of the cells is shown in Fig. 1. The cell (*a*) was bell shaped, turned out of a piece of steel shafting. The removable bottom (*b*) was perforated with holes one millimeter in diameter. These holes were countersunk toward the interior of the cell so as to facilitate the removal of air bubbles when the solution was run into the cell. When this steel disk (*b*) was in place, it left a smooth surface

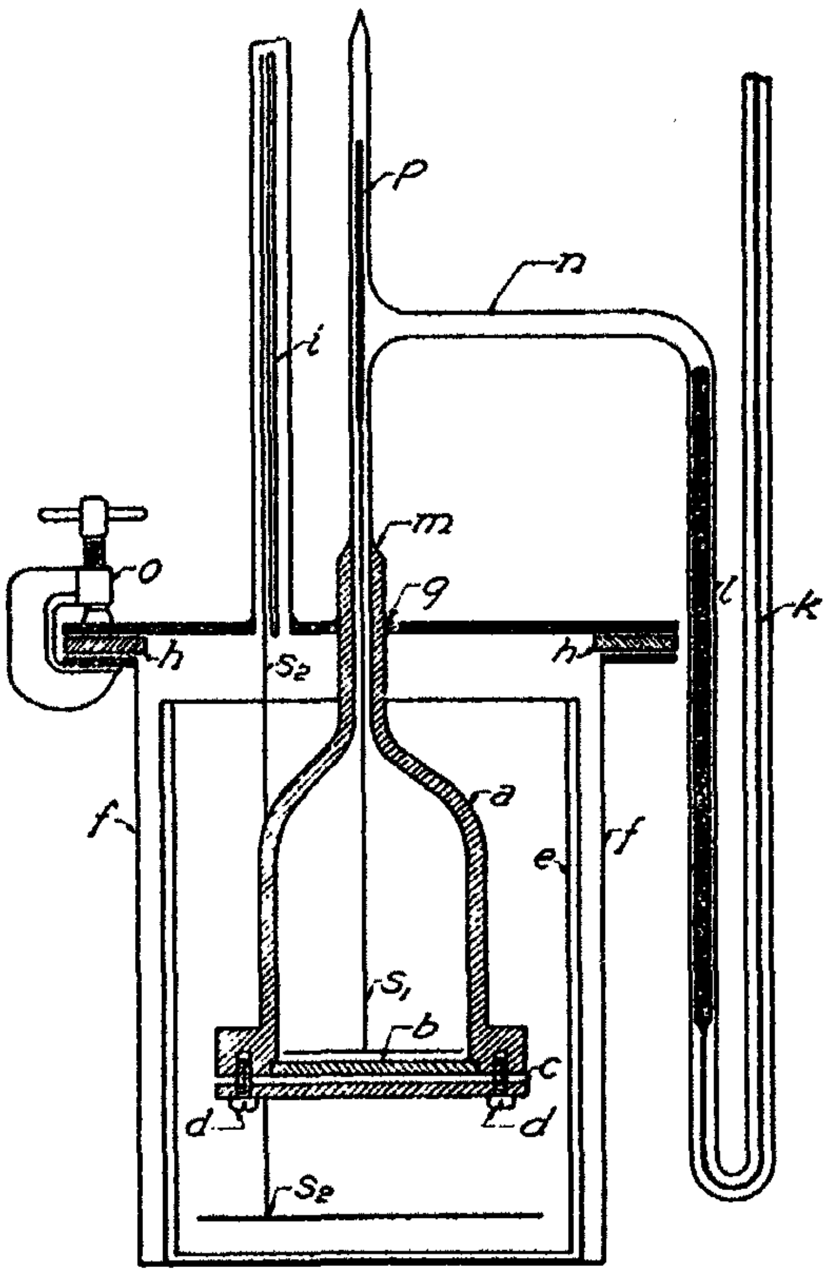

Fig. 1

on the outside of the cell, within the circle of eight holes for the screws (*d*). Upon this surface within the circle of screws, was laid the membrane consisting of a disk of rubber six and a half centimeters in diameter, the gaskets of rubber, and the muslin disks, the arrangement of which is described more fully in another place in this paper. The membrane was held in place by the steel disk (*c*), the central portion of which was perforated with holes like those of the cell bottom (*b*), although the holes of these two disks were not necessarily opposite each other. The holes in the disk (*c*) were countersunk toward the outside, so as to permit the outer liquid to come in contact with the membrane more readily. This disk (*c*) being about 3 mm thick was rigid and, when clamped on by eight screws which ran into the solid rim of the cell, held the membrane very firmly and evenly in place. The pyridine which bathed the outside of the membrane was put in the glass jar (*e*) which was set in the galvanized iron vessel (*f*). The stem of the cell was soldered into the hole in the center of the cover of this vessel (*f*) at the point (*g*). A heavy gasket of "rainbow" packing, well greased with vaseline, was laid between this and the flange of the vessel at (*h*) and the cover clamped on with six brass screw clamps like the one shown at (*o*). This kept the water of the thermostat from entering the iron vessel. On several occasions, a run covering a period of six to eight weeks was made and no water entered the vessel (*f*). The vertical tube, with the side arm for the manometer, and the manometer were made of glass. The joint between the glass and steel at (*m*) was made in the following way: A piece of glass tubing with the same internal diameter as the opening in the stem of the cell, was cut off straight so as to fit evenly on the steel. The outer surface of this tube for about 5 cm from the end was roughened by rubbing with a paste of glycerine and emery dust. This surface was then thoroughly cleaned and painted with a solution containing about three percent of platinic chloride and two percent of stearic acid in ether and alcohol, about two parts of ether to one of alcohol. The ether and alcohol evaporated very quickly leaving a thin coating of platinic chloride and stearic acid on the roughened surface of the glass. The glass was then heated gently in the flame of a Bunsen burner, to reduce the platinic chloride and finally heated to redness to burn off all the carbon. Upon the strongly adhering film of platinum, a layer of gold was deposited electrolytically. The gold was plated with a layer of nickel about a tenth of a millimeter thick. To stiffen the tube, a strip of zinc foil was wound about the nickel and soldered in place. Then the tube was soldered to the stem of the cell. The T tube, carrying the manometer on the side arm and giving a straight entrance to the cell through which a funnel was inserted for filling with the solutions, was fused to the upper end of the tube that was soldered to the cell. Whenever the cell was emptied, the manometer had to be broken off at (*n*) and, on refilling, fused on again.

The stirrer (s_1) for the interior of the cell was made of iron. To the upper end of the wire handle, was soldered a thicker piece of iron wire, which extended into the part of the glass tube above the side arm for the manometer. This stirrer was actuated by means of a helix, which was slipped over the sealed end of the glass tube. Through this helix a current was sent at intervals. Thus the contents of the cell were stirred as described in Kahlenberg's[1] experiments. The pyridine on the outside of the cell in the glass vessel (*e*) was kept in motion by the stirrer (s_2), the handle of which passed up through one of the copper tubes (*i*). The other tube was for the purpose of removing a sample of the outer liquid at any time without disturbing the progress of the experiment. These tubes extended about twelve centimeters above the water of the thermostat. The motion of this stirrer, as well as the interruptions of the current through the helix which operated the other, were brought about by gears driven by an electric motor which also served to keep the water of the thermostat in circulation. This arrangement is not shown in the drawings.

About 500 cc of pyridine were placed in the glass jar (*e*). The membrane having been put in place, the cell and the stirrer (s_2), with the cover (*g*) were adjusted and the latter clamped on with the six clamps like the one at (*o*). Several vigorous strokes with the stirrer removed the air bubbles from the holes in the disk (*c*), thus wetting the membrane with pyridine. In experiments where the bottom of the cell could be observed, it was found that this procedure was effective

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[1] Jour. Phys. Chem., 10, 141 (1906).

in removing the air bubbles. The manometer was sealed on at (*n*). Its large arm was filled with mercury to about the level of the bend. The other arm (*k*) was a 0.25 mm capillary open to the air above. Since the pyridine on the outside of the cell and the mercury in the capillary were open to the atmospheric pressure, the barometric changes had no effect on the readings.

The long drawn out stem of a thistle tube was inserted into the cell through the upright tube at the top and the solution, whose osmotic pressure was to be obtained, was poured in to within 3 cm of the top of the tube. The capacity of the cell was about 150 cc. Suction was applied at the upper end of the tube and suddenly released. Care had to be exercised not to suck the mercury around the bend in the capillary, which would allow air to enter. This alternate suction and sudden release was repeated a number of times and served to remove any air bubbles that might adhere to the interior of the cell, especially those in the holes in the steel disk, that lead to the membrane. The upper end of the glass tube, above the solution was then heated and drawn out to a long fine point. This tip was then filled with solution by means of a thistle tube with a very finely drawn out stem. With some practice, it was possible to seal off this tip without enclosing a bubble of air or at most about a cubic millimeter.

The manometer was supported by clamps on an upright iron rod which was fastened by clamps to the vessel (*f*). These supports are not shown in the drawing. The whole apparatus was then set in the thermostat and the necessary connections made for stirring the inner and outer liquids. The whole operation of filling and sealing a cell would require about thirty minutes.

The temperature of the thermostat was regulated by means of the ordinary toluene regulator and was kept constant to within 0.05°. It was found by experience that it was best to seal the cells at a room temperature a degree or two below that of the thermostat and thus obtain an initial pressure due to the thermal expansion of the solution, when it was raised to 25°, the temperature of the thermostat. This initial pressure was attained very rapidly, then the increase would be at a slower rate till the maximum was reached in from 24 to 72 hours. This is best shown by the curves in Fig. 2. When the initial pressure, due to thermal expansion happened to be higher than the maximum osmotic pressure of the solution, there was successively a rise of the mercury, a fairly rapid drop, a halt, and then a gradual falling off of the pressure. This is illustrated by curve No. 143 of Fig. 2. For any solution, the halt in the decrease in pressure would correspond to the maximum pressure attained when the cell was sealed at a temperature nearer to that of the thermostat, so that the pressure due to the thermal expansion was lower than the osmotic pressure.

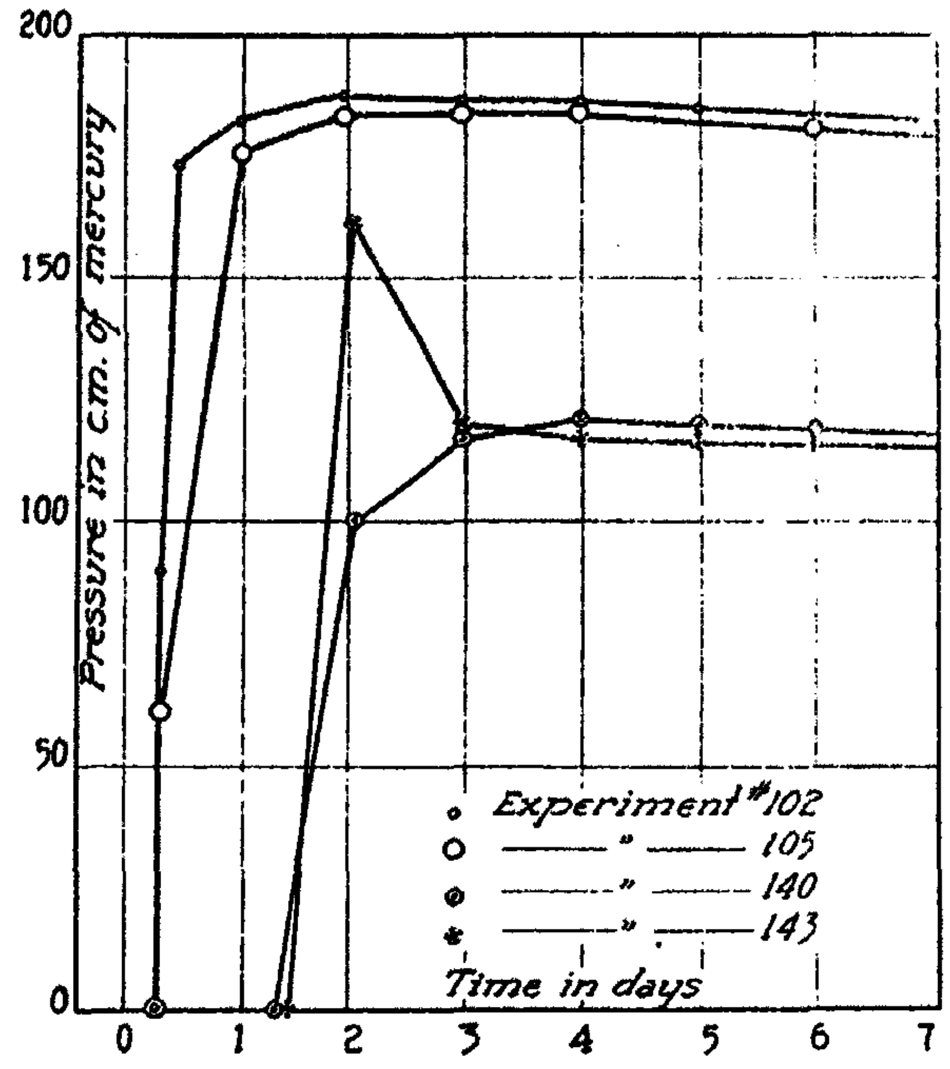

Fig. 2

The heights of the mercury in the capillary (*k*) and in the large arm (1), above the bottom of the thermostat were measured by means of a meter stick. The difference between these two heights gave the difference in the mercury levels. To this was added the capillary depression in the small tube. From the sum was subtracted the height of the solution from the level of the mercury in the wide arm to the top of the tube (*p*), reduced to the equivalent centimeters of mercury. For this reduction, the density of pyridine at 25° was taken as being near enough to that of the solutions used. The resulting length of the mercury was reduced to the value for 0° C, taking the average room temperature to be 23°. The room was steam heated and automatically regulated. Fluctuations of a few degrees would not change the results materially. The change of a column of mercury 100 cm long amounts to 0.017 cm per degree change in temperature.

The following example shows how the readings were made and corrected.

Height of the mercury in the capillary tube	148.5 cm
Height of the mercury in the wide arm	27.8 cm
Difference in level of the mercury	120.7 cm
Capillary depression (added), 1.5 cm	
Height of solution above the level of the mercury in the wide arm, reduced to its equivalent in mercury (subtracted), 1.8 cm	
True difference in level of mercury (at room temperature)	120.4 cm
Correction to reduce to mercury at 0° (subtracted), 0.48 cm	—0.5 cm
Corrected value for the pressure	119.9 cm

The Manometer Joint and the Adjustment of the Membranes

The development and the successful completion of this work centered around the arrangement of the membrane so as to make that part of the cell tight, and the production of a joint between the metal of the cell and the glass of the manometer so that this union would be absolutely tight.

The solution of the latter problem was accomplished first, for without a perfect non-leaking joint with the manometer, the action of the membrane could not be successfully studied. The work described in this paper is the result of over four years of experimentation of which nearly half was occupied in trying out various combinations of metals and methods of preparing the joint between the steel and the glass. The roughened part of the glass was not always uniformly coated by the reduction of the platinic chloride solution. On plating with copper, small bare or thin spots would often appear which would eventually plate over. The pyridine would gradually creep up between the copper and the glass. When gold was plated upon the film of platinum, the small bare spots became evident. The tube was then taken out of the plating solution, washed, the bare spots painted with the platinic chloride solution, and this coating reduced as previously described. If on further plating the gold did not form a continuous film, the above treatment was repeated. For some of the joints, copper was plated upon the gold and this soldered to the steel. Nickel is not appreciably affected by pyridine, so it was substituted for copper. It was necessary to make a strong coating of some other metal over the gold as the hot solder dissolves the gold off the glass. This platinum-gold-nickel combination was quite satisfactory, but it was further improved to overcome another difficulty. The weight of the manometers, which were two or three meters high, put a strain on the joint which sooner or later resulted in a leak, thus spoiling what would otherwise have been a good run. A strip of zinc, wrapped around the tube and soldered to the nickel all around, braced these joints so effectively that some of them lasted through over eight months of continuous use.

The following scheme for discovering leaks in the joint was found very useful. The cell was set up, as for a regular run, with a tenth-molecular solution of sugar. It was left out of the thermostat. The leaks could be located by the tiny globules of sticky syrup which gathered where the solution oozed out.

In summing up his researches, Raoult stated that the measurement of osmotic pressures was chiefly concerned with the soft membranes and that work with these offered such experimental difficulties that he hesitated to continue further experiments of this nature. It is because of these difficulties that quantitative measurements of osmotic pressure have been practically limited to such membranes as can be prepared according to Pfeffer's method of precipitation in the walls of a porous cup. In fact, the best results available at the present time, those of Morse, Berkeley, and their coworkers have almost all been obtained with one membrane, copper ferrocyanide, and with water as the solvent. Because of these facts, Professor Kahlenberg urged upon me the importance of continuing the present research till it was perfectly certain that the membrane used was so placed in the cell that there was no leakage; and, further, that the soft flexible rubber was so firmly and uniformly held in place that there could be no wrinkling or warping which could affect the results obtained. The final arrangement of the rubber disks, rubber gaskets, and muslin disks was, therefore, the result of long and careful experimentation. Some experiments were also made with a thicker rubber both for membranes and for the gaskets. This sheet rubber was like that ordinarily used on foot-power bellows and was about a millimeter thick when not stretched. The action with this thicker rubber was much slower. It became very sticky and gave lower pressures. This fact is in harmony with the conclusions drawn later, namely, that the longer the contact of the rubber with the pyridine the lower the osmotic pressures obtained.

Realizing the importance of the results of this work as exact quantitative measurements with a new membrane and a solvent other than water and that the apparatus described may be used in the investigation of other soft flexible membranes similar to rubber, the main outlines of the development of the placing of the membranes in the cells have been included in this paper.

At first a single disk of rubber dam was placed between the bottom of the cell (*b*) and the steel disk (*c*), Figs. 1 and 3. This rubber served as the membrane which separated the solution in the cell from the pyridine on the outside. With this arrangement, some pressure was developed but in no case was it very high, neither did the results for the same solutions agree. The pressures for a tenth-molecular sugar solution ranged from 30 cm to 90 cm. In fact, they resemble in magnitude and range those obtained by Cohen and Commelin[1] for the same solution, who give, for the tenth-molecular sugar solution, these pressures in centimeters of mercury: 82.3, 75.6, 71.9, 71.7, 67.1, 64.4, 63.2, 54.2, 50.8, 50.1, 47.8, 46.4. The pressures that they obtained for the 0.050 and the 0.025 molecular solutions show even greater variations. These workers used a membrane consisting of a single sheet of rubber clamped to the open end of a hollow cylinder by means of a perforated steel plate and a ring. More will be said of this work at another place.

The next improvement made in the present work was this: Between the membrane, which was cut in the form of a disk 6.5 cm in diameter, and the bottom of the cell were put two gaskets cut from the same rubber dam as the membrane. Each of these gaskets had the same outer diameter as the membrane and an opening in the center 4.5 cm in diameter, this opening being about the same size as the perforated region of the bottom of the cell and of the plate that held the membrane in place. A disk of strong closely-woven muslin was placed between the membrane and the outer plate. This arrangement is shown in cross section in Fig. 3. The pressures for a tenth-molecular solution of sugar now obtained varied from 130 cm to 160 cm of mercury. Finally, the circular

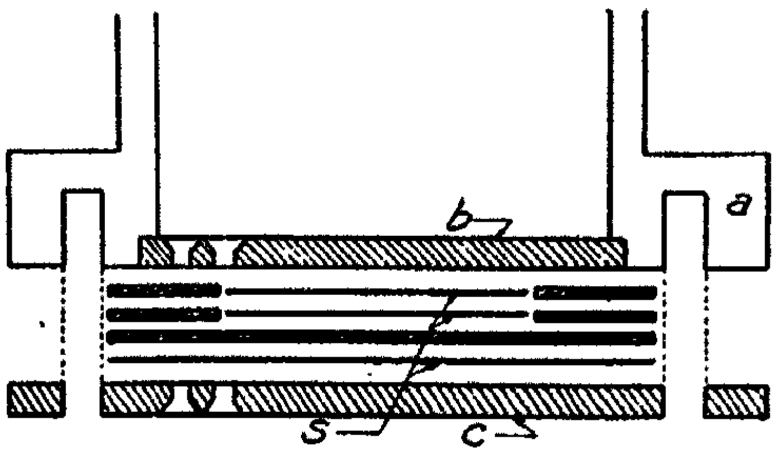

Fig. 3

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[1] Zeit. phys. Chem., 64, 1 (1908).

space, marked (*s*) in Fig. 3, inside of the gaskets was snugly filled with two disks of muslin, just the size of the openings in the rubber. The results obtained with this arrangement were fairly concordant and are those set forth in Table I of this paper. The rubber was used without any previous treatment with pyridine. Cohen and Commelin[1] state that in their work the rubber membrane was allowed to swell up in pyridine and, in this condition, was quickly put in place. Now this imbibed pyridine is given up very quickly by the fresh rubber so that the latter shrinks rapidly. Even though it may have taken only a fraction of a minute for them to put their membrane in place, their membranes must have shrunk somewhat due to loss of pyridine. Then when the pyridine solution came in contact with this membrane, the latter swelled and wrinkled, and there was no support on the inner side to prevent this. These wrinkles had to be pressed out by the pressure which was generated. This and the alteration of the rubber due to the action of the pyridine as explained later in this paper will no doubt account for the variations in the results obtained by Cohen and Commelin. The membranes used in the present work were so firmly clamped between muslin and steel plates that there was no chance of wrinkling or warping. Then, because of the fact that the experiments were all started with an initial pressure due to thermal expansion of the solution, there was a minimum entrance of solvent into the cell and consequently only a slight dilution of the solution whose osmotic pressure was to be determined. This was confirmed by experiment. The sugar solutions showed a decrease of only 0.03 to 0.08° in rotation in a tube two decimeters long, in experiments where osmosis had gone on for ten days to two weeks. The silver nitrate and lithium chloride solutions were found to be only slightly diminished in concentration after their osmotic pressure had been determined. Moreover, the outer liquid contained only traces of the solute. In all cases, the diminution in the concentration

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[1] Zeit. phys. Chem., 64, 1 (1908).

was much less than could have been detected by the accuracy with which the osmotic pressures could be measured.

The general behavior of the cells during the course of an experiment has already been briefly described and is shown in several typical cases by the curves in Fig. 2. In every experiment, when the cell had developed its maximum pressure, there was a gradual decrease in pressure, usually at the rate of about a centimeter per day. A cell filled with pyridine gave a pressure due to thermal expansion when it was placed in the thermostat but this pressure diminished to almost nothing in the course of twenty-four hours. This shows that a pressure developed by thermal expansion cannot be maintained, for the pyridine under pressure flows out through the membrane till equilibrium is established.

The following experiments throw some light on the cause of this decrease in the pressure after the maximum has been reached:

When a cell had developed its maximum pressure and this had begun to decrease, it was emptied. The membrane was allowed to dry for several days. The rubber was found to be elastic and apparently in the same condition as when fresh, as far as could be determined by ordinary means and by examination with a microscope. This used membrane was again placed in a cell filled with a fresh portion of solution, and set into pyridine. Such a membrane never developed as high a pressure as one cut from unused rubber. For example, a tenth-molecular solution of lithium chloride in pyridine gave a pressure of 81.7 cm the first time the membrane was used. This pressure fell to 68.0 cm in the course of several days. This same membrane with a fresh tenth-molecular lithium chloride solution gave 61.1 cm pressure which decreased to 39.9 cm in a little over a week. When used a third time this membrane gave a pressure of only 33.0 cm. In all these experiments, only traces of the solute had escaped through the membrane into the outer liquid. These amounts were entirely insufficient to account for the differences in the pressures developed. It would seem too that the change in the rubber, once started, keeps up even when not in contact with the pyridine, for it will be noted that the maximum attained in each of the above experiments is lower than the lowest pressure attained in the previous experiment. This may account in part for the variations in the results of Cohen and Commelin, previously referred to, for these workers soaked their rubber for some time before it was used. Thus it would seem that the different pressures developed by the same membrane when used more than once, might be caused by an alteration in the nature of the rubber due to its exposure to the pyridine. The following set of experiments also support this view. These experiments were made with a 0.075 molecular solution of sugar in pyridine. The pressures are the actual differences of the mercury levels of the manometer.

Experiment 1.—The maximum pressure attained was 120.7 cm. After three days the pressure had dropped to 119.4 cm. The contents of the cell were removed.

Experiment 2.—The cell was provided with a fresh rubber membrane and filled with the solution removed from the cell in Experiment 1, and the same outer liquid was used. The maximum pressure attained was 120.0 cm and this had decreased to 116.4 cm in five days after reaching the maximum.

Experiment 3.—The cell was provided with a fresh membrane and filled with the sugar solution used in Experiments 1 and 2 and the same outer liquid used in these two experiments placed on the outside. This time the pressure developed was 119.1 cm which decreased to 113.5 cm in the course of five days.

The same cell was used for these three experiments and all conditions were, as nearly as possible, identical. After having been used three times, the outer liquid contained only a trace of sugar. Several series of experiments of this kind were carried on with similar results. This would indicate that the decrease in pressure was due to an alteration in the nature of the membrane and not as Cohen[1] says, to a gradual accumulation of moisture in the outer liquid.

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[1] Loc. cit.

Permanence of Solutions

Something should be said here with regard to the keeping qualities of these solutions. A tenth-molecular solution of sugar in pyridine gave a rotation of 5.84° in a 2 dcm tube at 25° C. This solution was kept for a year in a well-stoppered bottle in a cupboard in the laboratory. At the end of the year a sample gave a rotation of 5.85° in a 2 dcm tube at 25° C. Each of these readings was the average of ten settings. The difference is no greater than that between some of the readings from which the average was determined.

The silver nitrate solutions were kept in dark brown bottles and in a dark cupboard. After two months, they were slightly cloudy with a grayish discoloration but showed no appreciable change in silver content. For these measurements, only freshly made solutions were used. As far as was possible to determine, the solutions of lithium chloride suffered no change on standing. When the stronger solutions of lithium chloride were left in contact with rubber for a long time, for a month or more, the solutions became yellow. The cause of this was not investigated.

Table I—Results

Conc.	T. P. in cm of mercury	Pressures, expressed in cm of mercury, found for solutions of:								
		Cane sugar			Silver nitrate			Lithium chloride		
0.200	371.84	—	—	—	—	—	—	179.2	173.5	149.9
0.150	278.88	253.0	251.6	251.0	242.0	242.0	223.5	117.1	116.6	—
0.125	232.40	213.4	212.6	212.0	170.5	165.2	164.0	—	—	—
0.100	185.92	191.9	186.5	185.1	138.5	137.4	132.0	82.9	80.9	80.8
0.075	139.44	119.9	119.2	118.3	117.7	115.4	108.5	76.7	75.8	—
0.050	92.96	60.3	59.0	58.9	—	—	—	58.5	46.9	45.7
0.025	46.48	34.5	25.8	24.3	—	—	—	17.4	—	—

The first column gives the concentration in gram-mols per liter, the next, headed T. P., gives the theoretical pressures as calculated from the gas laws, then follow the pressures found for the respective solutions. Other results, in cm of mercury, for the tenth-molecular solution of sugar, were:

184.6, 181.7, 179.6, 177.5, 176.3, 174.6, 173.5, 167.1, 162.7. Some of these results are also set forth in the curves in Fig. 4.

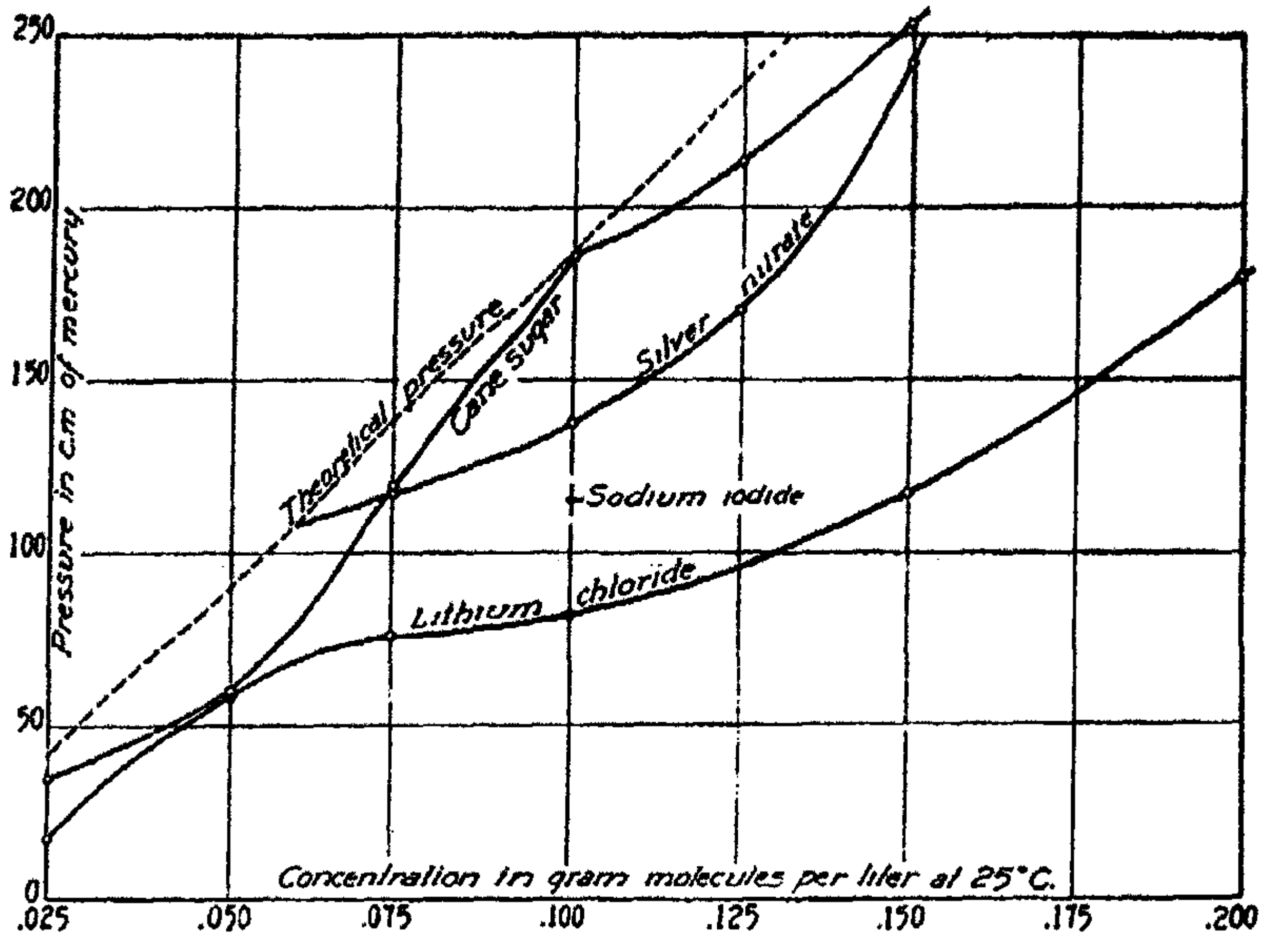

Fig. 4

Discussion of the Results

The osmotic pressures of the solutions of sugar in pyridine come the nearest to those demanded by the gas laws. In fact, in the case of the tenth-molecular solution the pressures are a little higher than the theoretical. Solutions of lower and higher concentration than the tenth-molecular yielded pressures lower than required by the theory. Molecular-weight determinations by Wilcox[1] show that sugar dissolved in pyridine has nearly a normal molecular weight. Hence, it should have a normal osmotic pressure, provided the gas laws hold. The curve in Fig. 4 seems to have a break at or near the tenth-molecular solution. The specific gravity, the specific rotation, and the molecular-weight determinations for these solutions show no such change at this concentration.

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[1] Jour. Phys. Chem., 5, 598 (1901).

The conductivity measurements for solutions of silver nitrate in pyridine have been made by Sakhanov,[1] Anderson,[2] and others. Sakhanov concludes that a tenth-molecular solution is about 18 percent electrolytically dissociated. Walden and Centnerszwer[3] found that solutions of this strength gave normal molecular weights for the silver nitrate by the boiling-point method. Schmuilow[4] from this molecular-weight determination concludes the salt is undissociated and un-ionized in pyridine. Sakhanov offers the usual explanation for the apparent 18 percent dissociation and the normal molecular weight by saying that the silver nitrate is polymerized just enough to offset the effect of the electrolytic dissociation. The osmotic pressures found in the present investigation are much lower than those demanded by the theory even if the molecular weight were normal. Walden and Centnerszwer[5] claim that the polymerization of the silver nitrate increases with the increase of concentration. Then the osmotic pressure ought to increase less rapidly as the concentration becomes greater. The reverse, however, seems to be the case for it increases more rapidly with the concentration.

Lithium chloride according to Sakhanov[6] and others, yields poorly conducting solutions in pyridine and apparently shows normal molecular weights by the boiling-point method. The osmotic pressures determined in this investigation are all much lower than the theoretical for an undissociated substance.

The curves in Fig. 4 show the relation of the pressures found to the theoretical values. In plotting these curves, the highest values obtained for each concentration were used.

Now, if a different membrane were used, it would seem to be possible to obtain an entirely different set of results for the osmotic pressures of these same solutions. Consequently

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[1] Jour. Phys. Chem., 21, 188 (1917).

[2] Ibid., 19, 753 (1915).

[3] Zeit. phys. Chem., 55, 321 (1906).

[4] Zeit. anorg. Chem., 15, 18 (1897).

[5] Loc. cit.

[6] Ibid.

attempts like those of van Laar,[1] to reconcile the results of Cohen to the gas laws by means of mathematical calculations, become quite meaningless. This possibility of obtaining different sets of results for the same solution when different membranes are used would be in accord with the chemical or selective theory of osmotic action as maintained by Kahlenberg in explanation of the researches he has carried out. Kahlenberg[2] says: "Whether osmosis takes place in a given case or not depends on the specific nature of the septum and the liquids that bathe it, and if osmosis does occur, these factors also determine the direction of the main current and the magnitude of the pressure developed."

Conclusions

1. An improved cell for the measurement of osmotic pressures with flexible sheet membranes, such as dental rubber, has been described.

2. The osmotic pressures, for solutions of sugar, silver nitrate, and lithium chloride in pyridine when separated from pyridine by rubber membranes, have been determined. The pressures for the sugar solutions were near those demanded by the gas laws but those for the silver nitrate and lithium chloride solutions were found to be much lower than those for the sugar solutions of corresponding molecular concentrations.

3. It was found that, after having reached a maximum, the pressure gradually decreased. This seemed to be due to an alteration in the nature of the rubber owing to its contact with the pyridine. Membranes used a number of times, with fresh solutions, did not give as high pressures as the unused rubber. The same solution used several times, each time with a fresh membrane, yielded practically the same pressure. This would lead to the conclusion, previously stated by Kahlenberg, that the magnitude of the pressure developed by a given

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[1] Zeit. phys. Chem., 64, 629 (1908).

[2] Jour. Phys. Chem., 10, 141 (1906).

solution depends upon the nature of the semipermeable membrane used.

The author wishes to take this opportunity to express his indebtedness to Professor Kahlenberg, at whose suggestion this work was undertaken and whose interest and encouragement made its development possible.

Laboratory of Physical Chemistry
University of Wisconsin
Madison, April, 1918

CRYSTALLOLUMINESCENCE

BY HARRY B. WEISER

The Crystalloluminescence of the Alkali Halides

It has long been known[1] that the crystallization of certain substances from solution is accompanied by an emission of light. This phenomenon is termed crystallization luminescence or crystalloluminescence. The nature and cause of this luminescence has been the subject of considerable discussion. Rose[2] who first attempted to explain the phenomenon arrived at the following conclusion: "Crystalloluminescent substances exist in at least two modifications, one of which is amorphous. If the amorphous modification separates from solution as crystals, the substance emits light. Accordingly, the emission of light is caused by the change from the amorphous to the crystalline modification." This hypothesis was modified slightly by Lehmann[3] who considered that the luminescence was caused by the transformation of one crystalline form into another. In the case of arsenious oxide he attributed the phenomenon to a change from rhombic to octahedral crystals but he did not test his view experimentally.

The Rose modification hypothesis remained unquestioned until 1894 when the matter was taken up by Bandrowski. In his first communication[4] on this subject he expressed the opinion that the luminescence was a spark accompanying the union of opposite charges on the ions: "On the basis of our knowledge of electrolytic dissociation I asked myself the question whether the luminescence during crystallization was not a series of electric discharges. Since the molecules of many substances in water solution dissociate into particles which would be separated by an electric current, the hypothetical deduction appears to me warranted, namely, that the separa-

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[1] Pickel: "Taschenbuch fur Scheidekunstler auf das Jahr, 1787," p. 55.

[2] Pogg. Ann., **35**, 481 (1835); **52**, 443, 585 (1841).

[3] Molekularphysik, **1**, 217 (1888).

[4] Zeit. phys. Chem., **15**, 323 (1894).

tion of the different substances from solution is complex, taking place in two steps. In the first step the ions originally free unite to form molecules which in the second step combine into crystalline complexes. The first step in this process, the union of the oppositely charged ions, might cause the luminescence." In support of this view he showed that the rapid precipitation of sodium chloride and potassium chloride is accompanied by light.

In a later communication,[1] Bandrowski disproved the hypothesis of Rose by showing that the crystallization of either crystalline or amorphous arsenious oxide from solution in hydrochloric, hydrobromic or sulphuric acid takes place with the emission of light. He further showed in the particular case of hydrochloric acid solution that the phenomenon is most marked when the constituents are in the definite proportion represented by the following equation: $As_2O_3 + 6HCl = AsCl_3 + 3H_2O$. In this case he does not specifically attribute the luminescence to the union of oppositely charged ions. "The water and acid must be present in definite proportions in order to produce light, which shows clearly that the cause of the luminescence must be sought in the chemical process which takes place among arsenious oxide, hydrochloric acid and water." At the same time Bandrowski pointed out that neither sodium sulphate nor potassium sulphate emit light when precipitated separately from solution but that a mixture of the two luminesces when the precipitated salt has the definite composition $2K_2SO_4.Na_2SO_4$. "Here also it appears that the cause of the luminescence is a chemical process since it depends on the formation of the double salt $2K_2SO_4.Na_2SO_4$. However, up to the present it has not been possible for me to investigate more fully the probable cause of the phenomenon. I am well aware that the investigations described throw light only on the qualitative side of the phenomenon. The establishment of its nature is probably reserved for physical-chemical investigation which I plan to take up during the winter semester. If, as I hope, I succeed

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[1] Zeit. phys. Chem., 17, 234 (1895).

in finding a larger number of analogous cases of crystalloluminescence, a broader basis will be provided whereby the explanation of these highly interesting facts can be more nearly realized.

"In conclusion a comparison of the luminescent phenomena observed may be appended. In the above described investigations (with arsenious oxide and $2K_2SO_4.Na_2SO_4$) the light appeared in the form of single sharply defined sparks, while that obtained by precipitation of a water solution of potassium chloride and sodium chloride with hydrochloric acid or alcohol, was more in the nature of a phosphorescence, sharp sparks appearing only during vigorous shaking. Hence, one might maintain that the two kinds of luminescence depend on different causes."

Bandrowski made no further contributions to this subject. Notwithstanding considerable uncertainty expressed or implied in the interpretation of certain of his observations, he is clearly of the opinion that the phenomenon of crystalloluminescence is essentially a chemical one.

Trautz[1] and Trautz and Schorigen[2] consider all cases of crystalloluminescence as cases of triboluminescence, "the property of many substances to give out light by contact, rubbing, crushing or smashing." They deduce this conclusion from the fact that most substances which luminesce when crystallized from solution likewise emit light when crystals of the substance are crushed or broken under suitable conditions. A survey of the known cases of crystalloluminescence leads Trautz to the following conclusion: "Some relation doubtless exists between chemical constitution and crystalloluminescence. Indeed the context shows that there is a causative connection between crystalloluminescence and the crystal form. But this brings me back to triboluminescence. For further conclusions in this field the crystallographic material is much too incomplete."

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[1] Zeit. wiss. Photogr., 2, 217 (1904); Zeit. phys. Chem., 53, 1 (1905).

[2] Ibid., 3, 80 (1905).

Guinchant[1] studied the crystalloluminescence of arsenious oxide and contrary to Bandrowski's observations, concluded that the solvent had nothing to do with the phenomenon. He believed that during the crystallization process, both monoclinic and octahedral crystals were formed and that the change from the monoclinic to the octahedral variety was accompanied by luminescence. This is essentially the same as Lehmann's modification of Rose's hypothesis. Guinchant's observations were not confirmed by Trautz.[2]

Gernez[3] observed a number of cases of crystalloluminescence and like Trautz, concluded that the phenomenon was a special case of triboluminescence.

Since none of the investigators who regard the luminescence during crystallization as a special case of triboluminescence have formulated a suitable hypothesis to account for the latter phenomenon, it seems to me that but little, if anything, is gained by such a classification. Pope[4] believes that the two phenomena are not identical. "There are, however, no grounds for attributing the phosphorescence of crushed crystals and that of crystallizing solutions to the same cause and the two classes of phenomena are apparently quite distinct." Bigelow[5] has summed up the situation as follows: "Over a hundred crystalline substances have been found to show this triboluminescence. It seems to have some connection with the crystalline structure but we do not know what." Of crystalloluminescence he says: "It is altogether probable that the cause of this whatever it may be is the same as the cause of triboluminescence whatever that may be."

Farnau[6] has compared the color of crystalloluminescence with the color of light obtained when sodium and potassium halides are subjected to the action of cathode rays and when

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[1] Comptes rendus, 140, 1101 (1905).

[2] Zeit. phys. Chem., 53, 37 (1905).

[3] Comptes rendus, 140, 1134, 1234, 1337 (1905).

[4] Jour. Chem. Soc., 67, 985 (1895).

[5] "Theoretical and Physical Chemistry," 516 (1912).

[6] Eighth Internat. Congress Applied Chemistry, 20, 133 (1912).

the metals are burned in the halogens. "The results as tabulated indicate the identity of the luminescence whether produced by cathode rays, chemical combination or precipitation." In a study of the flame reactions of sodium, Bancroft and Weiser[1] concluded that the blue luminescence in sodium flames was due to the reaction of sodium ion to the undissociated salt. However, they found that the observed crystalloluminescence was apparently distinctly less blue than that obtained by direct union of the elements. It was thought at the time that the color was so modified by the white color of the salt that the luminescence appeared white rather than blue. In a recent communication[2] it has been shown, however, that in most cases the color of faint luminescence cannot be determined even with approximate accuracy with the unaided eye. Accurate comparisons are particularly difficult if blue colors are concerned, which was the case in Farnau's experiments, since faint luminescence always appears blue.

Early in this investigation it was found that certain of Farnau's experiments could not be confirmed. His method of procedure was as follows: "After half an hour's wait in the dark room until the eyes became sufficiently sensitive 50 cc of saturated solutions of each of the salts, sodium and potassium chloride, bromide and iodide were shaken with 50 cc of alcohol in a 100-cc graduate and the glow appearing during precipitation was observed. In a similar manner concentrated hydrochloric acid was employed as precipitant of the chlorides of sodium and potassium."

Since sodium bromide is fairly soluble in alcohol and sodium iodide is very soluble (58.8 grams in 100 grams of 96 percent solvent), the question arose whether rapid precipitation would be obtained in these cases as Farnau claims.[3] Preliminary experiments were accordingly carried out to determine this point: Fifty cubic centimeters of the saturated solutions of the bromide and iodide of sodium and potassium were

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[1] Jour. Phys. Chem., 19, 310 (1904).
[2] Ibid., 22, 439 (1918).
[3] Ibid., 17, 649 (1912).

treated with an equal amount of 96 percent alcohol according to Farnau's directions. The bromide did not precipitate at once, but a relatively few flaky crystals came out slowly on standing. With the iodide no precipitate at all was obtained. Thinking that absolute alcohol might have been employed, the experiments were repeated with this precipitant with similar results. Finally, it was thought that Farnau's results might be confirmed at 0°. Fifty cubic centimeters of the salts saturated at this temperature were mixed in turn with an equal amount of alcohol likewise cooled to zero. No precipitate of sodium bromide was obtained at once either with 96 percent alcohol or with absolute alcohol and the slight precipitate which formed came out more slowly than at room temperature. With sodium iodide, of course, no precipitate whatsoever was obtained. No luminescence was observed with either salt even though the procedures were carried out as will be described subsequently, after the eyes had become very sensitive by remaining several hours in the dark room.

The results of these preliminary experiments together with the knowledge that conclusions based on the comparison of colors of faint luminescence may be open to some question made it seem advisable to carry out further experiments on crystalloluminescence in an attempt to substantiate the chemical nature of the phenomenon.

Experiments with Sodium Chloride

The crystalloluminescence of sodium chloride was first observed by Bandrowski,[1] who called attention to the necessity of precipitating the salt very rapidly with hydrochloric acid or alcohol. Because of the cheapness of the pure salt and the fact that the solubility changes but slightly with changing temperature, sodium chloride is well adapted for studying the effect of various factors on the intensity and duration of the luminescence. These effects will now be considered in detail.

