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THE MECHANISM OF THE COAGULATION OF SOLS BY ELECTROLYTES. I. FERRIC OXIDE SOL

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Two general theories of the mechanism of the coagulation of sols by electrolytes have been proposed: the adsorption theory of Freundlich and what may be termed the solubility theory of Duclaux and Pauli.

The Adsorption Theory. The widely accepted adsorption theory[1] assumes in the first instance that the particles of hydrophobic sols owe their charge to the preferential adsorption of ions from the intermicellar solution. Thus silver chloride formed in the presence of a slight excess of silver nitrate is positively charged because the particles adsorb silver ion more strongly than nitrate ion whereas silver chloride precipitated with a slight excess of sodium chloride is negatively charged because, in this case, the anion is the more strongly adsorbed. Similarly, hydrous ferric oxide thrown down in the presence of a slight excess of ferric chloride or hydrochloric acid is positively charged because of preferential adsorption of cations. The addition of suitable amounts of electrolytes to such colloidal systems causes coagulation as a result of preferential adsorption of the ions whose charge is opposite to that on the colloidal particles. This adsorption lowers the charge on the particles below a critical value and the colliding particles agglomerate into clumps sufficiently large to settle out. The ions whose preferential adsorption by the sol particles is responsible for their charge are called stabilizing ions while the added ions of opposite charge whose adsorption lowers the particle charge, are called precipitating ions. Since the ions of a precipitating electrolyte which have the same charge as the sol help to determine the critical concentration necessary for coagulation, the precipitation concentration or precipitation value of an electrolyte for a sol has been defined[2] as that concentration which results in sufficient adsorption of the precipitating ion to neutralize below a critical value, the combined adsorption of the original stabilizing ion and that added with the electrolyte. That the precipitating ions are carried down by the coagulated particles was demonstrated first by Linder and Picton[3] and then by Whitney and Ober[4] and has been confirmed repeatedly by a number of investigators.

To account quantitatively for the wide variation in the precipitating power of electrolytes of varying valence, Freundlich assumed that equal amounts of precipitating ions are adsorbed from equimolar solutions and that equivalent amounts of ions of different valence are carried down at the precipitation value. The evidence to support these assumptions was not con-

[1] Freundlich: "Kapillarchemie," 1st Ed., 345 (1909); 2nd Ed., 572 (1922).
[2] Weiser and Nicholas: J. Phys. Chem., 25, 742 (1921).
[3] J. Chem. Soc., 67, 63 (1895).
[4] J. Am. Chem. Soc., 23, 842 (1902).

clusive and it was demonstrated 10 years ago in the author's laboratory[1] that they are not generally true. Freundlich[2] has recently convinced himself that his original postulates are not in accord with the facts.

To account for the variation from equivalent adsorption during precipitation of sols, it was assumed[3] that the adsorption of equivalent amounts of the several ions was necessary to neutralize the charge below the critical value and that the observed variation from equivalence was due to varying adsorption of the several electrolytes by the agglomerating micelles. As will be pointed out in the experimental part of this paper, these assumptions are not borne out by the facts.

Since the two ions of the precipitating electrolyte are not adsorbed in equivalent amounts, the adsorption of the precipitating ion must be in part by exchange. Thus Linder and Picton[4] showed that chloride ion passes into solution by exchange when a ferric oxide sol prepared from ferric chloride is coagulated by potassium sulfate; with As_2S_3 sols, hydrogen ion enters the solution by exchange during coagulation.[5]

In concluding this brief survey of the adsorption theory of the coagulation process, it may be said that the theory furnishes a satisfactory semi-quantitative picture of the behavior of sols in the presence of electrolytes, but gives little insight into what actually takes place in any given case.

The Solubility Theory. The solubility theory of the mechanism of the coagulation process probably had its origin in a concept of Wyrouboff[6] that the various dialyzed ferric oxide sols are basic salts or chlorides of "condensed" ferric hydroxides. This idea was further developed by Duclaux[7] and especially by Pauli and his pupils,[8] who consider the stability of sols from the point of view of solubility. The colloidal particles are assumed to be highly complex colloidal ions resulting from the ionization of complex electrolytes allied to the Werner compounds. Coagulation in terms of this theory is believed to consist essentially of a chemical change involving the precipitation of a difficult soluble electrolyte.