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[1] Loc. cit.

Effect of the Concentration of Hydrochloric Acid.—Since the intensity of luminescence increases with increasing reaction velocity,[1] I expected to get the brightest light by precipitating the saturated salt solution with concentrated acid. Indeed, Farnau[2] recommends concentrated acid whereas Bandrowski used 23 percent acid. Some preliminary experiments with concentrated acid gave unsatisfactory results. Although a copious precipitate formed rapidly only a few sparks at the most were obtained. Accordingly, a series of experiments were carried out with acids of different strengths.

After a few preliminary trials it was found that particular care must be exercised to secure uniform mixing and stirring of the solutions if uniform results were to be obtained. For this purpose was employed a mixing apparatus designed and used by the author in previous investigations where rapid uniform mixing and stirring of solutions were essential. This apparatus which is described in a former article[3] consists essentially of two concentric glass tubes approximately 3.5 cm and 2 cm in diameter, respectively, closed at one end by a common stopper. One solution is placed in the outer compartment of the apparatus and the other in the inner. By quickly withdrawing the inner tube and moving it up and down very rapidly once or twice almost uniform mixing of the two solutions is obtained in minimum time. The original apparatus was improved somewhat by choosing tubes of such relative diameters that two small bulbs could be blown in the inner tube approximately 4 cm and 8 cm from the stopper. A coil of platinum wire was attached near the bottom of the inner tube.

It is difficult for the unaided eye to determine differences in intensity of luminescence with very great accuracy. Fortunately, however, the crystalloluminescence of sodium chloride is sufficiently bright under suitable conditions that it will fog a photographic plate. Advantage was taken of this

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[1] Trautz: Loc. cit.

[2] Loc. cit.

[3] Weiser: Jour. Phys. Chem., 21, 314 (1917).

fact to determine the relative intensity of light emitted under various conditions. For exposing the photographic plate to the luminescence a "camera" was constructed, a detailed description of which was given in a former paper.[1] It consists essentially of a vertical slit 7 cm long and 0.9 cm wide, cut in a board about 1 cm thick. On one side of this board is attached a sliding plate holder that can be moved over the slit in such a way that several images can be made on a single plate; on the other side is a holder for the mixing apparatus for the purpose of attaching the latter firmly in place during an experiment.

A saturated salt solution was prepared from pure sodium chloride by saturating at a higher temperature and cooling to 25°, the temperature at which the experiments were carried out. Acids of the different strengths were made by diluting the pure concentrated acid with distilled water. After bringing the acids to 25° in a thermostat the density of each was determined with a Westphal balance.

After thoroughly cleaning and drying the mixer, exactly 50 cc of the salt solution were placed in the outer compartment and an equal amount of acid in the inner compartment. This was set in the "camera" previously loaded with a Hammer Red Label photographic plate, and the solutions mixed. The experiments were carried out in total darkness after the eyes had become sufficiently sensitive. To facilitate the preparation for experiments without leaving the dark room, a portion of the laboratory table was faintly illuminated when necessary by a deep red light reflected from a small printing lamp. It was found that this did not materially diminish the sensitiveness of the eye. Furthermore, by this provision it was possible to remain in the dark room for hours at a time so that the eyes became particularly sensitive.

The results of the experiment are given in Table I and a portion of the photograph is shown in Fig. I, *a*. The entire photograph was not reproduced since a strip shows the different effects quite well and occupies much less space. The

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[1] Weiser: Jour. Phys. Chem., 22, 439 (1918).

luminescence always started faintly at first, increased rapidly in intensity up to the maximum brightness where it remained for a moment and then gradually died out. In every case the plate was exposed for 30 seconds. The very faint glow which in some cases, lasted for some time after this, was found to have little or no effect on the plate. The observations of the approximate time for a visible glow to appear and to disappear are included in the table for the purpose of comparison with similar observations under other conditions and with other salts.

TABLE 1

Hydrochloric Acid as Precipitant

No. on plate Fig. 1	Density of acid at 25°	Approximate time in seconds		Maximum intensity of luminescence
		Glow to start	Glow to disappear	
	1.1045	—	—	No light
I	1.1089	2	10	Faint
II	1.1145	2	90	Very bright
III	1.1190	2	Over 120	Brightest light
IV	1.1240	1.5	Over 120	Very bright
V	1.1295	1.5	75	Bright
VI	1.1342	1.2	45	Fairly bright
	1.1450	1	5	Faint
	1.1890	—	—	Streak of light

From the above series of experiments it is evident that the maximum intensity of luminescence was obtained with acid of specific gravity between the narrow limits 1.115 and 1.125 at 25°. The precipitations with acid of specific gravity 1.119 and with dilute and highly concentrated acids were observed in daylight. The mixing apparatus was used. With very dilute acid, crystals came out slowly; with very concentrated acid, there was apparently instantaneous precipitation; with the acid of medium concentration, there was no precipitation for a moment but crystals soon formed in rapidly increasing amount throughout the whole solution.

Since the intensity of chemiluminescence increases with increasing reaction velocity and since a greater amount of salt is precipitated in less time by the stronger than by the weaker acid, the results obtained in the above series of experiments would seem to disprove the assumption that the luminescence is the result of chemical action. As a matter of fact a closer examination of the process shows that the apparently contradictory results furnish a strong proof of the chemical nature of the phenomenon.

When a solution of hydrochloric acid is added to a saturated solution of sodium chloride the reaction which follows is a union of sodium ion with chloride ion to form the non-dissociated salt. Before the addition of acid the equilibrium that exists in the solution may be represented thus: $Na^+ + Cl^- = NaCl$. The addition of hydrochloric acid, of course, forces this reaction to the right. For securing the maximum velocity of this reaction uniformly distributed throughout the whole solution, it is necessary to secure the highest possible concentration of the ions above the equilibrium concentration that obtains for the reaction. Such a condition can be brought about only by the addition of relatively strong acid and in the absence of immediate precipitation. Under such conditions, the system will be in an unstable state in proportion to the excess concentration of the ions above the equilibrium concentration; and when precipitation starts thereby upsetting the unstable condition, the reaction may, by virtue of the excess concentration of the ions, attain to the critical velocity necessary to produce light. This explains why the intensity of the emitted light decreases both above and below a certain concentration of hydrochloric acid. With highly concentrated acid, the first drop that comes in contact with the saturated salt solution causes instant precipitation due to the high local concentration of chloride ion. When the solutions are mixed in the mixer practically complete precipitation follows in the immediate wake of the inner tube as it is rapidly withdrawn. Under such conditions it is, therefore, impossible to get a high concentration of chloride ion through the entire solution. The immediate formation of abundant crystal nuclei likewise prevents the piling up throughout the solution of a high concentration of chloride ion above the equilibrium concentration. It follows, therefore, that a high reaction velocity would obtain throughout only a relatively small region and that in consequence a flash following the inner tube is all that would be expected under these conditions. This is in accord with the experimental observations. Since the velocity at any instant and at any point in the solution is proportional to the concentration of the ions at that point it follows that the maximum reaction velocity and intensity of luminescence in a narrow region of the solution may be less than that attained throughout the whole solution under conditions that result in a large accumulation of ions in excess of the equilibrium concentration. With too dilute acid the velocity of the reaction with the formation of the non-dissociated salt may never attain to the critical velocity necessary to produce luminescence. Between these two extremes lie all the intermediate possibilities for obtaining a high concentration of ions throughout the solution, accompanied by a correspondingly high reaction velocity and intensity of light. The foregoing experiments clearly show the best concentration of acid to employ to secure the desired results.

Since a high reaction velocity and intensity of luminescence depend on securing a high concentration of ions in excess of the equilibrium concentration, it follows that any variation in the conditions of precipitation that increases or decreases this excess concentration will correspondingly affect the intensity of luminescence. Certain of these effects will now be considered.

The Effect of Stirring.—As before mentioned Trautz[1] considers that all cases of crystalloluminescence are produced by growing crystals "striking together, falling on each other and rubbing against each other." "Luminescence takes place of itself only when the concentration of the solution or melt is so great that there exists a movement of crystals in the solution, whether it be the precipitation of crystals or the crystals striking against each other as in molten sodium acetate."

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[1] Loc. cit.

If the crystalloluminescence of sodium chloride is excited by the crystals rubbing or striking together, one would naturally expect to get a more intense light in every case by vigorously stirring the crystallizing solution. To test this, experiments were carried out as previously described except that the solutions were stirred continuously by moving the inner tube rapidly up and down. But little light was obtained with any concentration of acid under these conditions. The photographic plate was not fogged at all. These results are what one would expect from the previous observations. Continuous vigorous stirring of the solution promotes the rapid formation and distribution of abundant crystal nuclei which prevents a large accumulation of ions in excess of the equilibrium concentration. Hence, at no stage of the process will the reaction attain as high a maximum velocity as in the absence of stirring.

This series of experiments emphasizes the necessity of rapidity in mixing the solutions in order to obtain the best results. With the mixer this was accomplished in an instant by jerking out the inner tube, immediately plunging it in and out again. As a further precaution the same apparatus was used in all the experiments.

The Effect of the Presence of Gelatine.—Trautz[1] observed that the presence of gelatine prevented the crystalloluminescence of barium chlorate when the salt precipitated from a solution containing 58 percent water, 40.5 percent barium chlorate and 1.5 percent gelatine. He attributed this effect to the increased viscosity of the solution: "If a barium chlorate solution is thickened with a small amount of gelatine no luminescence appears even though the salt separates very rapidly and almost no chlorate is reduced." Since this experiment was carried out by dissolving the salt at a high temperature and allowing it to crystallize out as the solution cooled, it is difficult to say what effects do come in, particularly since even a one percent solution of gelatine can vary in viscosity

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[1] Zeit. phys. Chem., 53, 25 (1905).

from a liquid almost as fluid as water when warm to a rigid gel when cold.

Zsigmondy[1] has observed the presence of small particles in a dilute gelatine solution. It seemed very probable, therefore, that the presence of a small amount of gelatine in a solution of sodium chloride would, by furnishing nuclei[2] affect the crystalloluminescence in much the same way as continuous stirring of the solution. This was tested experimentally:

To 50 cc of a saturated salt solution was added 0.3 gram of gelatine. The mixture was kept in the thermostat for 4 hours with occasional stirring. The milky "solution" that resulted was placed in the outer compartment of the mixing apparatus and was precipitated in the usual way with hydrochloric acid (specific gravity 1.119). Sufficient light was obtained to just fog the photographic plate. The experiment was repeated in daylight and it was found that crystallization started before the usual mixing process was completed. Two factors may enter in here: First, the actual presence of nuclei may start immediate precipitation as before suggested; and second, the salt solution rendered somewhat viscous by the presence of the gelatine may fail to mix uniformly, thereby producing high local concentrations at certain points which would result in the immediate formation of crystal nuclei just as happened when too concentrated acid was used. In the light of subsequent experiments it seems probable that the first factor is the more important. The crystals were examined microscopically and were found to be large and well formed. They settled to the bottom of the mixing apparatus quite as readily as in the absence of gelatine.

The effect of varying amounts of gelatine on the intensity of the luminescence was determined as above described. The results are recorded in Table II and a portion of the photograph obtained is reproduced in Fig. I, *b*.

To get comparable values of the relative viscosities of the different solutions the following procedure was adopted:

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[1] "Colloids and the Ultramicroscope," 195 (1909).

[2] Cf. Jaffé: Zeit. phys. Chem., 43, 565 (1903).

To 50 cc of saturated sodium chloride solution was added an equal amount of water and a weighed amount of gelatine. After standing in the thermostat 4 hours the density (d) and the "time of flow" (t), in an Ostwald viscosimeter were determined and the relative viscosity of the solutions compared to water at 25° was calculated from the expression

$$V_{\text{solution}} = \frac{(t \times d)_{\text{solution}}}{(t \times d)_{\text{water}}}.$$

The values of V so obtained are included in Table II.

TABLE II

The Effect of Gelatine

No. on plate Fig. I, *b*	Density of acid at 25°	Gram of gelatine	V	Intensity of luminescence
I	1.1190	0.0	1.315	Very bright
II	1.1190	0.05	1.346	Bright
III	1.1190	0.1	1.370	Fairly bright
IV	1.1190	0.2	1.425	Rather faint
V	1.1190	0.3	1.516	Faint

From Table II and the accompanying photograph it is clear that with gradually increasing gelatine content there is a gradual falling off in the intensity of the luminescence. That this decrease is not due to increased viscosity will be seen from the experiments which follow.

The Effect of the Addition of Cane Sugar.—To determine the effect of increased viscosity of the solution on the crystalloluminescence of sodium chloride, sugar instead of gelatine was dissolved in the salt solution before precipitation. In this way the desired viscosity was secured without the introduction of a colloidal phase and its accompanying influence. The experiments were carried out in the usual manner except that a weighed amount of cane sugar was completely dissolved in the 50 cc of salt solution before the precipitation with hydrochloric acid. Comparable values of the relative viscosities were determined as before described with solutions prepared by diluting 50 cc of saturated salt solution with an equal amount of water and adding a weighed amount of sugar. All experiments were carried out at 25°. The results are recorded in Table III and the photograph is reproduced in Fig. I, *c*.

By comparing the results recorded in Table III with those in Table II it will be seen that increasing the viscosity with a substance that does not introduce a colloidal phase has relatively little effect on the intensity of the luminescence at least up to a certain point. An experiment with a salt solution to which 20 grams of sugar was added showed only a slight decrease in the intensity. Indeed the observations

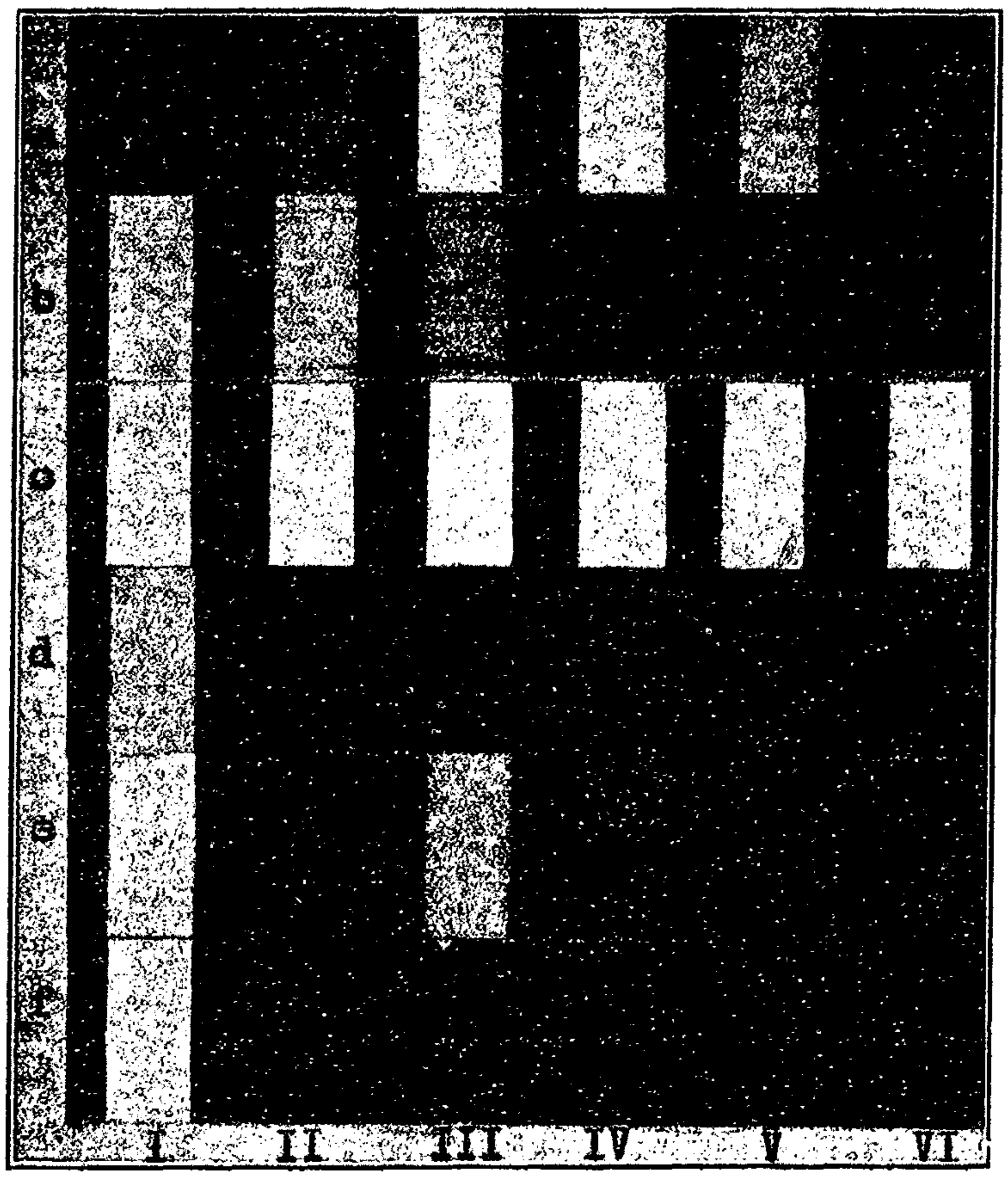

Fig. I

TABLE III

The Effect of Increasing the Viscosity with Cane Sugar

No. on plate Fig. I, *c*	Density of acid at 25°	Grams of cane sugar	V	Intensity of luminescence
I	1.1190	0	1.315	Very bright
II	1.1190	1	1.364	Very bright
III	1.1190	2	1.398	Very bright
IV	1.1190	4	1.479	Very bright
V	1.1190	6	1.560	Very bright
VI	1.1190	10	1.733	Very bright

seemed to indicate that up to a certain point, the intensity of the light was increased slightly by increasing the viscosity. This is what one might expect from the previous experiments. By increasing the viscosity slightly the tendency for immediate precipitation is reduced, which correspondingly favors the piling up of the ion concentrations. To test this point the precipitation was effected with acid of such concentration that a faint luminescence was ordinarily obtained. When the viscosity of the solution was increased by the addition of sugar a marked increase in the intensity of the luminescence was observed. The results are recorded in Table IV and the photograph is reproduced in Fig. I, *d*.

TABLE IV

No. on plate Fig. I, *d*	Density of acid at 25°	Grams of cane sugar	V	Intensity of luminescence
I	1.1190	0	1.315	Very bright
II	1.1342	5	1.519	Rather faint
III	1.1342	10	1.733	Fairly bright
IV	1.1342	15	1.996	Fairly bright

The results recorded in Table IV were confirmed by experiments with potassium chloride, which shows a decided increase in the crystalloluminescence with suitable increase in the viscosity of the solution. It is evident that increase in the viscosity above a certain point will have an opposite effect by cutting down the rate of mixing and diffusion.

Experiments with Alcohol as Precipitant.—When a saturated solution of sodium chloride was mixed with a suitable concentration of alcohol, crystalloluminescence was produced. Even under the most favorable conditions the intensity of the light was much less than the maximum intensity obtained with hydrochloric acid as precipitant. The photographic plate was barely fogged by one exposure to the brightest light obtained. This result was readily accounted for, since under the most favorable conditions it would ordinarily be possible to get a higher maximum value for the product of the concentration of the ions when the precipitation was effected by the addition of a common ion. The same conditions govern the effect of the concentration of the alcohol on the intensity of the luminescence as we saw held for hydrochloric acid. Several experiments were carried out with different concentrations of alcohol, to determine the best conditions for obtaining the maximum light intensity with this precipitant. The results are recorded in Table V. It will be noted that the time interval between mixing and the appearance of a visible luminescence was much longer than when precipitation was effected with a common ion.

TABLE V
Alcohol as Precipitant

Density of alcohol at 25°	Solution mixed, cc		Approximate time, seconds		Intensity of luminescence
	Alcohol	Salt	Glow to start	Glow to disappear	
0.792	50	50	4	15	Faint
0.804	50	50	4	20	Brighter than (1)
0.823	50	50	5	25	Faint
0.823	55	45	5	30	Faint
0.864	50	50	—	—	No light

The Effect of Temperature.—To determine the effect of temperature on the intensity of the crystalloluminescence of sodium chloride, experiments were carried out at 0° and at 50°. In this series of experiments the maximum intensity was obtained in the precipitation with suitable concentration of hydrochloric acid at 0°. However, the intensity was distinctly less than the brightest light obtained at 25°. This was due to a slower reaction velocity at the lower temperature. The observations disclosed that under the best conditions the luminescence remained at the maximum intensity considerably longer than at 25°, but at no time was the reaction velocity sufficiently high to produce so intense a light as at 25°. At 50° the luminescence started before the mixing process was complete. As one should expect under these conditions the results were similar to those obtained when too concentrated acid was used. The results of the series of experiments are tabulated in Table VI and the photographs with hydrochloric

TABLE VI
The Effect of Temperature

No. on plate Fig. I, *e*	Precipitant	Density of precipitant at 25°	Temp.	Approximate time in seconds for glow to		Intensity of luminescence
				appear	disappear	
I	HCl	1.1190	25°	—	—	Very bright
II	HCl	1.1089	0°	10	35	Rather faint
III	HCl	1.1145	0°	10	120	Bright
IV	HCl	1.1190	0°	10	60	Fairly bright
V	HCl	1.1240	0°	10	—	Flash
	HCl	1.1295	0°	—	—	Very faint flash
Fig. I, *f*						
I	HCl	1.1190	25°	—	—	Very bright
II	HCl	1.1145	50°	—	10	Rather faint
III	HCl	1.1190	50°	—	15	Fairly bright
IV	HCl	1.1240	50°	—	25	Fairly bright
V	HCl	1.1295	50°	—	25	Fairly bright
VI	HCl	1.1342	50°	—	10	Rather faint
	Alcohol (1)	0.792	0°	12	15	Faint
	Alcohol (2)	0.823	0°	15	40	Slightly brighter than (1)
	Alcohol*	0.823	0°	17	35	Brighter than (2)
	Alcohol*	0.864	0°	15	27	Faint

* 55 cc of alcohol and 45 cc of salt solution were mixed.

acid as precipitant at 0° and at 50°, respectively, are reproduced in Fig. I, *e* and *f*. Even under the best conditions with alcohol as precipitant, the intensity of the luminescence was insufficient to affect the photographic plate.

The Color of the Luminescence.—In a previous paper[1] the author has described a method for determining the color of faint luminescence that may be applied to the crystalloluminescence of sodium chloride. The method consists essentially of photographing the luminescence on a panchromatic plate, interposing a series of ray filters between the source of light and the plate. Since a preliminary test indicated that the luminescence was bluish violet, a photograph was taken with a graded set of filters that covered this region of the spectrum rather fully.

Since the experimental evidence indicates that the crystalloluminescence of sodium chloride is due to the union of the ions with the formation of the non-dissociated salt, it follows that if this reaction could be brought about in some other way, quantitatively the same luminescence would result. Wilkinson[2] burned sodium slowly in chlorine and obtained what appeared to be a light blue luminescence, instead of the familiar yellow color obtained by the rapid combustion of the metal. Because of the errors that may arise in determining the quality of faint luminescence by the unaided eye,[3] it seemed desirable to photograph the light from the slow combustion of sodium using the same filters that were used in photographing the crystalloluminescence. It has been shown[4] that the yellow luminescence of sodium is due to some stage in the reaction from sodium vapor to sodium ion. During slow combustion, the light intensity of this reaction is so low relatively, that so far as the eye can detect, it is completely masked by the blue luminescence produced by the reaction from sodium ion to the non-dissociated salt. However, the

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[1] Jour. Phys. Chem., 22, 439 (1918).

[2] Ibid., 13, 695 (1909).

[3] Weiser: Loc. cit.

[4] Bancroft and Weiser: Jour. Phys. Chem., 19, 310 (1915).

photographic method is so much more sensitive than the unaided eye, that it is difficult to eliminate the effect of the former reaction completely from a photograph. Furthermore, since the combustion is strongly exothermic, there is likely to be a purely thermal glow from minute particles of highly heated metal even when the reaction is going on relatively slowly. Owing to the "Purkinje phenomenon" this would appear blue and so would not be distinguished by the unaided eye. An attempt was made to render both of these effects negligible by photographing the faint glow that accompanies very slow combustion. The method of procedure was as follows: A strip of sodium 10 cm in length and 0.7 cm in width was fastened in a groove cut in a piece of wood that fit snugly in a piece of glass tubing 2.5 cm in diameter and 25 cm long. Since the alkalis do not react readily with dry halogens, a slow stream of chlorine was first conducted through a wash bottle containing water and then over the strip of sodium. The glow which resulted lasted but a short time, due to the deposition of a layer of salt over the surface of the sodium. To remove this a steel scraper attached to a glass rod was drawn back and forth over the surface. The faint glow was strikingly similar to the crystalloluminescence of salt. To the eye it appeared distinctly more white than blue just as did the glow during precipitation. An attempt was made to photograph this light using the apparatus previously described. Unfortunately the glow could be maintained only by scraping the surface of the metal rather forcibly. As a result fine threads of sodium were raked up by the scraper and these caught fire giving a yellowish glow that ruined the photograph. After numerous unsuccessful attempts to secure a good photograph with the apparatus variously modified, air was substituted for chlorine with much more satisfactory results. The procedure was as follows: A few grams of sodium were melted in a hard, glass tube 2.5 cm in diameter and 25 cm long. By means of a glass rod the molten metal was distributed over a portion of the inner surface of the tube, avoiding oxidation as much as possible. Moist air was then blown through the tube and a glow was secured that could be maintained indefinitely. The addition of heat was unnecessary as the heat of reaction was enough to maintain a sufficiently rapid combustion; but occasional stirring with a glass rod was beneficial. The luminescence appeared somewhat bluer than either the glow in chlorine or the crystalloluminescence. At first I was inclined to attribute this to a difference in intensity, but the photographs showed that there actually was slightly more blue in the former luminescence. Since halftones of this kind show so poorly on ordinary paper, the photographs were omitted and a description substituted. The filters used are listed in Table VII.

TABLE VII

Number	Color of filter	Light that passes through filter
1	Yellow	Red to the thallium line
2	Green	From lithium beta line to barium delta line. Small band in the red
3	Green	From lithium beta line to barium alpha line
4	Dark green	From calcium beta line to barium beta band
5	Greenish blue	From left of calcium beta line faintly to right of indium alpha line
6	Blue	From right of thallium alpha line to beyond the indium alpha
7	Purple	From strontium delta line through the extreme violet. Red to lithium alpha line
8	Blue	From thallium line to indium alpha line
9	Blue	From right of barium alpha line to right of indium alpha line
10	Blue (purplish)	From barium beta band to midway between strontium delta line and rubidium alpha line. Small band in orange
11	Blue	From left of barium beta band to lithium alpha line
12	Deep blue	Blue only

To determine the color of luminescence the photographs must be compared with a photograph of white light taken with the same filters. The crystalloluminescence produces a fogging behind filter number 7 that is distinctly more marked relatively than that produced by white light. The fogging behind 6 and 10 is slight, much less relatively than from white light. There is a little fogging behind 5, but the plate is unaffected behind all the rest. This fixes the color almost entirely beyond the indium blue line. The photograph of the slow combustion differs from that of the crystalloluminescence and also white light in showing a more marked fogging behind 6 than 7. Behind 10 the plate is fogged slightly more relatively than by the crystalloluminescence. There is also a slight fogging behind 5, 8 and 9 and a trace behind 11, but the plate is unaffected behind the others. It is evident that there is slightly more blue in the combustion luminescence than in the crystalloluminescence but the agreement is good considering the difficulties involved in photographing the former and the fact that in the two cases a different anion is concerned which is not without its effect.[1]

As before stated, Bandrowski[2] considered that crystalloluminescence was simply a series of electric discharges. If this were true it is probable that the light would be much more nearly like white light than it was found to be. Indeed, Bandrowski[3] believed that it was white. "I carried out investigations on the spectrum of the light in both cases. The same was white, hence, it follows that the light is white in all cases." In view of the foregoing experiments, it is evident that this conclusion is erroneous. Guinchant[4] did not go so far as Bandrowski. He considered that the crystalloluminescence of arsenic trioxide probably showed a continuous spectrum from which the violet and red were lacking because of the faintness of the light. Thinking that the crystalloluminescence of sodium chloride might contain some red or

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[1] Cf. Wiedemann and Schmidt: Wied. Ann., 56, 205 (1895); Lenard: Drude's Ann., 17, 203 (1905).

[2] Zeit. phys. Chem., 15, 323 (1894).

[3] Ibid., 17, 244 (1895).

[4] Loc. cit.

green light, a panchromatic plate was exposed to the luminescent reaction ten times in the same place. The photograph obtained merely confirmed the results previously reached with one exposure, namely, that there is no red, yellow or green in this luminescence.

Conclusion.—The results of the foregoing series of experiments on the crystalloluminescence of sodium chloride all tend to substantiate the view that the phenomenon is a purely chemical one, the luminescence resulting from the rapid union of the ions with the formation of the non-dissociated salt. As before stated, Trautz's classification of crystalloluminescence under the head of triboluminescence is of questionable value since he does not attempt to account for the latter. Because of the recognized similarity between the two phenomena, it is probable that all cases of triboluminescence are the result of chemical actions,[1] using the term in its broadest sense. Moreover, I am of the opinion that the cause of triboluminescence and crystalloluminescence is identical in the case of substances which show both phenomena. The only difference between the two, therefore, is in the actual way in which the chemical reaction which produces the light, is brought about. For example, sodium chloride may be partly ionized by fusion or by dissolving the salt in water. The recombination of the ions produces apparently identical luminescence although there is a difference in the way the results are accomplished. In like manner, it is by no means improbable that the relatively enormous forces which may be brought to bear in crushing a crystal of sodium chloride may cause a disruption of the molecule forming sodium ion and chloride which would recombine with emission of light identically the same as that obtained by cooling the fused salt or by precipitating it from solution. In certain cases it is not unlikely that the friction caused by crystals rubbing against each other during precipitation or stirring of suspended crystals, may be sufficient to bring about results similar to the more vigorous grind-

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[1] Cf. Bancroft: Jour. Franklin Inst., 175, 129 (1913).

ing in a mortar. This is unusual, however, since the known cases of so-called triboluminescence are numerous whereas the known cases of crystalloluminescence are relatively few and are confined for the most part to comparatively simple inorganic salts. That all triboluminescent substances are not also crystalloluminescent is due to the fact that the breaking up or disarrangement of the molecule (other than by ionization in solution), is usually accomplished only by the more vigorous rubbing or grinding of the dry crystals. Because of the faintness and transient nature of triboluminescence I have been unable as yet to establish experimentally, the identity of the two phenomena.

Experiments with Potassium Chloride

The crystalloluminescence of potassium chloride was first observed by Bandrowski[1] who calls attention to the experimental difficulties which he encountered: "In spite of numerous attempts with [hydrochloric acid solutions] of different concentrations, I have been unable so far to determine the most suitable conditions for obtaining the strongest luminescence. In a single favorable case a strong green luminescence resulted that appeared in places like a spark. Usually I observed only weak needles of light which appeared for a moment in different parts of the cylinder. The experiment is most likely to turn out well if a saturated potassium chloride solution is carefully mixed with an equal amount of hydrochloric acid (sp. gr. 1.12) and then shaken strongly and suddenly. Sometimes the effect is about like that obtained with sodium chloride." Judging from my experience with sodium chloride it seemed likely that the variable results obtained by Bandrowski were caused by using acid of the wrong strength and by lack of uniformity in mixing the solutions. This conclusion was borne out by the subsequent experiments. However, it was found that the luminescence, though similar in appearance to that of sodium chloride was very much fainter.

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[1] Loc. cit.

Indeed the photographic plates used were apparently unaffected by one exposure to the brightest light obtained. As in the previous experiments 50 cc of salt solution saturated at the chosen temperature was mixed in the mixing apparatus with an equal amount of hydrochloric acid solution or alcohol solution. The results under widely varying conditions are tabulated in Table VIII. Statements of the intensity of the luminescence are made without reference to the much brighter light obtained with sodium chloride under suitable conditions.

TABLE VIII

Experiments with Potassium Chloride

Precipitant	Density of precipitant at 25°	Temp.	Approximate time in seconds for glow to		Intensity of luminescence
			appear	disappear	
HCl	1.1089	25°	1	15	Faint
HCl	1.1145	25°	0.5	15	Fairly bright
HCl	1.1190	25°	0.5	15	Faint
HCl	1.1240	25°	0.5	7	Very faint
HCl	1.1295	25°	—	—	Trace
HCl	1.1342	25°	—	—	Trace
HCl	1.1089	0°	1	20	Fairly bright
HCl	1.1145	0°	1	35	Fairly bright
HCl	1.1190	0°	1	15	Fairly bright
HCl	1.1240	0°	—	—	Flash fairly bright
HCl	1.1342	0°	—	—	Flash
Alcohol	0.804	25°	—	—	No light
Alcohol	0.823	25°	—	—	No light
Alcohol	0.846	25°	—	—	Faint trace
Alcohol	0.864	25°	7	15	Fairly bright
Alcohol	0.877	25°	—	—	Few sparks
Alcohol	0.804	0°	—	—	No light
Alcohol	0.846	0°	—	—	Very faint
Alcohol	0.864	0°	—	—	Faint
Alcohol	0.877	0°	—	—	No light

The experiments with potassium chloride emphasized again the great importance of rapid, uniform mixing on the uniformity of the results obtained. With the mixing apparatus little difficulty was found in duplicating the luminescent effect under a given set of conditions even though precipitation started almost at once in every case. As we have seen, the last-mentioned condition is unfavorable for securing a high excess concentration of the ions and a consequent high reaction velocity. As a result the luminescence was faint and lasted but a short time under the most favorable conditions found. The most satisfactory luminescence resulted at 0° with acid of specific gravity 1.1145. Attention has been called to the fact that the intensity of the luminescence was increased by dissolving as much as 20 grams of sugar in the salt solution before precipitation. Fairly good results were obtained at 25° with alcohol, specific gravity 0.864.

Experiments with Potassium Bromide

Bandrowski[1] precipitated potassium bromide with 96 percent alcohol and obtained a few very faint, transient flashes of light. He mentioned having used hydrobromic acid as precipitant but gave no details. Trautz[2] was unable to get crystalloluminescence of alkali bromides: "The crystallization of alkali bromides shows little tendency to emit light. Thus, no light was produced when hydrobromic acid, specific gravity 1.49, was added to hot sodium or potassium methylate, ethylate, propylate, isobutylate and amylate. Alkali bromide separated out in every case. Stirring the mixture also gave no light." Again, it seemed that the conditions of precipitation were not chosen sufficiently carefully to get crystalloluminescence. Accordingly, the series of experiments tabulated in Table IX were carried out. Constant boiling hydrobromic acid solution was prepared and the solutions of different strengths were made up from this. As before 50 cc of each solution was mixed in the mixing apparatus and the effect observed. The results follow.

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[1] Loc. cit.

[2] Zeit. phys. Chem., 53, 19 (1905).

TABLE IX
Experiments with Potassium Bromide

Precipitant	Density of precipitant at 25°	Temp.	Approximate time in seconds for glow to		Intensity of luminescence
			appear	disappear	
HBr	1.433	25°	—	—	No light
HBr	1.385	25°	0.5	—	Very faint. Occasional flashes
HBr	1.365	25°	0.5	8	Fairly bright
HBr	1.337	25°	0.5	10	Brightest of series
HBr	1.303	25°	—	—	No light
Alcohol	0.792	25°	—	—	No light
Alcohol	0.804	25°	—	—	Occasional flashes
Alcohol	0.823	25°	—	—	Faint glow followed by occasional flashes
Alcohol	0.846	25°	—	—	Faint. Few flashes
Alcohol	0.864	25°	—	—	Very faint
Alcohol	0.877	25°	—	—	No light

The above results show that a crystalloluminescence can be secured with potassium bromide similar in every respect to that of sodium and potassium chloride. The most satisfactory glow, obtained with hydrobromic acid, specific gravity 1.337, lasted several seconds and was about the same intensity as with potassium chloride. With alcohol as precipitant the results were unsatisfactory at best.

Experiments with Potassium Iodide

Trautz[1] obtained a glow when hot sodium alcoholate and potassium alcoholate were treated with hydriodic acid. He found that this was not a crystalloluminescence but was produced by the action of alcohol with iodine formed by the decomposition of hydriodic acid. Farnau[1] obtained a faint light by precipitating potassium iodide with alcohol. I have

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[1] Loc. cit.

carried out experiments using both hydriodic acid solutions and alcohol solutions as precipitants. Constant boiling hydriodic acid solution free from iodine was first prepared and the more dilute solutions were made from this. The results of the series of experiments under varying conditions are given in Table X.

TABLE X

Experiments with Potassium Iodide

Precipitant	Density of precipitant at 25°	Temp.	Approximate time in seconds for glow to		Intensity of luminescence
			appear	disappear	
HI	1.672	25°	0.5	2	Fairly bright
HI	1.595	25°	0.5	5	Brightest of series
HI	1.534	25°	—	—	Faint
Alcohol	0.792	25°	—	—	No light
Alcohol	0.804	25°	—	—	Very faint trace
Alcohol	0.823	25°	—	—	No light

It may be seen from the above table that the precipitation with alcohol gives only a very faint trace of light. With hydriodic acid, however, a very satisfactory glow was observed that was similar in character and in intensity to the potassium chloride luminescence. This is in agreement with all the previous results. The addition of a common ion under suitable conditions, to the saturated salt solution, resulted in an ion concentration sufficiently high to cause the reaction with the formation of the non-dissociated salt to attain to the critical velocity necessary to produce light.

Experiments with Sodium Bromide and Sodium Iodide

Farnau claims to have observed crystalloluminescence with both sodium bromide and sodium iodide, by the addition of alcohol to the saturated solutions. As before explained, his results could not be confirmed under any conditions. Furthermore, no light was obtained by the addition of the respective acids to the saturated salt solutions. A relatively small precipitate formed slowly when a constant boiling solution of hydrobromic acid was added to saturated sodium bromide solution at 25°. No precipitate resulted when constant boiling hydriodic acid was added to sodium iodide solution. It is possible that the use of fuming acids would give sufficiently rapid reactions to emit light but this was not tried.

The results of this investigation may be summarized as follows:

(1) Crystalloluminescence is caused by chemical action.

(2) Nothing is gained by the usual classification of crystalloluminescence as a special case of triboluminescence without explaining the latter phenomenon.

(3) It is probable that all cases of triboluminescence are due to chemical action. The luminescent reaction is probably identically the same in the case of substances that show both triboluminescence and crystalloluminescence; the only difference is in the actual way in which the reaction is brought about.

(4) The specific reaction that produces the crystalloluminescence of the alkali halides is the recombination of the ions with the formation of the non-dissociated salt.

(5) Crystalloluminescence was observed with sodium chloride and with potassium chloride, bromide and iodide, but not with sodium bromide and iodide. The conditions for determining the maximum intensity of luminescence was determined in each case.

(6) A quantitative study has been made of the effect on the intensity of the crystalloluminescence of sodium chloride produced by (1) varying the nature and concentration of precipitant, (2) stirring the precipitating solution, (3) adding a colloid, (4) increasing the viscosity of the solution by the addition of a non-electrolyte, (5) varying the temperature.

(7) The maximum intensity of the crystalloluminescence results under conditions which favor the accumulation throughout the solution of the largest possible concentration of ions in excess of the equilibrium concentration; and which allow the luminescent reaction, once started, to go rapidly to com-

pletion. The actual conditions which are most favorable differ with different salts.

(8) The crystalloluminescence of sodium chloride is bluish white in color instead of being white light, like an electric spark, as Bandrowski supposed.

(9) The color of the luminescence produced when sodium is burned slowly in air is similar but slightly bluer than the crystalloluminescence of sodium chloride. The difference is due to the specific effect of the anion.

Department of Chemistry
The Rice Institute
Houston, Texas

SILICIC ACID GELS

BY HARRY N. HOLMES

Workers in various sciences have occasion to prepare special silicic acid gels but specific directions are lacking. Requirements for such gels made from the desired acid, setting in a convenient time, and of a definite silica content, should be met. This paper offers information for such needs as well as new work on the effect of high concentrations of the acid mixed with the sodium silicate and the comparative effect of weak and strong acids on silicic acid. A study of the influence of higher temperatures on silicic acid gels is also included.

Flemming,[1] under the direction of W. Ostwald, has made the most important contribution to this phase of the subject although Kohlrausch[2] studied the effect of age on water glass solutions as measured by change in conductivity and van Bemmelen[3] did invaluable work in connection with the dehydration and hydration of silicic acid gels. Maschke[4] added some work on the time of formation of these gels.

Methods of Work

A water glass solution sold for general purposes by a prominent chemical company was used for most of the experiments. Since carbon dioxide has a marked influence on the time of set of silicic acid gels it was necessary to have a water glass free from this substance. We diluted this sodium silicate, acidified and boiled. No carbon dioxide could be detected in the issuing gases. Some samples of commercial water glass contain iron salts in appreciable quantities but only a trace of iron was to be found in the product we selected. It was practically colorless. Analysis showed the composi-

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[1] Zeit. phys. Chem., 41, 427 (1902).

[2] Ibid., 12, 773 (1893).

[3] Zeit. anorg. Chem., 13, 233, 258 (1897); 18, 114 (1898); 59, 225 (1908); 62, 1 (1909).

[4] Pogg. Ann., 146, 90 (1872).

tion of this water glass to be 1 Na_2O, 3.66 SiO_2. Diluted to a density of 1.06 it required an equal volume of 0.52 *N* acid to neutralize it, using phenolphthalein as an indicator.

In making the gels it was our custom to pour the water glass into an equal volume of the acid desired, mixing quickly. The mixture was considered to have set to a gel when the container, a tube of 15 mm to 20 mm diameter, could be tilted and sharply tapped without a flow of the gel mixture. Flemming invented two rather complicated methods of observing the time of set, but, with a set of a few hours, their accuracy was probably no greater than by the simple method here given.

In the temperature study, water baths were improvised from granite kettles covered with asbestos paper and heated by micro burners. The flames were protected from drafts by curtains of asbestos paper. Test tubes of the gel mixture hung in the baths through holes in the wooden covers. Of course the solutions were heated to the desired temperature before mixing. With these baths, by close watching, we could hold the temperature to within 0.5 ° C of the desired point for temperatures below 50° C. Above 50° C the possible error was about 1 ° C.

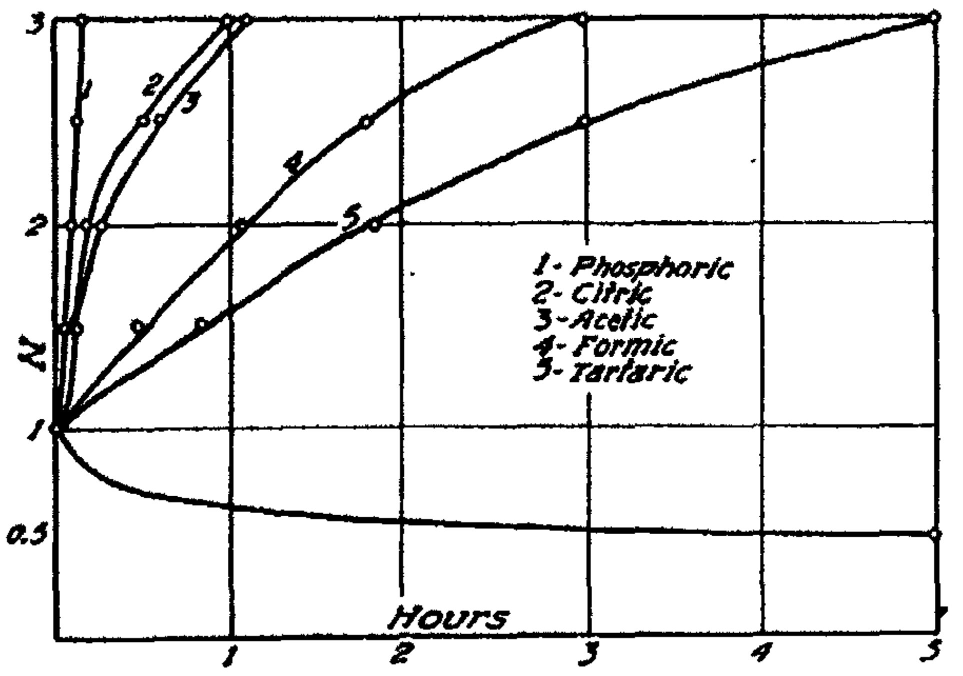


Fig. 1
Effect of varying acidity on the same concentration of SiO_2.
Acid mixed with an equal volume of 1.16 density sodium silicate at 20°

In Fig. 1 we plot the time of set for mixtures of the same water glass with five different acids, using concentrations of the acids differing by 0.5 *N* and below the 1 *N* decreasing in 0.1 *N* steps. It will be observed that with increasing acidity the set of the tartrate or formate gels is delayed more than with acetic, citric or phosphoric acids. Of course the normality reading on this chart does not represent the *excess* of free acid above that required to react with the sodium silicate but only the concentration of acid actually mixed with an equal volume of 1.16 density water glass. To read this excess of free acid one should subtract 1.4 *N*, the normality of acid required to neutralize an equal volume of the particular water glass used, and divide the result by two since the volume of the acid was doubled.

Flemming, working with hydrochloric and sulphuric acids, charted only the excess acid but as a source of convenient working directions this paper is confined to the actual concentrations mixed. It will be observed there that gels of almost immediate set are more than slightly basic, as it requires 1.4 *N* acid to neutralize an equal volume of the water glass used in Fig. 1. Flemming found that with gels of a much lower concentration of SiO_2 a slight excess of hydroxyl ion produced the quickest set. It is evident from Fig. 1 that the quickest set with more concentrated gels occurs in the presence of a much greater excess of hydroxyl ions. With increase in the excess of hydroxyl ions the time of set is delayed more rapidly than by the catalytic action of excess of hydrogen ions, that is, the curve quickly flattens. The curves for all these acids below the normal practically coincide as shown in Fig. 1.

This chart is similar to Fig. 1, but refers to different densities of the same water glass instead of 1.16 density alone. Due partly to the lower concentration of silicic acid, the time of set was much longer than with the 1.16 density water glass, in fact, the chart had to be drawn on the scale of one hundred hours instead of four hours as in Fig. 1. If it is desired to compare the effect of excess of different acids on silicic acid in this chart the comparison must be confined to one density, or concentration, of sodium silicate 1.08 for example. Naturally a lower concentration of silicic acid sets to a gel more slowly. For the 1.06 density subtract 0.52 *N* from the chart reading; for 1.08 density subtract 0.7 *N*; and for 1.10 density subtract 0.86 *N*. When these results are divided by two (because the volume of acid was doubled in mixing) the chart readings are changed from the concentrations actually used to the excess of acid present.

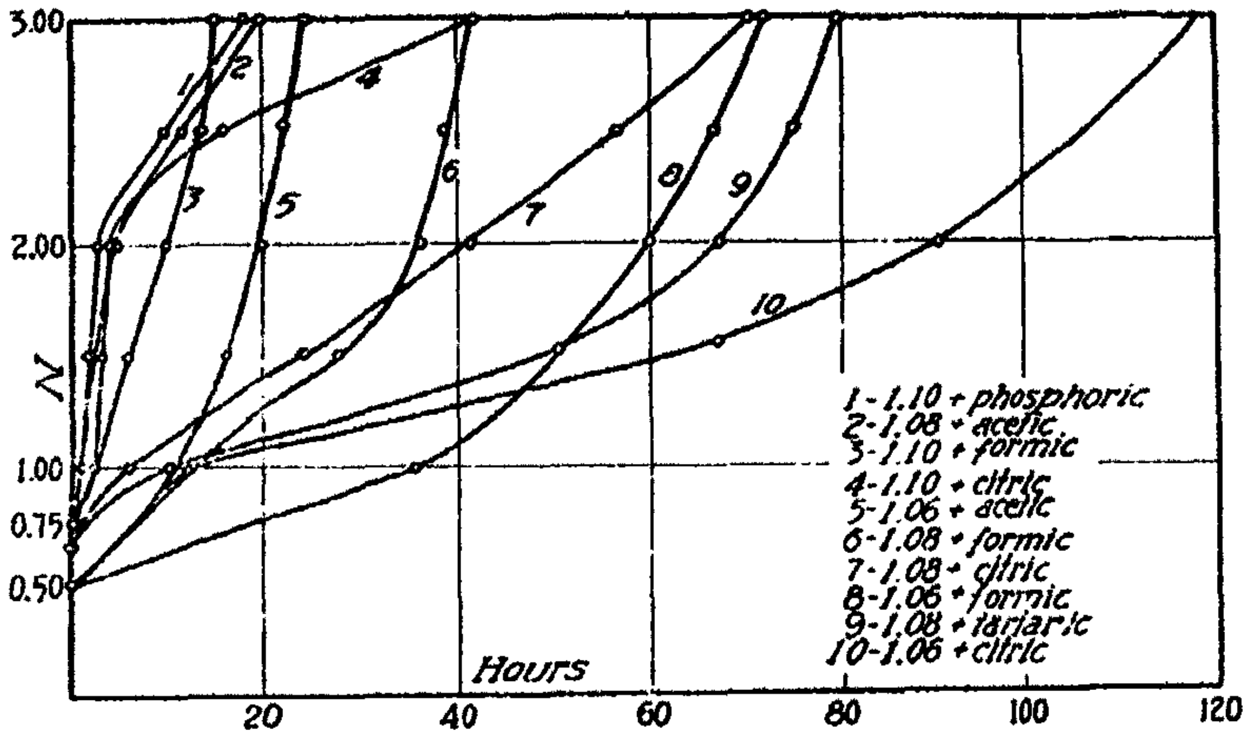


Fig. 2.

Effect of varying acidity on water glass of 1.06, 1.08 and 1.10 density at 20°

Using a water glass of approximately the same composition as that described here, any experimenter can select from the range of five different acids and four different densities of sodium silicate the particular mixture that meets his requirements in time of set. In some work a definite acid is desired.

Flemming considered the time of set to depend wholly upon the concentration of silicic acid liberated, and the catalytic effect of hydrogen or hydroxyl ions with, of course, a temperature influence. In this paper we raise the question whether the concentration of free hydrogen ions is not influenced greatly, in the weaker acids, by the presence of the sodium salt formed in the reaction. For example, the excess of free acetic acid must be greatly repressed in ionization by the sodium acetate formed. With sulphuric and hydrochloric acids, the only acids used by Flemming, this influence is slight.

The dehydrating influence of the molecules of the acid may have a great effect on the relative distribution of water between the two phases of the gel thus influencing the time of set. This influence must vary with the acid used and the concentration of its excess over the amount required to react with the water glass.

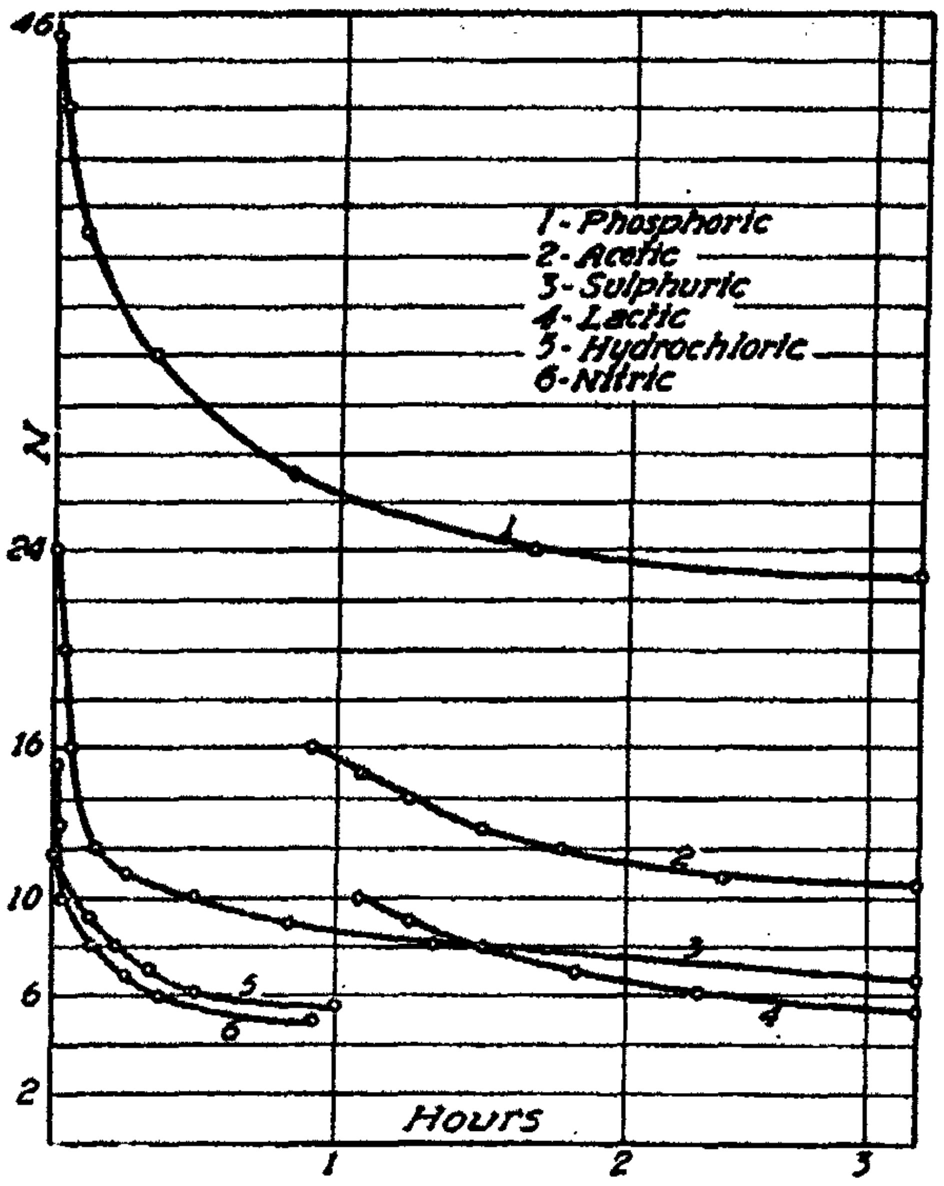


Fig. 3
Effect of extreme acidity on silicic acid gels
Sodium silicate of 1.16 density mixed with an equal volume of acid at 20°

Fig. 3 presents rather unexpected results. In Fig. 1 and Fig. 2 it is shown that gel mixtures containing only a slight excess of hydrogen ion set quickly but with increasing excess of hydrogen ion the set is greatly delayed. The curves soon flatten and run off the chart to an indefinite distance. Fig. 3 shows the return of the curves to the limits of the chart at still higher concentrations of acid. With hydrochloric or nitric acids this return, or rise from the horizontal, begins at about 5 *N*. For acetic acid the curve begins to rise at about 11 *N* but for phosphoric not until about 22 *N* is reached. It is remarkable that on mixing 45 *N* phosphoric acid (ordinary 85 percent syrup) with an equal volume of 1.16 water glass a gel of excellent texture results, setting almost immediately. Concentrated sulphuric acid coagulates the mixture into a rough lumpy mass but 24 *N* sulphuric yields a good firm gel, setting immediately. Glacial acetic acid is about 17 *N* hence the upper limit of that curve.

Flemming's belief that the catalytic effect of hydrogen or hydroxyl ions, the concentration of the silicic acid, and temperature, are the only factors influencing the time of set scarcely seems to explain the curves here given. He did not work at high concentration of the acids and so failed to plot the return of the curves to the vertical axis. It is quite possible that the catalytic influence of hydrogen ion is a very important factor but an increase in concentration of excess acid reaches a point where the number of molecules of the acid increase faster than the number of hydrogen ions. It is well known that sulphuric acid has its maximum specific conductivity in a 30 percent solution (approximate) and above this concentration the specific conductivity rapidly decreases. In other words, there is a concentration of the excess sulphuric acid, for example, below which hydrogen ions exert the most powerful influence on the set of silicic acid gel but above which the dehydrating influence of the nonionized molecules of sulphuric acid rapidly increases and finally preponderates. With the 1.16 density sodium silicate this point is reached apparently with about 7 *N* sulphuric acid. With phosphoric acid this point is reached at about 20 *N*.

Of course the ionization of the free acid is influenced by the salts present. With weak acids this repression of ionization is greatest. It is not inconceivable that there may be a catalytic effect exerted by other negative ions than hydroxyl to complicate the influences.

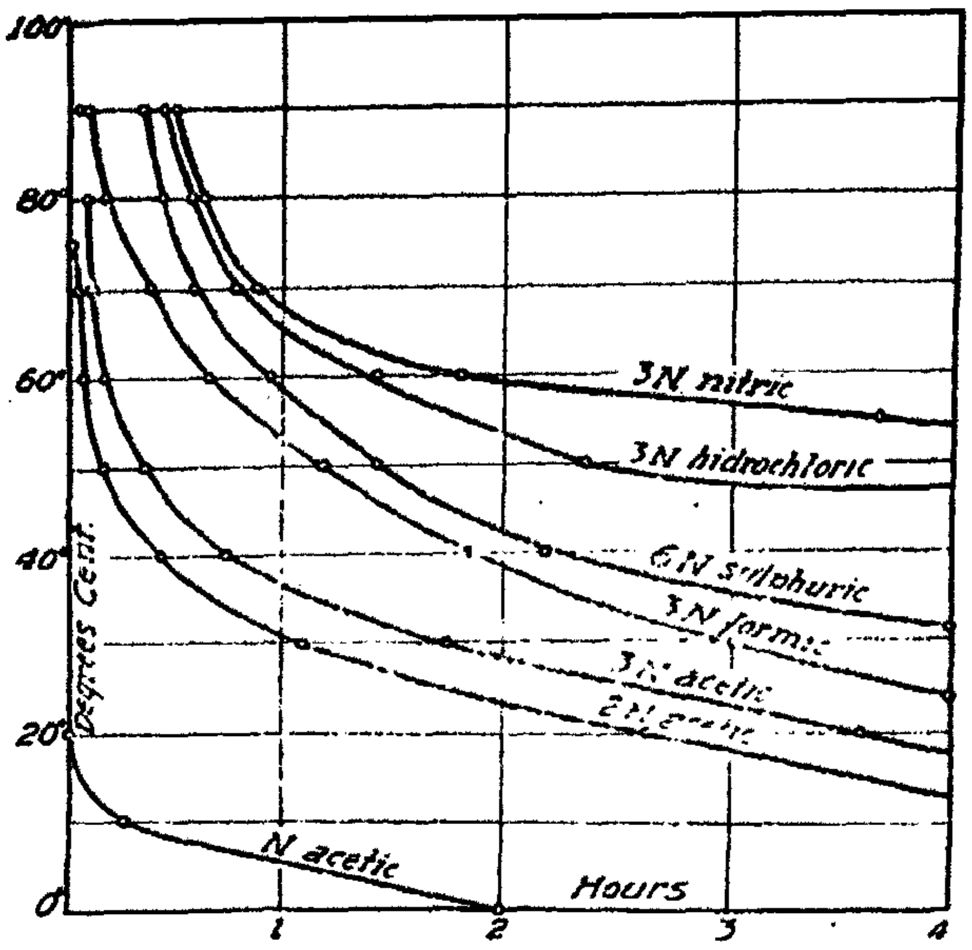


Fig. 4.
Temperature effect on silicic acid gels
Sodium silicate of 1.10 density mixed with an equal volume of acid

In Fig. 4 the curves all refer to the same concentration of silicic acid. It will be noted that a slight increase in temperature accelerates the time of set much more rapidly from 20° C to 60° C than above 60° C. In other words, the curve grows steeper above this middle range of temperature. The curves for formic and sulphuric acids are evidently quite unlike. Water glass of 1.10 density mixed with an equal volume of 3 *N* acetic acid sets more slowly than the less acid mixture with 2 *N* acetic although each gel contains more than enough acetic to liberate all the silicic acid. The curves for 3 *N* nitric and 3 *N* acetic are far apart, possibly because of the greater ionization of the strong mineral acid as well as the different dehydration influence of the two kinds of acid molecules.

At higher temperatures it is probable that dehydrating effects of nonionized molecules decrease and therefore the curves should approach each other as, in fact, they do. At any given temperature the gel from 3 *N* nitric sets more slowly than that from the much more acid 6 *N* sulphuric. This can hardly be explained on the theory of hydrogen ion catalysis.

When a water glass of a higher Na_2O content is acidified with sulfuric acid, for example, more sodium sulphate is formed as a by-product than when an equal volume of a water glass of the same SiO_2 content but a lower Na_2O value is acidified. The question arose whether two silicic acid gels formed as described and of equal SiO_2 concentration would set in the same time. They did this when a strong acid was used, but with a weak acid such as acetic the sodium acetate formed repressed the ionization of the excess acetic, lessening the catalytic influence of the hydrogen ion. Unequal amounts of sodium acetate were formed in the two cases and, as a result, one gel set much sooner than the other.

TABLE I

Sodium silicate mixed with equal volumes of acid

Acid	1.06 density sodium silicate		1.12 density sodium silicate	
	Gel set in 2 to 3 hours	Gel set in 8 to 10 hours	Gel set in 2 to 3 hours	Gel set in 8 to 10 hours
Hydrochloric	0.55 *N*	0.6 *N*	1.2 *N*	4.0 *N*
Nitric	0.55 *N*	0.6 *N*	1.2 *N*	4.0 *N*
Sulphuric	0.55 *N*	0.6 *N*	1.2 *N*	6.0 *N*
Phosphoric	0.75 *N*	1.5 *N*	2.5 *N*	3.0 *N*
Formic	0.70 *N*	0.9 *N*	1.5 *N*	2.0 *N*
Acetic	0.80 *N*	1.2 *N*	2.2 *N*	3.5 *N*
Chloracetic	0.80 *N*	1.0 *N*	2.2 *N*	3.5 *N*
Trichloracetic	0.55 *N*	0.6 *N*	1.2 *N*	1.4 *N*
Citric	1.00 *N*	1.2 *N*	2.5 *N*	3.0 *N*
Tartaric	0.80 *N*	0.9 *N*	2.2 *N*	......
Lactic	1.00 *N*	1.2 *N*	2.5 *N*	3.0 *N*

Using any sodium silicate one can determine the silica content and make gels setting in approximately the same time as those of equal silica content described in this paper—if strong acids are used. The particular water glass we used at a density of 1.06, yielded, when completely neutralized, gels containing 29.47 grams SiO_2 per liter.

This table is offered for further convenience in making gels. It adds to the data given by the curves. It is noteworthy that trichloracetic acid delays the gel set more than does the less ionized acetic, hence the lower concentration of trichloracetic given in Table I.

Dialyzed gels may be made in which there is only a small excess of any acid (other than silicic) or soluble salts, but the removal of these substances changes the time of set from the figures given in this paper. Hatschek dialyzed some mixtures of sodium silicate and acid and then secured a set at his convenience by adding a small amount of ammonia. For special purposes such a method may be of value.

Summary

1. Directions are given for the preparation of many types of silicic acid gels setting in any required time.

2. The temperature influence on these gels is plotted from 0° C to 100° C.

3. The effect of a great excess of acid on the time of set of the gel is plotted. As shown by other workers, gels containing a very slight excess of hydroxyl ions set in the shortest time, almost immediately if not too dilute, but with increasing excess of hydrogen ion, the time of set rapidly increases. With each acid mixed with sodium silicate there is a concentration of hydrogen ion which delays the set to an indefinite time. In this paper we show that at still higher concentrations of the same acid the time of set of the gel again becomes measurable, rapidly decreasing to an almost immediate set.

4. Contrary to Flemming and Ostwald's theory that the time of set of a silicic acid gel depends only on the concentration of SiO_2, temperature and the catalytic effect of hydrogen or hydroxyl ions, it is here shown that the dehydrating influence of nonionized molecules of the acid mixed with the sodium silicate is an important factor.

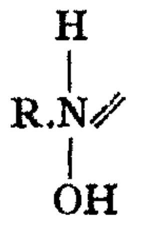
Oberlin College

THE RELATIVE MASSES OF PROTEIN ANIONS AND CATIONS[1]

BY A. R. C. HAAS

Investigation as to the mode of dissociation of protein compounds with inorganic bases and acids are of interest because they enable us to better understand the structural nature of such compounds. Conclusive evidence brought forward by Robertson[2] and Pauli[3] has shown that the salts which proteins form with inorganic acids and bases do not dissociate at the point of union of the inorganic radical with the protein but at some other place within the protein molecule. The dissociation is shown to yield not an inorganic and a protein ion, but two or more protein ions, in one or more of which the inorganic radical is bound up in a non-dissociable form.

When a direct current of about 1 milli-ampere was passed through a solution of potassium caseinate, it was found by Robertson[2] that the casein is deposited on the anode and that the amount of casein so deposited is proportional to the quantity of electricity that has passed through the solution. The fact that the deposition of protein in this case takes place on the anode instead of at both electrodes (as his hypothesis of the electrolytic dissociation of protein solutions would seem to require) is explained by Robertson in the following manner:



$$\begin{array}{c} \mathrm{H} \\ | \\ \mathrm{R.N}\!\not\!\!/ \\ | \\ \mathrm{OH} \end{array}$$

The anion migrates to the anode where it reacts with water, liberating oxygen and free casein which is eventually precipi-

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[1] From the Department of Biochemistry and Pharmacology, Rudolph Spreckels Physiological Laboratory, University of California.

[2] T. Brailsford Robertson: "Physical Chemistry of the Proteins," New York, 1918, Jour. Phys. Chem., 15, 521 (1911).

[3] Wo. Pauli and M. Hirschfeld: Biochem. Zeit., 62, 245 (1914).

tated as the uncombined and, therefore, insoluble protein; the cation R.COK^{++}, on reaching the cathode, reacts with water and liberates KOH, casein, and hydrogen, a condition which prevents the precipitation of free protein because the casein reacts with the excess of KOH to again form potassium caseinate which once more participates in carrying the current in each direction. Robertson concludes that the potassium or other univalent metal, which is carried along with the casein to the cathode, is there converted into the hydrate which then splits the ion, with which it has travelled, into two ions. The resultant cation is presumed to be retained in the cathodal region while the anion migrates back into the anodal region. Each cation which the cathodal region gains, gives up (provided the masses of the cations and anions are in every case equal), one-half its mass to the anodal region again. This theory, therefore, demands that the ratio of the anodal to the cathodal loss should be 2.

The refractive index method used by Robertson[1] for determining the amount of protein in the anodal and cathodal arms, has yielded only approximately the value of 2, the experimental error being quite considerable. At the suggestion of Dr. Robertson, the writer has repeated some of the experiments, using the same method which he used for determining the concentration of protein in solution and also an entirely different method. The results of the investigation confirm very satisfactorily the theory proposed by Robertson.

The apparatus adopted for the electrolysis of potassium caseinate solution was essentially the same as that used by Robertson in his experiments. The casein was prepared by Eimer and Amend as C. P. Casein "nach Hammersten" but was further purified.[2]

A 15 cc sample of the potassium caseinate solution was used as a control and was kept for 2 hours at 30° C as was the 35 cc of same original solution that was contained in the

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[1] T. Brailsford Robertson: Jour. Biol. Chem., 13, 469 (1909).

[2] T. Brailsford Robertson: Jour. Phys. Chem., 14, 528 (1910).

U-tube. The potassium caseinate solution used in each experiment was a 3 percent solution made neutral to litmus. This was prepared by dissolving 3 grams of casein in 100 cc of a solution made by diluting 15 cc of 0.1 *N* KOH to a volume of 100 cc. The solution was stirred in a mortar for $^3/_4$ to 1 hour and then filtered. Such a solution, neutral to litmus and freshly prepared for each experiment, was used rather than a solution neutral to phenolphthalein because of the possible error arising from hydrolysis and resolution of precipitated casein in the latter solution.

Three experiments were conducted in which the measurements of the amounts of casein in solution were made by the use of the refractometer method, the results of which are as follows:

	Number of experiment		
	1	2	3
Grams of casein lost from the anodal arm	0.2210	0.2763	0.2395
Grams of casein lost from the cathodal arm	0.1105	0.1197	0.1197
Ratio	2.00	2.30	2.00

The value obtained in the second experiment gives only very approximately the value 2 for the ratio. An improvement of technique was, therefore, essential if more conclusive data were to be obtained.

Accordingly, similar experiments were undertaken in which the nitrogen of each arm of the U-tube, as well as of a control, was separately determined at the end of the 2-hour period. The ratio of the grams of casein lost from the anodal arm to that lost from the cathodal arm is the same as the ratio between the nitrogen loss in each arm. In the official Kjeldahl method[1] that was used, a cold water extract of the cochineal insects (freshly made up for each determination) was found to

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[1] Bull. Bureau of Chemistry, 107, 5 (1912).

give sharper titration endpoints than the alcoholic cochineal indicator solution.

Since the nitrogen content of each arm was separately determined, it was necessary to ascertain accurately the volume of solution that each arm contained at the close of the electrolysis. The volume or displacement caused by the platinum electrodes and of the precipitated casein on the anode had to be taken into account in the calibration of the arms of the U-tube. Accordingly, the dry U-tube (bearing its dry platinum cathode and the spiral anode with its adhering dry precipitate of casein, in the cathodal and anodal arms, respectively) was calibrated with mercury. In this manner the exact volume of solution in each arm used for analysis after an electrolysis could be accurately determined. Prior to the adoption of this method of calibration, very variable results were obtained.

The results of the final four consecutive experiments with the improved technique, are as follows:

No. of Expt.	N content of 1 cc of control solution of potassium caseinate. No electrolysis. Results in grams	N content of 1 cc of potassium caseinate solution after electrolysis. Results in grams		Difference or N loss of 1 cc of potassium caseinate solution after electrolysis. Results in grams		Ratio of anodal to cathodal loss
		Anodal arm	Cathodal arm	Anodal arm	Cathodal arm	
1	0.00389	0.00315	0.00354	0.00074	0.00035	2.11
2	0.00372	0.00302	0.00337	0.00070	0.00035	2.00
3	0.00332	0.00259	0.00297	0.00073	0.00035	2.08
4	0.00350	0.00290	0.00321	0.00060	0.00029	2.06

It is evident that these results, obtained by a different method than that used by Robertson, fully confirm the theory proposed by him which requires that the ratio of the anodal to the cathodal loss should be 2. The good agreement with the theoretical ratio can be taken as confirmatory of the theory that the protein anions and cations are equal in mass at least so far as solutions which are neutral to litmus are concerned. The results of the investigation moreover afford evidence of the correctness of the view of Robertson that the protein is transported into the cathodal arm and, therefore, that the current is carried by protein ions in both directions.

I am indebted to Professor T. Brailsford Robertson for the constant interest that he has taken in this work, and to Harvard University for the grant of a Sheldon Traveling Fellowship which has given the financial aid in carrying out the investigation.

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NEW BOOKS

58.11. ; 62.11

Soil Conditions and Plant Growth. *By Edward J. Russell. 25 × 16 cm; pp. viii + 243. New York: Longmans, Green and Co., 1917. Price: $2.00.*—In the preface the author says that "considerable alterations have been made in the text and a new chapter has been added discussing the colloidal properties of the soil. It is abundantly clear that the soil investigator of the future will have to be thoroughly familiar with the ways of colloids, and I fully expect that much of the older work will require careful re-examination in the light of what has been done in this direction by chemists and physicists."

The second edition has already been reviewed (20, 625), so interest centers chiefly on the new chapter on colloids, from which two quotations are made, pp. 88, 93. "Van Bemmelen began by accepting Way's chemical hypothesis, and showed that soils with a high power of absorption usually contained a large quantity of easily decomposable silicates. Way's silicates would presumably be of this nature. Further, absorption of bases always involved displacement of other bases from the soil, a strong indication of chemical change. Later on, however, he made extensive studies of absorption by simple gels: silica, alumina, ferric hydroxide, tin hydroxide, etc., and found it closely to resemble absorption by soils; other studies of colloids were made and in each case the similarity to soil phenomena was so close as to leave no doubt that soil was essentially a colloid and soil absorption simply a manifestation of the colloidal properties. This new idea was soon found to explain many of the old discrepancies. Chemists had several times attempted to bring the phenomena of absorption equilibrium into line with those of chemical equilibrium, but the equations would not fit except for a narrow range of concentrations. Boedecker in 1859 had fitted an expression to Henneberg and Stohmann's results for ammonia absorbed and calcium displaced in the interaction between soil and ammonium sulphate, and Hull and Gimingham, dealing with the same reaction, showed that the ordinary formula for chemical equilibrium held over a limited range of concentrations; but Cameron and Patten found that it did not hold over a wider range. The absorption of potassium could not be fitted at all by the formula. When, however, the adsorption formula is used a complete fit can be obtained: Wiegner has gone over the recorded data and shown that all fit the equation....

"It has long been known that certain soils are acid to litmus paper but become neutral again on adding lime or calcium carbonate. Many cultivated plants, notably clover and its allies, fail to grow well on such soils and they succeed only after lime has been added. Azotobacter and other organisms are also adversely affected. The older chemists took the simple and obvious view that these soils contained an acid or acids, and, as 'high moor' peat showed the same property, they concluded that the acid was of the same general nature in both cases. It was assumed that the plant residues formed some acid substance at a certain stage in their decomposition, and this acid accumulated if the circumstances were such that decomposition became very slow, *e. g.*, in badly drained and badly aerated soils.

"But instances accumulated of acid soils, well drained and therefore not suffering from slowness of decomposition, containing so little organic matter that it was difficult to attribute acidity to organic compounds. It was therefore necessary to assume the presence of acid mineral substances in the soil, and a number of investigations were made showing that kaolin and similar silicates, which might be expected to occur in the soil, become more and more acid to litmus paper on treatment with CO_2 solution. Among recent papers is one by Gans where the literature of this particular problem is reviewed.

"Van Bemmelen's demonstration that humus is a colloid led Cameron to show that all the phenomena of soil activity could be explained as simple colloid manifestations and did not require the assumption of soil acids at all. It was only necessary to suppose that the soil colloids absorbed more readily than the acid from blue litmus and the whole phenomena are explained. In support of this view Cameron showed that cotton and other absorbents behaved like 'acid' soils slowly turning blue litmus red; the phenomenon was therefore a general property of a class of absorbents. Baumann and Gully applied this idea to the case of peat and showed that it fully explained all the known facts. . . .

"This physical explanation of acidity has not passed unchallenged. Rindall of Helsingfors, Sven Oden of Upsala, Tacke, and Ehrenberg have each argued in favor of definite humic acids in peat. Oden dissolved some purified humus in ammonia and showed that the conductivity phenomena indicated true salt, while Tacke showed that peat can not only invert cane sugar but can even give off hydrogen in contact with iron—two reactions difficult to explain on physical grounds. Truog finds, in the case of mineral soils, that equivalent amounts of different bases are required to neutralize the acid properties of the soil—which if generally true would be easier to explain by assuming an acid than an adsorption.

"Some writers have tried to combine both views and speak of 'positive acidity' when the phenomena are caused by an acid, and 'negative acidity' when they are due to absorption. It is difficult to make the distinction in practice and not easy to believe that it is real. The phenomena are so similar that it is easier to suppose the same cause at work in peats and in mineral soils. It will readily be conceded that such common bodies as acids are likely to occur in peat and in soil. But it must equally be admitted that the phenomena are more easily explained as adsorptions—all except Truog's observations, which may yet turn out to be the awkward facts that will shatter this otherwise eminently satisfactory hypothesis."

Wilder D. Bancroft

A Handbook on Antiseptics. *By H. D. Dakin and E. K. Dunham. 15 × 11 cm; pp. ix + 129. New York: The Macmillan Company, 1917. Price: $1.25.*—In the preface the authors say: "The unparalleled severity and frequency of wound infections in the present war has led to considerable advances in our knowledge of antiseptics and of methods for their successful employment. These advances have already proved to be of great value in the treatment of septic conditions in civil and industrial practice."

The chapters are entitled: general introduction; antiseptics of the chlorine group; the phenolic group of antiseptics; salts of the heavy metals as antiseptics; dyes as antiseptics; miscellaneous antiseptics; methods of testing antiseptics; certain applications of antiseptics.

When properly applied the antiseptics of the chlorine group have proved of genuine value to the surgeon. Dakin's solution, chloramine-T, and dichloramine-T are new developments of great importance. On the other hand no new properties of value have been observed in the phenolic group of antiseptics as a result of their employment in war surgery. With the exception of Rutherford Morison's bismuth paste, there has been no very extended use in the present war of the salts of the heavy metals as antiseptics. Among dyes malachite green has been used fairly extensively, especially in the naval service. Acriflavine has found application in the prophylactic treatment of fresh wounds as well as in cases where suppuration has developed. It has also been employed in the disinfection of the nasopharynx of carriers of the meningococcus. The authors believe that its germicidal action has been over-estimated. One of the most remarkable properties of acriflavine is that its germicidal action is apparently enhanced by admixture with serum though greatly diminished by pus.

The chemical disinfection on a large scale of contaminated or suspected water supplies for civilian, military, or naval use is now effected almost exclusively with substances belonging to the chlorine group. The problem of sterilizing small individual quantities of water such as are needed by cavalry or rapidly moving troops is a difficult one for the use of the chlorine antiseptics is generally impracticable owing to the instability of small tablets containing the required minute quantity of active disinfectant. The most suitable substance yet found is *p*-sulphondichloraminobenzoic acid, $Cl_2N.O_2S.C_6H_4.CO_2H$. Since the systematic name of this disinfectant is inconveniently long for ordinary use, it is called "halazone." Sodium bisulphate tablets were used by the New Zealand contingent in the South African War and subsequently to some extent by cavalry and mounted police and other mobile forces. They are frequently compounded with lemon oil and saccharin so that the resulting solution has some resemblance to lemonade.

One of the most interesting of the new disinfectants is dichloramine-T, toluene-*p*-sulphondichloramine. Like most other antiseptics of the chlorine group it is an active lymphagogue when placed on fresh wounds. As granulation tissue develops, the lymph discharge decreases and the wound becomes comparatively dry. It also possesses in marked degree the property of aiding in the removal of necrotic tissue. The first application of the oil solution causes a smarting sensation, which passes away in a few minutes. Wounds treated with the oil fill rapidly with granulation tissue of healthy color which shows no tendency to exuberant growth nor to become sodden....

"Dichloramine-T in oil solution has been tried extensively in the early treatment of injuries, not only of the soft parts but of tendons, bones, and joints. At the primary dressing of these wounds, after the excision of dead tissue and obvious foci of infection, the wound is liberally flooded with the oil and then closed without drainage. In Lee's experience primary union follows in at least 75 percent of these sutured wounds if treated within three hours of their infliction. If signs of infection should appear, one or more stitches are removed and oil is introduced by means of a grooved director to the focus of infection once in 24 hours. With wounds treated after a longer interval the question of their closure becomes a matter of surgical judgment. Dichloramine-T in oil has also been found decidedly useful in the treatment of boils and carbuncles with minimal incision, in osteomyelitis, non-tuberculous empyema, and in the control of post-operative wound infection. More recently it has been used by Lee for the treatment of burns, and in these cases it is advisable to cover the burn with one layer of a coarse-meshed gauze previously soaked in paraffin wax. In this way the exudate easily comes through the open mesh and the dressings do not stick. It is an advantage if such wounds can be exposed to the air. The absence of suppuration and freedom of drainage in these cases is significant....

"It will be well, perhaps, to refer to the way in which the antiseptic action of dichloramine-T in oil solution is exerted. It is well recognized that antiseptics incorporated with or dissolved in oily substance usually possess little, if any, antiseptic activity because intimate contact with the infected matter is hindered by the oil. When, however, such oil solutions of dichloramine-T as will be described are brought in contact with aqueous media, the partition coefficient between the oil and the water is such that a certain amount of the dichloramine-T passes into the water and there exerts its germicidal action. The amount of dichloramine-T thus passing from the oil is enhanced by the presence in the aqueous medium of substances capable of taking up chlorine. The oil solution serves as a store of the antiseptic which is drawn upon to maintain the germicidal activity of the aqueous medium with which it is in contact. Thus the amount of active antiseptic leaving the oil solution is dependent, to a considerable extent, upon the rate at which it is used up in the aqueous medium."

Wilder D. Bancroft

A Short Handbook of Oil Analysis. *By Augustus H. Gill. Revised eighth edition. 21 × 14 cm; pp. 209. Philadelphia: J. B. Lippincott Company, 1918. Price: $2.50.*—The general headings are: physical and chemical tests; derivation, description and examination of certain oils. In the second part the sub-heads are: petroleum products; oils and fats; waxes. In the preface the author says: "The changes in this edition embrace a description of the new MacMichael viscosimeter, and a means of the reduction of viscosimetrical readings to absolute units or poises. One or two tests for lubricating oils have been added. The special tests, methods of analysis, and the description of the special oils and greases have been revised where necessary, particularly in the case of the drying oils; and the methods of the analysis of edible and hardened oils included, so as to bring the book thoroughly up-to-date."

On p. 177 we read: "It is claimed for them [the hydrogenated oils] that they can be heated hotter (to 455° F.) without smoking than ordinary fat: this cooks the outside of the food more quickly and prevents the grease from soaking in. Consequently it is less greasy, more digestible, dry and crisp. Another claim is that one-fourth less is used of these fats than of butter; further, that it is all fat, while butter contains 5 to 16 percent of water. Finally, hydrogenated vegetable oils seem to offer a satisfactory substitute for animal fats to those who object to the latter from prejudice or religious scruples."

Wilder D. Bancroft

METHANE

BY WILLIAM MALISOFF AND GUSTAV EGLOFF

Introductory

The systematic study of methane, looked upon as the parent substance of organic compounds, the simplest and at the same time the most baffling of the hydrides of carbon, has now well passed the century mark. The aims of the men who pursued investigations on the subject have been as varied as the results have been restricted, and consequently a mass of data has accumulated, which perhaps is fairly complete but entirely uncoördinated. The aim of the present communication is to formulate the result of research on methane up to date, to indicate thereby the future of research on methane both theoretical and practical, and to introduce the necessary data and theoretical discussion leading to a series of papers on the researches of the authors.

The Scope of Past Research

The theoretical and practical aims of the various investigators on methane were mixed at the outset. Hence, for clarity we may classify the researches up to the present along the following lines:

A. Physical Characteristics of Methane.
    1. Physical Constants.
    2. Specific Properties.
    3. Gas Properties.
    4. Application of Physical Characteristics Industrially.
B. Chemical Characteristics of Methane.
    1. Combustion and Explosion of Methane.
    2. Solubility of Methane in Various Solvents.
    3. Occlusion of Methane.
    4. Miscellaneous Physico-Chemical Properties.
    5. Industrial Reactions of Methane.
        Oxidations.
        Halogenation of Methane.
        Formation of Carbides.
        Cyanides from Methane.

C. Synthesis and Decomposition of Methane.
  1. Direct Union of Carbon and Hydrogen.
  2. Synthesis not Directly from the Elements.
  3. Catalytic Production Indirectly.
  4. Electrosyntheses from Methane.
  5. Formation of Methane Electrically.

D. Miscellaneous on Methane.
  1. Biological Data.
  2. Sources and Supply of Methane.

E. Research Possibilities on Methane.

A. PHYSICAL CHARACTERISTICS OF METHANE

1. Physical Constants

The work of Guye[1] and of Baumé and Perrot[2] on methane, made from CH_3MgI, and carefully cleared of all traces of air, gave as an average of a series of determinations the values of 0.7168 g as the weight of 1 liter of methane at 0° C, 760 mm, sea level, 45° parallel. Up to the present no other check upon this value by any other method has been made. The value is an important one in view of the fact that it is used in a large number of thermodynamic calculations on the gas.

Baumé and Perrot[3] also determined the melting point, —184° C, at which temperature methane becomes a colorless, mobile liquid.

Wahl,[4] in his optical investigation of crystalline nitrogen, etc., found that methane (solidifying at —186° C) forms crystals in the regular system, usually setting in from many centers, forming beautiful spherulites.

Similar values are given by Moissan and Chavanne,[5] who set the freezing point at —185.8° C and the boiling point at —164° C at 760 mm pressure. Olszewski[6] gives the melting point as —184° C.

Some interesting theoretical deductions may be drawn from the work of the above investigators, especially from that of Wahl. Indeed the latter's work may be of important application to theories dealing with the configuration of the atoms in the molecule of methane. Though all the four hydrogens have to be considered as chemically the same, yet the molecular valencies may be such that the carbon could display a valence of six. The world may well be grateful to one who will show the vital relation between its structure and reactivity, beyond the usual, merely qualitative explanation.

2. Specific Properties

Further details on methane are given by Cardoso,[7] who gives the critical temperature as —82.85° C, critical pressure as 45.60 atmospheres, critical density as 0.1623. His method is a very accurate one and would indicate that the value given by Goldhammer[8] for critical density, 0.1519, is incorrect. Goldhammer's method, however, gave a precision of within 1 percent.

The formula for critical density was as follows:

$$\frac{(q_1 - q_2)^3}{q_1 + q_2 - 2q_K} = 27\, q^2{}_K\, q_K = \text{critical density}$$

The triple point of methane has been determined by Crommelin,[9] who puts it as —183.15° C and 70 mm of mercury pressure. Olszewski[10] gave —185.8° C and 80 mm pressure.

The study of the critical constants and even of the coefficients is likely to be of great use in the determination of the scientific reasons for the stability of methane. The hydrogen in methane is located very close to the carbon atom. The substitution of a heavier atom for a hydrogen as in the case of the halogen derivatives, increases greatly the *electrochemical field of the molecule.* Such a consideration would also help one to understand the formation of the higher substituted halogen derivatives from the lower substituted ones rather than from methane itself. If the above data on the critical constants of methane could be supplemented by a set on the critical constants of the halogen derivatives, the mathematical chemist might readily fall into his stride.

8. Gas Properties

In his work on the coefficients of expansion of gases, Leduc[11] included methane. He gives the true coefficients times 10^6 as $\alpha = 3687$, and $\beta = 3681$. The average coefficients $\alpha_{0° - 100° \text{C}} = 3681$ and $\beta_{0° - 100° \text{C}} = 3679$. These values, again, are significant in the thermodynamic calculations on methane.

Friendly physicists have produced some rather important data on methane which might at any time prove of unexpected value when applied to the consideration of the reactions of methane.

W. H. Bragg and W. T. Cooke[12] have worked out the ionization curve of methane. It is a gas more suitable for such research than air because it shows the four ionization steps more definitely. Similarly, the particles of high velocity are inhibited less by methane than low velocity particles, compared to air. The deductions therefrom are not altogether clear. Further data may throw some light on the subject. However, an explanation may be volunteered for the fact that the rapidly moving particles are less stopped by methane than the slow ones, by considering, in view of the work of Wahl, Bragg, and others, that the structure of the methane molecule must be very compact (work of Wahl). In such a case the probability of impact by fast-moving particles would be less, hardly any time being given for the linking of the fields indicating impact because of the smallness of the field of relatively inactive substance.

Himstedt and Dechend,[13] in trying to obtain the spectrum of methane, found that its decomposition gave hydrogen ions and the Swan spectrum. To all appearances, it seems, they did not speculate as to the nature of the hydrocarbons giving the Swan spectrum.

Noteworthy is the work on the dispersion of light in gases by Loria.[14] Values were obtained for several wavelengths and the constants in Cauchy's formula determined:

Wave-Length $\lambda \times 10^{-5}$ =
6.585 6.375 5.9355 5.718

In Cauchy's formula $n - 1 = a(1 - b/\lambda^2)$, $a = 0.000042607$, $b = 1.441 \times 10^{-10}$.

Von Bahr[15] investigated the effect of pressure on absorption of ultra-red rays by gases. Great effect was shown and gases were proved to have a maximum absorption for certain pressures. It should be pointed out that this observation is of exceeding importance in determining the optimum pressure for chemical reactions of methane which are furthered by ultra-red rays.

E. Parr Metcalfe[16] found an additive law showing the effect of molecular grouping on the ionizations of methane, ethane, etc.

The results obtained by Soddy and Berry[17] on the heat conductivity of rarefied gases indicates a better conductivity for methane than for hydrogen. The number of calories which are conducted at 0.01 mm pressure through a cubic centimeter for 1° C temperature difference between surfaces is as 2.7 in the case of methane to 2.29 in the case of hydrogen. For higher pressures hardly any data are available. Such would be of use in the theoretical treatment, at least, of the velocity of flame propagation, and ignition of methane.

4. Application of Physical Characteristics Industrially

The data concerning the boiling point and freezing point of methane will assume greater importance, as a commercial process is developed, for the liquefaction of methane. There are further possibilities for the use of methane as a constant temperature liquid bath for reactions and investigation at low temperatures. A process may indeed be developed for the purpose of obtaining low temperatures by the expansion of the liquid methane to a gas. It comes in conveniently between the ranges covered commonly in low temperature work. Whether the liquefaction of methane for such purposes would be a commercial proposition would be more easily seen after some development. Considering the volume relations for a methane explosion, and the limits of explosibility, the transportation of the liquefied gas is likely to be attended with no greater danger, and probably with less danger, than that of any other highly compressed gas. There is therefore considerable room for exploiting the physical properties of methane to a greater extent commercially.

B. CHEMICAL CHARACTERISTICS OF METHANE

1. Combustion and Explosion of Methane

The burning and explosion of methane has always been a serious problem. Aside from the natural interest taken in the prevention of mine accidents, other useful practical applications have been sought for.

The study of the lower and upper limits of inflammability of methane with mixture of nitrogen or oxygen or air by Parker,[18] Taffanel and LeFlock,[19] Coward and Brinsley,[20] LePrince-Ringuet,[21] Burgess and Wheeler,[22] Wheeler,[23] Burrell and Robertson,[24] produced a mass of rather contradictory data on the subject. The results may, however, be summarized as follows: According to Prof. Enrique Hauser in his Leçons sur le Grisou (Madrid, 1908) one gets different limits of inflammability depending on the direction in which the flame has to travel. The variations arising therefrom are enough to change values 5.4 percent to 6.0 percent or 13.4 percent to 14.8 percent equivalent to a 10 percent variation. With this in view the data of the various workers may be consulted more intelligently. Some other generalizations are possible, as, that the lowering of the temperature of the gas raises the lower limit of inflammability. The condition necessary for the ignition of explosive mixtures is that the temperature of the constituents should be raised, at least locally, to a degree at which the mass of the gas self-heats by combination until it bursts into flame, *i. e.*, until chemical action becomes autogenous or self-propelling.