Ferric oxide sol formed by adding ammonium hydroxide to ferric chloride solution followed by dialysis, has been investigated extensively from this point of view. Pauli[9] determined the chloride content of the sol by direct analysis and by a potentiometric method and measured the conductivity of the sol at various dilutions. It was found that not all of the chlorine could be detected potentiometrically as chloride ion. The possibility that a part of the chloride was adsorbed[10] and so would not be subject to potentiometric measurement

[1] Weiser and Middleton: J. Phys. Chem., 24, 30, 630 (1920).
[2] Freundlich, Joachimsohn, and Ettish: Z. physik. Chem., 141, 249 (1929).
[3] Weiser and Middleton: Loc. cit.
[4] J. Chem. Soc., 87, 1908 (1905).
[5] Whitney and Ober: J. Am. Chem. Soc., 23, 842 (1902).
[6] Bull., 21, 137 (1899).
[7] J. Chim. phys., 5, 29 (1907); 7, 405 (1909).
[8] Pauli and Matula: Kolloid-Z., 21, 49 (1917); Pauli and Walter: Kolloidchem. Beihefte, 17, 256 (1923); Pauli and Rogan: Kolloid-Z., 35, 131 (1924).
[9] Loc. cit.
[10] Cf. Maffia: Kolloidchem. Beihefte, 3, 85 (1911).

was ruled out and instead, it was assumed that the sol was merely an incompletely dissociated electrolyte which yielded only a fraction of its chlorine as ion.

In support of the dissociation theory, Pauli showed that the addition of an electrolyte to the sol which is equally concentrated in chloride ions causes no displacement of the chloride ion concentration of the sol. Moreover, under certain conditions the cations of an added electrolyte with a common anion may also decrease in concentration, a phenomenon which is attributed to a driving back of the dissociation by the common ion of the ferric oxide sol. As Freundlich[1] points out, neither of these arguments is conclusive. For if the chloride ion is in adsorption equilibrium, it is only natural that the equilibrium should be maintained if the chloride ion concentration remains unchanged. Furthermore, the fact that the anions in the intermicellar liquid are sufficiently free to drive back the dissociation of an added salt with a common anion is likewise in entire accord with the adsorption equilibrium which exists in the sol. Finally, Pauli and Matula[2] emphasize that the behavior of sols as regards conductivity cannot be interpreted simply from the point of view of the dissociation theory. Thus a mixture of ferric oxide sol and alkali chloride containing equivalent amounts of chloride ion exhibits a conductivity higher than the arithmetic mean of the conductivity of the components. This is probably due to higher mobility of the colloidal particle owing to an increase in charge by adsorption of a portion of the added cations.

In this connection Lottermoser[3] found the specific conductance of ferric oxide sols to be higher than that of the ultrafiltrates, the differences being regarded as the true conductivity of the micelles. If the micelles P are considered to be complex electrolytes, the equivalent conductivity at infinite dilution may be calculated from the equation, $\Delta_{P\infty} = 1000K_P/K_{Cl}$, where K signifies specific conductance. The mobility of the micelles was found to rise abnormally with purified sols containing but small amounts of chlorine. This fact indicates that the micelles are really adsorption complexes, the abnormality being due to the displacing of the adsorption and hydrolysis equilibria by dilution.

The general formula of a ferric oxide sol is written by Pauli $[xFe(OH)_3.yFeOCl.FeO]^+ + Cl^-$. The addition of sufficient electrolyte such as potassium sulfate, to the sol causes coagulation and the amount of sulfate dragged down is the same as the amount of chloride in the supernatant solution after coagulation. The precipitation is attributed to the formation of a complex insoluble sulfate in accord with the equation $[xFe(OH)_3.yFeOCl.FeO]Cl + K_2SO_4 = [xFe(OH)_3.yFeOCl.FeO]_2SO_4 + 2\ KCl$. Actually, of course, the alleged insoluble sulfate is not thrown down until a critical concentration of sulfate is added. This anomalous behavior as compared with that in the precipitation of simple insoluble compounds calls for an explanation. "The