Dixon and Coward[25] (1909) state that the temperature at which ignition occurs lies within a very narrow range in cases where the mechanism of combustion is probably simple, for example hydrogen and carbon monoxide, and within the limits of experimental error they are the same for air as for oxygen (Hydrogen 580°–590° C; Carbon monoxide 640°–658° C). However, if the mechanism of combustion is very complex, as in the case of hydrocarbons, the ignition range is either fairly large or materially lower in oxygen than in air (for methane in air, 650°–750° C; in oxygen, 556°–700° C). An explanation for this is to be found in the fact that the combustion is not simple, because of the fairly rapid interaction between the inflammable gas and the oxygen before the ignition point is reached. If such interaction were to be suppressed somehow, or made very rapid, as it is in the case of ethylene, the ignition range would become smaller (ethylene 542°–547° C in air; 500°–519° C in oxygen).

Besides the method of ignition by heating the constituents separately and then mixing, or by heating some one spot in the mixture, two other methods have been used: ignition by adiabatic compression and more commonly, by sparking. Nernst recommended the first of the two alternative methods, provided (1) the ignition is not produced merely locally, and (2) the piston of the apparatus does not move appreciably after the gas has been raised to the ignition temperature. This method is a rather difficult one because of the last proviso mentioned. Consequently considerable doubt has been cast on the results obtained by this method, as the work, for instance, of Falk in America showing that hydrogen peroxide is first formed in the combustion of hydrogen and oxygen.

The mathematical relation for estimating the temperature of ignition from the initial temperature and the initial and final volumes is

$$\left(\frac{T_2}{T_1}\right) = \left(\frac{V_1}{V_2}\right)^{j-1} \quad j = 1.41$$

Dixon's photographic analysis of the flame in hydrocarbon combustions showed that it took time for the flame to spread. This indicated that even more refined precautions for stopping the piston were necessary in the method discussed above, because the real ignition point is not synchronous with the appearance of the flame. The pre-flame period is negligible only in the fastest burning mixtures.

That ignition may not be a thermal problem purely is indicated from results obtained by Dixon, Bradshaw and Campbell.[26] The addition of hydrogen and nitrogen raised the ignition temperature of various mixtures. This can be explained by considerations of dilution and the fact that hydrogen has a high thermal conductivity. The addition of oxygen, however, lowered the ignition point. A possible explanation would be that perhaps some polymeride of oxygen is formed. This is difficult of proof, but the fact in itself seems to warrant the conclusion given above.

The pressure and temperature may vary over a rather wide range without affecting explosibility. Variations are introduced in the results by the method of ignition, nature of the source of ignition, size and shape of the containing vessel. Inaccuracies in the mixing and analyzing of the gases may be avoided. The largest range of inflammability has been obtained by Burrell and Oberfell[27] (making spark at the bottom of a box by pulling two wires apart, carrying 7 amperes at 220 volts) with a minimum of 4.9 percent of methane to a maximum percentage of 15–15.4 percent.

The above studies dealt principally with the explosibilities of mine mixtures. A further application would lie in the development of a motor not to run on methane (natural gas) but on a mixture of methane and other hydrocarbons and air. With the certain development of alcohol motors, the introduction of a percentage of methane (dissolved or under some pressure in the alcohol) is sure to be of aid. Of somewhat greater importance perhaps would become the work on the velocity and mode of propagation of the methane flame; by Parker and Rhead[28] who found a maximum flame velocity of 70 cm per second; by Burgess and Wheeler,[29,30] Parker;[31] and the work on ignition temperatures of gases by Dixon and Coward,[32] who found the value for methane in air to be from 650° C to 750° C, with 10° C variation, depending on the rate of flow of the gas, and independent of the form, material, or surface of the apparatus; or the work of Bucher[33] showing the negative influence of hydrogen on the velocity of ignition of methane; or that of Thornton[34] on the ignition of coal gas and methane by momentary electric arcs, showing that at 20 volts no ignition occurs and hence electrical signalling is safe.

2. Solubility of Methane in Various Solvents

A field, which is very promising and has not as yet been covered as it should, before being dropped, is the investigation of the solubility of methane in various solvents. A. S. McDaniell[35] gives the solubilities of methane in methyl, ethyl and other alcohols, benzene, toluene, *m*-xylene, hexane, heptane, and pinene. McDaniel's determinations were very carefully made in a specially designed apparatus, making certain of the saturation of the liquid with methane, and with a certainty that air was excluded from the experiment. The figures for the ratio of the volume of gas to liquid in these cases are:

Solvent	$\frac{\text{cc gas}}{\text{cc solvent}} = A_{25°}$ C.
CH_3OH (99%)	0.4437
C_2H_5OH (99.8%)	0.4581
(Iso) $C_3H_7OHCH_3OH$	0.4584
$C_5H_{11}OH$	0.4500
C_6H_6	0.4844
$C_6H_5CH_3$	0.4852
(*m*) $C_6H_4(CH_3)_2$	0.5096
C_6H_{14}	0.5918
C_7H_{16}	0.7116
Pinene	0.4623

The values of $\frac{dA}{dt}$ vary greatly for the same liquid in many instances, and therefore predictions as to the solubility at other than observed temperatures are unsafe. In general, however, absorption increases as the temperature decreases. The solubilities, of course, have a negative temperature coefficient.

A good many solvents have as yet to be tried out. In particular the authors would recommend mixtures of various solvents. Some values precisely obtained are:

1 volume of water at $t°$ absorbs
$0.05449 - 0.001807t - 0.000010 28t^2$ volumes of methane
1 volume of alcohol at $t°$ absorbs
$0.522586 - 0.0028655t - 0.0000142t^2$ volumes of methane

It may be of some importance to point out that substances of high molecular weight, saturated and unsaturated, would probably give higher coefficients of absorption (e. g., oleic acid, linoleic acid). There is also likelihood of a relation existing between the index of refraction, the viscosity, and the critical constants, on the one hand, and the absorption coefficient on the other. This likely relationship would show up on further research of an experimental character on the above physical constants.

The solubility of methane in various solvents may have tremendous industrial application. A solution of methane in pentane, heptane, benzene, or ethyl alcohol under pressure may be an ideal motor fuel for aeroplane engines which are subjected to sudden temperature changes of 60° C or more in a relatively short interval of time.

The reseaches merge into more strictly chemical lines when we find the work by Worstall[36] on the absorption of methane by fuming sulphuric acid. He was interested in showing that the absorption was within the limit of error in analysis. However, there is a very small absorption, which hardly can be explained as a chemical reaction and must be explained on the grounds of solubility.

The effect of oxidizing agents, as nitric and chromic acids, has been studied but little. Though the action may be very slight ordinarily, there seems to be no reason why it could not be accelerated catalytically. There is a total lack of data on this field.

There is no essential reason in the opinion of the authors why methane should not be capable of nitration and sulphonation directly. It is a known fact that even the lower aliphatics may be sulphonated, by the use of oleum. The conditions required are

1. Sufficient concentrations of the reacting substances.
2. Very intimate mixing.
3. Proper temperature.
4. Catalyst.

In case of gaseous constituents the effect of pressure is obvious. The syntheses which could be carried out with such a process as a starting point would produce valuable products like formaldehyde simply and more complex compounds by coupling.

8. Occlusion of Methane

A property of physico-chemical interest is the occlusion of methane by metals. B. Delanchal[37] has studied the occlusion of methane by some common metals.

From 1,000 grams of tin he obtained on heating:

	Cc
Methane	2.80
Hydrogen	3.25
Carbon monoxide	2.05
Carbon dioxide	1.44
Nitrogen	1.56

From 144 grams of commercial platinum:

	Cc
Methane	3.67
Hydrogen	0.47
Carbon monoxide	4.05
Carbon dioxide	0.70
Nitrogen	1.31

The gases were obtained from commercial specimens and very little was done to check occlusion by *pure* metals. However, it is possible that the methane is not occluded by the metals, but forms during the heating from hydrogen and carbon monoxide previously occluded. Since the equilibrium between hydrogen, carbon monoxide and methane differs with the temperature, further work along this line will aid in discovering the truth of the matter, if various temperatures were to be tried in the expulsion of the occluded gases. The bearing a further research on the occlusion of methane would have on the catalytic ignition, burning and oxidation of methane, is likely to have significance industrially.

The ideas on occlusion may have a rather important bearing on the choice of material for methane reactions. It seems that occlusion by palladium and other catalyst metals has not been investigated. In the search for catalysts, of course, the numerous oxides and organo-metallic compounds which have found such wide application elsewhere should be tested.

Among the non-metallic substances which occlude methane is coal. The latest discussion of the matter may be found in a pamphlet by S. H. Katz.[39] For further information as to earlier experiments, the reader is asked to refer to Richters,[40] Thiessen,[41] Le Prince-Ringuet,[42] Graham,[43] Porter and Ovitz,[44] Mahler,[45] Porter and Ralston[46] and Winmill.[47]

Katz reports a series of experiments on the absorption of gases from the various mixtures of Pittsburgh bituminous coal:

1. At ordinary temperatures newly mined coal quickly absorbed methane from an atmosphere of air containing about 5 percent of admixed methane, the absorption being about 0.08 cc per gram of coal. Equilibrium was obtained after 4 hours.

2. Under the same conditions, coal that had been exposed to the action of room air for 5 weeks, with resulting loss of methane, absorbed 0.16 cc or twice as much methane. Equilibrium attained in 4 hours.

3. The coal in equilibrium with nitrogen absorbed methane in amounts that increased with increase in the partial pressure of the methane.

4. With absorption of the methane there was an evolu-

tion of nitrogen in amounts somewhat less than the amount of methane.

5. Coal in equilibrium with a mixture of nitrogen with methane absorbs gas with a fall in temperature and evolves gas with a rise in temperature.

6. If the temperature is held constant at a certain point, then allowed to vary and again held constant at that point, a definite equilibrium between coal and gas is repeatedly established. The author claims that the absorption of gas by coal is closely analogous to the absorption of gases by charcoal.

It would be desirable that such investigations should be conducted with a somewhat different point of view. Coal, gram for gram, is a better "solvent" for methane than the usual liquid solvents. And besides, why not try coal as a catalyst in methane reactions?

4. Miscellaneous Physico-Chemical Properties

L. T. Wright[48] has investigated the luminosity of methane and found about 5.2 candles per 5 cubic feet per hour.

Some little work on the catalytic ignition of methane of practical application has been done by Dixon and Lowe[49] on the effect of incombustible dust on the ignition of methane.

Even the radioactivity of methane has been investigated. J. Satterly[50] gives some interesting results. It is marsh gas, however, that is radioactive rather than methane.

5. Industrial Reactions of Methane

Oxidations

Only a few chemical reactions of methane have been utilized commercially. Some are, however, of great promise.

Lance,[51] English patentee, deals with the making of methyl alcohol from methane. He uses hydrogen peroxide, with or without ferrous sulphate or monopersulphuric acid, or with monopersulphuric acid alone.

An important patent of the Sauerstoff und Stickstoff Industrie Hausmann und Co.[52] deals with the production of formaldehyde, and eventually methyl alcohol and formic acid from methane mixtures of air or oxygen. The gases are passed over granulated copper at 600° C. If fatty substances are used as contact masses, as for example, tan bark, the process may be carried on at 30°–50° C.

A patent by von Unruh[63] deals with the oxidation of methane by tan bark and similar materials.

Halogenation of Methane

Halogenation of methane in various stages has offered and still offers a fruitful field of research. Patents[64-65] on the formation of chloroform and of carbon tetrachloride have been taken out in numbers. Methyl alcohol may also be made from methyl chloride which comes from methane. To complete the series one may mention the work of F. Swarts[66] on fluorine derivatives of methane and that of A. Byden[67] and G. Guerin[68] on bromine and iodine derivatives of the gas.

A review of the work on the lower chlorides of methane from natural gas is given by various writers, notably C. W. Bedford,[69] Baskerville and Riederer.[70] The evolution of the subject and its present state are as follows: Berthelot, in 1858, found that unless chlorine and methane were made to interact very slowly explosions took place with a separation of carbon. This was not very encouraging and practically nothing of consequence was done till 1893 by Phillips, who chlorinated methane without light at 300°–400° C, obtaining only the first and last chlorides. Walter[71] bases his patent on the fact that water retards the reaction, and the fact that if the chlorine is added gradually it reacts selectively with the already chlorinated product rather than methane to form carbon tetrachloride.

Baskerville and Riederer[70] found that the blue end of the spectrum was more suitable than the ultraviolet in chlorination reactions. They have a process of making carbon tetrachloride and then reducing to chloroform. The reason why decomposition occurs is found in the fact that according to thermochemical calculations there would be a rise of 2000° C if all the heat of the reaction were to go toward the raising of the temperature of the mixture. As the temperature rises, of course, the methane begins to decompose. If thin tubes are used the radiation takes care of the rise of temperature and decomposition is avoided. In reactions involving the making of chloroform, the temperature must be low enough to condense out the chloroform. This is equivalent to getting it out of the sphere of action and thus avoiding chlorination to carbon tetrachloride. C. W. Bedford[69] found that the less chlorine used, the stronger the light necessary. Very good results may be obtained by using ice cooling and strong light, as the white flame arc. According to his patent, methane and chlorine are caused to react in a chamber filled with pieces of ice and having a window and curtain for regulated admission of actinic light. Various other halogenation reactions may be similarly carried out with gaseous materials, starting with methylene chloride to make chloroform or with methane to make carbon tetrachloride, or with ethane or methyl chloride and chlorine and using either ice or a shower of water to control the temperatures of the reacting materials and thus regulate the degree of chlorinations. By keeping the temperature and supply of chlorine low in chlorinating methane, methyl chloride nearly free of higher chlorination products of methane may be obtained.

Carbides Formed from Methane

Various carbides have been prepared from methane. J. Novak[72] notes that the decomposition of methane begins at 600° C in presence of magnesium. MgC_2 forms in traces at 733° C. A maximum formation of Mg_2C_3 occurs at 760° C. S. Helpert and J. Paunesen[73] prepared the carbides by manganese by heating the metal in the presence of a current of methane. Five percent of the carbon in methane is absorbed at 600° C. At 700° C the carbon content of the product is 25 to 28 percent. At 900° C a 50 percent mixture of hydrogen and methane is 15 percent reacted upon by the metal. When the products containing up to 8 percent are put in dilute hydrochloric acid, methane is obtained and a small percent of ethylene. The products containing more than 8 percent carbon gave a carbon slime and fatty substance and a very small percent of unsaturated hydrocarbons.

An observation which may turn out to be of some importance in the production of lamp-black from methane is that during the formation of magnesium carbides, carbon separates out very strongly at 20° C.

Of interest may be then the carbides of magnesium. MgC_2 has its limit of existence at 600° C. It can, however, be shown to be present in traces up to 1030° C. Its decomposition starts at 490° C. No suitable solvent has been found for MgC_3 up to the present. It is decomposed energetically by water. Magnesium carbide (Mg_2C_3) is also not stable at high temperatures. The decomposition starts at 700° C and at 780° C it is found present only in traces. In spite of this it can be shown to be present up to 1200° C; and both carbides can also be produced by the action of magnesium upon alcohols, ketones, aldehydes, acetylene, ethane, etc., by heating carbon and magnesium at 530° to 740° C.

The decomposition of manganese carbides might lead to similar results. The reaction of making carbon from methane may therefore take place in two steps, or the metals, manganese and magnesium, may be introduced in such a manner as to bring this about in one so-called catalytic reaction.

The above investigation should be pushed by all means since it has apparently an important bearing on the possible catalytic transformation of methane into fatty substances, the metal acting as a condensing agent.

The types of reaction occurring in the electric arc or under varying temperature and pressure conditions will be taken up in the subsequent portions of the paper.

Cyanides from Methane

The processes for making cyanides from methane are varied in that in some cases nitrogen alone is used, in other cases air, in others hydrogen is added to the nitrogen, and in still others ammonia is used.

Some representative processes follow: Gow (U. S. Pat. 801,728) mixes natural gas (95 percent methane) with nitrogen or air and passes the mixture through an arc, a sputtering arc giving the best results. Sinding-Larsen (U. S. Pat. 1,042,723), passes nitrogen and the vapors of hydrocarbons through the system. He obtained thereby nitrides of aluminium and silicon and in the volatile constituents ammonia and hydrocyanic acid. Moscicki and Jablczynski, U. S. Pat. 1,050,978, manufactured hydrocyanic acid from a repeatedly used gas mixture containing nitrogen, hydrogen and hydrocarbon at high temperature and subsequent cooling, preventing increase of the hydrogen by removing the same from time to time. The heating is done in an electric furnace having a revolving high tension flame, the temperature reaching 2500 to 3500° C.

Attempts have been made to use catalysts, such as copper. Commerical results are claimed to be obtainable at 500° C. (Beindl, U. S. Pat. 1,144,457.)

Liebknecht (U. S. Pat. 1,235,342) has a process for the production of hydrocyanic acid from nitrogen, hydrogen, and hydrocarbons in an electric furnace containing a high voltage arc at a pressure of approximately 1.6 atmospheres. 50 grams of hydrocyanic acid per kilowatt hour were produced from a mixture of 5.3 percent carbon monoxide, 8.3 percent methane, 33.7 percent hydrogen and 42.7 percent nitrogen.

Amongst foreign processes, the Lipinski process has received the most consideration. Lipinski reports that on passing an electric discharge through a mixture of nitrogen, hydrogen and methane, the last mentioned may be changed to hydrocyanic acid entirely. A favorable mixture is 10 percent of hydrogen, 20 percent of methane, and 70 percent of nitrogen. The yield of hydrocyanic acid is equivalent to 19 percent of the mixture. The large excess of nitrogen is necessary to prevent the separation of free carbon. Evidently ordinary coal gas can form a basis for the preparation of such a mixture.

Roessler reports that 4 liters of a gas mixture of nitrogen and marsh gas passed through a flame of 1000 volts; 0.8 ampere gave 0.75 gram of hydrocyanic acid.

An experimental apparatus is described by Muthmann and Schaidauf which consisted of a 1500 cc glass alembic containing 4 tubes, of which only two carry electrodes, while the other two serve as inlet and outlet tubes. In the reaction vessel an excess pressure of 40 cm is maintained during the operation. The current source was an alternating current of 50 cycles per second, which furnished at 93 volts a maximum of 43 amperes. The electrodes consisted of wires of silver, gold and platinum which were screwed into cooled copper rods. The outgoing gases were analyzed and from the results the amount of decomposition occurring in the flame was calculated. The reaction between methane and nitrogen by this method gave just hydrogen cyanide and hydrogen.

RÉSUMÉ OF PHYSICAL-CHEMICAL CONSTANTS OF METHANE

Specific gravity (air = 1)	0.559
Boiling point	—164° C, 760 mm
Melting point	184° C
Freezing point	—185.8° C
Solidifying point	—186° C
Triple point	—183.15° C, 70 mm
Triple point	—185.8° C, 80 mm
Critical temperature	—82.85° C
Critical pressure	45.6 atmospheres
Critical density	0.1623
Critical density	0.1519
Coefficient of expansion	$3681/10^6$ $3679/10^6$
Specific gravity of liquid	0.415
Heat of formation at constant pressure	21,750 cals.
Heat of formation at constant volume	21,170 cals.
Heat of combustion	213,500 cals.

CH_4 forms a hydrate with water at —2° C under 30 atmospheres

C. SYNTHESIS AND DECOMPOSITION OF METHANE

1. Direct Union of Carbon and Hydrogen

In spite of the fact that Dalton, as far back as 1809, investigated the methane equilibrium with its elements, no work of any great consequence was done till recently.

Bone and Coward[74] initiated a long series of experiments when starting with very pure carbon and hydrogen; they succeeded in turning 75 percent of the carbon to methane at 1100°–1200° C. In their experiments no doubt a part of the gases were lost through the walls of the reaction tube. For example, they obtained 422 cc of methane from 0.306 g carbon. They also noted that platinum furthered the reaction.

J. N. Pring[75] discovered that at 1200° C the reaction velocity was very slow, that is, it took 22 hours to form 0.35 percent methane. Under these conditions the rate of decomposition was even slower. At 1500° C 2 hours equilibrium gives 0.17 percent. Greatest values were obtained using platinum between 1050°–1500° C. At 1200° C 0.55 percent and at 1500° C 0.30 percent were obtained from both sides. Above 1550° C more and more methane is obtained because of the decomposition of acetylene, although the amount of the latter at 1850° C is too small for analysis. It can be shown, however, that above 1500° C acetylene is converted into ethylene and methane. Incidentally it was observed that carbon monoxide seemed to have no influence on the equilibrium of methane at the temperatures under consideration, and that it did not change the velocity of reaction.

The relationship used by Pring was as follows:

$$K_T = -18{,}507 + 5.9934T \log T + 0.002936T^2 + RT \log \frac{CH_4}{(H_2)^2}$$

The constant K was found in the above equation to be 21.1 by Mayer and Altmayer. The apparatus used in the experiments was a rod of carbon or graphite tube with a narrow slit along the top, inside of which the carbon to be used was placed. All contact between the heated carbon and everything else but the hydrogen was carefully avoided by the experimenters. The percentage of methane was determined by removing the hydrogen present by means of palladium; acetylene by formation of cuprous acetylide or silver acetylide; and the other gases by suitable means, and finally exploding the methane present with oxygen. The carbon used in the experiments was derived from sugar charcoal carefully purified by alternately treating one hour with chlorine, nitrogen and hydrogen at 1550° C and then for one-half hour *in vacuo* at 1220° C. When using amorphous carbon, upon which platinum was deposited as a catalyser, and heating to 1050° C for one and one-half hours, characteristic results gave 0.052 percent of carbon monoxide and 0.866 percent of methane.

Further work by Pring and Fairlie[76] on the synthesis of hydrocarbons at high temperatures has an important bearing upon the equilibrium of methane. According to their experimental results carbon and hydrogen combine to form methane between 1200° C and 1500° C while ethylene forms at temperatures above 1700° C. In the presence of hydrogen either ethylene or acetylene forms methane at temperatures above 700° C.

The authors attempted to apply Haber's equation to the equilibrium of methane:

$$\log_e K = \frac{Q_o}{R_t} - \frac{\sigma \log_e T}{R} - \frac{\sigma_I T + \sigma_{II} T^2}{R} + \frac{K}{R}\ K = \frac{CH_4}{p(H_2)^2},$$

where Q_o is the heat of reaction at absolute zero, and $\sigma, \sigma_I T + \sigma_{II} T^2$ are the sums of the specific heats at constant pressure of the substances disappearing, carbon and hydrogen; and the substance, methane, appearing. The constant K is a quite indeterminate value, known as 21.1 between the temperatures of 250° C and 850° C. At the temperature of 1200° C Haber's equation gives the equilibrium ratio $CH_4/(H_2)^2 = 0.07$.

The specific heat value was omitted because it was not known. Furthermore, it was recognized that the variables of the equation were not sufficiently precise for calculations involving high temperatures.

The materials used were of the following purity: The hydrogen analyzed 98 percent with the balance as nitrogen. The carbon gave a two percent impurity composed of the oxides of silicon, iron and other substances. The methane was generated by the action of water upon aluminium carbides which gave a number of other gases such as hydrogen sulfide, acetylene, etc., which were removed by the usual means. The residual gas was liquefied and the methane evaporated off.

The furnace used in the experiments was of special design, having a capacity of 750 cc, and pressures of 100 to 200 atmospheres were applied during operation. At a temperature of 1275° C an analysis of the gas gave 0.002 percent acetylene and 21 percent of methane.

The synthetic formation of methane from the elements proceeded with greatest rapidity at high gaseous pressure. The equilibrium of methane formation was reached after a period of two hours with the use of carbon in a compact form, with or without catalyst, at temperatures of 1200° C to 1300° C and pressures 30 to 50 atmospheres. At temperatures above 1400° C equilibrium was reached in fifteen minutes while at 200 atmospheres the reaction was much more rapid in reaching equilibrium. When carbon was used in a finely divided condition with hydrogen at high temperatures, the reaction reached equilibrium with great rapidity, the reaction being endothermic in character. Under the conditions of temperatures of 1100° C to 1200° C and pressures up to 200 atmospheres no other saturated paraffin hydrocarbons were formed except methane. The ratio of $CH_4/(H_2)^2$ under the above conditions was found to be constant and represents the true equilibrium constant K. The change of free energy in the transformation of carbon into graphite increases rapidly in the range of temperatures from 1200° C to 1600° C; however, the values for amorphous carbon are not quite so definitely known for graphite on account of the gradual transformation which the former undergoes into the latter at the temperatures utilized in this set of experiments.

By application of Kirchhoff's law relating to specific heats one can see that the mean specific heat of amorphous carbon must be much higher than that of graphite between

0° C and 1200° C and that this difference increases with increase of temperature.

The 0.002 percent of ethylene formed at 1275° C does not exert any appreciable effect upon the methane yield, the latter being 21.5 percent. At temperatures between 1800° C and 2100° C by exerting high pressures upon the system no appreciable effect was noted on the yield of ethylene and acetylene when the results are compared with those obtained in earlier work at atmospheric pressure.

The work of Pring and Fairlie may be summarized in the statements

1. Acetylene is not formed below 1200° C.
2. Methane forms about one hundred times as rapidly as ethylene.
3. At 1400° C the ratio of ethylene to methane is 1 : 10.
4. At 1650° C acetylene appears.
5. Methane probably forms directly from the elements.

Similar results are reported elsewhere by Pring and Fairlie[77] for temperatures 1100° C to 2000° C and pressures of 10 to 200 atmospheres. They point out that the velocity of methane formation increases very rapidly with increase of pressure and that the ratio of $CH_4/(H_2)^2$ is constant for any given temperature and pressure. Furthermore, when amorphous carbon was used the percentage yield of methane was greater, a fact which they attributed to a metastable condition. No appreciable effect was noted upon the percentage yields of acetylene or ethylene with increase of pressure and no other hydrocarbon formation was observed. The term "metastable equilibrium" was used to cover the same multitude of sins now more popularly covered by such terms as "free energy," "surface action," and a host of et ceteras.

Of no less interest is the direct synthesis of methane with the aid of catalysts. Ipatiev[78] is responsible for some work with metals and the oxides of the metals. Disagreeing apparently with Mayer and Altmayer, who assume that the synthesis of methane in the presence of nickel is aided through the hydrogen compounds of this metal, he explains the phenomena through the coöperation of the metallic oxide which can produce catalytic oxidation and reduction. The outline of reaction is as follows:

Actor H_2 — NiO catalyser : Actor H_2 — C acceptor

The nickel oxide oxidizes the carbon present to carbon dioxide and the latter is reduced by the hydrogen according to the reversible reaction

$$CO_2 + 4H_2 \rightleftarrows CH_4 + 2H_2O.$$

The water formed during the reaction in turn oxidizes the metal to the oxide which means the regeneration of the metallic oxide. This process being a continuous one, a small amount of oxide can cause a relatively large percentage yield of methane. Support of the correctness of this view was sought in the fact that at least a small amount of water was necessary in this as well as in many other well-known reactions, and that the reaction represented by the above equation is reversible. This is proved by numerous experiments made at different temperatures and pressures with varying concentrations of gases. The carbon used in the experiments was of a 99 percent purity and the hydrogen was further purified from extraneous gases present by potassium hydroxide, potassium permanganate, copper sulphate, sulphuric acid, and cupric chloride. The synthetic production of methane from the elements in the presence of reduced nickel under high pressure takes place at temperatures of 510° C to 520° C. The following examples are illustrative:

A. Three grams of nickel oxide at 510° C and 110 atmospheres pressure gave at the end of twenty-six hours 6.5 percent of methane.

B. Three grams of stannous oxide at 515° C and 102 atmospheres pressure gave at the end of seventeen hours 6.2 percent of methane.

Further experiments showed that the higher the temperature the greater the yield of methane, but that there is a temperature limit beyond which the reaction cannot be carried because of hydrogen diffusing through the walls of the reaction zone. Experiments further indicated that methane in the presence of reduced metals and water can be decomposed with separation of hydrogen, but with zinc dust at a temperature of 502° C no decomposition took place.

The following general conclusions may be drawn from the above work:

1. From a large excess of hydrogen in relationship to the carbon dioxide no complete reduction of the carbon dioxide can take place.

$$CO_2 + 4H_2 \longrightarrow CH_4 + 2H_2O$$

2. With too great excess of carbon dioxide, free hydrogen was always found to be present, less being present the larger the original concentration of the carbon dioxide.
3. The use of catalysers as nickel oxide and reduced nickel acted similarly in reducing carbon dioxide but the action of cupric oxide was much weaker than the nickel catalysers.
4. With concentrations of hydrogen and carbon dioxide which approach the theoretical values, reduction approaches a certain limiting value.

The work done by others before Bone and Coward is as follows: 1809, Dalton and William Henry[79,80] studied the decomposition of methane and ethane by subjecting them to the action of electric sparks. 1839, Marchand[81] proved that the ultimate resolution of hydrocarbons into elements at high temperatures is not in general the immediate result of a single chemical change. He obtained much methane on decomposing ethylene. 1860, Buff and Hofmann[82] supported the above conclusion. The decompositions were performed by means of platinum wire. V. B. Lewes also remarked that the denser hydrocarbons were formed at incipient red heat. 1863–69, Berthelot[83-86] maintained that hydrocarbons are never directly resolved into elements. The primary change is either polymerization (*e. g.*, acetylene to benzene) or coalition of two or more molecules to form denser hydrocarbons with the elimination of hydrogen and so on to carbon.

$$2CH_4 = C_2H_2 + 3H_2 \qquad 2CH_4 = C_2H_6 + H_2$$
$$C_2H_6 = C_2H_4 + H_2 \qquad 2C_2H_6 = 2CH_4 + C_2H_2 + H_2$$
$$C_2H_4 = C_2H_2 + H_2 \qquad 2C_2H_4 = C_2H_6 + C_2H_2$$

1873, T. E. Thorpe and S. Young showed that primary decomposition gives olefine and lower paraffin.

$$CH_3CH_2CH_2CH_3 = CH_3CH_3 + CH_2CH_2.$$

1886, Armstrong and Miller[87] suggested the formation of benzene directly from hexane, no acetylene being present in oil gas from petroleum. 1894–5, V. B. Lewes[88,89] adduced evidence as to the formation of acetylene from methane. 1896, Haber[90] noted that on the primary decomposition of *n*-hexane between 600°–800° the elimination of methane was involved,

$$CH_3CH_2CH_2CH_2CH_3 = CH_3CH_2CH_2CHCH_2 + CH_4$$

and that, the tendency in the aromatic series was toward the formation of more complex molecules.

$$2C_6H_6 = C_{12}H_{10} + H_2.$$

1897, Bone and Jerdan[91,92] stated that at 1000°–1200° C methane is the only hydrocarbon formed synthetically.

Some of the conclusions reached by Bone and Coward are

1. Methane is the most stable of the hydrocarbons. It is the principal product of the decomposition of the three hydrocarbons considered, acetylene, ethylene, and ethane, especially above 800° C. Methane is decomposed mainly into carbon and hydrogen with evidence of a surface reaction.
2. The decomposition of acetylene, ethylene, and ethane is not a surface one.
3. Acetylene is the principal product of the decomposition of ethylene and not of methane and ethane, Lewes' equation being disproved thereby.
4. Acetylene polymerizes at low temperatures, the maximum value being attained at 600°–700° C, and little being in evidence at 1000° C.

5. Acetylene and ethylene show a tendency to combine with hydrogen at low temperatures to form ethylene and ethane, respectively. This tendency is found to be negligible at 1000° C.
6. One of the principal factors at 800° C and above is the direct hydrogenation of residues as $\vdots CH$, $:CH_2$ and possibly $.CH_3$ to methane when the atmosphere is rich in hydrogen.
7. Berthelot's theory is disproved. (Berthelot's theory is that hydrocarbons are never resolved into their elements directly.)
8. No single equation will do to express these reactions.
9. Equations may, however, be given for intervals, *e. g.*,

   $$C_2H_6 \longrightarrow C_2H_4 + H_2 \longrightarrow C + CH_4 + H_2.$$
10. The primary effect of temperature on C_2H_6 and C_2H_4 is to form $:CH_2$ and $\vdots CH$ which may (*a*) form $H_2C:CH_2$ and $HC\vdots CH$, (*b*) break down to C and H, (*c*) be hydrogenized to CH_4, or (*a*), (*b*), and (*c*) simultaneously.

The reactions may be written:

$$\begin{array}{l} H:H \\ HC\vdots CH = 2(:CH_2)_2 + H_2 = \\ H:H \end{array} \begin{cases} (a)\ C_2H_4 + H_2 \\ (b)\ 2C + 2H_2 + H_2 \\ (c)\ \text{plus } H_2 = 2CH_4 \end{cases}$$

$$\begin{array}{l} H:H \\ HC:CH = 2(\vdots CH) + H_2 = \end{array} \begin{cases} (a)\ C_2H_2 + H_2 \\ (b)\ 2C + H_2 + H_2 \\ (c)\ \text{plus } 2H_2 = 2CH_4 \end{cases}$$

11. C_2H_2 polymerizes as follows:

$$HC\vdots CH = 2(\vdots CH) = \begin{cases} (a)\ 2C + H_2 \\ (b)\ \text{plus } 3H_2 = 2CH_4 \end{cases}$$

For these compounds the rate of decomposition is much slower than the rate of combustion. This explains why a flame is propagated by them, and why oxidation takes precedence.

Contact Catalysis of Methane

The phenomena of contact catalysis is of highly theoretical and industrial significance. In hydrocarbon reactions, contact surfaces play a more important role than is generally believed; for widely different results are obtained when a clean iron tube is used or when covered with carbon, or filled with some metallic or metallic oxide substance. Slater[93] in a series of experiments on the influence of different surfaces on the decomposition of methane used in a finely ground state, silica, anhydrous alumina, magnesium, calcium and barium oxide, wood charcoal, graphite, carborundum, iron and copper.

According to our present ideas of contact catalysis as enunciated by Bancroft,[94] catalysis in the presence of graphite should be less than in other cases, *i. e.*, in the direction of the formation of methane. This seems to be borne out by the following figures. Carbon as a product of the decomposition of methane favors least its synthesis.

Catalyst	Percent hydrogen	Catalyst	Percent hydrogen
CaO	15.6	Iron	73.1
MgO	11.4	Charcoal	69.4
Tube, empty	11.0	CaO	35.2
SiO_2	8.7	Tube, empty	10.1

Catalyst	Percent hydrogen	Catalyst	Percent hydrogen
Charcoal	33.9	Graphite	66.0
CaO	23.9	SiC	44.0
Tube, empty	16.2	Copper	27.9
SiO_2	12.3	Tube, empty	18.0
MgO	12.0	SiO_2	15.0
Al_2O_3	10.4		
BaO	6.5		

Hamburger[95] studied the influence of adding small amounts of methane and carbon monoxide to a tungsten lamp filled with nitrogen. He found that concentrations of methane as low as 0.14 percent were highly injurious, due to a carbide of tungsten forming and decomposing to carbon at high temperature. At a temperature of 3000° C the formation of cyanogen and hydrogen cyanide occurs in the presence of small amounts of methane and tungsten in a nitrogen-filled lamp.

2. Synthesis of Methane not Directly from the Elements

The work which established some of the physical constants and served perhaps as suggestion of the researches discussed in the previous section was that of Mayer and Altmayer.[96] This work was on the synthesis of methane from calcium hydride.

The calcium hydride used was made by passing hydrogen over metallic calcium at ordinary temperature or at "dark red heat." When hydrogen is passed over specially prepared calcium it is absorbed at a temperature of 240° C and more quickly at rising temperatures, but at 675° C calcium hydride is decomposed and it is best to keep the temperature above 270° C until the reaction ceases. The gray powder with carbon monoxide at a temperature of 500° C gave a methane yield of 65.6 percent but upon further increase of temperature the percentage yield of methane decreased. However, when the velocity of the gas is increased at 500° C the amount of methane increases, but there is obviously a limit to the velocity of carbon monoxide passage for increased yield of methane. The other products of the reaction are carbon and calcium carbide.

When carbon dioxide and calcium hydride react the maximum yield of methane occurred at 500° C of 60.24 percent. The following equation expresses some of the reaction products:

$$2CO_2 + 4CaH_2 \longrightarrow CH_4 + C + 2H_2 +$$

In this case calcium carbide is formed in lesser quantities, but there are traces of calcium formate formed and considerable quantities of calcium carbonate. At a temperature of 270° C soot and calcium hydride give hydrogen as a reaction product but methane is also formed at higher temperatures, the maximum yield being 40.68 percent at a temperature of 500° C. At the same temperature in a current of hydrogen 19 percent of methane was formed. During the reaction some calcium nitride was also produced, due to some nitrogen being present as an impurity.

The above constituted a first step in the direction of investigating the nature of catalytic formation of methane with the belief that it is promoted by the formation of hydrides.

In a series of papers, Mayer, Heuseling, Altmayer and Jacoby[97] investigated these and similar questions further and adduced the following facts:

1. Halogen substitution products of methane are reduced by hydrogen.
2. Berthelot obtained methane by the reduction of acetaldehyde and acetone.
3. Methane may be obtained by passing gaseous carbon disulfide with hydrogen sulfide over dark glowing copper.
4. Methane may be produced by the passage of carbon disulfide and antimony hydride through glowing pipes.
5. Methane may be produced from aluminium and manganese carbides with water.

In general, that reduction reactions will yield methane or in the case of hydrolysis, carbides will also do the same. Therefore the syntheses of methane from carbon monoxide, carbon dioxide and water or hydrogen were to be expected.

They observed that the velocity of methane formation from carbon monoxide and hydrogen, and from carbon dioxide and hydrogen proceeded with the same rapidity with nickel oxide as with nickel. When iron was used only small amounts of methane were formed which indicated that the iron was oxidized by oxides of carbon present. The greatest speed of reaction in methane formation occurred when finely divided carbon from the decomposition of carbon monoxide was used, while from graphite and from carbon obtained electrolytically methane was produced in small amounts only.

With the same catalysts further investigations were carried on, using water vapor in the form of steam in place of hydrogen.

$$CO + H_2O \rightleftarrows CO_2 + H_2$$
$$C + 2H_2O \rightleftarrows CO_2 + 2H_2$$
$$CO_2 + 4H_2 \rightleftarrows CH_4 + 2H_2O$$

The discoveries thus obtained were then extended experimentally to illuminating gas and the possible technical applications were discussed also with respect to the water gas process.

By thermodynamical applications these relations were more closely studied in the analysis of methane. Similarly the equations between carbon, carbon dioxide, and carbon monoxide were subjected to a new valuation. Finally they showed theoretically that through the combination of carbon dioxide and methane the quantitative relationship of the reactions may be established. If this last equation is combined with the expression of the water gas reaction, one obtains the equation for methane analysis:

$$CO + 3H_2 \rightleftarrows CH_4 + H_2O$$
$$CO_2 + 4H_2 \rightleftarrows CH_4 + 2H_2O$$

The thermodynamic equations of Mayer and Altmayer and their co-workers were used in the preceding discussions.

A further review of the values tabulated by Mayer and Altmayer may be worth while. It will be remembered that the thermodynamic equation for the equilibrium shows that with decreasing hydrogen pressure the equilibrium pressure of methane rapidly falls. For instance, at 850° C a decrease of hydrogen pressure from 0.9841 to 0.1 atmosphere lowers the methane content from 1.59 to 0.16 percent and, looking over their table, one sees that as hydrogen and methane are frequently 82 to 90 percent of the coal gas product, some of the data given are applicable. At 604° C the rate of decomposition of methane per degree rise in temperature is at a maximum. Of course the hydrogen liberated by the decomposition of methane prevents by its accumulation of partial pressure the further decomposition of methane. Thus above 607° C the retarding action of $(H_2)^2$ pressure is already greater than the effect of heat in driving the reaction forward. As a result at 800° C there is less increase in the rate of decomposition per degree of temperature than at 400° C.

At the higher temperatures all tests show higher methane content than the equilibrium would lead us to expect. Several explanations could be suggested.

1. While some parts of the coal are at a moderate temperature, the methane produced there is not decomposed with sufficient rapidity during the time the gas is in the retort to correspond with equilibrium proportions. The truth of this contention may be indicated by an experiment showing that less methane is decomposed (about $^1/_3$ as much) in a packed tube than in an unpacked one in say 25 minutes.
2. The presence of hydrogen assists the decomposition of ethylene into methane and this secondary formation of methane would go to swell the methane content provided it were with drawn from the retort with sufficient rapidity to prevent the further decomposing effect of heat.
3. There is also a possibility of the steam reacting with the methane, namely,

$$CH_4 + H_2O \rightleftarrows 3H_2 + CO.$$

Tests, furthermore, show that at higher temperatures the yields of hydrogen and carbon monoxide are increased. There is, moreover, a gain in luminosity of the gas. It has been claimed, especially in carburetted water gas, that carbon monoxide has advantages in developing luminosity. The following reactions may occur in the interaction between the constituent gases in the luminous flame:

$$2CO + 2H_2 \rightleftarrows CH_4 + CO_2$$

A practical investigation on the synthetic production of methane was carried on by E. Erdmann.[98] Water gas freed from carbonic acid was conducted at 250° C over finely divided metallic nickel with the necessary amount of hydrogen to complete the equation

$$CO + 3H_2 = CH_4 + H_2O.$$

A difficulty was encountered in the fact that water gas produced in the usual way does not contain carbon monoxide and hydrogen in the correct proportions. Theoretically $3H_2 : CO$ are required, but practically 5 : 1 is needed. Furthermore, the nickel catalyst used was poisoned by the sulphurous gases, or by the deposition of a coat of carbon. Pure hydrogen was considered as too expensive for use. The hydrogen and carbon monoxide were segregated from blue water gas by physical means in correct proportions. The water gas is deprived by condensation at the temperature of liquid air of an amount of carbon monoxide to produce an escaping gas of only 17 percent carbon monoxide. The condensed carbon monoxide is then gasified and used for driving compressors. The extreme cooling also removed sulphur present. And finally the precipitation of the carbon can be prevented by diluting the carbon monoxide with hydrogen.

The above facts are made use of in the Bedford process. In this process the water gas is first purified in a water tower and then sawdust is used to remove the tar present. The carbon dioxide present is removed by compression to 10 atmospheres, the residue of 0.1 percent being removed by the use of lime, or subsequent liquefaction and absorption in cold alcohol. The gas now free of carbon dioxide contains 41 percent monoxide, 54 percent hydrogen and 5 percent nitrogen. At ten atmospheres pressure it is made to enter a Linde apparatus for the separation of carbon monoxide and hydrogen. The liquid carbon monoxide and nitrogen are collected in a receiver. The gas is split up into 2 parts, one 93 percent carbon monoxide, the other 5–14 percent carbon monoxide. These proportions depend on the adjustment of the expansion valves. In working, the valves are adjusted so as to obtain a final gas of 17 percent carbon monoxide, 79 percent of hydrogen and 4 percent of nitrogen.

The reduction apparatus consists of three silica tubes 1½ m 120 cm each containing 20 g. of finely divided nickel pumice. The tubes are arranged vertically in a casing and provided with electrical heating (temp. 280–300°). Since the reaction is exothermic there is a suitable arrangement for allowing the dissipation of all extraneous heat, after the process is started. The water formed in the reaction is condensed. The resulting products are: traces of carbon monoxide and carbon dioxide, 30 percent methane, 62 percent hydrogen, and 6–7 percent nitrogen. The nickel, when coated with carbon, can be restored to its original catalytic properties if a gas weak in carbon monoxide is passed through the tube. The earlier figures on the cost of the synthetic methane were 4,484 cc for 3 s. 1.8 d., or 8.5 d. per liter.

P. Sabatier[99] confirmed a great many of the facts of the Bedford process.

Along similar lines, but more strictly theoretical and still possibly of industrial application, is the work of G. W. Andrews[100] on the water gas equilibrium in hydrocarbon flames.

1. The constant $K_t = \frac{C_{CO} \times C_{H_2O}}{C_{CO_2} \times C_{H_2}} = 3.98$ is found to be independent of the nature of the hydrocarbon mixture or pressure of the gas before ignition; also of the maximum flame temperature.
2. The constant does not correspond to the maximum flame temperature but is characteristic of a hypothetical temperature which is probably between 1500–1600° C.
3. No calculation is attempted of the flame temperature, which is, however, estimated as not above 1600° C.
4. The reaction proceeds with rapidity during the cooling period of hydrocarbon flames, and the adjustment of the equilibrium down to a comparatively low temperature is prompt.
5. The amount of methane in the final gases never exceeded 1.05 percent (being usually only 0.3–0.6 percent). No conclusions could be drawn.

6. The most general conclusion is that the explosion combustion of many hydrocarbon oxygen mixtures gives rise to products which approximately at least conform to water gas equilibrium with a value of 4 for K_t and that this value is not greatly altered even when large quantities of carbon are separated or a considerable percent of methane formed in the ultimate products.

The author quoted Bone on secondary reactions: "At higher temperatures of flame secondary thermal decompositions come into operation at an earlier stage and play a more important rôle than in slow combustion, but they do not precede the onslaught of the oxygen on the hydrocarbon, but arise in consequence of it."

3. Catalytic Production of Methane not by Direct Synthesis

There is a series of patents, notably by M. L. Vignon,[101-107] on the production of methane by the reaction of carbon monoxide with steam in the presence of lime, which serves as a catalyst. The reaction is carried on at 1000° C with steam. The yields are about 88 percent hydrogen and 12 percent methane from a gas consisting of 99.1 percent of carbon monoxide and 0.9 percent hydrogen. The results for various catalyzers are as follows:

Catalyzer	Temp. ° C	Percent by volume CH_4	Percent by volume H_2	Percent by volume CO
Al_2O_3	950	3.8	5.9	90.3
MgO	900	6.7	4.7	88.6
SiO_2	750	8.4	10.9	80.7
Fe	950	11.2	20.3	68.5
Ni	400	12.5	1.5	86.0
Cu	700	6.3	2.2	91.5

Probably in the case of iron, aluminum oxide, and silicon dioxide an intermediate carbide is formed.

4. Electrosyntheses from Methane

Thenard and Berthelot[108] passed a silent electric discharge through methane and carbon dioxide and claimed that they obtained an insoluble carbohydrate. Berthelot[109] observed a trace of butyric acid in the reaction products. The residual gases consisted of a little acetylene and of considerable carbon monoxide.

Similarly from a mixture of methane and nitrogen (100 CH_4 and 100 N_2) Berthelot[110] obtained 117.7 hydrogen, 3.4 methane, 74 nitrogen and a solid body approximately of the composition $C_8H_{12}N_4$.

Striking is the work of W. Loeb,[111] who subjected moist methane under ordinary pressure to the influence of the silent discharge and obtained an insoluble, white substance which separated out on the sides of the vessel. Its composition seemed to be $C_9H_{15}O$. Previously Losanitsch had produced from methane and acetylene an insoluble compound which absorbed oxygen and passed into carburetted hydrogen gas. This compound showed no traces of being caused through the formation of the spark, but contained traces of ash, due to the glass being attacked by the discharge. These traces were considered as making the carbon content rise to 2 percent and water to 0.3 percent. The formation of the esters of aliphatic acids such as butyric, caproic, and others, can be understood by the changes methane undergoes.

1. $CH_4 + H_2O = CO + 3H_2$.
2. $CO + H_2O = HCOOH = CO_2 + H_2$.
3. $HCOOH + (CH_2 : CH_2)x = CH_3(CH_2)_{2x-1}\,COOH$.

In these experiments the sides of the vessel were 2 mm apart. The electrisator was filled with distilled water, so that the methane was compressed from a definite volume and the lower part of the discharge tube remained full of water. The gaseous products were removed every 2–4 hours, the other substances at the end of a week. The substance is readily removed by shaking with water and alcohol. At the end of 20 hours, 0.2 to 0.3 g was obtained. This substance ($C_9H_{15}O$) is not changed by boiling with alkalies or dilute acids, but concentrated H_2SO_4 darkens and dissolves it. The gaseous products consist of CO_2, $C_n\,H_{2n}$, CO, C_nH_{2n+2}, and about 35–45 percent hydrogen.

Duration	Cc CH_4	Gas after expt.	Cc CO_2	C_nH_{2n}	CO	H_2	$CH_4 + C_2H_6$
4 hrs. 30 min.	52.0	60.4	0.5	0.1	0.8	36.90	9.00
2 hrs. 40 min.	50.5	57.4	0.6	0.7	1.1	39.48	12.20
2 hrs. 30 min.	49.2	57.3	0.1	0.4	1.4	43.92	12.96

Maquenne[112] passes mixtures of methane and oxygen through the silent discharge and obtains HCHO and HCOOH.

Losanitsch and Jovitschitsch[113] on subjecting mixtures of methane and carbon monoxide to the silent discharge obtained acetaldehyde and its condensation and polymerization products.

Similarly, Hemptinne[114] reports the formation of an aldehydic substance from methane in the silent discharge.

5. Formation of Methane Electrically

Loeb and Lorenz[115] report that on electrolysis of an aqueous solution of methyl alcohol containing $KC_2H_3O_2$, besides carbon monoxide and carbon dioxide there were obtained methane and KCH_3CO_2.

Lassar-Cohn[116] on electrolyzing fused $KC_2H_3O_2$ found carbon dioxide at the anode and carbon, hydrogen and methane at the cathode.

Clark and Smith[117] on electrically oxidizing succinic acid in alkaline solution obtained oxygen, carbon monoxide, carbon dioxide, ethylene, methane, tartaric and oxalic acids.

Truchot[118] on decomposing ethyl ether found ethylene, hydrogen and methane.

Loeb[119] on sending a voltaic discharge in air between carbon points obtained formic acid, 39 percent methane and 45 percent hydrogen, and small quantities of carbon dioxide, carbon monoxide and acetylene.

Maquenne[120] reports the following products from methyl alcohol on silent electric discharge being passed through:

Pressure	3 mm	100 mm
CO	24.3	19.6
CO_2	0.0	0.0
$C_2H_2 + C_2H_4$	4.3	0.9
CH_4	51.0	36.7
H_2	20.4	42.8

Similarly,[121–122] methane has been obtained from: formic methyl ester, formic ethyl ester, acetic methyl ester, glyceric acid, ethyl alcohol, propyl alcohol, isopropyl alcohol, allyl alcohol, glycol, acetaldehyde, paraldehyde, propylaldehyde.

S. M. Losanitsch[123] reports that isopentane on being exposed to silent electric discharge condenses to higher products (when going through at the rate of 3 or 4 bubbles per minute). The separated gas consists of hydrogen, methane and about 5 percent by volume of unsaturated hydrocarbons. The condensed product, after distillation of the unchanged isopentane, remains as an oily, perfumed liquid, which is soluble in ether and less so in alcohol. This is separated by distillation into a volatile and non-volatile substance, the latter being a thick, yellow, clear mass; the former, colorless, mobile and fragrant liquid, from which is obtained C_8H_{18}, C_nH_{2n}, $C_{20}H_{38}$, $(C_8H_{14})_n$. These analyses show that the electric condensation products of isopentane have the same properties as other electrocondensation products.

Similarly there have been described in detail decompositions of hexane, ethyl ether, acetaldehyde, ethyl acetate, ethylene, benzol, methylal, acetal, mixtures of the above with hydrogen and ammonia, giving rise along with other interesting products, also *methane*.

Aside from the scientific interest in the methane equilibrium, there is the industrial interest in the products of decomposition. The investigation, as to the products formed on electrical discharge of various types through the gas, is still in a very incomplete state (see Sections on electrosyntheses for the white substance obtained by Loeb, etc.). The thermal equilibrium, however, has been analyzed above.

The industrial application of the above data has not been worked out at all satisfactorily, though much experimentation, principally unpublished, has been done. The chief aim of methane decomposition is to obtain a special grade of carbon, for printers' ink and the like. As an example, E. Szarvasy claims in U. S. Pat. 1,199,220 that *pure retort carbon* is produced from methane by heating, to a glowing temperature, particles of carbon previously produced by the same process and then passing methane over the carbon to dissociate the methane and build up the particles; particles of smaller size are submitted intermittently. The necessary temperature is maintained by supplying hydrogen and air or oxygen before introducing the methane. The reaction is preferably carried out in an inclined rotating retort. One would be inclined to doubt the commercial success of this process. Similarly G. Fernekes in U. S. Pat. 1,066,894 claims to get lampblack from methane by decomposing it at atmospheric pressure, at temperatures 1300° C to 1700° C. This is very doubtful in view of the facts given previously. A great deal is still to be expected on the *industrial side* in producing carbon in any form but coke.

U. S. Pat. 1,023,783 I. N. Knapp, passes natural gas through incandescent carbon to convert methane into acetylene, benzene and other hydrocarbons.

A. Heinemann (U. S. Pat. 1,134,677), produces propylene from acetylene and methane by passing a mixture of equal parts of acetylene and methane through catalytic contact mixtures of platinum, copper, aluminum or magnesium on pumice at temperatures 100–200° C, claiming a 70 percent yield.

D. MISCELLANEOUS ON METHANE

1. Biological

The occurrence of methane in the breath of sheep, in the intestinal gases, indicates the existence of methane-forming bacteria. Methane fermentations have been investigated to some extent, in particular by Omelianski.[124] His experiments cover the methane fermentation of cellulose and the methane fermentation of ethyl alcohol by anaerobic bacteria. As an example of his results the following will serve: the fermentation of the fecal matter of rabbits on one percent ethyl alcohol gave after two weeks a gas which was 87.4 percent methane, 11.5 percent carbon dioxide and 1.1 percent hydrogen. The material obtained at the bottom of this culture was transferred to fresh media and a gas of 12 per cent carbon dioxide and 88 percent methane was obtained. Similar results were reported with garden soil.

Giglioli and Masoni[125] have published a series of papers on the biologic absorption of methane. They describe the conditions of burning of methane by bacteria, not enzymatic in character, however.

N. L. Söhngen[126] has published observations on the rôle of methane in organic life, showing that all fatty acids of an even number of carbon atoms give methane on fermentation.

$$CaC_4H_6O_4 + H_2O = 2CH_4 + CO_2 + CaCO_3$$

and

$$2CaC_2H_2O_4 = CH_4 + CO_2 + 2CaCO_3, \text{etc.}$$

Whenever hydrogen was added more methane was formed. The reaction of $4H_2 + CO_2 = CH_4 + 2H_2O$ was thereby verified independently. Furthermore, the ravages of *bacillus methanicus* were described, namely $CH_4 + 2O_2 = CO_2 + 2H_2O$.

The distribution of the various methane organisms is described by Giglioli and Masoni.[127]

2. Sources and Supply of Methane

Methane gas issues out of the earth in practically every part of the globe. Wherever organic matter is found in a state of decomposition methane is one of the by-products. It is found in volcanoes, extinct craters, coal mines, stagnant pools, and oil fields throughout the world. Billions of cubic feet of natural gas from wells and coal mines are lost daily. Up to the present no commercial method has been developed to utilize the methane gas which is found in coal beds and mines.

Our most prolific source of methane gas is from natural gas wells and from casinghead gas. In the year 1916 there was produced and sold 753,000,000,000 cubic feet of gas and for the year 1917 approximately 900,000,000,000 cubic feet valued at $145,000,000. It has been estimated that 1,000,000,000,000 cubic feet of natural gas would be produced and sold in the year 1918. Analyses[128] of thirty-two samples of natural gas from twenty-five cities in the United States, the percentage of methane ranged from 50.6 to 97.3 percent with an average of 78.2 percent. The main use of natural gas or methane gas at the present time is for power, heating and lighting, with smaller quantities being used for making lampblack or carbon black.

The use of natural gas for fuel is a simple, direct and, at present, economical one, but one may question its use for the production of carbon black, the burning of brick, use in the cement and glass industry or for the smelting of metals. May we not yet see practically all of our power and heating done by the use of coke from by-products coke ovens recovering thereby also the liquid products from thermal decomposition of coal? May we not find higher forms of utilization of our natural gas than its present use? May we not divert at least a part to the various uses outlined above? Would not this be true conservation?

E. RESEARCH POSSIBILITIES ON METHANE

The following demand further or new research:

1. The checking of the density determinations of methane.
2. The establishing of a table of densities and volume of methane in natural gas of different compositions.
3. The establishing of the electro negative-positive valency of carbon. Some work indicates valency of six for carbon in methane.
4. Determination of the conditions for liquefying methane.
5. Design of methane refrigeration system.
6. The study of the relation between the ionization of methane and its reactivity.
7. The study of the effect of various wave-lengths on the reactivity of the gas, especially the ultra-red.

8. The study of the effects of pressure on absorption of rays, and hence on reactivity.

9. The effect of the substitution of various groups for the individual hydrogens. (A reaction series of methane substitution products.)

10. Effect of X-rays on methane. (See 7.)

11. The determination of the relation between heat conductivity and velocity of flame propagation.

12. Determination of the effect of moisture and other factors on the explosibility of mine gas.

13. The solubility of methane in solvents and solvent mixtures.

14. Methane in internal combustion engines.

15. Solutions of methane for use in internal combustion engines.

16. The effect of oxidizing agents on methane.

17. Methane combination with other hydrocarbons.

18. The combination of methane with unsaturated compounds.

19. The nitration and sulphonation of methane.

20. The occlusion of methane by metals.

21. The occlusion of methane by coal and other materials.

22. The effect of radium on explosibility and reactivity of methane.

23. The catalytic production of methyl alcohol from methane.

24. The production of intermediate oxidation products of methane on incomplete combustion.

25. Incomplete halogenation of methane precisely controlled.

26. Indirect formation of lampblack from methane.

27. Direct formation of lampblack from methane.

28. The formation of nitrifiable carbides from methane.

29. The most direct process of turning methane to benzol.

30. The transformation of methane to fatty substances.

31. Further research on the methane equilibrium with special attention to catalysis.

32. The effect of a large series of surfaces on methane stability.

33. The formation of carbohydrates from methane electrically.

34. The formation of complex nitrogen compounds from methane electrically.

35. Thorough investigation of the effect of the silent discharge on methane.

36. Reactions of methane in the silent discharge with nitrogen.

37. Reactions of methane in the silent electric discharge with carbon monoxide.

38. Reactions of methane in the silent discharge with carbon dioxide.

39. Reactions of methane in the silent discharge with ammonia.

40. Reactions of methane in the silent discharge with other hydrocarbons.

41–46. as 35–40 with different types of discharge.

47. Oxidation of methane in the silent discharge and others.

48. Producing higher hydrocarbons from the lower ones by the action of heat, by catalysts and in solution.

49. Bacterial oxidation of methane.

50. Bacterial nitrifying of methane.

51. Mixed methane fuels.

52. Cyanates from methane.

53. Efficient methane preparation and purification.

REFERENCES ON METHANE

1. Chem. Zentr., **1909**, I, 977.
2. Jour. Chim. phys., **7**, 369–74.
3. Comptes rendus, **148**, 39–42.
4. Proc. Roy. Soc., **87A**, 371–81.
5. Comptes rendus, **140**, 407 (1905).
6. C. A., **1913**, 3868.

7. Arch. sci. phys. nat., **36**, 97–100; **39**, 400–4; Atti acad. Lin., **24**, I, 1056–7.
8. Zeit. phys. Chem., **71**, 577–624.
9. Proc. Akad. Wetenschappen, **15**, 666.
10. C. A., **1913**, 3868.
11. Comptes rendus, **148**, 173–5.
12. Phil. Mag., **14**, 425–7.
13. Physik. Z., **9**, 852–3.
14. Anzeiger Akad. Wiss. Krakau, **1908**, 1059–67.
15. Ann. Phys., (4) **29**, 780–96.
16. Phil. Mag., (6) **18**, 878–9.
17. Proc. Roy. Soc. London, **83A**, 254–64.
18. Jour. Chem. Soc., **105**, 1002–9; Proc., **30**, 75.
19. Gas World, **59**, 125.
20. Proc. Chem. Soc., **30**, 176.
21. Comptes rendus, **158**, 1793–6, 1999–2001.
22. Jour. Chem. Soc., **105**, 2591–96, 2596–2605.
23. Ibid., **105**, 2606–13.
24. Jour. Ind. Eng. Chem., **7**, 417–9 (1915).
25. Jour. Gas Lighting, **107**, 323.
26. Jour. Chem. Soc., **105**, 2027 (1914).
27. Bureau of Mines, Tech. Paper **119**.
28. Jour. Chem. Soc., **105**, 2150–8.
29. Ibid., **105**, 2591–6.
30. Ibid., **105**, 2596–605.
31. Ibid., **107**, 328–37.
32. Ibid., **95**, 514–43.
33. Zeit. Ver. deut. Ing., **55**, 1110–8.
34. Electrician, **70**, 62–6; Jour. Gas Light, **120**, 295–7; Eng., **94**, 348.
35. Jour. Phys. Chem., **15**, 587–610.
36. Jour. Am. Chem. Soc., **21**, 275 (1899).
37. Comptes rendus, **148**, 561–64.
38. Zeit. Elektrochemie, **17**, 497–502.
39. Bureau of Mines, Tech. Paper **147**.
40. Dingl. polyt. Jour., **195**, 315–331 (1870).
41. Bureau of Mines, Bull. **82**.
42. Comptes rendus, **158**, 573–6.
43. Coll. guard., **112**, 513.
44. Bureau of Mines, Tech. Paper **2**.
45. Comptes rendus, **150**, 1521–23.
46. Bureau of Mines, Tech. Paper **65**.
47. Coll. guard., **106**, 626–7.
48. Proc. Chem. Soc., (3) **21**.
49. Mem. Manch. Phil. Soc., **57**, 1–10; Jour. Chem. Soc., 106, II, 192.
50. Proc. Camb. Phil. Soc., **16**, 356–9.
51. Eng. Pat. 7297 (1906).
52. Ger. Pat. 214,155.
53. U. S. Pat. 891,753.

54. U. S. Pat. 220,397.
55. Am. Phil. Soc., Mar. 11 (1893).
56. Comptes rendus, **134**, 9, 514.
57. Ger. Pat. 24,872.
58. Liebig's Ann., **107**, 212.
59. Comptes rendus, **91**, 1071.
60. Swed. Pat. 40,494 (1916).
61. Norw. Pat. 27,040 (1916).
62. Comptes rendus, **146**, 1037–9.
63. Ibid., **92**, 42, 145.
64. Jahresb. Chem. Techn., **1881**, 971.
65. Am. Chem. Jour., **11**, 362.
66. Bull. Acad. roy. Belg., **1910**, 113–23.
67. Jour. prakt. Chem., (2) **83**, 1911, 421–4.
68. J. Pharm. chim., (6) **29**, 54–5 (1909).
69. Jour. Ind. Eng. Chem., **10**, 1090 (1916).
70. Ibid., **5**, 5–8 (1911).
71. Chem. Centr., **1910**, ii, 255.
72. Zeit. phys. Chem., **73**, 513–46.
73. Ber. deutsch. chem. Ges., **46**, 3479–86.
74. Proc. Chem. Soc., **24**, 222.
75. Jour. Chem. Soc., **97**, 498–511.
76. Ibid., **101**, 91–103.
77. Proc. Chem. Soc., **27**, 305 (1911).
78. Jour. prakt. Chem., (2) **87**, 479–87 (1913); J. Russ. Chem. Soc., **45**, 433–42.
79. New System, I, 440, 447.
80. Phil. Trans., **99**, 446 (1809).
81. Jour. prakt. Chem., **36**, 478.
82. Liebig's Ann., **113**, 129 (1860).
83. Ann. Chim. Phys., (3) **67**, 53 (1863).
84. Ibid., (4) **9**, 413, 455 (1866).
85. Ibid., (4) **12**, 5, 122 (1867).
86. Ibid., (4) **16**, 143, 148, 153, 162 (1869).
87. Jour. Chem. Soc., **49**, 74.
88. Proc. Roy. Soc., **55**, 90 (1894).
89. Ibid., **57**, 394 (1895).
90. Ber. deutsch. chem. Ges., **29**, 2691.
91. Jour. Chem. Soc., **71**, 41 (1897).
92. Ibid., **79**, 1042 (1901).
93. Ibid., **109**, 160–164 (1916).
94. Jour. Phys. Chem., **21**, 573, 644, 734 (1917).
95. Chem. Weekblad, **12**, 62–73 (1915).
96. Ber. deutsch. chem. Ges., **41**, 3074–80.
97. Jour. Gasbel., **52**, 166–71, 194–201, 238–45, 282–5, 305–13, 326.
98. Chem. Trade Jour., **49**, 175.
99. Comptes rendus, (9) **134**, 514–16.
100. Jour. Chem. Soc., **105**, 444–56.

101. Bull. Soc. chim. de France, (4) **9**, 18–20.
102. Comptes rendus, **157**, 131–134.
103. Fr. Pat. 416,699.
104. Add. to above.
105. Add. to above.
106. Jour. Soc. Chem. Ind., **1912**, 117, 481.
107. Comptes rendus, **152**, 871–74.
108. Ibid., **82**, 1360.
109. Ibid., **126**, 561.
110. Ibid., **126**, 567.
111. Ber. deutsch. chem. Ges., **41**, 87–90.
112. Bull. Soc. Chim., **37**, 298.
113. Ber. deutsch. chem. Ges., **30**, 135.
114. Bull. de l'Acad. roy. Belg., (3) **34**, 275.
115. Electrochem. of Org. Comp.
116. Liebig's Ann., **251**, 358; Ber deutsch. chem. Ges., **37**, 325.
117. Jour. Am. Chem. Soc., **21**, 967.
118. Comptes rendus, **84**, 714.
119. Ber. deutsch. chem. Ges., **34**, 915.
120. Bull. Soc. chim., (2) **37**, 298.
121. Ibid., (2) **40**, 64.
122. Zeit. phys. Chem., **22**, 358.
123. Ber. deutsch. chem. Ges., **42**, 4394–4400.
124. Ann. Inst. Pasteur, **30**, 56–60.
125. Staz. sper. agrar. ital., **42**, 589–609.
126. Rec. Trav. chim. Pays-Bas, **29**, 238–74.
127. Staz. sper. agrar. ital., **42**, 589–606.
128. Bureau of Mines, Tech. Paper **109**.

ADDITIONAL REFERENCES ON PROPERTIES OF METHANE

Riesenfeld: "Silent Electrical Discharge in Gases," Zeit. Elektrochemie, **17**, 725–31.

Denham: "Temperature of Combustion of CH_4 in Presence of Pd," Jour. Soc. Chem. Ind., **1905**, 1202–5.

Nernst, "Chemical Constants (CH_4 = 2.5)," Jour. Chim. phys., **8**, 228–67.

Leiser: "Electric Cracking of Carbon Compounds," Abhandl. deutsch. Bunsengessell. Nr. 4.

FURTHER REFERENCES ON REACTIONS OF METHANE

"Methane into Hydrogen Cyanide," Gas World, **60**, 157.

Briner and Wroczynski: "Gas Systems at High Pressures," Jour. chim. phys., **9**, 105–42.

Massol and Faucon: "Absorption of Ultraviolet Rays by Br_2 Derivatives of Methane," Comptes rendus, **165**, 92–4.

Vignon: "Cat. Production of Methane," Gas World, **60**, 771.

Holgate: "Production of Methane," Jour. Gas Lighting, **106**, 25, 84.

Sabatier: "Low Temperature Production of Methane," Chem. Zeit., **37**, 148 (1913).

Losanitsch: "Electrosyntheses," Ber. deutsch. chem. Ges., **43**, 1871–4.

Gautier: "The Effect of Heat on CO," Comptes rendus, **150**, 1383–88, 1564–9.

Parker and Campbell: "Preparation and Analysis of Methane," Jour. Chem. Soc., **103**, 1292–7 (1913).

Von Wartenberg: "Calculation of Hydrocarbon Equilibria," Zeit. phys. Chem., **61**, 366–72; **63**, 269–72.

Lacy: "Some Experiments on the Bunsen Flame," Zeit. phys. Chem., **64**, 633–40 (1908).

Pappenberg and Stephan: "On Explosives," Zeit. ges. Schiess. u. Sprengst., **4**, 281–5, 305–10.

Walter: "Methane Wells (Austria)," Zeit. Ver. Bohrtechn., **18**, 20.

Mickwitz: "Methane Wells (Finland)," Bull. Acad. St. Petersburg, **1908**, 188–90.

Rybak: "Poisoning by Fire Damp," Lek. Roshledy, 1912; Zentralbl. Biochem. Biophys., **13**, 716.

"Spark Discharge through Methane," Hoffman and Buff: Liebig's Ann., **113**, 129; Berthelot: Ibid., **123**, 211; Brodie: Ibid., **169**, 270; Wilde: Bull. Soc. chim. Paris, (2) **5**, 267.

"Methane Fermentation," Hoppe-Seyler: Zeit. physiol. Chem., **11**, 561 (Ca Acetate, Lactate); Baginsky: Ibid., **12**, 457, 461 (Milk Sugar); Nencki and Sieber: Monatsheft, **10**, 562 (Albumin); Hasebroek: Zeit. physiol. Chem., **12**, 148 (Choline); Mitscherlich: Monatsheft Akad. Wissen., **1850**, 104 (Cellulose); Popoff: Pflüger's Arch., **10**, 113 (Cellulose); Tappeiner: Ber. deutsch. chem. Ges., **16**, 1734, 1740; **15**, 999 (Cellulose).

"The Carbides of Al, Be, Ce, Mn, La, etc.," Moissan: Proc. Roy. Soc., **60**, 156; Moissan: Comptes rendus, **131**, 595; Berthelot: Ibid., **132**, 281.

PATENTS: CYANIDES FROM METHANE OR MIXTURES OF METHANE WITH OTHER HYDROCARBON GASES

British	United States	German	Swiss
264	500,651	190,555	20,911
1,032	598,195	197,394	44,225
1,089	615,266	199,973	52,110
2,598	654,466	220,354	55,749
3,735	801,728	228,539	60,534
4,409	889,096	229,057	64,929
5,037	889,097	254,068	65,918
8,767	1,042,723	255,073	68,325
11,010	1,050,978	260,599	
11,107	1,144,457	262,325	
12,541	1,169,817	263,692	Norway
12,604	1,206,155	268,277	2,911
12,946	1,226,811	281,723	11,692
13,069	1,235,342	285,931	13,026
14,855			18,956
15,040			19,985
15,513	Austria	French	23,792
16,049	71,147	199,977	25,585
16,275		202,700	25,704
18,945		210,365	
19,804		262,949	
22,039	Sweden	294,979	
23,835	39,866	417,794	
26,326		458,546	
26,371			

MISCELLANEOUS PATENTS ON METHANE

United States	French	German	British
220,397	353,291	217,157	13,861 (1906)
427,744	355,325	222,919	14,971 (1908)
880,900	356,471	237,499	17,017 (1909)
891,753	400,654	260,477	27,045
956,734	416,699		
983,199	420,933		
989,755	427,774		
1,009,428			Canadian
1,023,783			131,896 (1911)
1,066,894		Norway	
1,134,677	Sweden	26,837 (1916)	
1,199,220	40,495 (1916)	27,040 (1916)	

CRYSTALLOLUMINESCENCE. II

BY HARRY B. WEISER

Triboluminescence and Crystalloluminescence

The term triboluminescence was first applied by Wiedemann[1] to the property which many crystalline substances possess of emitting a characteristic phosphorescent light when rubbed or crushed. The earliest observers of this phenomenon took it for granted that the light was caused by small particles of the solid becoming heated to incandescence by friction. However, it was demonstrated as early as 1792 by Saussure[2] that in certain cases light could be obtained under such conditions that a pure temperature radiation was altogether unlikely. Thus, by fusing a mixture of chalk and phosphoric acid he obtained a substance which glowed when stroked with a quill.

Dessaignes[3] attempted to show that the light obtained by grinding glass, adularia and pumice stone in a mortar was an electrical effect. "He says, that a stronger light is obtained in a metal mortar than in a nonconducting one of porcelain and that better results are obtained in dry weather than in wet; if the powder obtained in a metal mortar is strewn on a hot plate it no longer luminesces, whereas that obtained in a porcelain mortar glows well under the same conditions. In the first case the electric fluid on which the phosphorescence in general depends will have had an opportunity to escape entirely because of the good conductivity of the metal"[4] These experiments have not been confirmed.

Henrick[5] made an exhaustive study of the phenomenon of triboluminescence but reached no definite conclusion as to the cause. However, he emphasized the fact that the light

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[1] Wied. Ann., 34, 446 (1888).

[2] See Kayser: "Handbuch der Spektroscopie," 4, 672 (1904).

[3] Delamentherie: Jour. Phys., 68, 444; 69, 5 (1809).

[4] Kayser: "Handbuch der Spektroscopie," 4, 673 (1908).

[5] Die Phosphorescenz der Korper, 4, 425-570 (1820).

was not caused by the heat resulting from rubbing or grinding. "Henrick reviews and then criticizes the previous explanations of triboluminescence and gives his own: The light in so far as it is not a burning or glowing is due, 1, to the separation of particles caused by friction (to the cracking off of rough places on the crystals; 2, to the electricity resulting from friction; 3, to the chemical decomposition produced by this means. The first mentioned cause is the most important. It is evident that Henrick explains nothing whatsoever, since he merely says that rubbing phosphorescence comes from rubbing."[1] It is interesting to note that Henrick recognized the possibility of some chemical action entering into the process even though he did not take the matter seriously.

Schneider[2] attempted to show that the phenomenon was due neither to electrification nor heating. By rubbing different diamonds together he found that there was apparently no connection between the tendency to luminesce brightly and the degree of electrification. He again pointed out that certain siliceous rocks often emit light under conditions that could not result in an appreciable rise in temperature.

More recent investigators have endeavored to establish some connection between triboluminescence and the crystal structure. Among the first investigations carried out with this end in view was Pope's[3] study of saccharin. He found that there was apparently no connection between the luminescence and crystal structure; however, the results of his work are particularly important since he shows that the luminescence is not caused by a number of things that were later suggested as explanations. "The method by which the crystals are broken seems without influence on the flashing; phosphorescence occurs when the crystals are hacked with a knife, rubbed together, crushed between the fingers or between pieces of glass, and also when they are caused to crack

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[1] Kayser: Handbuch der Spektroscopie, 4, 675 (1908).

[2] Pogg. Ann., 96, 282 (1905).

[3] Jour. Chem. Soc., 67, 985 (1895).

by rapid heating either in the air or in the acetone mother liquor from which they crystallize. There seems to be no plane in the crystal parallel to which breaking occurs without phosphorescence; no matter how carefully a crystal is cleaved along the very perfect cleavage on a(100), so that parting shall only occur parallel to the cleavage, vivid phosphorescence always occurs, and on carefully cutting the crystals in the two directions perpendicular to the cleavage, so that very little parting occurs along this plane, a brilliant flash almost invariably results.

"An exhaustive examination of the properties of the crystals was made in order to allow of some cause being assigned to this peculiar phenomenon; it was at first thought that the crystals might be hemimorphic or hemihedral and that the phosphorescence might be in some way related to the polar properties inseparable from hemimorphism. Some support seemed to be given to this view by the fact that the crystals are usually very unsymmetrically developed, the forms r(101) and c(001) being frequently represented by only one face each, and a hollow often taking the place of one of the faces of the basal plane; but these anomalies can only be accidental, for such a distribution of planes does not indicate any of the kinds of symmetry possible in the monosymmetric system.

"The completely holohedral nature of the crystals is shown pretty conclusively by the following methods: No evidence of pyroelectricity is obtained on heating and testing by Kundt's method; further, on cleaving a crystal parallel to a(100) and dusting with the electrified mixture of red lead and sulphur, no indication is obtained that the two surfaces acquire a difference of electrical potential such as might be expected if this form were perpendicular to a pyroelectric axis; no pyroelectricity is observed on heating the two cleaved surfaces. These facts seem to indicate that the phosphorescence is in no way connected with pyroelectric polarity, for the crystals phosphoresce brilliantly when parted along the plane a(100) although no evidence of pyroelectricity is obtained from the two parted surfaces."

Andreocci[1] found that dextrorotatory and levorotatory ethyl santonin are triboluminescent but the racemic modification is not. Brugnatelli[2] observed triboluminescence of a number of derivatives of santonin that was similar to the light emitted by saccharin. He was of the opinion that there was no connection between the luminescence and the optical activity, although the phenomenon was not observed with racemic modifications of the substances studied. He thought that there might possibly exist some connection between cleavage and triboluminescence since the luminescent santonin derivatives all show good cleavage and a particularly bright light resulted when the crystals were broken perpendicular to the axis of symmetry. He found on the other hand, that many substances like phenacetin which possess a good cleavage do not luminesce when crushed, while others which have no cleavage like dichlormethyl-paratolylsulphone show the phenomenon to a marked degree. In a later investigation of the triboluminescence of santonin derivatives Andreocci[3] concluded that there was some connection between the phenomenon and optical activity. His conclusions may be summarized as follows: 1. Two optical isomerides which are antipodes show the same behavior as regards luminescence; either both are triboluminescent or neither. 2. Crystals of racemic forms do not exhibit triboluminescence even though they may be derived from triboluminescent forms. 3. Optically active isomers which are not antipodes do not behave similarly with respect to triboluminescence. 4. Optically active double forms resulting from two non-antipodal components may be triboluminescent.

Tschugaeff[4] examined 400 organic substances and 110 inorganic substances for triboluminescence. He found that 30 percent of the former and only 5 percent of the latter were

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[1] Gazz. chim. ital., 25, 462-568 (1895). See pages 494, 513, 524.

[2] Zeit. Kryst. Min., 27, 78 (1897).

[3] Gazz. chim. ital., 29, 516 (1899).

[4] Ber. deutsch. chem. Ges., 34, 1820 (1891); Jour. Russ. Phys. Chem. Soc., 36, 1245 (1904).

triboluminescent, from which he concluded that the property was more particularly associated with organic compounds. "The phenomenon of triboluminescence is especially associated with certain cyclic atomic groupings. In my investigations the phenomenon was observed in 36 percent of the aromatic and hydroaromatic compounds and in only 13 percent of the aliphatic compounds." The intensity of the emitted light is in general greater in cyclic than in open chain carbon compounds.

"Furthermore, there appear to be certain atomic groups which may be termed lumiphores that exert a particularly favorable effect on the triboluminescence. To such groups belong hydroxyl, carbonyl and especially secondary and tertiary bound nitrogen. In harmony with this may be mentioned the fact that in the group of natural alkaloids the phenomenon occurs frequently and is often quite bright."

Tschugaeff pointed out additional examples of racemates that were not triboluminescent even though derived from triboluminescent forms. However, he states that: "These remarkable relations which appear to indicate the simultaneous destruction of the light due to the two optical antipodes, require additional confirmation; and notwithstanding the fact that my results agree with Andreocci's, the final solution of the matter can be reached only by the aid of new facts."

Gernez[1] examined 74 inorganic salts and 26 metallic salts of organic acids and found that every one emitted light when rubbed in a glass mortar with a platinum rod. From these results he concluded that the property of triboluminescence is not manifested especially by organic substances as suggested by Tschugaeff. Gernez[2] also tested the conclusion of Andreocci and of Tschugaeff that, when two optically active forms of a substance are triboluminescent the racemic compound is in general not triboluminescent. He points out that there are but six authentic cases that conform to the above rule as compared with a large number in opposition to it. I

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[1] Comptes rendus, 140, 1337 (1905).

[2] Ibid., 147, 11 (1908); Ann. Chim. Phys., (8) 15, 516 (1908).

have tabulated his results in Table I. D, L and R are the dextrorotatory, levorotatory and racemic forms, respectively. (+) means that the substance is triboluminescent and (—) denotes the opposite.

TABLE I

Substance	D	L	R
Tartaric acid	+	+	—
Neutral tartrates of K and NH_4	+	+	—
Double tartrates of Na and K	+	+	—
Neutral tartrates of Na and Tl	+	+	+
Acid tartrates of NH_4, K, Rb, Na and Tl	+	+	+
Double tartrates of NH_4-Li, SbO-K, Cs-Li, Li-K, Li-Rb, Li-Na, Li-Tl, Rb-Na, Na-Tl	+	+	+
Neutral tartrate of Li	—	—	+
Neutral tartrate of Rb	+	—	+
Neutral tartrates of quinine, strychnine and brucine	+	+	+
Acid tartrates of quinine, strychnine and brucine	+	+	+
Erythrytol	+	+	+

From the above results it is evident that there can be no hard and fast relation between molecular symmetry and triboluminescence. However, Ostromisslensky[1] is of the opinion that racemic modifications of triboluminescent substances are always non-luminescent. He gets around the numerous exceptions by assuming that they are not racemates but only physical mixtures of the two components. He admits that actual racemates may exhibit temporary luminescence and that the optically inactive compounds of such types as meso-tartaric acid may be triboluminescent.

Trautz and Schorigen[2] and Trautz[3] have called attention to the fact that many newly-formed crystals of certain substances show the phenomenon of triboluminescence quite well but that the property diminishes or even disappears with time. I will quote the views of Trautz on the possible nature of the phenomenon since they have a bearing on the later discussion:

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[1] Jour. Russ. phys. Chem. Soc., 42, 591, 607 (1910).

[2] Zeit. wiss. Phot., 3, 80 (1904).

[3] Zeit. phys. Chem., 53, 1 (1905).

"The known cases of triboluminescence may be considered as resulting from: 1. Gradual transformation into a form with another degree of symmetry. 2. Supersaturation phenomena. 3. Solid solution.

"Let us consider the first. In crystallography there are cases known in which one and the same substance shows a higher degree of symmetry of the crystal at higher than at lower temperatures. By lowering the temperature the angle of the plane of symmetry gradually changes. It is conceivable that this would produce a state of strain. In connection with this a potential difference may arise which may lead finally to a discharge within the crystal. This explains the readiness with which triboluminescence sometimes disappears but it is not quite clear why no luminescence appears by artificially changing the form of the crystal, since strained conditions must result from this also.

"The latter difficulty disappears by considering it a supersaturation phenomenon or a phenomenon of suspended transformation. Triboluminescent substances exhibit to a marked degree the tendency to supersaturate in solution and to supercool in the molten state. All the substances I studied exhibited this property.

"For temporary triboluminescence it is essential that sparks do not go entirely through the crystal but only to the interior. Accordingly the fissures which originate within the crystal frequently run exactly radially as I was able to observe very well in freshly prepared arsenic trioxide. Moreover, temporary triboluminescence results only in crystals which are formed in the regions of supersaturation—in regions where there is a marked decrease in temperature, as on the walls of the vessel the contents of which is not stirred. Furthermore, the refractive index of such isotropic crystals can not be determined sharply with the refractometer. This indicates that there may be a difference between the refractive power of the inside and outside of the crystal. This would agree with the conception that the interior of the crystal was in equilibrium in contact with a much more concentrated solution than the exterior; and that the equilibrium between the layers of the solid crystal itself can not keep up with the growth of new layers on account of the slowness of adjustment of equilibrium between solid substances. Hence there would be a difference between the inside and the outside of the crystal that would vanish with rising temperature, with time and with rubbing of the crystal. Corresponding to this is the possibility of a greater electrolytic dissociation in one part of a crystal than in another part; hence there may be an unequal distribution of ions which would distribute themselves equally after a while and probably recombine at least in part corresponding to the phenomenon in gases observed by Gunkell.[1] On account of the unequal distribution, potential differences are certain to result. Unfortunately the measurement of the dielectric constant of crystals is impossible since the difference to be expected would fall within the limit of experimental error.

"Analogous to this ion hypothesis, it is conceivable that in many triboluminescent crystals there may be solid solutions which undergo changes in concentration. As an example of this we may have a crystal containing K_2SO_4 and $KHSO_4$, the inside of which has a different composition than the outside. Under these conditions a state of strain may result."

In a later review of the subject of triboluminescence, Trautz[2] concludes that every case of triboluminescence is probably caused by small electric sparks induced by differences of potential resulting from irregularities in the crystal. Such irregularities may be produced by such things as thermal after-effects and by the presence of foreign substances or different modifications of the same substance. He expresses the opinion that the proximate cause of triboluminescence may differ in different cases, but the immediate cause is probably the difference of potential produced by strain.[3]

From a study of the triboluminescence of mineral sub-

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[1] Inaugural Dissertation, Marburg, 1905.

[2] Ion, 2, 77 (1910).

[3] Cf. Lindener: Bull. Acad. Sci. St. Petersburg, 6, 999 (1910).

stances Karl[1] concludes that pure substances are not triboluminescent[2] but that the property is always associated with solid solutions of a certain degree of dilution. Analogous to phosphorescence, he considers that triboluminescence requires the coexistence of large quantities of diluent with small quantities of impurity, which he terms the triboluminogen. This view is open to question, particularly since marked triboluminescence has been observed in substances that are apparently quite pure.[3]

As one might expect in dealing with a phenomenon of this kind, the results of different investigators do not always agree.[4] Indeed, Trautz found that different samples of the same substance even when crystallized from the same solution behaved differently. From this he concluded that triboluminescence is not a property of certain substances, but a property of certain samples of substances.

Vernadsky[5] associates the property of triboluminescence with the electrical properties of crystals; thus where triboluminescence occurs in crystals having a center of symmetry, pyroelectric and other electric properties also occur.[6] He believes that the luminescence is a surface phenomenon and that temporary triboluminescence is the result of a gradual alteration in the physical character of the crystal surface.

Ostromisslensky[7] believes that the property of triboluminescence depends only upon the system and structure of the crystal, the composition affecting it only in so far as the latter influences the crystalline form.[8] He maintains that permanent triboluminescence occurs only in those crystals which have no

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[1] Comptes rendus, 146, 1104 (1908).

[2] Cf. Pope: Nature, 59, 618 (1899).

[3] Cf. Trautz: Ion, 2, 77 (1910).

[4] Tschugaeff: Loc. cit.; Gernez: Loc. cit.; Trautz: Loc. cit.; Phys. Zeit., 10, 255 (1909).

[5] Bull. Acad. Sci. St. Petersburg, 6, 1037 (1910).

[6] Cf. however, Pope: Jour. Chem. Soc., 67, 985 (1895).

[7] Jour. Russ. Phys. Chem. Soc., 42, 591 (1910).

[8] Cf. however, Imhoff: Phys. Zeit., 18, 78, 374 (1918); Science Abstracts, 20A, 226,531 (1918).

center of symmetry. Exceptions to this rule observed by Tschugaeff, Trautz, Gernez, Karl, Vernadsky and others, he considers are either cases of temporary luminescence or are cases in which the crystalline form has not yet been determined accurately.

Theoretical

From the above survey one can not help being impressed by the unsatisfactory nature of the various hypotheses advanced to explain the cause of triboluminescence. On account of the small amount of friction necessary to produce the phenomenon in certain cases it can be due neither to a temperature radiation nor frictional electricity. It is apparently not a question of the crystal structure, since it is associated with various forms of crystals of both inorganic and organic substances. Indeed triboluminescence is not confined to crystalline substances, but is shown by a small number of amorphous substances which also exist in crystal form.[1] The conception that the cause is a difference of potential due to strain is open to the objection already quoted from Trautz's paper. Furthermore, if the light is merely an electrical discharge between oppositely charged portions of a crystal, one might ordinarily expect to get white light, whereas the luminescence is very seldom white but is red, orange, yellow, or varying shades of blue and violet, depending on the substance.

It seems altogether probable that the failure to arrive at anything like a satisfactory explanation of the cause of triboluminescence is the result of an attempt on the part of almost all investigators in this field to trace it to a purely physical origin. However, Bancroft[2] has deduced from analogy with other cases of chemiluminescence that, "it seems safe to assume that crystalloluminescence and triboluminescence are cases of chemiluminescence." As I pointed out in a recent communication,[3] it is usual to consider the phenomenon of crystallo-

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[1] Imhoff: Loc. cit.

[2] Jour. Franklin Inst., **175**, 129 (1913).

[3] Weiser: Jour. Phys. Chem., **22**, 482 (1918).

luminescence as a special case of triboluminescence.[1] In the absence of a suitable theory to explain the latter phenomenon, such a classification is of doubtful value except in so far as it calls attention to a probable similarity between the two. In my paper above referred to, it was demonstrated that crystalloluminescence is the result of chemical action; and since all crystalloluminescent substances show the phenomenon of triboluminescence, it was suggested that triboluminescence was also the result of chemical action; and in the case of those substances that exhibit both phenomena, that the two are identical so far as the chemical reaction and hence the luminescence is concerned, differing only in the physical process employed to bring about the reaction. It is an interesting fact that practically all the well-defined cases of crystalloluminescence are to be found among inorganic salts that undergo electrolytic dissociation. The reaction which emits the light when these are precipitated from solution is the rapid recombination of the ions with the formation of the non-dissociated salt. If, as suggested, the triboluminescence is identical with the crystalloluminescence, then the trituration must result in a splitting apart of the molecules the recombination of which emits light. This is not at all unlikely. It is evident that a state of strain may exist in crystals as a result of conditions attending their formation. In the passage above quoted, Trautz has called attention to some of the things that may contribute to this. When force is applied to a crystal from without it adds on to the greater or less strained condition that already exists; and when the crystal breaks down under what may be relative enormous internal forces, it is altogether likely that certain molecules will be split apart. We know that a similar thing happens when cathode and anode rays act on salts. The impact of the particles decomposes molecules and the recombination results in the emission of light.[2]

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[1] Trautz and Schorigen: Loc. cit.; Trautz: Loc. cit.; Gernez: Comptes rendus, 140, 1134 (1905); Ann. Chim. Phys., (8) 15, 514 (1908).