[1] "Kapillarchemie," 621 (1922).
[2] Kolloid-Z., 21, 498 (1917).
[3] Z. Elektrochemie, 30, 391 (1924).

addition of sulfate and similar acting salts to the sol, says Pauli and Walter,[1] "causes precipitation owing to the formation of insoluble compounds. The anomalous behavior as compared to simple electrolytes, namely that an amount of sulfate almost equivalent to the entire chlorine content of the sol is necessary for flocculation, is explained by a peculiar equilibrium between the complex bound and the ionic chlorine as well as by the peptizing action of the undischarged complex. The coagulated sol has the formula of a complex double salt, a chlorine-poor and sulfate-rich chlor-sulfate. The ratio of chlorine to sulfate is in the first instance a function of particle size. It increases with particle size since the analytically determined maximum exchange of chlorine (with excess sulfate) decreases with the growth of the particles." The coagulating action of an alkali chloride is attributed to a driving back of the dissociation of the salt and a similar action is assumed to account for the precipitation with alkali nitrate.

It will be noted that Pauli's interpretation of the coagulating action as a chemical precipitation process, involves the use of the phrases "peculiar equilibrium between the complex bound and the ionic chlorine" and "peptizing action of the undischarged complex." It would be interesting to know just how Pauli visualizes the "peculiar equilibrium" relations and the "peptizing" action referred to.

The general point of view of Pauli is accepted by Wintgen, Rabinowitsch, and others. Considering the micelles to be ordinary ions, Wintgen[2] determines the amount of colloidal substance deposited by one Faraday of electricity and designates this the electrochemical equivalent or "equivalent aggregate" of the colloid. The number of electrochemical equivalents of colloid per liter is called the normality of the colloid, N. This value is obtained by applying Kohlrausch's law, $1000\ K_m = N(u + v)$. K_m the specific conductance of the micelle is estimated from the conductance of the colloidal system before and after ultrafiltration; u the mobility of the colloidal particle is gotten from U-tube measurements; v the mobility of the anion is known, and N is calculated. The similarity between colloidal behavior and ordinary ionic reactions in solution is indicated. Thus colloidal chromic oxide is regarded as an amphoteric electrolyte which reacts with either acids or bases to give salts.[3] It is pointed out that equi-normal colloidal solutions containing oppositely charged particles should mutually precipitate each other.

Whatever merits Wintgen's formulation of the constitution of colloids and the mechanism of the coagulation processes may have, it should be pointed out that his work is vitiated by a methodical error. Laing[4] showed that the fraction of the current carried by any charged body whether ion, colloid, wall, or bubble is equal to the ratio of its actual conductivity to the total conductivity of the system. That is

$$\text{fraction of current} = c_i f_i/\mu,$$

[1] Kolloidchem. Beihefte, 17, 291 (1923).
[2] Z. physik. Chem., 103, 250 (1922); Wintgen and Biltz: 107, 403 (1923); Wintgen and Löwenthal: 109, 378 (1924); Wintgen: Kolloid-Z., 40, 300 (1926).
[3] Wintgen and Weisbecker: Z. physik. Chem., 135, 182 (1928).
[4] J. Phys. Chem., 28, 673 (1924).

where c_i is the concentration and f_i is the conductivity of unit concentration and μ is the sum total of all such cf terms for all constituents present. The bodily movement n_i differs from the above by a factor m which is the number of units to one electrical charge. Thus

$$\text{bodily movement} = n_i = c_i m_i f_i/\mu.$$

McBain[1] points out that Wintgen and his pupils neglected this factor m. They should have divided their mobilities by m_i to find the conductivity. A further error was made in interpreting U-tube experiments on cataphoresis. Both Lash Miller and G. N. Lewis showed that the law of conservation of matter requires that the "moving boundary" method must give results which are identical with those derived from the Hittorf method of quantitative analysis. These errors and the neglect of the Donnan equilibrium makes Wintgen's numerical values for the charges on the particles something like ten times too large.