[2] Wiedemann and Schmidt: Wied. Ann., 56, 203 (1895); Wilkinson: Jour. Phys. Chem., 13, 691 (1909).

In the case of substances which show only temporary triboluminescence, so-called, the particularly strained conditions that exist in certain newly formed crystals (but gradually disappear on standing) is essential for getting a sufficiently violent destruction of the crystal to cause a breaking up of molecules. Indeed, in certain cases this state of strain may be so great that the application of relatively little outside force is necessary. But altogether apart from this, certain salts and certain samples of the same salt are more triboluminescent than others, just as certain salts show the phenomenon of cathodoluminescence or anodoluminescence to a much greater extent than others. This is due to two things: The comparative forces necessary to break up the molecule in different cases; and the magnitude of the conversion factor for light in the recombination reaction. However, I should expect a substance that shows a marked triboluminescence to show a marked cathodoluminescence or anodoluminescence; and a substance which shows only temporary triboluminescence to show the property of cathodoluminescence or anodoluminescence to a marked degree when newly formed than when old. I hope to get definite evidence on this in the near future.

So far as the luminescence of simple inorganic salts is concerned, the evidence indicates that the light is produced by the reaction of recombination rather than the reverse process of decomposition.[1] When it comes to the various classes of organic compounds the nature of the reaction which produces the triboluminescence must vary widely in different cases. However, some progress has been made in determining the specific reaction which produces the triboluminescence of certain organic compounds. This will be considered in a subsequent communication.

That all triboluminescent substances are not also crystalloluminescent; and that all the well-defined cases of the latter phenomenon are to be found among inorganic salts, are due to the fact that the breaking up or disarrangement of the

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[1] Wilkinson: Loc. cit.; Bancroft and Weiser: Jour. Phys. Chem., 18, 213, 281, 762 (1914); 19, 310 (1915).

molecule (other than by ionization in solution) is usually accomplished only by the more vigorous rubbing or grinding of crystals.

If, as suggested, triboluminescence is due to chemical action and the specific reaction is identical with that which causes crystalloluminescence in those substances which show both phenomena, then it follows that the light emitted during precipitation and during trituration of a given substance should be quantitatively identical. The results of the experiments which will now be described, confirm this conclusion.

Experiments with Arsenic Trioxide

The Crystalloluminescence of Arsenic Trioxide.—The crystalloluminescence of arsenic trioxide was first observed by Rose,[1] who believed that the luminescence was the result of the transformation from the amorphous to the crystalline modification.

This hypothesis was disproven by Bandrowski,[2] who showed that the crystallization from a solution of either the crystalline or amorphous substance in hydrochloric, hydrobromic or sulphuric acid, was accompanied by an emission of light. He further showed in the particular case of the solution in hydrochloric acid that the best results were obtained when the constituents were in the definite proportion represented by the equation $As_2O_3 + 6HCl = AsCl_3 + 3H_2O$.

Of the procedures tried the following proved to be the most successful: Sixty grams of arsenic trioxide were dissolved in 260 cc of hydrochloric acid, specific gravity 1.12, and to this was added 340 cc of hot water. After bringing the solution to the boiling point, it was set aside in the dark room to cool, without agitation. After fifteen or twenty minutes occasional sparks appeared. When these had become quite numerous, the beaker was immersed for several seconds in a freezing mixture at a temperature of approximately $-5°$. It was then withdrawn and the solution stirred vigorously.

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[1] Pogg. Ann., 35, 481 (1835); Ann. Chim. Phys., (2) 61, 288 (1835).

[2] Zeit. phys. Chem., 17, 234 (1895).

The rapid precipitation was accompanied by a marked luminescence throughout the solution.

Since it has been found that spectrographs of the strongest phenomena of crystalloluminescence and triboluminescence cannot be obtained,[1] the color of the emitted light was determined by a method previously described in detail,[2] which consists in exposing a panchromatic plate to the luminescence, interposing a series of different colored ray filters between the source of light and the plate. By comparing the photograph so obtained with a photograph of white light made with the same filters, the color of the faint luminescence may be determined with a degree of accuracy limited only by the number and choice of the ray filters employed. The luminescence of arsenic trioxide was photographed in a "camera" similar to that previously used.[3] The apparatus formerly described was so modified that an 80 cc beaker in which the precipitation was carried out, could be held firmly in place about 5 mm from the plate. The amount of the plate exposed and the width of the filters were materially increased. Wratten and Wainwright panchromatic plates were employed. The filters used are listed in Table II, and the photographs of white light and of the luminescence are reproduced in Figure I, *a* and *b*, respectively.

It is evident from the photographs that there is no red or yellow light in the luminescence, since the plate was not fogged behind filters 1, 2 and 3. There is also relatively little green since there was little fogging behind filters 4, 5 and 6. The fogging was less behind 4 than behind 6, which allows more blue-green through. From the blue-green, through the violet the luminescence is very similar to white light. To show this more conclusively, a plate was exposed to the luminescence a number of times in the same place. The resultant photograph is reproduced in Figure I, *c*. As may be seen, the plate was very much overexposed behind the blues, but it was

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[1] Trautz: Zeit. phys. Chem., 53, 101 (1905).

[2] Weiser: Jour. Phys. Chem., 22, 442 (1918).

[3] Ibid., 22, 443 (1918).

unaffected behind the red and yellow and was fogged but little behind the greens.

TABLE II

Number	Color of filter	Light that passes through filter
1	Red	Red to lithium beta line
2	Orange	Red to left of calcium beta line
3	Yellow	Red to thallium line
4	Green	From lithium beta line to barium delta line. Small band in red
5	Green	From lithium beta line to barium alpha line
6	Green	From lithium beta line to barium beta band
7	Greenish blue	From left of calcium beta line faintly to left of indium alpha line
8	Blue	From right of thallium alpha line to beyond the indium alpha line
9	Blue	From thallium line to indium alpha line
10	Purple	From strontium delta line through the extreme violet red to lithium alpha line
11	Blue	From left of barium beta band to midway between indium alpha line and rubidium beta line
12	Blue	From left of barium beta band to indium alpha line
13	Blue	Blue only

The Triboluminescence of Arsenic Trioxide.—Triboluminescence of arsenic trioxide is readily obtained, particularly if newly formed crystals are rubbed or crushed. In order to obtain a photograph of the light with the color screens, it is necessary to effect the breaking up of the crystals in such a way that a uniform glow will result. This was accomplished in the following way: A carefully chosen 800 cc pyrex beaker was filled with a boiling solution of arsenic trioxide in hydrochloric acid of the composition above suggested. The solution was allowed to cool slowly until considerable luminescence was observed, after which the beaker was placed in ice water, where it was kept until the solution cooled to 15°. By this means the sides of the beaker were coated uniformly with crystals of arsenic trioxide that adhered firmly. After pouring out the solution and rinsing the beaker several times with water, the latter was inverted and allowed to drain thoroughly. To secure a uniform luminescence it was only necessary to rub the coated sides of the beaker with uniform pressure.

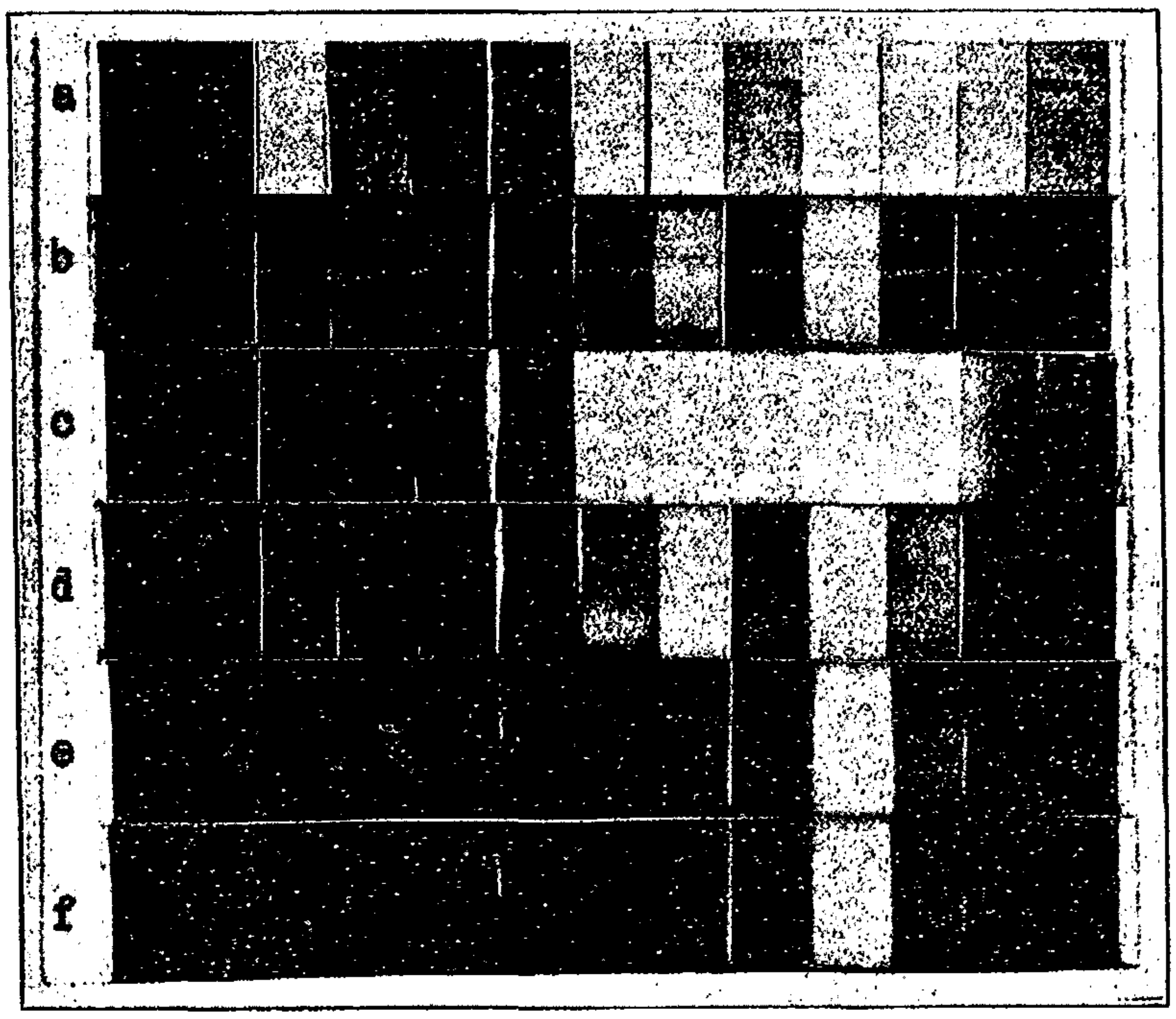

Fig. 1

This was accomplished with a glass tube 5 cm in diameter and 12.5 cm in length, the ends of which were rounded to prevent scratching the beaker. To expose the plate, the loaded "camera" was first placed flat on the table and the beaker was laid on the side, above the plate, after which the glass tube was moved back and forth over the crystals causing them to emit a relatively bright light. After preliminary trials showed that a uniform exposure of the plate could be secured in this way, a photograph was taken, using the same filters as were used in photographing the crystalloluminescence. The photograph is reproduced in Figure I, *d*. A comparison of the photographs shows that the color of the triboluminescence is quantitatively identical with the crystalloluminescence. It is evident also that Guinchant's[1] conclusion as to the color of the triboluminescence of arsenic trioxide, is incorrect, namely that: "the emitted light appears to be identical with the incandescence of a solid body; indeed the origin is the same."

The Combustion of Arsenic in Oxygen.—When metallic arsenic is heated in a current of oxygen it catches fire, burning with a blue flame. Depending on the rapidity of the combustion, the color of the luminescence may be modified to a greater or lesser degree by the lemon-yellow vapors of arsenic and the solid particles of arsenic trioxide which may be heated to incandescence. Similar to the flame reactions of sodium, it is probable that arsenic ion is an intermediate product in the combustion of the metal and that the reaction which emits the characteristic blue is that from arsenic as ion to the nondissociated oxide or salt.

When an arsenic compound like the oxide, chloride or hydride is fed into a coal gas or hydrogen flame, the latter is colored a distinct blue, similar to the luminescence obtained by the direct union of the metal and oxygen. Since, under suitable conditions arsenic oxide may be precipitated on a cold tube from the hottest part of the flame and arsenic trioxide from the cooler portion,[2] it is evident that the reaction from arsenic ion to the non-dissociated oxide or salt is taking place within the flame, giving to the flame the characteristic blue color. Of course, any "arsenic" flame is modified[3] by the vapors of metallic arsenic and particularly by the white light resulting from the incandescence of solid particles of arsenic trioxide.

The obvious conclusion to be drawn from the above

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[1] Comptes rendus, 140, 1170 (1905).

[2] Bancroft and Weiser: Jour. Phys. Chem., 18, 256 (1914).

[3] Cf. Bancroft and Weiser: Jour. Phys. Chem., 18, 281 (1914).

experiments is that the blue crystalloluminescence, triboluminescence, and flame luminescence are due to one and the same chemical reaction, the only difference being in the actual way in which the reaction is brought about.

Experiments with Potassium Sulphate

The Crystalloluminescence of Potassium Sulphate.—Crystalloluminescence of potassium sulphate was first observed by Pickel.[1] Rose[2] fused potassium sulphate with other salts (*e. g.*, sodium chloride, sodium sulphate and potassium carbonate) and observed crystalloluminescence when the resulting mixtures were allowed to crystallize from their solutions in water. Bandrowski[3] studied the crystalloluminescence of a solution of potassium sulphate to which sodium sulphate was added and found the best results when the crystallization took place from a solution containing two mols of potassium sulphate to one of sodium sulphate. The precipitated crystals under these conditions had the composition of $2K_2SO_4.Na_2SO_4$. Gernez[4] found that sodium sulphate could be replaced by other salts and that the phenomenon was exhibited by potassium sulphate alone.

After numerous attempts to get a good crystalloluminescent solution that would deposit crystals sufficiently triboluminescent to photograph, the following procedure was adopted, which is essentially the same as recommended by Bandrowski: A quantity of the sulphates of sodium and potassium in the proportion of two mols of the former to one of the latter, was placed in a three-liter beaker and completely dissolved in water. After evaporating until crystals began to separate, the solution was poured into 800 cc pyrex beakers and set in the dark room to cool slowly, without agitation. After flashes began to appear in rapid succession, the beakers were set in ice water for a short time, after which they were

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[1] Taschenbuch fur Scheidekünster, 55 (1787).

[2] Pogg. Ann., 52, 433, 585 (1841).

[3] Zeit. phys. Chem., 17, 238 (1895).

[4] Comptes rendus, 140, 1234 (1905).

removed and the contents stirred vigorously. The luminescence was bright, but less so than with arsenic trioxide, so that more exposures were necessary to get a good photograph. The same filters were used as in the previous experiment. The photograph is reproduced in Figure I, *e*. It will be seen that the luminescence is similar to that of arsenic trioxide in that it contains no red or yellow. It differs from it, however, in that it contains no green and comparatively little blue-green.

The Triboluminescence of Potassium Sulphate.—The crystals obtained from the above solution were quite triboluminescent and a photograph was obtained by the method previously described. The crystals do not adhere to the walls of the beaker so well as the arsenic trioxide crystals; accordingly the loose ones were poured on a Büchner funnel and dried. From time to time during the trituration process, small portions of the loose crystals were distributed evenly among those stuck to the walls of the beaker. In this way good results were obtained. The photograph obtained is reproduced in Figure I, *f*. As may be seen, the color of the light is the same as that emitted during precipitation.

Similar experiments could be carried out with other salts, but the above are sufficient to show that in the case of those substances which exhibit both crystalloluminescence and triboluminescence, the two phenomena are identical so far as the chemical reaction and hence the color of the luminescence are concerned.

The conclusions to be drawn from this investigation are as follows:

(1) Triboluminescence like crystalloluminescence, is caused by chemical action.

(2) In the case of substances which show both triboluminescence and crystalloluminescence, the chemical reaction and hence the color of the luminescence are identical.

(3) The identity of the crystalloluminescence and triboluminescence of arsenic trioxide and of potassium sulphate have been shown photographically.

(4) The color of the luminescence is specific, depending on the chemical reaction by which it is caused.

(5) A large number of substances exhibit the property of triboluminescence, but relatively few show crystalloluminescence. All the well-defined cases of the latter are to be found among the simple inorganic salts.

(6) The crystalloluminescence of inorganic substances is due to the rapid reformation of molecules broken up by the process of electrolytic dissociation; triboluminescence of the same substances is due to the rapid reformation of molecules broken up by violent disruption of crystals.

(7) All crystalloluminescent substances show the property of triboluminescence, but the reverse is not true. That all triboluminescent substances are not also crystalloluminescent is due to the fact that sufficient breaking up or disarrangement of molecules (other than by ionization in solution) is usually accomplished only by the grinding or crushing of crystals.

(8) Due to conditions attending their formation, a state of strain may exist in certain newly-formed crystals that will disappear with time. If outside force is applied to such crystals before the internal forces have become adjusted, the combined effect may result in a particularly violent disruption of the crystal with a correspondingly marked molecular decomposition and consequent triboluminescence.

(9) The intensity of triboluminescence varies widely in different substances. Two causes contribute to this: The comparative forces necessary to break up the molecule in different cases; and the magnitude of the conversion factor for light in the luminescent reaction.

Department of Chemistry
The Rice Institute
Houston, Texas

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NEW BOOKS

Physical Chemistry of Vital Phenomena. *By J. F. McClendon. 23 × 15 cm; pp. viii + 240. Princeton: Princeton University Press, 1917. Price: $2.00.* —In the preface the author says that the need for special teaching in the application of the simpler aspects of physical chemistry to biology was first realized by himself while attempting to teach physics and physiology to the same group of college students in 1906. The purpose of the book is not to go far in physical chemistry but to develop a tool for physiological research. The titles of the chapters are: introduction; electrolytic dissociation; osmotic pressure; hydrogen and hydroxyl-ion concentration and carbon dioxide pressure; surface tension and adsorption; electrolytes, non-electrolytes and colloids; enzyme action; changes in permeability of plant cells; negative osmose and the polarization of membranes in relation to the biological phenomena, stimulation, absorption, and secretion; cytolysis and disinfection; ameboid motion and tropisms, cell division, fertilization, and parthenogenesis; muscular contraction, oxidation and heat and light production; blood and other cell media.

It is rather a pity that the author did not get some candid friend to revise his physical chemistry. On p. 4 he says that ions of opposite charge combine when they meet. This is a staggerer for the electrolytic dissociation theory, if true. The same idea appears on p. 17. "If silver nitrate is added to the solution of any chloride, a white cloud of $AgCl$ is instantly formed because $Ag^{\cdot}$ unites with Cl', the two being drawn together by their electrical charges." On p. 14 there is another surprising statement. "The greater the hydration of an ion the less is its speed, hence the speed is supposed by some writers to decrease with decrease in concentration until maximal hydration occurs. When such a dilution is reached, further dilution evolves no heat and the solution is called dilute." It may be true to say, p. 24, that weak electrolytes obey the law of mass action and therefore their ions must obey it, but it is an unfortunate phrasing. Rudolphi and van't Hoff suggested different forms of the dilution law and neither form coincided with the one ascribed to them, p. 25.

It is not true to say, p. 25, that it was found by de Vries, Pfeffer and others that one gram-molecule of a non-electrolyte, such as dextrose, dissolved in water to make one liter has an osmotic pressure of 22.4 atmospheres at 0°. On p. 31 is the remarkable statement that the Beckmann thermometer has the disadvantage that the zero point must be determined every year. The discussion of adsorption, p. 58, is distinctly bad and since sodium chloride does not dissolve in benzene any way, it seems a waste of time to deduce, p. 93, that benzene will take no sodium chloride from an aqueous solution at infinite dilution.

On the other hand there are a great many interesting things in the book as the following quotations will show, pp. 118, 124, 128, 132, 138, 148, 155, 183, 184:

"The electromotive forces produced by living matter have always been a subject of interest, if not amazement. The shock of some electric fish is several hundred volts, and may be felt while the fish is entirely submerged in sea water. On the other hand the ordinary electric potential differences observed in living matter never reach 0.1 volt. The secret of the electrical organ lies in the connection of the cells in series. Brünings observed that if one frog's skin is laid on another, the electromotive force is doubled. In the same way he found the electromotive force of two concentration cells with porcelain membranes to be doubled when they were connected in series."

"The rate of propagation of the excitatory impulse may be 1 mm per second in some plants and 12,000 in mammals. It is probably very slow over the bodies of nerve cells and motor end plates, as there is some delay in conduction through these regions. Mayer found that nerve conduction varies almost as the concentration of electrolytes around the nerve. Lillie supposed nerve conductions to vary with electric conductivity but Mayer has not observed an exact parallel."

"Modern theories of electrical stimulation depend on membrane polarization. Nernst accidentally passed through his body a high frequency Tesla current of enormous voltage and observed no stimulation. This led him to formulate his theory of electric stimulation, according to which the current must carry a certain number of coulombs of electricity per unit cross-section before it is reversed, in order to stimulate. In other words, stimulation is due to polarization of membranes and the polarization must reach a certain minimal value."

"If the turgor of living cells is due to electro-endosmose, dead cells should dry in air sooner than live ones. This fact is the teleological principle involved in the instinct of certain wasps who store spiders with the eggs so that the larvae may have food. If the spiders are killed, they dry up before the eggs hatch, hence the necessity of keeping them alive. The wasp stings the spider in its central nervous system so that it remains alive in a paralytic condition."

"Although Battelli and Stern claim that anesthetics precipitate proteins, Traube and Köhler, and Traube assert that anesthetics help in the solution of proteins....They have arranged anesthetics according to their power of hastening the swelling and isolation of gelatin jelly (and retarding gelatin of sols). It is found that they are with few exceptions in the order of anesthetic power."

"It was shown by Quincke that movements of drops of fluid, resembling ameboid motion, could be produced by localized changes in surface tension. A local reduction in surface tension produces a protrusion of the affected surface—a localized increase produces a flattening. By a combination of such changes in surface tension, combined with adhesions to the substratum and to food particles, Rhumbler has imitated all forms of ameboid motion. In imitating food taking, Rhumbler found that his artificial amebae would take only such food as adhered to them. A chloroform drop would engulf a piece of shellac but would not take a piece of glass. If a piece of glass is coated with shellac, the chloroform drop will engulf it, but after the shellac is dissolved off it will reject the glass. In this way the process of defecation by the ameba is imitated. Such a process also imitates the shell building of some protozoa. These shells are formed of defecated particles which cover the surface of the protozoon. If chloroform is shaken with powdered glass and dropped into water, the drops are found to be surrounded by shells composed of particles of glass."

"The perception of light is perhaps beyond the pale of physical chemistry at present. It should be noted, however, that many of the devices used in photography were first used in the construction of the eyes of animals. Even the Lumière plate for color photography is represented by the retina of turtles and diurnal birds, which is covered with red and orange oil droplets. These are absent in the eyes of nocturnal birds. The rods and cones beneath a red oil drop can be affected by red rays only and those beneath a yellow drop by yellow rays only, whereas those not covered by oil drops would be affected chiefly by the more effective blue rays. In this way a mechanism for color vision is provided, but whether it functions as such has not been determined."

"Hasselbach and Gammeltoft observed a lowering of the CO_2 tension on a meat diet. This suggests an explanation of the so-called dynamic action of protein (Lusk). On passing from a protein-poor to a protein-rich diet the heat output of the body is increased even though the available energy of the food is not. Since the CO_2 tension of the alveolar air is decreased, the lung ventilation must be increased and the oxygen carried to the tissues increased as well. Perhaps the greater heat production is the direct result of this increased oxygen supply. If this be true, we may suppose that the amino acids arising from digestion of the protein increase the hydrogen-ion concentration of the blood, and stimulate the respiratory center, increasing lung ventilation, this in turn increasing oxidation. Since the respiratory center is more sensitive to changes in hydrogen-ion concentration than any apparatus available for measuring it, a failure to determine any increase in the hydrogen-ion concentration of the blood is to be expected. It was shown by Haldane and Priestley that a 0.2 percent rise in the CO_2 tension of the alveolar air doubles lung ventilation. This causes only a minute change in the hydrogen-ion concentration (a change too small to measure with certainty on a carbonated fluid like the blood). We may conclude from the foregoing that the buffer value of the blood is lowered by a meat diet. The same seems to be produced during exercise, acclimatization to high altitudes, diabetic coma, and other conditions of acidosis. On the other hand the experiments of Van Slyke, Cullen and Stillman indicate that the buffer value of the blood is increased during protein digestion. This may be due to the passage of chlorine ions from the blood to the stomach with consequent increase in the bicarbonate content of the blood."

"It is maintained by A. B. Macallum that the salt composition of the blood of mammals is the same as that of the sea during the Cambrian period. In passing from the marine invertebrates (the osmotic pressure and the proportions of whose blood salts is the same as those of the sea) to the mammals, there is a gradual lowering of the osmotic pressure and of the magnesium content of the blood. Macallum supposes that the evolution of the sea took the reverse direction and the osmotic pressure and magnesium content was low during the Cambrian period. The osmotic pressure is constantly increased owing to the accumulation of salts carried in by rivers, which now carry a greater proportion of calcium and magnesium salts. But the calcium is constantly being precipitated since the sea is about saturated with calcite and the magnesium content alone is relatively increasing."

The author is to be congratulated upon trying to write a book like this. While the book would have been better had he taken more pains with it, it is an interesting and suggestive one, even if not authoritative. *Wilder D. Bancroft*

Electric Furnaces in the Iron and Steel Industry. *By W. Rodenhauser, J. Schoenawa and C. H. Von Baur. Second edition. 23 × 16 cm; pp. xix + 429. New York: John Wiley and Sons, 1917. Price: $3.75.*—The first edition of Von Baur's translation of Rodenbauser and Schoenawa's German work, which appeared in 1913, was undoubtedly the most valuable book in English which we possessed in this field. It has already been reviewed (18, 78). In the preface to the present edition, the author and translator says:

"The belief expressed in the writer's preface five years ago has been well borne out. To-day there are over 212 electric furnaces in the iron and steel industry in the United States and Canada out of a total of 562. Over half a million tons of electric steel are being made annually the world over, and production only started less than a score of years ago.... The average size of furnaces has also steadily increased, together with the number of days they are in operation yearly. Several newcomers have made their appearance, with the usual pain and effort accompanying such creations."

In the present edition the first has been more or less rewritten and considerably enlarged. It has been brought down to date by the inclusion of a chapter on the Rennerfelt furnace (pp. 161–171) and descriptions of the Greaves-Etchells and Snyder furnaces (pp. 261–263). The chapter on electrometallurgy of iron and steel has been enlarged to include some of the more recent Scandinavian and Californian developments.

The second edition is fully equal in quality to the first one and should continue to be the standard of reference in one of the most interesting and rapidly developing fields of electrochemistry. *T. R. Briggs*

Principles of Quantitative Analysis. *By W. C. Blasdale. Second revised and enlarged edition. 19 × 13 cm; pp. xii + 402. New York: D. Van Nostrand Company, 1917. Price: $2.50.*—The plan, as outlined in the first edition, is to present the entire field of quantitative analysis "from the standpoint of a comprehensive scheme of classification, which is based upon the different types of chemical and physical equilibrium." In the preface to the second edition the author expresses his belief that this method of presenting the subject of quantitative analysis is "an improvement over that heretofore in general use, at least when students of a sufficient degree of maturity are concerned and where the training which it is desired to give them is not of a specialized character."

The subject is divided into ten sections: general features of gravimetric processes; gravimetric gas-evolution processes; gravimetric precipitation processes; gravimetric solution and extraction processes; partition processes; general features of volumetric processes; volumetric processes involving precipitation; volumetric processes involving neutralization; volumetric processes involving oxidation; physicochemical processes.

It seems to the reviewer that too much stress has been laid on quantitative theory. The average student will probably get the idea that shaking out with ether depends upon the distribution coefficient being a constant, p. 221, in spite of the rather perfunctory paragraph on p. 224. In a great many places ions are brought in without any obvious necessity for it. The book is written to bring in as much physical chemistry as possible whereas this should be kept down to the minimum. A few errors have crept in. The definition of consolute liquids is wrong, p. 221. Methyl orange is a weak base and not a strong acid, p. 290. No hint is given, p. 308, why glycerine or mannitol should increase the acidic properties of boric acid.

There is an interesting paragraph on p. 238. "A principle which can be used to great advantage in volumetric processes is that of counteracting the errors involved in the actual determination by equal errors in the standardization of the solutions used. Assuming that there is always a discrepancy between the true and the observed endpoint, it will generally be true that this discrepancy will be constant so long as the conditions remain constant. If the solution is standardized under exactly the same conditions as those which must obtain in the actual determination, practically all errors are eliminated as the standard solution used becomes merely an instrument, by means of which the strengths of two solutions of the same substance, one representing a known amount of a pure compound and the other the solution of unknown concentration, are compared. Considered from this point of view it is preferable to standardize the solution by comparing with a known weight of the substance being determined, and wherever it is possible to use the same solution for the determination of a number of substances, strict accuracy would demand that the solution be re-standardized for every one of the substances, for which it is to be used."

Wilder D. Bancroft

Van Nostrand's Chemical Annual. *By John C. Olsen. Revised fourth edition. 19 × 13 xm; pp. xviii + 778. New York: D. Van Nostrand Company, 1918. Price: $3.00.*—In the preface the author says: "In the preparation of the fourth issue of the Chemical Annual a very thorough revision of all tables has been made. Molecular weights and factors have been recalculated in accordance with the 1917 table of atomic weights. All physical constants of the elements have been revised in accordance with new data which have been published. New compounds have been added to the tables in the endeavor to include substances which have come into common use. In many cases this has not been possible because the properties of such compounds have not been studied or the results of such studies published. About 48 new tables have been added. Some of these replace tables previously published as the newer tables are considered more accurate or reliable. The new tables include tables on the properties of the elements, tables bearing on calibration and the true volume of glass vessels, the use of indicators, the properties of oils, alloys, glass, etc., specific-gravity tables, vapor pressure, units of weights and measures, the capacity of tanks, conversion of units of heat, electricity, temperature, etc., freezing-point mixtures, etc."

That is a very impressive list of changes and it is to be hoped that the 1918 Annual will have the sale to which it is entitled. *Wilder D. Bancroft*

THE COLORS OF COLLOIDS. I

BY WILDER D. BANCROFT

Introduction

The colors of colloids are the colors of bubbles, drops, grains, filaments, and films. The literature on the subject is so scattered that it has seemed desirable to bring together what we know about the colors of two-phase systems.

When white light passes through a material, homogeneous medium of appreciable but not too great thickness, there is always a certain amount of light absorbed; but we ordinarily speak of a substance as transparent if it transmits the range of wave-lengths known as the visible spectrum without appreciable absorption. If a sufficiently thick layer be employed, a so-called transparent liquid will often show absorption in the visible spectrum.[1] Pure water is one of the most transparent substances we have; but a long column of it appears distinctly blue, showing that it absorbs the red end of the spectrum more or less completely. Most varieties of glass show absorption when a sufficiently thick layer is examined. The definition of transparency is therefore an arbitrary one, there being no such thing in nature as a perfectly transparent substance.

The so-called transparent liquids often show powerful absorption in the infra-red and ultra-violet regions, though this cannot be detected by the eye. When there is a marked absorption in the visible spectrum, the substance is called colored, the color being that of the transmitted light. This has been discussed at some length by von Bezold.[2] Suppose we have sunlight passing through a slit in a window shutter and then through a prism to a screen in an otherwise dark room. "If one places a red glass (a so-called flashed glass, colored with cuprous oxide) before the slit in the shutter,

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[1] Wood: "Physical Optics," 436 (1911).

[2] "Die Farbenlehre," 40, 46 (1874).

only red light and no white light comes into the room. If this light passes through the prism, only red and orange are to be seen in the spectrum, the other colors being missing. The red and the orange have not changed their position or their extension, as can be shown by only covering the upper half of the slit with the red glass. We get then the complete spectrum of white light and, close above, the light which has passed through the red glass. It is easy to see that the other colors have disappeared. There are two possible explanations for this phenomenon. Either the red glass has cut out and absorbed all the rays except the red or it has converted these other rays into red. It is easy to determine which of these two hypotheses is right. If one throws the spectrum of the sun upon the screen in the usual way and if one then passes a narrow strip of the same red glass through the rays, the glass casts no perceptible shadow on the screen so long as it is in the path of the red and orange rays; but it casts a black shadow upon the screen when the strip is placed in front of the green, blue or violet rays. [This formation of a shadow in the blue, for instance, is not accompanied by any increased brightness in the red portion of the spectrum.] So far as the red and orange rays are concerned, the red glass behaves just like ordinary colorless window glass, whereas, it behaves like an opaque substance to all other rays, like a black glass, in fact. Red glass therefore lets red and orange rays through and destroys all the other colors of the spectrum.

"It must therefore be a matter of indifference whether one puts the red glass in front of the slit or whether one puts a sheet of the same glass across the light rays anywhere between the prism and the screen. The same spectra are obtained in the two cases. There is still another way in which this point of view can be tested. If the action of the red glass is due solely to the fact that it is transparent for certain rays and not for others, it is immaterial at what point between the source of light and the eye the glass is inserted. One can place the red glass close to the eye and look through it at the spectrum projected on the screen. Again one sees only the red end of the spectrum because the light from the other portions does not get through the red glass.

"Similar results are obtained if one substitutes a glass of another color or a clear but colored liquid in a bottle or cell. One always sees spectra in which certain colors of the solar spectrum are lacking and that color predominates which the unaided eye recognizes as that of the colored substance. For instance, if a blue cobalt glass is used, one obtains a spectrum with the whole middle cut out. Only blue comes through and a very narrow strip of red. . .

"Pigments and colored substances in general take out of the light falling upon them certain rays of definite wave-length and absorb them, letting through or reflecting back[1] the other rays, depending on whether they are transparent or opaque. The process taking place in a dye is the arithmetical one of substraction. Certain simple rays are taken out of the incident light and sent back while the others are destroyed. If the incident light lacks those rays which the substance can reflect back, the substance appears black. If the source of light contains some of them but not all, the substance will appear of a different color from that shown in white light and which we call its characteristic color. These two generalizations can be illustrated by a number of very simple experiments and account for many well-known facts.

"It is now easy to see why white is the brightest of all colors. The study of a white strip of paper by means of the prism shows that such a paper reflects all the rays, though not in full intensity but at least cut down uniformly, whereas all other colors destroy some part of the incident light and weaken the other rays at least as much as white substances do. It is also easy to see why white substances always appear the color of the light which falls upon them. If one illuminates a white surface with red light by means of a red flame or by letting the light pass through a red glass, the surface appears red. If, however, differently colored substances are illuminated by

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[1] [As we shall see later, this statement in regard to reflections is not quite accurate, for a substance may reflect rays which it absorbs. W. D. B.]

monochromatic light, they all appear in more or less light shades of that color, depending whether they absorb more or less of the monochromatic light which is assumed to fall upon them. The simplest way to obtain really monochromatic light is to put sodium chloride in an alcohol flame or, better still, in a non-luminous gas flame. Such a flame emits a pure yellow light having the wave-length of the D lines. The spectrum consists of a single yellow line, which corresponds exactly with the dark D line of the solar spectrum and which like that can be broken up by a powerful spectroscope into three lines very close together.

"If one lights such a flame in an otherwise completely dark room, one sees gradations from yellow to black but no other colors. The whole room with all its contents produces the effect of a picture painted in gray on gray, seen through a yellow glass. Red-vermilion reflects back very little yellow light in this wave-length, and therefore a surface painted with vermilion appears a pure gray in this light. The human face seems livid and red cheeks sunken and hollow. A sample color chart shows only gray. If one now lights an ordinary candle or a piece of wood, the manifold colors appear again and the spectator feels himself freed from discomfort and pressure. From these experiments on the absorption by colored materials, it is easy to see that a substance shows its color most brightly when it is illuminated by light of the same color. In this case the minimum possible of the light is absorbed and practically all of the light either passes through or is reflected back. Every colored substance behaves like a white one towards light of its own color. If one illuminates red figures on a white ground with red light, the figures disappear.

"The simplest way to obtain light of a color like that of the characteristic color of a substance is to have light reflected from that substance. If the light which has been reflected from one portion of a given substance is reflected again from another portion, it is weakened very much less the second time. Since the colored light is usually accompanied by a good deal of white light after the first reflection, this latter is what is absorbed mostly at the time of the second reflection. By repeated reflections at surfaces of the same kind, it is possible to cut down more and more the percentage of white light and to make the colored light more and more pure, or, as painters say, deeper and more fiery. Artists are quite familiar with this and they know that in the folds of hangings the color is not only darker, but is deeper and more saturated. The same thing is true if a garment that is illuminated by light reflected from a substance of the same color. A red mantle in a red room appears much more fiery on the side towards the wall than on the side towards the window. A gilded niche is a much deeper yellow than a plane surface with the same amount of gold. Gold ornaments on concave surfaces are much more effective than on convex ones. Flat gilded frames have quite a different color from frames which are gilded the same way but which are modelled in high relief so that there are deep hollows and channels to increase the contrast. The inside of a golden beaker has a very different color from the outside. It would not occur to anybody to gild a silver cup on the outside only, whereas people delight to gild the inside and to leave the outside untouched, because in this case the striking properties of both metals are brought out to good advantage, the lustre of the silver and the color of the gold.

"If a substance is illuminated by colored light containing several spectrum colors, it will only appear the same color as by daylight in case the source of light emits all the rays which the substance can reflect. In candle light and lamp light, the blue and violet are relatively more scanty than in daylight. Consequently red and yellow fabrics appear about the same color under this illumination as in the day time, while blue materials can often scarcely be distinguished from green ones by lamp light and violet ones appear red or an unpleasant gray, depending on the dye in question. Green pigments reflect chiefly green and blue light and blue pigments the same two, though in different proportions, and often some violet. If the light contains but little blue and violet, both the green and the blue substances will reflect only green and each will appear green. Under these conditions an erroneous estimate may convince the spectator that both are blue. The violet pigments usually reflect blue and red or blue and violet. In the first case the material will appear reddish by candle light or reddish brown if the light is not bright, while in the second it will appear gray."

Color screens may be used with white light to give us selected portions of the spectrum or they may be used to separate the monochromatic constituents from a source of light such as the mercury arc.[1] "There are countless absorbing substances at our disposal such as solutions of aniline dyes and of colored salts which can be used in glass cells made by cementing glass plates to annular strips cut from heavy glass or brass tubing. The following substances are very useful: cobalt chloride, copper chloride, nickel sulphate, potassium permanganate, chromium chloride, potassium bichromate, picric acid, sodium chromate, neodymium chloride, and praseodymium chloride. When the last two are combined with other filters, they are useful for sharpening the edges of absorption bands. . . .

"For separating the radiations of the mercury arc the following solutions will be found useful. Potassium bichromate transmits the green line and the two yellow lines. Addition of a neodymium salt removes the yellow lines without reducing the intensity of the green line in the least. Cobalt glass plus aesculin solution transmits the 4359 line. Guinea green B extra plus quinine sulphate transmits 4916. Nickel sulphate is also useful. Chrysoidine plus eosine transmits the yellow lines 5790. The chrysoidine should be dilute and the eosine added until the green line disappears. A very thick cell with a saturated solution of potassium bichromate is perhaps as good. Methyl violet 4R very dilute, and nitrosodimethyl aniline transmits the ultra-violet line 3650. Methyl violet with quinine sulphate as separate solution transmits 4047 and 4078, and 3984 faintly. . . .

"A film of silver, deposited chemically, upon a quartz lens

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[1] Wood: "Physical Optics," 15 (1911).

or plate, is practically opaque to all radiations except the ultra-violet region 3160–3260. The film should be of such thickness that a window backed by a brilliantly lighted sky is barely visible through it. Lenses prepared in this way have been used by R. W. Wood for photographing the moon, landscapes, and various objects in ultra-violet light. Very dense cobalt glass combined with a layer a centimeter or more in thickness of a saturated solution of potassium bichromate cuts off everything except the extreme red above wave-length 6900. This screen has been used by Wood in making infra-red landscape photographs. A clear blue sky is nearly black through it, while sunlit foliage comes out very bright. A saturated solution of iodine in carbon bisulphide is opaque to all visible radiations, while transmitting the infra-red freely."

While light of a given wave-length always has the same color, it is possible to get the sensation of that color by using a combination of light of other wave-lengths. A mixture of red and green lights in proper proportion will give a yellow which can scarcely be distinguished from the yellow of the sodium flame.[1] "A screen can easily be prepared which transmits the red and green only, and in about the right proportions to produce the sensation of 'subjective yellow,' as it is called. Canada balsam, boiled down until it will solidify on cooling, is stained with brilliant green and naphthalene yellow in the same proportions as used for making dichromatism prisms and a small quantity pressed out between two warm glass plates until the color of the transmitted light is yellow. Examination with a small spectroscope reveals the fact that in reality no yellow light is transmitted, only red and green. We have then the important distinction that while wave-length determines color, color does not necessarily determine wave-length.

"Lord Rayleigh recommends a mixture of an alkaline solution of litmus with chromate of potash. If a window, backed by well-lighted clouds, is viewed through such a solution and a prism it presents a most splendid appearance, for

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[1] Wood: "Physical Optics," 10 (1911).

the red and green images are widely separated, the region where they overlap being colored with the compound yellow. A screen transmitting only the yellow region is difficult to prepare. A mixture of bichromate and permanganate of potash answers fairly well and can be made to match the first screen. A sodium flame is invisible through the first screen and easily visible through the second. Both together are practically opaque, even with very intense white light."

In certain cases we may easily have contrast colors. The simplest case is that of the colored shadows.[1] "If one places an opaque substance so that daylight casts a shadow of it on a white paper and places a lighted candle near it so that this also casts a shadow on the paper the second shadow will appear blue and the first one yellow. That one of them is yellow is not surprising because the place that is protected from daylight is illuminated by the yellow light of the candle. It is different with the blue shadow due to the candle. This portion of the white paper is illuminated by daylight just as much as though the candle were not lighted. That this is the case can be seen by looking at this portion of the white paper through a narrow tube blackened on the inside. If one sees no portion of the white paper that is illuminated by the candle, the shaded part looks exactly the same whether the candle is lighted or not. The blue color of the shadow is therefore an apparent color and not a real one. The place where the blue shadow is seen is lighted only by the white daylight, the bulk of the paper is lighted also by the yellow candle-light and the second shadow only by the candle. The reason that the one shadow does not look white and the other yellow is because we know that the paper looks white when it is illuminated by white light and we, therefore, believe that it is still white, even though it is really illuminated by yellowish light. Our judgment in regard to white is disturbed and the spot that is really white we consider blue."

This experiment is even more striking with electric light than with a candle. If one lights an electric light with a yel-

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[1] Von Bezold: "Die Farbenlehre," 177 (1874).

lowish shade on a gray day in winter, the shadows cast on a white table-cloth by objects between the electric light and the cloth will appear spots of blue ink. The effect is very startling the first time. A more familiar phenomenon is the purple shadow of a large cloud on a green mountain side or on a green sea. This color is so intense that everybody has noticed it and very few people believe that there is no red in the shadow and that what one thinks one sees is the complementary color of the sunlit woods or sea. Still fewer believe that the color disappears if one looks only at the shadow through a tube blackened on the inside. Many years ago I knew an enthusiastic amateur painter who insisted on painting exactly what he saw. So he painted his sunlit part as he thought he saw it and the shadow as he thought he saw it without reflecting that the two colors would then react on each other. Of course the result was atrocious; but he was a logical man, though not a good painter, and he stuck to it that the mountain side looked that way to him, which was a bit pathetic, because we knew it didn't.

Von Bezold goes on to say that "if one uses a colored flame instead of the yellow and candle light, the shadow cast by the daylight will appear of the complementary color. If the flame is red, the two shadows will be red and green respectively. If the flame is green, the colors will be reversed and the two shadows will be green and red respectively. Instead of coloring the flame, which can only be done with certain salts, it is simpler to use a colored glass. With colored glasses the experiments on colored shadows can be done very easily in another way. If one supports a large colored glass plate at an angle on a table near a window, tipping away from the window, and if one covers the part of the table underneath the glass with a piece of white paper, the paper is illuminated both by the daylight which is colored by passing through the plate and by the light which is reflected from the ceiling and walls of the room. An object in that space therefore casts two shadows, one the color of the glass plate and the other the complementary color. It is advantageous to select for the substance to cast the shadow an object which gives great variation in the depth of the shadow case. A half-opened roll of stiff paper works admirably. When the experiment is done in this way, the paper itself does not seem white but the color of the glass, while the shadow on the side towards the observer shows the complementary color very distinctly, even when one does not see the other shadow at all. This experiment is especially successful when one uses a blue glass. The shadow on the side toward the observer then appears a beautiful sulphur-yellow and what is especially striking, it appears even brighter than the blue ground even though it really receives less light.

"Another way of showing the same thing is to lay a sheet of glass with not too deep a color on a flat glass or metallic mirror and then to hold some object, preferably a small rod, in such a way that one sees the reflected image, in which case one always has two colored images, one the color of the glass and the other the complementary color. One of the images is reflected from the upper surface of the colored glass and the other from the mirror. This second image is due to light which has passed twice through the colored plate and is therefore colored quite intensely, while the first image really has its natural color. Since the observer does not know which of the two is the colored image, he distributes the actual color difference over the two images. This experiment works best if one lays the plate so that one sees the reflection of the clear, or better, the overcast, sky and the images of the shaded side of the rod.

"Still another simple and effective way of showing contrast phenomena is to fasten two pieces of white cardboard together so that one lies horizontally and the back one stands vertically, and to place between them a colored glass plate at such an angle that one can see the horizontal surface by looking through the glass and the image of the vertical surface reflected from the surface of the plate. If one has painted a black figure on each of the pieces of white cardboard, for instance a not too narrow black ring, it is easy to find a position of the glass plate such that the image of the one figure appears close beside the figure seen through the glass or that the image covers the figure partly. The reflected image is seen in the color of the glass and the other in the complementary color. If the glass is green, the reflected image of the ring appears green and the one seen through the glass a rose-red. This very surprising fact depends upon the same error of judgment as in the case previously described experiments with colored shadows. Actually the ground on which one sees the two rings is pale green, for the green light coming through the colored glass from the lower surface mixes with the white light reflected from the surface. This latter is missing at the point where the black ring is reflected and only green light comes from there. The black ring which is seen through the glass sends out no light and consequently from points on the glass in line with this ring, the eye only receives the weak light reflected from the upper surface of the glass. One would therefore expect to see a deep green and a gray ring on a pale green ground. That does not happen because our judgment leads us into an error that we cannot avoid. We consider the predominant color of the ground either as white or as whiter than it really is and transfer to the gray ring the actual difference of color between it and the ground, making the gray ring appear rose-red.

"There is another very interesting and instructive variant of this experiment. If one replaces the vertical cardboard by a perfectly black surface and if one then looks through the colored glass at the horizontal surface, there is no contrast color or only traces of it. The ring appears black on a green ground. As soon as one replaces the black surface by a perfectly white one, the contrast color appears, though not so strikingly as in the first case. The intensity of the contrast color depends very much on the amount of admixed white light. By turning the whole apparatus, the amount of admixed white light can be varied and it is an easy matter to find a position where the ratio is the most favorable one. This is a very important experiment because it shows that no contrast colors develop upon a perfectly black surface and that an admixture of white is absolutely essential. If the contrast is to be marked, it is desirable to have an admixture of white in the colored light. This can be shown by making one of the figures white on a black ground. It is then possible to arrange things so that the image of the white covers the black figure which is seen direct. While the ring still appears of the complementary color, the apparent color is by no means so intense as when the whole of the reflected surface is white. This shows that simultaneous contrast is more marked with pale colors than with saturated ones. . . .

"There is a less effective but very simple way of showing that contrast colors are not very marked unless there is an admixture of white. If one lays a piece of matt black paper on a colored ground, there is only a trace of contrast color to be seen; but the contrast color appears markedly if one covers the whole thing with translucent white paper. Instead of a piece of paper one can use black letters printed on a colored ground. The contrast color can also be developed without superposing a white paper if one holds the printed paper at such an angle that the printed paper appears lustrous. This fact is important in the textile industry, for it shows that the production of a pure black is more difficult, the more the structure of the threads and the cloth tends to seem lustrous. Black figures on a violet ground appear markedly yellowish green if done in satin or in twill, much blacker if done in velvet. If one wishes to avoid this, one must give the black a light tint which neutralizes the contrast color, by mixing in some of the color of the ground. If one wants a pure black drawing on a red ground, one must use a reddish black; on a blue ground one must use a bluish black. It is worth noting that differently colored grounds have different powers of producing contrast colors. The effect is most marked with the so-called cold colors, green, blue and violet, while red, yellow, and yellow-green give rise to much less marked contrast colors."

Colors due to absorption have been called pigment colors because the colors of pigments are due to absorption. While it is probably true, as Wood[1] says, that the colors of most natural objects result from absorption, there are many cases where the color is not due to this cause. Thus the colors of the rainbow, the blue of the sky, the reds of the sunset, the white of snow, the brilliant colors of oil films, the fiery tints of the opal, and the iridescence of mother-of-pearl are not pigment colors. Such colors as these are called structural, optical, or physical colors, the first being the best name. These structural colors occur more often in nature than most of us suppose.

As far back as 1854 B. Altum laid stress on this point.[2] "The color of feathers may depend on the physical structure of the feathers or of the surfaces. It is this, hitherto unrecognized, possibility which I wish to emphasize. To make myself clear I call attention to the well-known colors of the rainbow, the spectrum, soap-bubbles, weathered glass, heated steel, mother-of-pearl, etc. Nobody will claim that these colors are due to red, yellow, blue, and other pigments. . . I maintain definitely that the iridescent colors of birds' feathers are due solely to the colors of thin films and to grating colors. If arguments from analogy are to have any scientific weight we must deduce and refer similar results to similar causes. A ray of white light is decomposed by a glass prism into six main colors, red, orange, yellow, green, blue and violet; and these colors always appear in the same order. The thin-filmed or grooved surface of many substances show us the same phenomena clearly and constantly. When the iridescent feathers of birds show us the same colors in the same order on varying the angle of the incident light, we must refer the color phenomena to physical structure and not to the presence of a pigment. It is true that the color depends on the thickness of the plates in the case of thin films, while the thickness remains constant in the feathers; but the distance that the light has to travel varies with the angle of incidence,

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[1] "Physical Optics," 439 (1911).

[2] Naumannia: "Archiv. für die Ornithologie," 1854, 293.

and that gives the same result. If we take a peacock's feather, which appears dark blue in one position and turn it a little, it becomes greenish blue. On turning it further it appears successively green, yellowish green, yellow, and orange. The only reason that we do not see the two ends of the spectrum, violet and red, is because the light does not reach our eye at the angles in question. It is of course, probable that there is a pigment beneath the thin plate and it is also possible that the scales which act as a grating or as thin films may themselves be colored by a pigment, though that is still to be proved. The change in colors cannot be explained by a deposit of pigment. Against this theory people have put forward the iridescence of *Limenitis iris*, which depends upon a structure of the scales having nothing to do with grating colors or the colors of thin films. I reply that the two iridescences also have nothing in common. I know very well the reason for the surprising change of color in *L. iris* and *L. ilia*, from a black to a beautiful blue. . . . I permit myself to remark that the iridescence of butterflies' wings has nothing to do with that of birds' feathers because no butterfly iridesces in the colors of the spectrum; they do not show first a red, then an orange, yellow, green, blue, and violet color with the intermediate changes. The change is an abrupt one between two colors which are not adjacent in the spectrum (or are so only accidentally). I have in my collection a *Colias edusa* from the Tyrol, which iridesces orange and violet. Orange and violet are of course spectrum colors; but are separated by red and are never neighboring colors.[1] With *Colias edusa*, there are no intermediate stages.

Gadow[2] says: "The colors which we observe in the things surrounding us may result from various sources, according to which they may be divided into two classes. The first class consists of so-called objective, chemical,

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[1] [It is evident that Altum never heard of anomalous dispersion. It is possible though perhaps not probable, that orange and violet should be adjacent colors in some spectra. W. D. B.]

[2] Proc. Zool. Soc. London, 1892, 409.

[pigmental] or absorption colors. Such colors do not change or vary under any position of the light or eye; they receive their color always from a coloring matter. They may exist in the form of a solution or as pigment. Animal objective colors are mostly due to pigment. The second class has been variously described as subjective, physical, or structural colors. They are the result of reflected or broken light. This may take place in various ways:

1. Total reflection of light, *e. g.*, the gloss on a polished surface.
2. The light may be broken infinitely often and be totally reflected. The result of this is white.
3. Diffraction by a prism.
4. Interference of colors. By this theory are explained the colors of extremely thin transparent plates, and those which are produced by a system of narrow ridges, *e. g.*, iridescence of mother-of-pearl, the blue heat stage of steel, and the color of soap-bubbles."

Krukenberg[1] says: "The cases where the colors of animals are due to pigments are undoubtedly the most simple theoretically. These so-called subjective chemical absorption colors include all of the blacks and brown tints and most of the red, orange and yellow ones.

"In addition to the fluorescence and phosphorescence phenomena a comparative chromatology of the organisms must also take into account the objective and subjective structural colors, which, with the exception of a few doubtful cases are different by transmitted light and by reflected light. The most brilliant of the animal colors are not dependent, or usually not, on the presence of special substances which are colored owing to their chemical nature; but are due to special structural relations (fibers, ridges, enclosed air-spaces, etc.) which is the reason why they can be damaged or destroyed by mechanical attacks (pinching, hammering, powdering, etc.), whereas they resist chemical reagents in so far as they do not affect the structural relations. Nowhere in the whole animal kingdom are the

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[1] "Vergleichend physiol. Vorträge," 111 (1886).

structural colors so varied and so surprising in their effects as in the plumage of birds, for which reason we shall take most of our illustrations from feathers.

"The objective structural colors differ from the subjective ones in that the first do not vary in any way with the position of the eye or with the angle of the incident light, while the subjective structural colors change under changing conditions. The simplest case of an objective structural color is pure white, which is caused by the presence in the tissues of an opaque substance which reflects back all the constituents of the incident sunlight to a great extent and without relative change. The same effect is produced often, in all white feathers and in white hair for instance, by the tissues being filled with air spaces, sometimes to such an extent that the tissue is reduced to a delicate network.

"Many white colors among animals are interpreted as adaptation phenomena, and others as forming desirable backgrounds for the color displays upon them. Outside of amorphous calcium carbonate there is scarcely a substance occuring in animal cells, which, on account of its chalky and opaque color, is better adapted to serve as a background for color cells than guanin, a substance occurring in large quantities in the epidermis cells of fishes, amphibia and reptiles. An objection to generalizing this idea is found in the fact that in many animals (batrachians, snakes) the under portion of the body is chiefly the one containing guanin and not the upper side where the color development occurs. We do not know definitely how the chalky particles in the skin of caterpillars are formed; but it is certain that they are not due to deposits of guanin as Leydig believed.

"While pure guanin changes the skin covering of batrachians, reptiles, and selachians in places to a white opaque mass on which the chromatophores or chromatoblasts develop, the crystals of calcium guanin give the beautiful silvery lustre to the outer skin of the bony fishes. In the *Cephalopodensclera* there are spindle-shaped crystalloids which have a similar effect and whose chemical nature is not known except that they do not contain urates or guanin. An investigation should be made to determine how far the silvery lustre is due to interference or to total reflection in which case the calcium guanin would act like the air-filled pores on the under sides of the *Hydrophilides*, *Dyticides*, and *Hydrometra*.

"Among the objective structural colors must also be included the light to dark blue of many birds' feathers (*Irena puella*, innumerable species of *Psittacides*, *Pitta moluccensis*, etc.) and bare portions of skin on birds (for instance, with *Casuarius*) and with animals (for instance, with the Mandrill). The physical conditions necessary to produce the intense blue color of the skin have not been studied; it will be very difficult and probably impossible to determine how these colors occur in the feathers of birds through the many absorptions and refractions which the incident rays undergo in the feather until they reach either the black pigmented layer or our eye. We know only that in all such feathers, the blue color occurs exactly at those spots where there is a black or brown layer of pigment under a layer of prismatic or cone-shaped hollow spaces (the enamel described by Fatio and considered as large polygonal cells; Gadow's prismatic cells or prismatic columns). Usually the blue color is confined to the barbules of the feather which do not have at these points further branches and interlocking spurs, and consequently spread out broader and flatter.

"The data in regard to the sudden turning gray of men's hair are now so complete as to establish beyond question the occurrence of this often disputed phenomenon. We have a very careful paper by Leonard Landois in regard to a man suffering from delirium tremens whose hair turned white in a single night. The change in color was due to the fact that large numbers of air bubbles formed throughout the marrow of the blond hair and to some extent in the rind, while the hair pigment remained unchanged. These air bubbles gave the hair an exquisite gray appearance. In rare cases there has been noticed a banded bleaching, so that the hair was alternately dark and white at intervals of about one millimeter. Landois found in one of these cases that the white places were due to the marked development of small air-bubbles in the medullary canal and the surrounding rind, while the pigment was unchanged."

Poulton[1] says: "The colors of animals are produced in various ways. By far the commonest method is the *absorption* of certain elements of light by means of special substances which are called *pigments*, or *coloring matters*. The color of each pigment is due to those elements of the light which it does not absorb, and which can therefore emerge and affect the eye of the spectator. Black is, of course, caused by the absorption of all the constituents of light, so that nothing reaches the eye. The color of red pigment, like that of red glass, depends upon the fact that red is less absorbed than any other element of the light which passes through. If a sheet of red glass be placed upon white paper, the light traverses the glass, is reflected from the surface of the paper, retraverses the glass, and emerges. Similarly, in painting, bright effects are produced by covering the surface of Chinese white with the desired color. The light passing twice through the thickness of the color, absorption is far more complete than when only one thickness is traversed, as in a piece of red glass held up to the light. Absorption being more complete, the red color is deeper. Animal pigments are nearly always twice traversed by the light, and therefore a very thin layer produces a considerable effect.

"Animal colors are therefore generally due to precisely the same optical principle which causes the color of a wall-paper, a carpet, or a picture. Certain transparent animals are, however, for the most part colored by light which passes but once through them, upon the same principle as the colors of a stained-glass window. The beautiful transparent blue of many pelagic animals, such as the Portuguese Man-of-war (*Physalia*), is caused in this way. . . .

"The production of white is due to a different principle, for we know that when light passes through a body without any absorption, the body is transparent and invisible rather

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[1] "The Colors of Animals," 1 (1890).

than white. When all the light passes through, the body is completely invisible. Whiteness is due to reflection of the whole visible series of vibrations, unaccompanied by the absorption of a part of them, as in the production of colors. But regular reflection, *viz.*, reflection from a polished surface like that of a mirror, does not cause whiteness, it renders the surface itself invisible, but produces images of surrounding objects. A white appearance is produced by irregular reflection, which causes the light to be scattered or reflected in all directions. To produce such a result there must be an immense number of surfaces in an immense number of different directions. If a colored substance be reduced to powder of various degrees of fineness, the color will diminish in intensity, and the whiteness will increase, according to the fineness of the powder; this is because the number of reflecting surfaces is increased, while the thickness of the grains is diminished. This will be clear from the following consideration. When a beam of light falls on a sheet of glass, a known fraction (about 4 percent) of the light is reflected back from the first surface; the larger portion, however, enters the glass, and, after suffering a certain amount of absorption, reaches the second surface and is again partially reflected. If the glass be powdered, the number of surfaces will be so immensely increased that all the light will be reflected by a small thickness of the powder. The light reflected from the second surface of each grain of colored glass will still be colored by absorption, but not sufficiently to produce any visible results, when the thickness of the grain is very small.

"Reflection is the *immediate* cause of whiteness, and the amount of reflection is due to the difference between the refractive powers (*viz.*, the power of changing the direction of rays of light) possessed by the grains of glass and the substance, such as air or water, which lies between them. Thus the refractive powers of glass and water are much nearer than those of glass and air, hence a dry powder will reflect far more than a wet one, and will appear much whiter.

"To take a few familiar examples: snow is white, because of the minute globules of air which refract very differently from the crystals between which they are entangled, ice, on the other hand, is transparent. If snow be compressed, the air is driven out, and the mass becomes transparent; if ice be powdered it becomes white like snow. The froth of a colored liquid is not colored like the latter, but is white. Milk and fat are white because light is scattered from the surfaces of the countless oil globules, which refract very differently from the substance which lies between them. The surface of well-polished glass is almost invisible, because it reflects regularly, but a scratched surface is very visible, because there are surfaces in many different directions, which therefore scatter the light, while the far more numerous surfaces of ground glass scatter the light far more effectually and produce a white appearance.

"The white markings of animals are produced in various ways. White hairs and feathers owe their appearance, like snow, to the number of minute bubbles of gas which are contained in their interstices. Fat is also made use of to give a white appearance; and the same result may be obtained by the presence of minute granules, probably akin to pigment, but differing widely from it in optical properties, in that no absorption takes place.

"It has been stated already that when light traverses a sheet of glass surrounded by air, a certain proportion of it is reflected back at the first surface and a certain proportion at the second surface. The light will be reflected in the same direction from both surfaces. It is believed that the vibrations of ether, some of which affect us as light, are in the form of undulations of different lengths; if, therefore, the sheet of glass be sufficiently thin, some of the undulations reflected from the second surface will interfere with those started from the first surface. This will happen when the sheet is of such a thickness that the wave of light reflected from the second surface is half an undulation behind that reflected from the first surface; for then the two sets of undulations will be in opposite directions, and will therefore neutralize each other.

This will be quite clear if we apply the same reasoning to those visible undulations from which the name itself has been borrowed—the waves on the surface of water. If a set of ripples is started by the motion of an object in still water, and then another set is started from another object moved, so that the ripples succeed each other at exactly the same rate as the preceding set, and if the second set is begun when the first has advanced half a complete ripple (*viz.*, a movement up *and* down), it is clear that the upward movement of the second will correspond to the downward movement of the first and *vice versa*, so that, if the objects are so placed that the two sets of ripples are traversing the same sheet of water, they will neutralize and destroy each other.

"If we compare a number of sheets of glass which are successively thinner and thinner, interference will first occur among the longest undulations of light, because half an undulation will of course require a greater distance (or thickness) than when the undulations are shorter. As thinner and thinner sheets are examined, interferences will gradually pass through the whole spectrum from red to violet, destroying sets of waves with shorter and shorter undulations. The color seen in each case will be due to the other sets of waves which are not destroyed. The amount of reflection, and therefore of interference and of color produced, depends upon the difference between the refractive power of the thin sheet and the substance on each side of it. Such interference colors are seen in a soap-bubble, and the colors change as the bubble becomes larger and the film thinner; they differ, too, on the various parts of the bubble, because the thinness also varies. A bubble of melted glass may be blown thin enough to produce the same effects, which are also well seen when a thin layer of air is enclosed between two sheets of glass between the plates of some crystals, or when a drop of oil is allowed to spread out into a thin film on the surface of water. When a substance has a laminated structure, and sufficiently thin films are enclosed between the laminae, very marked effects are seen. Thus the metallic appearance of the laminated flakes which are formed on the surface of glass which has been long buried in the earth, is accounted for. If these brilliant flakes are wetted the color fades away, because the thin films of air between the laminae are displaced by water, with a refractive power much nearer to that of the glass, and the amount of reflected light is therefore diminished.

"Interference colors due to thin films are certainly very important among animals, but the extent to which they occur is imperfectly known. The iridescent colors of many beetles' wings are probably due to thin films of air included between layers of a horny consistence. Such colors are unaltered in dried specimens. In other cases the chinks between the layers are kept open by films of less powerfully refractive liquids. When the tissue becomes dry the films evaporate and the color disappears. We must suppose that the denser layers come together, obliterating the chinks and excluding the air; otherwise the colors would be more brilliant than ever, because the refractive power of air is even lower than that of the liquids. The brilliant metallic appearance of many chrysalides, especially in the genus *Vanessa*, is caused by a large number of films of liquid enclosed between the laminae of the dense outer layer. If the pupa be kept in spirit or water the color remains, but disappears directly it is dry, although it can be renewed any number of times by wetting. This may even occur in a living animal, for Dr. Sharp has just directed my attention to an interesting observation made by Dr. Nickerl, who found that a brilliantly golden beetle (*Carabus auronitens*) lost all its lustre after hybernating in captivity, but entirely regained it after drinking some water.

"When white light falls upon a surface on which there are a number of fine parallel grooves the reflected light appears colored, the color varying with the angle at which the light falls on the surface, and with the angle at which it is seen. This is due to the light reflected from different portions of the surface having distances to travel before reaching the observer, and when (as occurs when the grooves are very close together) these differences amount to half a complete undulation for any particular length of vibration, interference is caused, and the vibration of that particular rate is wanting from the reflected light, which therefore appears colored. Opinions differ as to the relative importance of animal colors due to thin plates and to diffraction. Many which were believed to result from the latter are in all probability due to the former. The iridescent colors on the inner surface of many shells (mother-of-pearl) are at any rate partially caused by diffraction, for an accurate cast of the surface exhibits traces of the colors.[1] The shell is, however, a laminated structure, and the colors may therefore in part be caused by thin plates.

"When light passes through a wedge-shaped transparent substance (or prism) with greater refractive power than the surrounding medium, it is bent in the same direction at both surfaces, but its different constituents are bent unequally. The slowest vibrations (red) are bent least, the most rapid (violet) most; and when the substance possesses a sufficiently high refractive power, all the colors of white light are seen arranged like the rays of a fan in the order of their rates of vibration. Prismatic colors, like those of the diamond, are due to refraction. It is doubtful how far the colors of animals are caused by this principle, but Dr. Gadow has given strong reasons for supposing that the metallic colors of birds' feathers are produced in this way,[2] and there are scales on the wings—cases of certain beetles (*Pachyrhyncus*) which also may owe their colors to refraction.

"All these causes of animal colors may be conveniently grouped under two heads—(1) *pigmentary*, and (2) *structural*. The first head includes colors caused by absorption, and the effects produced vary with the chemical nature of the substance (pigment). The second head includes the colors or appearance produced in all other ways, the efficient cause be-

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[1] Professor C. Stewart informs me that he has repeated Brewster's original experiment, upon which the above statement depends. He found that the color was due to a thin layer of shell which had been stripped off and adhered to the surface of the wax.

[2] Proc. Zool. Soc. London, 1882, 409.

ing the structure of the substance rather than its chemical nature."

The same idea is developed in more detail by Newbigin.[1] "The color of the rose, for example, is due to a red pigment present in the cells of the petals, which can be extracted from those cells. This is the simplest form of color production, and is the one which commonly occurs in plants. Colors so produced are called pigmental colors and can be recognized by the following characters. Pigmental colors are those produced by pigments, or substances of definite chemical composition, which can be extracted from the colored tissues by appropriate reagents, and which react to light in the same way whether they are within the tissues or outside of them. Tissues or organisms showing only pigmental colors never have a surface gloss, and the color is not altered by immersion in any medium which does not directly attack the pigment.

"Although the great majority of the colors of plants are produced in this simple way, yet even among them we have indications of that other kind of color-production which reaches its climax of splendor in birds and butterflies. The gorgeous tints of the humming-birds, which change during life with every movement, are not produced by the dyeing of the feathers with pigment, but are phenomena of the same order as the colors of the gems after which some of the birds are named. We all know that the colors of the opal and of many minerals are not due simply to a prime property of the substance concerned, but are optical effects dependent upon various external conditions for their full manifestation. Many of the most brilliant tints of animals are similarly optical colors, but as they are produced by the special structure of the colored parts, they are more frequently known as structural colors.

"Structural or optical colors in organisms can be recognized by the following tests. They usually vary either with the angle of incidence of the light or with the change from reflected to transmitted light; tissues or organisms showing

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[1] "Color in Nature," 7 (1898).

these colors have a very marked surface gloss, and the color is usually destroyed by injury to this surface; immersion in a neutral medium, whose refractive index is different from that of air, also usually destroys the color. Optical colors may further be recognized by the negative character that the colored tissues do not yield to any reagent a pigment of the same tint as that which they themselves possess. A peacock's feather affords an excellent example of a type of structural coloration which is widely spread in birds. If the reader stands in front of a window and holds a peacock's feather in his hand nearly on a level with the eye, and then, still with the feather at arm's length, slowly describe a semicircle on his own axis, he will note that the colors of the feathers undergo a complete cycle of change. In this case, therefore, the colors change with the change of the angle of reflected light. If the feather be now held up to the light, it will be seen that the colors disappear, to be replaced by a dull brown or black tint. Thus the feather changes color according as it is viewed by reflected or transmitted light. The presence of a marked surface gloss is, of course, very obvious, and, though the size of the colored particles is too small to make it easy to note the effect produced by injury to this surface, yet the disappearance of the color when the surface is thoroughly wetted with water or oil can be observed very readily.

"Having now distinguished generally between the colors due to pigment and those which are the result of a special structure, we must proceed to consider these different methods of color production in detail. As much less is known of the structural colors than of pigmental, we shall devote the remainder of this chapter to the former, leaving the latter for a further chapter.

"*White* is probably the simplest and most readily understood of all structural colors, and, except in rare cases, is always structural. The colors of the lily, of white feathers, of Arctic mammals, are all due to the same cause, namely, the total reflection of light produced by the intercalation of numerous bubbles of air, or some other gas, among colorless solid particles. Thus in the lily the colorless cells are separated by very numerous intercellular spaces containing air. This is one of the simplest forms of structural color, not only because it is so readily explicable physically, but also because there is no complication arising from the presence of pigment in the tissues, and because the modification of structure necessary to produce it is of the simplest nature. Most people are familiar with the analogous process of producing a white color by pounding up colorless glass, or crystals of blue sulphate of copper, while the whiteness of snow, which has produced so many metaphors, is produced in a precisely similar manner.

"The fact that the whiteness of all these substances is due to an optical effect and not to a pigment should be thoroughly grasped, otherwise those not accustomed to dealing with color phenomena will find much difficulty in comprehending structural colors in general. White sunlight is produced by the combination of all the tints of the rainbow. When objects permit light to pass completely through them, we call them transparent; when they reflect all the rays of the light uniformly, we call them white. This whiteness may be produced in one of two ways. A substance such as Chinese White is white because it is a property of the particles of which it is composed to reflect equally all the rays of incident light, it is further a familiar fact that Chinese White can be employed to impart its own color to other objects, that is, it can be employed as a pigment. Snow, on the other hand, is white, not because its individual particles reflect the light—on the contrary, they are transparent—but because these transparent particles are separated by bubbles of air. The incident light in passing from the one medium to the other is bent or refracted, and the result is the appearance of whiteness. A white color in organisms, except in very few cases, is similarly produced, and is not due to pigment.

"Other structural colors are to be accounted for in a closely similar fashion. Glass is a colorless or transparent substance: when powdered it is white; when cut with prismatic edges it displays all the colors of the rainbow; yet the qualities of the glass remain unaltered. These are, of course, very familiar facts, but it is important to realize also that many of the most brilliant colors or organisms are produced in a similar fashion—are adventitious and not due to the essential properties of the colored substance. It is only in rare cases, however, that bright colors are produced in a way capable of simple physical explanation. There are usually complications arising from the presence of some amount of pigment, from the superposition of tissues or from the complex nature of the individual tissues. Such brilliant optical colors occur apparently only in cuticular structures. It is a curious fact that, although such structures are of course not cellular, nor living, yet their color frequently fades very rapidly after death; that dragon-flies, for example, lose in a very short time all their gorgeous tints is a fact only too well known to collectors. This may be due to loss of water or to changes in the underlying tissues.

"Structural colors are most brilliant and conspicuous in birds and insects, but it is chiefly in the former that they have been studied. Dr. Gadow has especially studied the structural colors[1] of birds, and he divides them into two classes, according to their behavior as regards incident light. Thus certain structural colors, such as green and blue, are unchanging in reflected light, and are then not readily distinguishable from pigmental colors. These Gadow classifies as *Objective Structural* colors. Again many colors change in tint according to the angle at which they are viewed. Such metallic colors may be classified as *Subjective Structural* colors.

"Of *Objective Structural* colors, green and blue afford the best examples. Green seems to usually produced by a combination of a yellow pigment and a structural modification, wherefore green feathers usually appear yellowish in transmitted light. The display of blue color again seems, at least in birds and probably in insects, to be always associated

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[1] For a purely physical treatment see a pamphlet by B. Walter.

with the presence in the tissues of a dark-colored pigment. A blue color in the feathers of birds is always confined to certain parts of the feather, and its presence is associated with considerable modification of feather structure. Blue is not, however, confined to the feathers; but may occur also on bare patches of skin, as in some of the Paradise birds, in the cassowary, etc. Curiously enough, a blue color in the skin seems to be particularly unstable, fading as rapidly after death as does the blue color in the abdomen of some dragon-flies. The exact physical cause of green and blue colors is still doubtful, but the fact that the colors are structural is readily perceived both by the strong surface gloss and by the disappearance of the color in transmitted light.

"While unvarying blue and green tints in birds rather heighten the general effect than display in themselves great beauty, the *Subjective* Structural colors, on the other hand, display the most exquisitely varying tints, and it is to them that many birds and insects owe their wonderful flashing beauty. These colors glow with all the changing tints of the rainbow and change with every changing ray of light. Such metallic colors are of course not uncommon phenomena in the inorganic world, and are displayed, for example, with extraordinary brilliancy on a polished slab of the mineral Labradorite; among organisms, although suggested elsewhere, they attain their maximum brilliancy in birds and insects. In birds their degree of development varies greatly, for we find them ranging from the dull greenish gloss of some of the female humming-birds to the gorgeous coloring of many of the males in humming-birds and birds of Paradise. Among birds metallic color is apparently always associated with the presence in the feathers of dull brown or black pigments, which are necessary for the production of the colors. It is also associated with a modification of the feather structure which in many cases renders the feathers unfitted for the purpose of flight. Here, as in the case of objective structural colors, the exact physical causation of the colors is unknown. In insects the colors are equally bright, but have had little attention bestowed upon them; it is still doubtful whether the colors in them are or are not associated with the presence of a dark pigment.

"The presence of a pigment is not, however, essential to the production of structural colors; the common earthworm, for example, exhibits a faint iridescence which is due to the presence of numerous fine lines on its colorless cuticle, these fine lines producing interference of light. Although the coloring is very slight in the earthworm, it is well known that some of the marine worms, *e. g.*, the sea-mouse (*Aphrodite*) are covered with numerous bristles which exhibit brilliant iridescent colors. Again, the colors of mother-of-pearl are of course produced by structure only, without any assistance from pigment. For convenience of reference, Structural Colors may perhaps be arranged as follows, retaining Gadow's distinction of objective and subjective colors.

Structural Colors:

1. Those not dependent upon the presence of a pigment.
    - (*a*) Due to total reflection; white color of some flowers, of some feathers, of hair, etc.
    - (*b*) Due to striation of the surface, occurrence of thin plates, etc.; iridescence of bristles and cuticle of worms, of mother-of-pearl, etc.
2. Those dependent on the presence of a pigment.
    - (*a*) Objective structural colors; blue and green feathers.
    - (*b*) Subjective structural colors; metallic colors of many birds and insects.

"Structural colors are of extreme interest, not only on account of their wonderful beauty, but also on account of the difficult questions connected with their origin. It is to some extent possible to correlate pigment production with the physiology of the organism; but this seems extremely difficult in the case of structural coloration. We may note, however, that structural coloring attains its greatest perfection among birds and butterflies, and both groups are noted for the extraordinary development of their cuticular structures. The delicate beauty of the sculpturing of butterflies' scales has been extolled by most possessors of a microscope, while savage and civilized races are alike in their admiration for the feathers of birds. The fact that organisms so widely separated as birds and butterflies are alike in exhibiting both exquisite structural coloration and a wonderful development of structures arising from the cuticle suggests that the colors are in origin merely a result of extreme differentiation of the cuticle and therefore produced by the same cause which gives rise to this differentiation. The presence of brilliant iridescence in some of the mud-inhabiting worms is therefore not quite inexplicable, for here also we find that the cuticle shows a considerable amount of differentiation. We can also further understand how it is that the highest pitch of perfection is attained in birds and butterflies, when we consider that in both cases the coloring occurs in connection with structures which are of supreme importance to the species, that is, with the feathers of the birds and the scales, which are but outgrowths of the wings, in butterflies."

Cornell University

THE ATOMIC WEIGHT OF LEAD FROM SAMARSKITE

BY ARTHUR L. DAVIS[1]

The object of this work is an extension of the investigations on the atomic weight of lead of radioactive origin. We have determined the atomic weight of lead from a source hitherto not employed—the mineral Samarskite.

The problem involves the separation of the lead from this mineral, its purification, and determination of its atomic weight by analyses of the pure lead chloride obtained.

Parallel experiments with ordinary lead are included, thus showing the relative values under the same conditions of experimentation.

Finally, in order to correlate the results with the theory of radioactive changes involved, the percentages of uranium and thorium in the mineral were determined.

Historical[2]

Richards and Lembert,[19] with the great care that is characteristic in the determination of atomic weights at Harvard, have determined the atomic weights of samples of lead of widely distributed origin, geographically. They found that all of the radioactive specimens possessed a lower atomic weight than that of ordinary lead determined under identical conditions and in one case that the deficiency amounted to as much as 0.75 of a unit. The radioactivity of the various samples was determined quantitatively but no simple relationship between the amount of radioactivity and the atomic weight was found. The ultraviolet spectrum of a typical radioactive sample was compared with that of ordinary lead in a quartz spectrograph, but no difference was found in the spectra of the specimens. They infer that radioactive lead

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[1] Abstract of a thesis submitted in partial fulfilment of the requirements for the degree of Master of Arts, University of Missouri, 1918.

[2] The references are summarized in a bibliography.

contains an admixture of some substance different from ordinary lead, and very difficult to separate by chemical means. It has later been shown that the product of one thousand and six fractional crystallizations of radioactive lead has the same atomic weight as the original material, thus proving conclusively that no separation is possible by chemical means. The results obtained were contrary to experience with a number of other elements, notably copper, silver, iron, sodium and chlorine, each of which has a constant atomic weight, no matter what the geographical source may have been.

Soddy and Hyman[23] extracted the small quantity of lead present in Ceylon thorite, a hydrated silicate of thorium, and determined the atomic weight relative to ordinary lead by a standard method. They obtain an atomic weight of 208.4 compared with 208.2 calculated from the percentage of thorium and uranium present. Out of some twenty-four determinations on the atomic weight of lead, referred to by Brauner[4], seven give values between 206.8 and 206.95, six between 206.95 and 207.1, none between 207.1 and 207.35 and six between 207.35 and 207.6, showing quite considerable variation.

Hönigschmid and Mme. St. Horovitz[13], [14], [15] have obtained samples of radio-lead from primary minerals in order to obtain specimens as free from ordinary lead as possible. Lead obtained from crystallized uranium oxide gave an atomic weight of 206.06, showing the practical absence of outward contamination. A sample from bröggerite gave 206.08 and a portion of the same sample distilled gave a result of 206.066, showing very closely agreeing values.

M. Curie,[6] on the examination of lead extracted from pitchblende, carnotite, yttriotantalite and monazite sand, found it to give an atomic weight of 206.64, 206.36, 206.34 and 207.08 for the respective samples.

Richards and Wadsworth,[20] on determining the atomic weight of a number of samples of radio-lead, obtained essentially the same results as previous experimenters. Every sample used, except the ordinary lead, possessed radioactivity. In conclusion, their results show that the most carefully prepared samples seem to give lower values, this being strong evidence that the higher results obtained were due merely to the accidental admixture of ordinary lead in varying proportions.

The foregoing results are summarized on the following page.

DETERMINATIONS OF ATOMIC WEIGHT OF LEAD OF RADIOACTIVE ORIGIN

Richards and Lembert[19]	
North Carolina uraninite	206.40
Joachimsthal pitchblende	206.57
Colorado carnotite	206.59
Ceylonese thorianite	206.82
English pitchblende	206.86
Soddy and Hyman[23]	
Ceylon thorite	208.40
Hönigschmid and St. Horovitz[14]	
Joachimsthal pitchblende	206.405
Uraninite, Morogoro, G. E. Africa	206.059
Bröggerite, Moss, Norway	206.083
Bröggerite ($PbCl_2$ distilled)	206.066
Curie, Maurice[6]	
Yttrio-tantalite	206.34
Carnotite	206.36
Pitchblende	206.64
Monazite sand	207.08
Richards and Wadsworth[20]	
Australian carnotite	206.34
American carnotite	207.00
Norwegian cleveite, Moss	206.08
Norwegian bröggerite, Langesund	206.12

The published analyses[7] of samarskite indicate the complex nature of the mineral. It is regarded as a complex niobate and tantalate of the rare earths, and contains a considerable amount of uranium with a small percentage of thorium. Most of the older analyses fail to show the presence of either thorium or lead, but both of these elements are probably found in all samples of samarskite. In the earlier analyses of the mineral these constituents were doubtless separated with the rare earth elements.

Being a primary mineral deposited by magmatic intrusion, the lead present may be considered as the end products of the uranium and the thorium series rather than a secondary deposit.

Separation of Radio-Lead

Samarskite was readily decomposed and the lead separated by the following procedure:

One and one-half times the amount of hydrofluoric acid necessary to combine with the bases present was added and the mixture evaporated nearly to dryness in platinum dishes. Dilute hydrofluoric acid was then added to the residue to take up soluble fluorides, the presence of the acid being necessary to prevent the hydrolysis of these fluorides. The mixture was filtered through a rubber funnel and thoroughly washed till free from acid, the filtrate and washings being collected in a platinum dish. The residue was transferred to a platinum dish with the smallest quantity of water possible, evaporated to dryness and then heated to fuming with concentrated sulphuric acid which has been found to be entirely free from lead. This mixture was cooled and the soluble sulphates extracted with hot water; the insoluble sulphates boiled with sodium hydroxide, the mixture treated with nitric acid, diluted, filtered and evaporated to dryness. This residue was taken up with water, acidified with hydrochloric acid and the lead precipitated by saturation with well-scrubbed hydrogen sulphide. The freshly precipitated lead sulphide was boiled with strong hydrochloric acid and the solution evaporated to dryness. From 1100 grams of samarskite, fourteen grams of the crude lead chloride was obtained.

Purification of Lead Salts

The impure lead chloride of radioactive origin was dissolved in water, saturated with hydrogen sulphide and the sulphide formed dissolved in nitric acid; the sulphate formed being dissolved, the lead precipitated as the sulphide and treated with nitric acid as before.

The lead was recrystallized as the nitrate four times, converted to the chloride and as such submitted to three more crystallizations. Baxter and Grover[2] have shown this procedure to be efficient and very satisfactory in their preparation of samples for the determination of the atomic weight of ordinary lead. All filtrations were made through a platinum sponge and the later recrystallizations were carried on entirely in platinum.

In order to obtain a sample of ordinary lead, galena, from Commerce, Oklahoma, was treated with nitric acid. The nitrate obtained was recrystallized six times as such, converted to the chloride and recrystallized twice. In all cases the final products of crystallization were kept in a vacuum desiccator over fused potassium hydroxide.

Analysis of Lead Chloride

The method involves the conversion of samples of lead chloride into silver chloride. The data required are the weights of the samples of lead chloride used, and the equivalents of silver chloride obtained. The calculations are based upon the atomic weights of silver and chlorine.

The method and procedure followed is almost in detail the same as used by Baxter and Grover.[2]

After the preliminary drying in a vacuum desiccator, the final drying is accomplished by fusion in an atmosphere of thoroughly dried hydrogen chloride and slowly replacing the hydrogen chloride by means of a stream of carefully scrubbed and dried air.

The apparatus consisted of five drying tubes containing concentrated sulphuric acid for the final drying of the hydrogen chloride generated by dropping concentrated sulphuric acid into the purest concentrated hydrochloric acid; two drying tubes containing silver nitrate solution for the removal of hydrogen sulphide from the air, one containing solid potassium hydroxide for the removal of carbon dioxide and two tubes containing concentrated sulphuric acid for the final drying of the air; connected to the so-called bottling apparatus. All connections were fused or ground glass joints.

A platinum boat, previously heated to constant weight and weighed in a weighing bottle, was filled with the dry lead chloride and placed in the combustion tube with the weighing bottle in place. The apparatus was completely filled with hydrogen chloride by the passage of a gentle stream of the dried gas and then the chloride was gradually heated till a perfect state of fusion was reached, under which condition it was allowed to remain for 10 minutes. The apparatus was allowed to cool very slowly, still with the passage of hydrogen chloride. When perfectly cool the hydrogen chloride was replaced by a gentle stream of scrubbed dried air. Without disconnecting the apparatus, the boat was placed in the weighing bottle and then the bottle removed to a desiccator. The weighing of the bottle, boat and fused chloride was then made.

Solution of the fused chloride was effected by attaching a platinum wire to the boat and suspending in 500 cc of double distilled water, slightly acidified with nitric acid, contained in a liter Erlenmeyer flask, heated by means of a hot plate. When the solution was complete, the boat was thoroughly washed with hot water and removed. The precipitation of the chloride was made by the addition of a very slight excess of fiftieth normal silver nitrate solution. After standing several days in a dark place, with occasional agitation, the silver chloride was collected on a platinum sponge crucible. The silver chloride was dried at 235° for sixteen hours, cooled and weighed.

The results obtained are summarized in the following table: The weights given are reduced to vacuo, and the

ANALYSIS OF LEAD CHLORIDE

Number of analysis	Weight of $PbCl_2$	Weight of AgCl	Factor $PbCl_2$: AgCl	Atomic weight
Ordinary lead.				
1.	0.94411	0.97264	0.97066	207.354
2.	1.24607	1.28454	0.97010	207.186
				207.27
Radioactive lead.				
3.	1.06795	1.10199	0.96683	206.246
4.	0.73514	0.76011	0.96722	206.363
				206.30

weights of silver chloride have been corrected for the traces held in solution.

The calculations are based on the atomic weights of silver and chlorine as 107.88 and 35.457, respectively.

Uranium and Thorium Content of Samarskite

A very good method of separation of the elements present in a complex niobate and tantalate was found, but since a fusion with acid potassium sulphate is made, it was deemed hardly applicable under the circumstances with the possible convenient use of hydrofluoric acid.

By the use of the following procedure very satisfactory results were obtained:

Duplicates of 1 g of 200-mesh samarskite were decomposed in platinum dishes with a considerable excess of hydrofluoric acid. After evaporating nearly to dryness, a little dilute hydrofluoric acid was added, and the insoluble fluorides filtered off. The filtrate was discarded. The fluorides were then washed into a platinum dish, evaporated to dryness, and heated to fuming with sulfuric acid. After cooling, the sulphates were boiled with water, the insoluble residue filtered off and discarded. To the filtrate containing the sulphates of U, Th, and Ce and Y earths, ammonium chloride and ammonia were added and boiled. After settling, the precipitate was filtered off, and dissolved in hydrochloric acid. After dilution, the solution was heated to boiling and a slight excess of ammonium oxalate added. After standing 12 hours, the precipitate of thorium and rare earth was filtered off and washed. Nitric acid was added to the filtrate and evaporated to dryness. After taking up with water, a little ammonium chloride was added and the uranium precipitated with ammonium hydroxide.

After drying and ignition, the uranium was weighed as the green oxide U_3O_8.

The precipitate of thorium and rare earth oxalates was washed from the filter and evaporated to dryness with an excess of nitric acid present. It was then dissolved in water and an excess of sodium thiosulphate added. After settling, the thorium-bearing precipitate was filtered off, dried, ignited and weighed as ThO_2.

The following percentages of uranium and thorium were obtained by the foregoing method:

U_3O_8	12.14	12.29	Av., 12.21%
ThO_2..............	1.12	0.94	Av., 1.03%
Atomic percentages...	U = 91.7%		Th = 8.3%
Radioactive percentages.	U = 97%		Th = 3%

Discussion

Since thorium decays at a slower rate than uranium—approximately 0.36 as fast—the quantity of end product resulting from the thorium present in our sample of samarskite, assuming that both end products result in stable forms of lead, would be only three atoms per hundred on the basis of the analytical data obtained. On this assumption, the atomic weight of the lead from our samarskite, taking 208 as the atomic weight of the thorium lead and 206 for the uranium lead, should have come out 206.06. Lead from the samarskite, however, gave an atomic weight of 206.30. The experimental value corresponds to a mixture of approximately three parts of radio-lead to one part of ordinary lead.

If eight percent of the uranium is transformed along the actinium series, resulting in a stable isotope of atomic weight 210, the value 206.38 would be obtained, which comes nearer to the value found. But the experimental value is in still better agreement with the supposition that either or both of the isotopes of lead in the thorium series are relatively short-lived, and that the lead in samarskite represents a mixture of radio-lead of the uranium series, atomic weight 206, and the actinium series atomic weight 210. This conclusion, however, is not in agreement with the value 206.04 found by Hönigschmid for the atomic weight of lead from crystallized uraninate from Morogoro, G. E. Africa. His result points to the conclusion that the radio-lead of the actinium series is unstable.

Finally, I wish to express my thanks to Dr. Herman Schlundt, Professor of Physical Chemistry, University of Missouri, for the suggestion of the problem and his valued supervision of the work.

Chemical Laboratory
University of Missouri

BIBLIOGRAPHY.