If one insists on regarding ferric oxide sols merely as electrolytes with complex ions it must be emphasized that there is a fundamental difference between sols and non-colloidal complex electrolytes such as potassium ferrocyanide, the cobalt amines, the complex platinous salts, etc. formulated by Werner. There is also a distinct difference between a colloidal ferric oxide and such colloidal electrolytes as the soaps and Congo red in that the latter contains ionic micelles made up of groups of ions of definite composition and carrying one charge for each equivalent of the ion, whereas the micelle of the former has no definite composition and may carry hundreds or thousands of equivalents for each free charge.

In conclusion, there seems no justification for assuming the absence of adsorption in a system such as colloidal ferric oxide where an adsorption equilibrium between minute solid particles of hydrous ferric oxide and the surrounding solution, must certainly exist.

It was believed that further light could be thrown on the structure of colloidal systems and the mechanism of coagulation by following the change in composition on adding a precipitating electrolyte stepwise to a sol. Since the precipitating ion is taken up in exchange with chloride in ferric oxide sol prepared from ferric chloride solution, Rabinowitsch and Kargan[2] followed the change in the chloride ion concentration potentiometrically on adding sulfate and other ions stepwise to a measured portion of the sol. The procedure was as follows: A 20 cc portion of sol in which was some suspended calomel, was placed in a beaker containing mercury thus making one half of a calomel concentration cell. The other half was a saturated calomel electrode. The difference in potential was found with a potentiometer at the outset and shortly after each addition of a small amount of electrolyte. From the potential measurements, the concentration of chloride ion at each step was calculated using the Nernst equation. Typical curves obtained by Rabinowitsch

[1] Colloid Symposium Monograph, 4, 14 (1926).
[2] Z. physik. Chem., 133, 203 (1928).

for the titration of two different sols with N/2 sodium sulfate are given in Fig. 1. The straight line represents the concentration of sulfate added while the irregular curves represent the changing concentration of chloride. It will be noted not only that the curves are irregular but that they run above the sulfate line indicating that considerably more chloride is displaced than there is sulfate added. Indeed special attention is called to the observation that

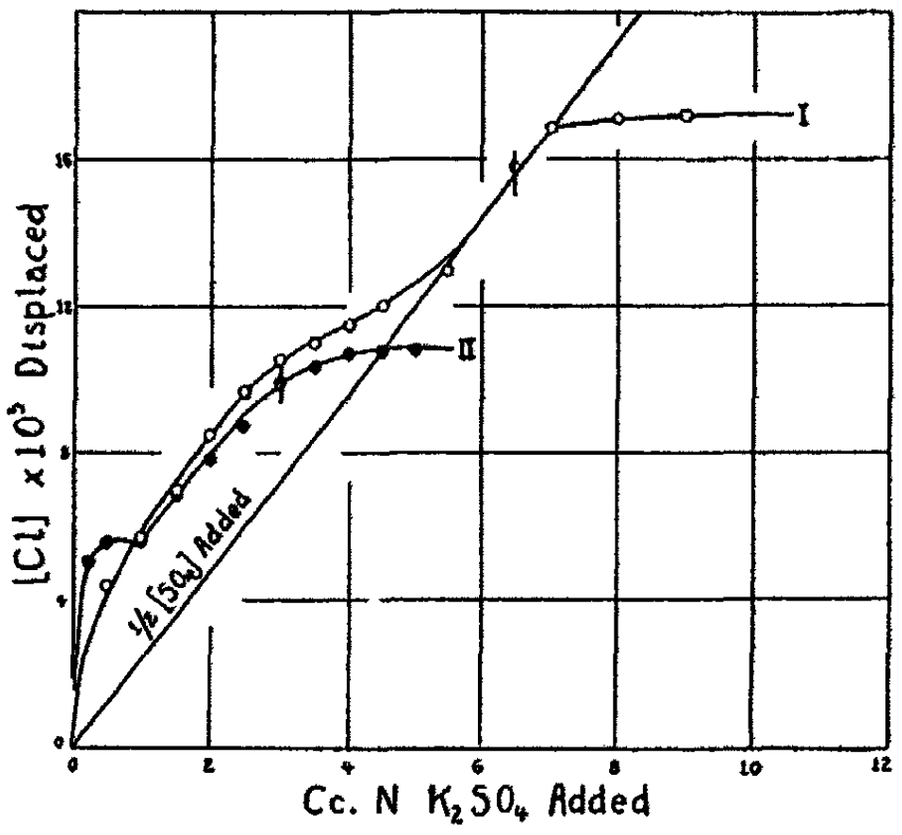

FIG. 1
Titration curves of Fe_2O_3 sols with K_2SO_4 (from data by Rabinowitsch and Kargan)