1. O. D. Allen: Am. Jour. Sci., [3] **14**, 131 (1877).
2. G. P. Baxter and F. L. Grover: Jour. Am. Chem. Soc., **37**, 1027 (1915).
3. C. W. Blomstrand and W. C. Brogger: Min. Surnorw. Granitpeg, 142 (1906).
4. Brauner: Abegg's "Handbuch," **3**, II, 613.
5. K. v. Chrustschoff: Verh. Kais. russ. min. Ges., **31**, 412 (1894).
6. Maurice Curie: Comptes rendus, **158**, 1676 (1914).
7. Doelter: "Handbuch der Mineralchemie," **3**, 256 (1913).
8. K. Fajans: Ber. deutsch. chem. Ges., **46**, 422 (1913).
9. W. F. Hillebrand: Proc. Col. Sci. Soc., **3**, 38 (1888).
10. G. C. Hoffman: Am. Jour. Sci., [3] **24**, 475 (1882).
11. A. Holmes and R. W. Lawson: Phil. Mag., **28**, 823 (1914); **29**, 673 (1915).
12. Hönigschmid: Monatshefte, **33**, 253 (1912).
13. Hönigschmid: Sitzungsber Akad. Wiss., Wien., **123**, IIa, 1 (1914).
14. Hönigschmid and St. Horovitz: Comptes rendus, **158**, 1798 (1914).
15. Hönigschmid and St. Horovitz: Monatshefte, **36**, 355 (1915).
16. B. M. Margosches: Die Chemische Analyse, **14-15**, 302 (1912).
17. G. Pisani and A. Lacroix: Comptes rendus, **152**, 559 (1911).
18. C. F. Rammelsberg: Zeit. deutsch. geol. Ges., **29**, 817 (1877).
19. T. W. Richards and M. E. Lembert: Jour. Am. Chem. Soc., **36**, 1329 (1914).
20. T. W. Richards and C. Wadsworth 3rd.: Jour. Am. Chem. Soc., **38**, 2613 (1916).
21. J. L. Smith: Am. Jour. Sci., [3] **13**, 362 (1877).
22. F. Soddy: Chem. News, **107**, 97 (1913).
23. F. Soddy and H. Hyman: Jour. Chem. Soc., **105**, 1402 (1914).
24. G. P. Tschernik: Jour. Russ. Phys. Chem. Ges., **34**, 684 (1902).

FLAME REACTIONS: SELENIUM AND TELLURIUM IN THE HYDROGEN-AIR FLAME

BY JACOB PAPISH

In a recent paper by the author[1] experiments were described in which elementary selenium and tellurium were precipitated from a Bunsen flame charged with the oxides of these elements. From these experiments it has been concluded that the characteristic flame reactions of selenium and tellurium are due to the existence of the free elements in the flame. In order to throw more light on the nature of these reactions, it was deemed desirable to extend the experimental work to the behavior of some of the compounds of selenium and tellurium, and of the elements themselves, in the hydrogen-air flame.

Selenium Dioxide.—This substance, prepared as described elsewhere,[2] was placed in a hard-glass tube provided with a platinum tip. Hydrogen, generated from zinc and sulphuric acid and washed through a solution of silver nitrate, was passed through the tube and ignited above the platinum tip. The selenium dioxide was now heated with a flattened Bunsen flame. After a short while the flame of the burning hydrogen, which had become charged with vaporized selenium dioxide, was seen to consist of a deep blue inner zone surrounded by a pale blue middle zone. The outer zone was greenish. But when the selenium dioxide in the hard-glass tube was heated more highly, thus causing more selenium to volatilize, the outer zone became red in color. No selenium was deposited on the cold object when the outer zone was depressed. The red variety of selenium was obtained when the cold object was introduced in the middle

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[1] Jour. Phys. Chem., 22, 430 (1918).

[2] Ibid., p. 431. The method of preparing tellurium dioxide is also given on the same page. Elementary selenium and tellurium used in the following experiments were prepared by dissolving the purified oxides in hydrochloric acid and precipitating the elements with sulphur dioxide. They were then thoroughly washed and fused.

and in the inner zones. Vapors of selenium dioxide were seen to escape from the outer zone of the flame.

The selenium dioxide, which had been volatilized in a current of hydrogen, was not reduced by the hydrogen to such an extent as to allow free selenium to enter the hydrogen-air flame. The mass which condensed just beyond the space in the glass tube where the selenium was heated, was contaminated very slightly with amorphous selenium, indicating slight reduction, but it was followed by a ring of pure crystalline selenium dioxide. When the flame above the platinum tip was blown out without interrupting the heating of the selenium dioxide in the glass tube, fumes of selenium dioxide were seen to escape. These fumes were allowed to condense in a long glass tube and were found to consist of pure selenium dioxide, as the deposit was not discolored by any of the varieties of selenium. The purity of the deposit also tends to prove that no hydrogen selenide found its way into the flame.

Tellurium Dioxide.—When the experiment just described was repeated with tellurium dioxide in the place of selenium dioxide, the flame was seen to consist of the following: A slender inner zone, green in color, and surrounded by a lilac-colored middle zone. This lilac zone was surrounded by a green outer zone, which constituted the upper half of the flame. Vapors, undoubtedly tellurium dioxide, were seen to escape from the green zone of the flame. On the introduction of the cold object in the outer zone no deposition of tellurium took place. But when the cold object was introduced in the middle zone and especially into the green inner zone, a voluminous deposit of tellurium in the form of a dark mirror was obtained.

No conclusions can be drawn from the above experiments as to the behavior of tellurium dioxide in the hydrogen-air flame, because the tellurium dioxide was readily reduced when heated in the current of hydrogen. The substance that entered the flame and imparted to it the colors described was in the main elementary tellurium.

Hydrogen Selenide.—The introduction of hydrogen selenide in the hydrogen-air flame reminds one of Marsh's test for arsenic and antimony. Selenium dioxide when introduced in the hydrogen generator is reduced very readily by the nascent hydrogen according to the equation:

$$SeO_2 + 4H = 2H_2O + Se,$$

but the quantity of hydrogen selenide formed is negligible, although it can be detected by the characteristic odor and by the colored flashes it imparts to the hydrogen-air flame. For this reason it was found necessary to mix hydrogen and hydrogen selenide, the latter generated from aluminum selenide and water, and burn the mixture as it was issuing from a glass tube provided with a platinum tip. The details of the experiment are as follows:

Aluminum selenide was prepared by heating, in a covered porcelain crucible, a mixture of 5 parts by weight of finely powdered aluminum and 22 parts of powdered selenium. The reaction, which is exothermic in nature, takes place energetically. Fonzés-Diacon[1] suggests the use of a magnesium ribbon to start the reaction. This was found satisfactory for small quantities of the mixture, but in the case of larger quantities the reaction was far from complete. As aluminum selenide is very readily acted upon by moisture, it was sealed off in glass tubes for subsequent use.

Hydrogen, generated from zinc and sulphuric acid and washed through a solution of silver nitrate, was allowed to bubble briskly through an Erlenmeyer flask of 500 cc. capacity half filled with water. This flask, fitted with a three-hole rubber stopper, was provided with a safety tube of 8 mm inner diameter and with a platinum-tipped glass tube for the burning of the escaping gases. The apparatus is no more than a modification of the kind used for the production of the "philosopher's candle." The stream of hydrogen was adjusted and ignited at the point of escape. The result was the ordinary, barely visible, hydrogen flame. Coarsely granu-

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[1] Comptes rendus, 130, 1314 (1900).

lated aluminum selenide was introduced into the Erlenmeyer flask through the safety tube. Shortly after, the flame above the platinum tip assumed a characteristic color and was seen to consist of three distinct zones. The inner zone, which was comparatively short and slender, was very faintly blue. The middle zone, comprising the main portion of the flame, was deep blue, and the outer zone surrounding it was greenish. When the outer zone was depressed with the cold object no deposit of selenium was obtained, but the middle blue zone furnished large quantities of amorphous selenium when subjected to the same treatment.

The structure of the flame can be very strikingly illustrated by depressing the flame longitudinally and horizontally with a glazed paper. The image thus obtained will be seen to consist of a colorless inner cone, of a deep red middle cone, and of a faint red outer cone. Colorless, deep red and pale red rings are obtained when the flame is depressed horizontally. From this it is to be inferred that the inner zone contains the unburned hydrogen selenide, while the middle zone is rich in elementary selenium.

Hydrogen Telluride.—Aluminum telluride, which was used as the source of hydrogen telluride, was prepared by fusing together a mixture of powdered aluminum and tellurium in proportion of 1.6 of the former to 11 of the latter. The combination between these elements takes place with explosive violence, and for this reason, small portions of the mixture should be fused at a time. The apparatus was set up as in the case of hydrogen selenide, and the coarsely granulated aluminum telluride was introduced into the Erlenmeyer flask through the safety tube. As hydrogen telluride is still more unstable than the corresponding selenide, a large quantity of it was decomposed with the precipitation of tellurium before the flame became colored. At last the flame was seen to consist of a slender inner zone, sky-blue in color, surrounded by a lilac zone. The outer zone which formed the upper half of the flame was green in color. When the cold object was introduced into the outer green zone, no deposition of tellurium took place. But when the middle zone or the blue inner zone was depressed, a bright metallic mirror of tellurium was deposited on the cold object.

Selenium.—Selenium was heated in a stream of hydrogen and introduced in the hydrogen-air flame. The inner zone of the flame became blue, while the surrounding middle zone assumed a pale violet color. The outer zone which was not very distinct, except at the top, was greenish, while white fumes, undoubtedly selenium dioxide, were seen to escape from the flame. When the flame was extinguished without interrupting the heating of the selenium, a slight odor of hydrogen selenide could be detected from the escaping gases. This indicates that in addition to free selenium some hydrogen selenide found its way into the flame. The formation of hydrogen selenide in this way is in accordance with the investigations of Pélabon[1] and of Bodenstein.[2]

No deposit of selenium was obtained when the greenish outer zone was depressed with the cold object, but a voluminous deposit of amorphous selenium was obtained from the middle and inner zones.

Tellurium.—When the preceding experiment was repeated with tellurium in the place of selenium the following results were obtained: The inner zone was green; the middle zone was lilac; and when more tellurium was volatilized by applying higher heat, this zone was seen to be resolved into a red zone surrounded by a blue zone. On extinguishing the flame a slight odor of hydrogen telluride was noticed. The results obtained on depressing the flame with the cold object were as follows: No tellurium was obtained from the outer green part of the flame. A mirror of tellurium was obtained when the middle and inner zones were depressed.

A summary of the results is given in the following table:

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[1] Comptes rendus, 118, 142; 119, 73 (1894); 121, 401 (1895); 124, 360 (1897).

[2] Zeit. phys. Chem., 29, 429 (1899).

Substance volatilized	Inner zone		Middle zone		Outer zone	
	Luminescence	Deposit on cold object	Luminescence	Deposit on cold object	Luminescence	Deposit on cold object
SeO_2	Deep blue	Se	Pale blue	Se	Greenish[1]	None
H_2Se	Very faint blue	None	Deep blue	Se	Greenish	None
Se	Blue	Se	Violet	Se	Greenish[2]	None
TeO_2	Green	Te	Lilac[3]	Te	Green	None
H_2Te	Blue	Te	Lilac	Te	Green	None
Te	Green	Te	Lilac[4]	Te	Green	None

Conclusions

It is impossible to say with certainty just what the causes are of the different luminescences described in this paper. In the case of the outer zones of the flames charged with the compounds of selenium and with the element itself, it may be concluded that the greenish luminescence is due to the existence of the oxide, or oxides, of selenium in these zones. The blue luminescence of the middle and inner zones is undoubtedly due to the formation and existence of elementary selenium. The formation of selenium is a process of dissociation and reduction, while the disappearance of elementary selenium in the outer zone is a process of oxidation, and these may account for the different luminescences.

Turning our attention to the luminescence due to tellurium and its two compounds used, we notice again a similarity in the different outer zones and in the middle zones. The outer zones are green and the middle zones are lilac, whether the flame be charged with tellurium dioxide, hydrogen telluride, or with tellurium. It is true that tellurium dioxide and tellurium gave identical results due to the reduction of

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[1] Becomes red if much selenium dioxide is volatilized.

[2] Occasional red flashes.

[3] Accompanied by red flashes.

[4] Also red surrounded by blue when much tellurium is volatilized.

the dioxide in the current of hydrogen, and for this reason the only substances to be considered are tellurium and hydrogen telluride. Here again processes of dissociation, reduction and oxidation are back of the luminescences of the different zones.

Department of Chemistry
Purdue University
Lafayette, Indiana

NEW BOOKS

Heredity and Environment. *By Edwin G. Conklin. Revised second edition. 21 × 15 cm; pp. xvi + 550. Princeton: Princeton University Press, 1918. Price: $2.00.*—The headings of the chapters are: facts and factors of development; cellular-basis of heredity and development; phenomena of inheritance; influence of environment; control of heredity—eugenics; genetics and ethics.

Upon the fundamental likeness between the life processes of man and those of other animals are based the wonderful advances in experimental medicine, which may be counted among the greatest of all the achievements of science. The experimental study of heredity, development and evolution in forms of life below man must certainly increase our knowledge of and our control over these processes in the human race. If human heredity, development and evolution may be controlled even to a slight extent, we may expect that sooner or later the human race will be changed for the better. At least no other scheme of social betterment and race improvement can compare for thoroughness, permanency of effect, and certainty of results with that which attempts to change the natures of men by establishing in the blood the qualities which are desired.

The entire individual—structure and functions, body and mind—develops as a single indivisible unity; but for the sake of clarity, it is desirable to deal with one aspect of the individual at a time. For that reason we shall consider first the development of the body, and then the development of the mind. In practically all animals and plants individual development begins with the fertilization of a female sex cell or egg by a male sex cell or spermatozoon. After its entrance into the egg, the sperm nucleus moves toward the egg nucleus until the two meet, when they divide by a complicated process known as mitosis or indirect nuclear division. After the germ nuclei have divided, the entire egg divides by a process of constriction into two cells. This is the beginning of a long series of cell divisions, each of them essentially like the first, by which the egg is subdivided successively into a constantly increasing number of cells. From this stage onward the course of development differs in different classes of animals. Usually the many cleavage cells form a hollow sphere, the blastula, and this in turn becomes a gastrula, in which at first two, and later three, groups or layers of cells may be recognized. By further differentiation of the cells of these layers and by dissimilar growth and folding of the layers themselves, the various organs of the embryo begin to appear. This very brief and general statement of the manner of embryonic development applies to all vertebrates, man included. In one respect the development of the human being or of any mammal is apparently very different from that of a bird or frog or fish, viz., in the fact that in the former the embryonic development takes place within the body of the mother, whereas in the latter the eggs are laid before or soon after fertilization. This difference is not a fundamental one for in different animals there are all stages of transition between these two modes of development. While in most fishes, amphibians and reptiles the eggs are laid at the beginning of development and are free and independent during the whole course of ontogeny, there are certain species in each of these classes in which the development takes place within the body of the female before the eggs are laid, and there are mammals (monotremes) which lay eggs, while in others (marsupials) the young are born in a very imperfect condition.

The development of the mind from the activities of the germ cells is certainly most wonderful and mysterious, but probably no more so than the development of the complicated body of the adult animal from the structure of the germ. Both belong to the same order of phenomena and there is no more reason for supposing that the mind is supernaturally created than that the body is. Indeed, we know that the mind is formed by a process of development, and the stages of this development are fairly well known. There is nowhere in the entire course of mental development a sudden appearance of psychical processes, but rather a gradual development of these from simpler and simpler beginnings. The most fundamental phenomenon in the behavior of organisms is irritability or sensitivity, which is the ability of receiving and responding to stimuli: this is one of the fundamental properties of all protoplasm. Another general characteristic of protoplasm is the capacity of storing up or registering the effects of previous stimuli. A single stimulus may produce changes in an organism which persist for a longer or shorter time, and if a second stimulus occurs while the effect of a previous one still persists, the response to the second stimulus may be very different from that of the first. The embryos, and indeed even the germ cells of higher animals, may safely be assumed to be endowed with protoplasmic and organic memory out of which, in all probability, develop associative and conscious memory in the mature organism. Even the intellect and reason which characterize man so strongly have had a development from relatively simple beginnings. All children come gradually to an age of intelligence and reason. Another characteristic, which many persons regard as the supreme psychical faculty, is the will. This faculty also undergoes development and from relatively simple beginnings. The will of the child has developed out of something which is far less perfect in the infant and embryo than in the child. The most complex of all psychic phenomena, indeed the one which includes many if not all of the others, is consciousness. There seems good reason for believing that the continuity of consciousness, the continuing sense of identity, is associated with the continuity of organization, for in spite of frequent changes of the materials of which we are composed our sense of identity remains undisturbed.

These are some of the facts of development. The factors of development may be classified as intrinsic in the organization of the germ cells, and extrinsic as represented in environmental forces and conditions. The intrinsic factors are those which are commonly called heredity, and they direct and guide development in the main; the extrinsic or environmental factors furnish the conditions in which development takes place and modify its course more or less.

This brief summary of the first chapter will give some idea of the style and scope of the book. The author has summed up the third chapter himself, p. 306. "The principles of heredity established by Mendel are almost as important for biology as the atomic theory of Dalton is for chemistry. By means of these principles particular dissociations and recombinations of characters can be made with almost the same certainty as particular dissociations and recombinations of atoms can be made in chemical reactions. By means of these principles the hereditary constitution of organisms can be analyzed and the real resemblances and differences of various organisms determined. By means of these principles the once mysterious and apparently capricious phenomena of prepotency, atavism, and reversion find a satisfactory explanation."

On p. 329 there is an account of an interesting but rather unpleasant experiment. "If the fertilized egg is whirled rapidly on a centrifugal machine it may be subjected to a pressure several thousand times that of gravity. Under such conditions the heavier particles are thrown to one side of the egg and the entire surface of the egg becomes stratified into layers or zones. In the ascidian egg, where the different kinds of protoplasm give rise to different tissues and organs, this rearrangement of the egg substances may lead to a marked dislocation of organs; the animal may be turned inside out, having the endoderm on the outside and its ectoderm or skin on the inside, etc."

The author's views on education are quite definite, pp. 364, 466, 497. "In education we are strangely blind to proper aims and methods. Any education is bad which leads to the formation of habits of idleness, carelessness, and failure, instead of habits of industry, thoroughness and success. Any religious or social institution is bad which leads to habits of pious make-believe, insincerity, slavish regard for authority and disregard for evidence, instead of habits of sincerity, open-minedness and independence. * * No given environment or training can be good for every individual, nor for the same individual at every stage of development. Every individual is unique and if the best results are to be had must have unique environment and training, which must be supplied by omniscient intelligence. However, the impossibility of securing the absolutely best conditions of development need not prevent society from securing better conditions than those which now prevail."

"Already a few enthusiastic persons have begun to apply these doctrines [of heredity] to practical affairs. We are told that children should never be admonished or punished, for they do only what their natures lead them to do; the nature of the child must be respected and must be allowed to manifest itself in its own way. Lying and stealing will cure themselves like mumps, or they will remain incurable, in which case the germ plasm is to blame and nothing could have been done anyway. Laziness is due to inheritance or to hookworms; the latter kind may be cured but not the former. Thriftlessness, alcoholism, and uncleanness run in families and can be cured only by extermination. Men who prey upon society were born with wolfish instincts and cannot help but eat the lambs. Villains, law-breakers, murderers should be pitied but not punished; if blame attaches to their deeds, it falls upon the marriage bureau and the parents. The world needs hospitals and sanatoria and sterilization institutes for the criminal and the vicious, but not courts and prisons, and all punishments should be visited only upon the parents to the third and fourth generations. * * * There are many similarities between such an extreme view and the old doctrine of preformation, and it contains a like absurdity. It practically denies development altogether."

"This debilitating philosophy in which everything is predetermined, in which there is no possibility of change or control, in which there is hypertrophy of intellect and atrophy of will, is a symptom of senility whether in men or nations. We need to return to the joys of a childhood age in which men believed themselves free to do, to think, to strive, in which life was full of high endeavor and the world was crowded with great emprise. We need to think of the possibilities of development as well as of the limitations of heredity."

The possibilities of development are emphasized on p. 486. "Will is indeed the supreme human faculty, the whole mind in action, the internal stimulus which may call forth all the capacities and powers. And yet the will does not directly create nor even discover these powers; they are produced by the factors of development, by heredity, environment and training; and they are usually discovered by accident or under the stress of necessity. How often have we surprised ourselves by doing some unusual or prodigious task! What we have once done we feel that we can do again. We realize more or less clearly, depending upon our experience, that what we habitually do is far less than we could do. It is this reserve upon which we can draw on special occasions that gives us the sense of freedom."

While there may not be much physical chemistry as such in this book, it is a book which will interest all physical chemists and which should be read by them.
Wilder D. Bancroft

Lecithin and Allied Substances. The Lipins. *By Hugh Maclean. 25 × 16 cm; pp. vii + 206. New York: Longmans, Green & Co., 1918. Price: $2.25.*— The present monograph on "lecithin and allied substances" is the latest addition to the excellent series of monographs on biochemistry, edited by Plimmer and Hopkins. In it Maclean has collected and correlated the chaotic literature dealing with the so-called "Lipoids," a difficult task, which was not made easier by the fact that the author was called to France before the work was completed.

Lipins are substances of a fat-like nature, yielding on hydrolysis fatty acids or derivatives of fatty acids and containing in their molecule either nitrogen or nitrogen and phosphorus.

Maclean uses the term lipin as a class name to include the cerebrosides and phosphatides. He wisely omits cholesterol and many other bodies, natural and artificial, which are alcohol- and ether-soluble, and often time included in the term lipin (Rosenbloom), because as he states (p. 2), the term then ceases to have any significance, since the only relationship between these bodies is limited to the physical one of common solubilities in certain solvents.

While no final classification of the lipins can be adopted until research has succeeded in ascertaining the chemical constitution of these substances, Maclean provisionally adopts the following:

A. Phosphatides.
  I. Monoaminomono phosphatides.
    1. Lecithin.
    2. Cephalin.
  II. Diaminomono phosphatides.
    1. Sphingomyelin.
  III. Monoamino diphosphatides.
    2. Cuorin (whose existence as chemical compound is questioned.)
B. Cerebrosides.
    1. Phrenosin.
    2. Cerasin.

Lecithin as the term is ordinarily used, signifies that fraction of the tissue, which is soluble in alcohol and ether and insoluble in acetone. This material, however, has been shown by various investigators (Maclean, Moruzzi, Levene and West), to be a mixture of two substances, lecithin and cephalin (presence of amino nitrogen). They may be separated by using different solubilities of the cadmium chloride compounds in ether (Macelan). A pure lecithin has also been obtained from the lecithin fraction which remains dissolved in the egg oil, by precipitating with acetone, and crystallizing the cadmium chloride compound from alcohol-ethyl acetate (Levene and West). While Maclean was unable to obtain pure cephalin from the mixture, its presence has been shown by isolating amino ethyl alcohol as the gold salt (Maclean, Levene and West). The study of this mixture is more easily carried out on the reduced lecithin. By repeated fractionations Levene and West obtained a product with less than 1 percent of amino nitrogen and from the more soluble fractions of the lecithin mixture (unpublished work) a nearly pure reduced compound (Ritter, Levene and West) may be obtained. Since on hydrolysis these yield only stearic acid, this leaves little doubt that lecithins contain only fatty acids with 18 carbons. Bailly claims to have shown that egg lecithin is a mixture of at least two isomers containing the symmetrical and asymmetrical varieties of glycero-phosphoric acid, and states that the inactive asymmetrical form predominates. Whether these two forms are associated with the mixture of lecithin and cephalin, or whether there are two forms of lecithin, remains to be established. The nature of the base, choline, is definitely established.

The chemistry of *cephalin*, the ether-soluble, alcohol-insoluble fraction of the extract, is less satisfactory.

All the investigations agree that the cephalin molecule probably consists of stearic and linolic (or an isomer) acids, aminoethyl alcohol and glycero-phosphoric acid. A comparison of the theoretical values with those actually obtained shows that a considerable discrepancy exists, particularly with regard to the percentage of C and H. The carbon is at least 5 percent less than the theoretical requirements. Thudichum realized this difficulty and endeavored to account for the difference by assuming that each mole of cephalin contained 5 moles of water. With such an assumption, the hydrogen content is much too low. At present the available evidence tends to suggest that the difference is largely due to oxidation of the unsaturated acid in the molecule, but the question must be left an open one.

The existence of *cuorin* is questionable. The tissue contains small amounts of a body closely resembling cephalin in physical and chemical properties, but having considerable more phosphorus than cephalin (Erlandsen, heart; Maclean, kidney, egg-yolk; Baskoff, liver. Whether these bodies are mixtures, or in some cases artificial products, is at present undecided. The method of preparation is such that the complete removal of cephalin is practically impossible; this makes one hesitate to accept the chemical individuality of cuorin.

Sphingomyelin is the only crystalline phosphatide thus far isolated from the brain. Because of its close resemblance in physical properties to the cerebrosides it was believed by many early investigators that these formed a definite compound, *protagon*. Recent work, however, has cleared this point. As yet, however, no one has been able to obtain a pure sphingomyelin. Levene's best sample contained, in addition to lignoceric acid, a low melting acid, which could not be obtained pure. Whether the molecule is of the nature of a diphosphatide, containing the two fatty acids, or whether it is a mixture of two phosphatides, differing only in their fatty acids, is still to be determined. The phosphatide contains in addition to the fatty acids, phosphoric acid (but no glycerol), choline and sphingosine. A peculiar behavior of sphingosine during the process of hydrolysis has been observed by Levene, who found that the base loses a molecule of water, and gives rise to a base of the nature of anhydrosphingosine. Maclean (p. 59) apparently believes that Levene has confused the formula of this compound; Levene really analyzed the dihydro derivatives and so states in his paper.

At the close of this chapter, Maclean gives detailed directions for the ordinary methods of drying tissue and the extraction, separation, and purification of the various phosphatide.

The term cerebroside (Rosenheim) has been adopted in preference to cerebrogalactodide (Thudichum) or galacto lipine (Leathes). The two members of these series are phrenosin and cerasin. There is probably no question but that phrenosin has been obtained pure. Its compounds are: cerebronic (phrenosinic) acid, galactose and sphingosine. While Rosenheim feels that he has likewise obtained pure cerasin, the recent work of Levene and West makes this appear doubtful. The components of cerasin are, without question, lignoceric acid, galactose, and sphingosine. That is, the two cerebrosides differ only in nature of the fatty acid, a fact recognized by Thudichum as being probably true. Cerebronic acid has been shown to be the hydroxy derivative of the higher homologue of lignoceric acid. The constitution of lignoceric acid is unknown. The structure of sphingosine has been shown to probably be,

$$C_{12}H_{23}CH — CH — CH(OH)CH(OH)CH_2NH_2,$$

although the position of the amino group relative to the two hydroxyl groups is not known.

The history of *protagon* is fully given, and the work which finally led to the conclusion that it was nothing more than a mixture of cerebrosides and sphingomyelin with traces of other bodies. "Carnaubon" (Dunham) is simply so-called "protagon" and represents a variable mixture of Lipins. *Para-nucleo-protagon* (Ulpiani and Lilli) is probably a protagon-protein mixture. The many compounds of Fränkel and his collaborators are justly classed together as insufficiently characterized lipins, for, as Maclean states (p. 146), Fränkel has produced no reliable evidence whatever that any of his alleged new bodies exist. It is now certain that several of these were mixtures of lecithin with other substances. While future research may show that some of these ill-characterized bodies do really exist in the tissues, at present the evidence does not favor their inclusion among the well defined lipin bodies. Among these may be named: *Vesalthin*, *Neottin*, *Sahidin*, *Leucopoliin*, *Jecorin*, and other to which no individual name has been given.

Our present knowledge of plant lipins is extremely limited, and we do not yet know with any certainty whether or not plant and animal lipins are identical. While there is a certain amount of evidence pointing to the conclusion that no essential difference exists between the lipins of the two kingdoms, this view is by no means universally accepted.

The question as to the nature of the plant lipins opens up what promises to be a fertile field for future research. The application of some of the newer methods used in the case of animal organs may result in the solution of many of these problems. The little work already done deals chiefly with the plant phosphatides.

The chapter on the function of the lipins leads Maclean to the assertion that, so far, the special part played by the lipins in the activity of the organism is entirely unknown to us. There is hardly a statement made on this problem by one investigator, which is not contradicted by some other observer. From the physical point of view the colloidal nature of the lipins is of importance in regulating certain processes in the cell. The presence of unsaturated fatty acids in the molecule is also suggestive, since the chemical reactivity of the molecule is thereby increased. The function of the lipins in the following biological functions is discussed: metabolism and growth, narcosis and in certain oxidative processes, respiration of plants, action on the digestive ferments (proteolytic, diastatic, lipolytic lipase) and the coagulation of the blood.

A 22-page bibliography is appended. The book sums up clearly and thoroughly the present state of our knowledge of the lipins; as one reads, one can but wonder at the gaps in our knowledge and at the great amount of work necessary to clear up all the questions raised by Maclean. The methods of extraction and separation of the individual lipins must be worked out and improved. New methods of hydrolysis must be developed and the product of hydrolysis separated. Then the relation of the lipins of the various organs of a given species of the same organs in different species, and of the different kingdoms must be established. Owing to the difficulty of the work it will probably be many years before even a part of this program can be accomplished.

Clarence J. West

Airplane Characteristics. *By Frederick Bedell. 24 × 16 cm; pp. 125. Ithaca: Taylor and Compnay, 1918. Price, $1.75.*—In the preface the author says: "It is the author's purpose to present the principles of airplane sustentation and stability, and the characteristics of an airplane in flight in a way that is direct and simple and at the same time reasonably precise, laying particular stress on that which is vital." There are four chapters, entitled: sustentation; relations in flight; resistance; lateral stability; and directional stability. In addition there are four appendices: glossary; thrust characteristics; power characteristics; control and other diagrams.

If an inclined plane is driven fast enough through the air, the vertical component or lift will be greater than the force of gravity and the plane will rise. A flat plane disrupts the air, both the entering edge, and, to a lesser extent, the trailing edge tending to produce air eddies. The turbulence produced by such a plane increases the wing-resistance and decreases the lift. By giving the wing more or less of a stream-line form, an increase in lift and decrease in wing-resistance can be obtained. This is done by arching the wing from front to back. A wing thus arched is called a cambered wing and is always used in airplane construction.

A cambered plane exerts a lift even at a small negative incidence. Zero lift is usually obtained when the incidence is between —2° and —4°; but in extreme cases the incidence may be decreased to —6° or —8° before zero lift is reached. Although in most cases an airplane flies with a positive incidence, at high velocities it may fly with zero incidence or with a small negative incidence; but not within two or three degrees of the point of zero lift. In approaching the point of zero lift there is danger of going too far, so that the air strikes the surface of the wing causing the machine to take a nose dive. The upper limit of maximum lift is possible but it usually is only approached because there is an increasing danger of stalling, leading to a fall or tail slide.

Some early machines had a very small speed range, from perhaps a minimum of 35 to a maximum of 50 miles per hour, giving a speed range of 15 miles per hour. A gust from behind of more than 15 miles per hour would reduce the relative speed below the requisite 35 miles per hour necessary for sustentation, so that the machine would have no support. This is the cause of the so-called holes in the air.

For mechanical reasons wings are made with fixed area and camber. A practical wing with either of these adjustable would do much to advance the art of flying, for it would make possible a great increase in speed range both by increasing the maximum and decreasing the minimum speed. These improvements have long been considered, the adjustable camber now seeming the more promising of the two. With adjustable wing-area the pilot would use large area for low speed and small area for high speed. With adjustable camber the pilot, at low speed, would use such camber as would give maximum lift. For high speed he would flatten out the wing and so get less lift without a dangerous reduction in incidence. This flattening out of the wing would also bring about a reduction of wing-resistance, a highly important advantage at high speeds. For the present, however, it is necessary to be content with wings of fixed area and camber.

The wings of an airplane are its first essential for they create the lift; but they cause wing-resistance while creating lift. Although not a cause of lift, wing-resistance is a necessary concomitant, being the price paid for the lift. Unfortunately this is not all. In addition to wings an airplane must have other parts—body, landing gear, struts, wires, etc.—all of which have a resistance; but, unlike the wings, these parts do not contribute to the lift. The resistance of these parts is called parasite resistance and one of the important problems in design is to make this parasite resistance as low as possible, for parasite resistance, though small at low velocities, is very great at high velocities, being perhaps fifty percent more than wing-resistance at ordinary maximum flying velocities. While about two-fifths of the power delivered through the propeller by the engine is used in airplane flight in pushing the wings through the air, approximately three-fifths of the power is used up in parasite resistance which is therefore the biggest obstacle to high-speed flight.

. In the case of a cylindrical strut or wire, a large part of the resistance of the strut to motion the air is due to the turbulent region of low pressure behind it. The more nearly a body conforms to stream-line flow the less is its resistance because the turbulence and suction back of the body is then reduced to a minimum. Only a little is gained by tapering the front side of a cylinder or strut. Note the blunt breast and tapering tail of a bird and the shape of a fast swimming fish that can dart through the water with scarcely a ripple. For low resistance wheels and body should be enclosed; these, as well as every strut and wire, should be stream-lined so far as possible. A small cylindrical wire may offer much more resistance than a larger wire that is well stream-lined.

The law for parasite resistance is summed up in the statement, determined by experiment, that parasite resistance varies as the square of the velocity. This applies to the airplane as a whole, as well as to the separate parts. If a certain airplane, for instance, has a parasite resistance of 64 pounds when flying at 40 miles per hour, it will have a resistance of 256 pounds at 80 miles per hour.

Lateral control might well be obtained by shifting the center of gravity; but this is not done. It has been obtained by warping (*i. e.*, distorting) the planes; but lateral control is generally obtained now by means of auxiliary planes or *ailerons* which may be independent of the main planes. To roll the machine the pilot turns the aileron on one wing down and the other aileron up simultaneously, thus giving more lift to one wing so that it rises and less lift to the other so that it descends. This movement of the ailerons is effected usually by pushing the control stick or by turning the control wheel to left or right. The term "warping" is used frequently to include this control of ailerons.

In a machine with one propeller, the rotation of the propeller in one direction, tends, when the power is on, to make the whole machine rotate in the opposite direction. This may be corrected for easily in the control by the pilot or automatically by a difference in the lift of the two wings. When flying, any correction is made unconsciously by the pilot. When starting, however, the correction may be noticeable, for the amount changes as the engine accelerates. It is also particularly important to keep both wings even while near the ground. When there are two propellers rotating in opposite directions, the effects of propeller torque are neutralized.

Turning causes banking because the outer wing has the higher velocity and greater lift, therefore tending to rise on a turn while the inner wing tends to descend. Also the pressure on the keel surface during a turn tends to keel the machine over provided the keel center is above the rolling axis, as is usually the case. If a machine is banked too much for a particular turn, it will slip in and down on account of the horizontal component there is to the lift and the decrease in the vertical component. This may result in a nose dive. If a machine is not banked enough, it will skid out and (in some cases, due to the inertia of the machine) up, this being likely to happen on sharp turns and at high speeds. This may end in a stall, as the relative wind strikes the machine less from the front and more from the side, thus giving less support to the machine on account of its decreased forward velocity.

When the wings are inclined, whatever the cause, the lift on the wings not only has a vertical component but also a horizontal sideways component, which tends to move the machine horizontally toward the side that is down, thus deflecting the flight path. This becomes more pronounced in machines with large keel surface. By placing large keel surfaces both forward and aft, certain machines are turned entirely by banking and are provided with no rudder.

The propeller and revolving parts of the engine form a gyroscope, so that a sudden turn of the machine sideways will cause it to pitch or rear. Similarly any sudden pitching or rearing will cause the machine to turn to one side because the application of a force suddenly perpendicularly to the axis of a gyroscope causes the axis to swing sideways at right angles to that force. The direction of this effect will depend upon the direction of rotation of the revolving parts and so may be opposite in different machines. The effect will be but small when the controls are not jerked suddenly and they should not be operated suddenly on account of the severe stresses produced.

The book is written clearly and simply. To the layman it seems like a good book. There is an occasional slip in the glossary. Under "fuselage" we are told to look under "body;" but there is no reference there to "fuselage."

Wilder D. Bancroft

James Woodhouse, a Pioneer in Chemistry. *By Edgar F. Smith. 20 × 14 cm; pp. iv + 299. Philadelphia: The John C. Winston Company, 1918. Price: $1.50.*—In the preface the author says: "Offering to readers the biography of a man who ceased to live one hundred and nine years ago may call for explanation; if so, the reasons are at hand. First, the subject of this sketch was a chemist; second, the status of chemical science in our country, at present, is excellent, and in the future is bound to rise to an even more exalted position, so it is hoped that the student of its history, upon inquiring as to its rise and development, will welcome the facts pertaining to the labors and successes of its earliest pioneers. 'However, the records of these are widely scattered, and what is more, are rapidly disappearing. To assemble those still extant would require much time and enduring patience. The material presented in the life story of James Woodhouse has been gathered through many years, and as it has grown and been studied there shone forth in it innumerable evidences of a splendid, masterly leadership, with data of exceptional value. For instance, if chemists were to pause and ask—were there chemists on these shores who took an interest and participated in the struggle waged about the new chemistry, as set forth by Lavoisier and his associates, when it was arrayed against the strange doctrine promulgated by Becher, Stahl, and hosts of devoted experimenters in many lands, the answer, so far as we are concerned, would be found in the labors of Woodhouse, who was foremost in establishing the teachings of the French School upon American soil? And he was also a genuine leader in other lines of chemical endeavor, for he was a real investigator, who independently isolated potassium and published facts of unusual importance. To-day, it is true, many of his observations would be held as trivial, but compared with contemporaneous contributors at home and abroad they rank exceedingly high. Further, Woodhouse introduced Robert Hare, Benjamin Silliman and others into chemical science; and it is conceded that they, too, became leaders in this field of research.'"

Woodhouse was born in Philadelphia in 1770 and graduated from the University of Pennsylvania in 1787. In 1795 he was elected Professor of Chemistry, a position which he held until his death in 1809. He was the founder, and the only president of the Chemical Society of Philadelphia, the first chemical society in the world. He seems to have begun his research work by studying the action of poison ivy as a cure for consumption. His most important contributions to science were his attacks on the phlogiston theory, though his letter showing that a supposed artificial wall in North Carolina is really basalt might serve as a model to-day. The article on the value of chemical knowledge, p. 214, is one that everybody should read. In 1808 Woodhouse obtained particles of potassium independently by heating a mixture of soot and potassium carbonate. He was also interested in all sorts of miscellaneous subjects, such as indelible ink, cooling of water by evaporation, the making of bread, the burning of anthracite coal, the refining of camphor, etc. *Wilder D. Bancroft*

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A Text-Book of Inorganic Chemistry. *By H. F. V. Little. Edited by J. Newton Friend. Vol. IV. 22 × 16 cm; pp. xx + 485. Philadelphia: J. B. Lippincott Company, 1917. (Charles Griffin and Co., Ltd.) Price $5.00.*—"The present volume aims at giving a tolerably complete and readable account of the inorganic chemistry of the elements of the third group of the Periodic Table, together with cerium and the tervalent rare earth elements. Where they are of particular interest or importance, however, various organic compounds of these elements have also been described, particularly in dealing with the rare earth elements. So far as was possible without overburdening the text, the results of modern physico-chemical work have been included. It is hoped that the bibliography relating to the pure chemistry—inorganic and physico-chemical— of the elements described is practically complete and that no important references are omitted. The discussions of mineralogical, technical, and analytical chemistry are of necessity very brief, but it is to be hoped that the bibliographies attached to them will be of service to the reader.

"The chapters dealing with the rare earth elements together constitute more than half the book, and form the most complete account of the chemistry of these elements that has yet appeared in English. No apology is needed for the somewhat lengthy discussion of the spectra of these elements. The nature of the cathodic phosphorescence spectra has been purposely discussed in considerable detail, and it is hoped that the description of Urbain's beautiful researches on this subject may assist English chemists in realizing that the atmosphere of mystery and romance which they have so long associated with these elements has at last been dispelled."

The first nine chapters are entitled: introductory; boron; aluminum; clay and ceramics; ultramarine; gallium; indium; thallium; scandium. Then come five chapters on the rare earth elements and the book ends with a chapter on actinium and its disintegration products. The book is an admirable one and surprisingly complete. If the other volumes are as good as this one, the set will be an extremely valuable one. *Wilder D. Bancroft*

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Theories of Energy. *By Horace Perry. 19 × 14 cm; pp. vii + 231. New York: G. P. Putnam's Sons, 1918. Price: $1.75.*—Each chapter is entitled the theory of something: energial propagation; energetic atom; energy; energizement; spectral lines; energial motion; chemical reaction; gravity; magnetism; electricity; reflection; color; double refraction; polarization; edgetal deflection. The quality of the book may be judged by a paragraph on the methods of energizement, p. 39.

"It [matter] may be energized centroatomically by both qualities of all or some of the manners of the engaging energy, which may be called centroatomic energizement, and the matter may be said to be centroatomically energized. It may be energized transatomically by both qualities of all or some of the manners of the engaging energy, which may be called transatomic energizement; and the matter may be said to be centroatomically energized. The matter being composed of different substances, mixed together, one may be energized centroatomically by both qualities of some of the manners of the engaging energy, and transatomically by both qualities of the other manners thereof and of the centroatomic energy of the rest of the matter, and the other substance, or each of the other substances, if more than one, may be energized controatomically by both qualities of the other manners of the engaging energy (each substance, if more than one, being so energized by different manners) and transatomically by both qualities of the other manners thereof and of the centroatomic energy of the rest of the matter, or, one more of the substances being so energized, the other substance or substances may be energized transatomically by both qualities of all the manners of the engaging energy and of the centroatomic energy of the rest of the matter. This may be called misceous (mixed) energizement, and the matter may be said to be misceously energized. Translucency results from this method of energizement by light."

Wilder D. Bancroft

Text-Book of Inorganic Chemistry. *By A. F. Holleman. Translated by H. C. Cooper. Fifth English edition. 23 × 16 cm; pp. viii + 521. New York: John Wiley and Sons, Inc., 1916. Price: $2.25.*—Through an oversight this new edition was not reviewed promptly. In the preface the translator says that "very many of the descriptive portions have been rewritten, notably those on sulphur, ammonia, the nitrogen oxides and the phosphorus sulphides, as well as the sections on atomic and molecular weights, colloids, noble gases and rare earths, while the subjects of gaseous equilibrium, association, metallic state and intermetallic compounds, and atomic structure furnish new material. The chapter on metal-ammonia compounds is reprinted as approved by Professor Werner for the third edition. The physical data have been revised by the author. On melting points, however, the disagreement is still annoying. The word 'aluminum' is so widely used in the trade and everyday life that the more classic spelling has been abandoned in this edition."

Holleman has long been recognized as a most satisfactory writer of chemical text-books, and a revised edition of so admirable a book is always welcome, especially when the translation is done as well as Professor Cooper does it.

Wilder D. Bancroft

Principles of Chemistry. *By Joel H. Hildebrand. 19 × 13 cm; pp. ix + 313. New York: The Macmillan Company, 1918. Price: $1.75.*—"It seems to the author that the ideal text-book would consist of two volumes, one of general principles, the other of descriptive chemistry. Since, however, the descriptive material is available in so many existing books, the limit of the author's present ambition is a presentation of the principles of chemistry in such a way as to allow, in its use, the maximum flexibility consistent with the subject. It is hoped that the treatment of these principles in this volume is such that the various chapters and sections can be used with almost any arrangement of descriptive material."

The general headings are: kinds of matter; the gas laws and the kinetic theory; weight relations in chemical reactions, and atomic theory; volume of gases, and molecular weights; types of chemical compounds; valence, and writing equations; chemical nomemclature; quantitative relations involving solutions of known concentrations; thermochemistry; behavior of substances dissolved in water, and the ionic theory; the speed of chemical reactions; the effect of concentration on chemical equilibrium; chemical equilibrium, and properties which may effect concentration; the effect of pressure and temperature on chemical equilibrium; oxidation and reduction; periodic system; the constitution of the atom; dispersed systems.

There are very few mistakes. On p. 141 it is unwise to imply that the kinetic theory accounts satisfactorily for the increase of reaction velocity with rising temperature. On p. 160 it is unfortunate to compare chemical equilibrium with the swing of the pointer of the balance, because a student will consider that chemical equilibrium is reached after oscillations and not asymptotically. On the other hand, there is an admirable paragraph, p. 244, on oxidizing power and speed of oxidation. "There are some substances, like hydrogen peroxide, which would have great oxidizing power if they could react rapidly enough. It is important to distinguish between an oxidizing agent that is 'strong' because it is rapid, and one which is strong but slow. Thus iodine will often react more rapidly than chlorine, and hence produce more oxidation in a given time. Its true oxidizing power is much less, as shown by the fact that it will not oxidize ferrous ion completely, whereas chlorine will. The oxygen acids, like nitric and sulphuric acids, are not rapid oxidizing agents. This seems to be connected with the fact that they are highly ionized. Nitrous acid, which is not a stronger oxidizing agent in the true sense of the term is nevertheless a much more rapid oxidizing agent, and is, at the same time, much less dissociated."

The book seems to be well written and logical and yet it is a bit disappointing. It is good and worthy but uninteresting. This may be the fault of the author, or it may be that the assumption of the desirability of two distinct volumes is wrong. The reviewer admits his inability to put his finger on the trouble and yet it seems certain that the book does not measure up to what one had expected of the author. *Wilder D. Bancroft*

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