0.05 cc N/2 Na_2SO_4 displaced more than 4.6 times the equivalent of chloride in one sol. There is no apparent reason for this behavior and Rabinowitsch's explanation of it is not satisfactory. Moreover, as will be discussed later on, Rabinowitsch and Kargan either do not give all the facts or there is some error in their calculations of chloride concentrations from the observed potentials. In any event, the general method seemed to offer a fruitful method of approach to the problem of what takes place when an electrolyte is added to a sol. The results of investigations along this line are reported in the next section.

Experimental

Preparations of Sols. Three ferric oxide sols were used in the course of this investigation. The first was prepared by dissolving 100 grams of pure ferric chloride in approximately 500 cc of water, filtering, and adding dilute ammonia just short of precipitation. The concentrated sol was diluted to 4 liters and dialyzed in four Neidle dialyzers using cellophane bags which held approximately one liter. The dialysis proceeded with a continuous change of water for two days when the chlorine content was found to be approximately

0.015 normal. The sol was set aside in a pyrex flask for four months before using. The second sol was prepared by the same procedure outlined above except that the ageing following the dialysis was accomplished by heating for a week on the steam hot-plate. Loss by evaporating was prevented by attaching a reflux condenser to the mouth of the flask. This sol was used within a month after preparation. The third sol was formed by dissolving 75 grams of ferric chloride in 500 cc of water and adding slowly to 3500 cc of boiling water. After dialysis at 90° for two days, the sol was set aside for three months before using.

The sols were analyzed for the Fe_2O_3 content and the chlorine content as follows: The ferric oxide in 25 cc portions of the sols was coagulated by ammonia and the precipitate was collected, washed, ignited and weighed in the usual manner. The chlorine content of 25 cc portions of sol was obtained by first adding a small excess of silver nitrate followed by adding nitric acid and heating. This process dissolved the oxide leaving a precipitate of silver chloride. After diluting, the silver salt was collected in a Gooch crucible, dried and weighed. The analyses are given in Table I.

TABLE I

Analysis of Ferric Oxide Sols

Sol number	Fe_2O_3 grams per liter	Cl mols per liter
I	6.46	0.0158
II	6.92	0.0166
III	4.08	0.0047

Method of Titration. Preliminary experiments disclosed quite promptly that satisfactory data could not be obtained by adding the electrolyte to the sol stepwise and measuring the change in chloride ion potentiometrically after a few minutes. The reason is obvious when one considers that it takes time to establish equilibrium at the calomel electrode. Indeed it is always recommended that the newly prepared standard calomel half element be set aside at least a day and preferably several days before use. Accordingly the procedure adopted by Rabinowitsch and Kargan was discarded as unsatisfactory and the following method adopted: In general, the method consists in mixing separate portions of sol with gradually increasing amount of electrolyte and making the observations on the separate samples. In the sol was suspended a small amount of freshly precipitated calomel. This was prepared by the interaction of pure mercurous nitrate and hydrochloric acid followed by thorough washing with the aid of the centrifuge in the presence of a small amount of mercury, first with water and then with the sol. To secure rapid uniform mixing of the sol with electrolyte 20 cc of the former was placed in the outer compartment of an all-glass mixing apparatus and a definite amount of electrolyte diluted to 5 cc in the inner compartment. After mixing, the mixture was transferred to a small bottle which was placed in the thermostat

at 25° and shaken at intervals for a period of two days in order to saturate with calomel. It was then transferred to an electrode vessel like that shown in Fig. 2. This was prepared by rounding out the bottom of a 30 cc weighing bottle to prevent its breaking, followed by sealing in a small platinum wire. After placing mercury in the bottom of the vessel, the sol-electrolyte mixture was poured in and allowed to stand in the thermostat 24 hours before making the potentiometric measurements. Thus an interval of three days elapsed between the mixing of sol with electrolyte and the determination of the chloride ion content.

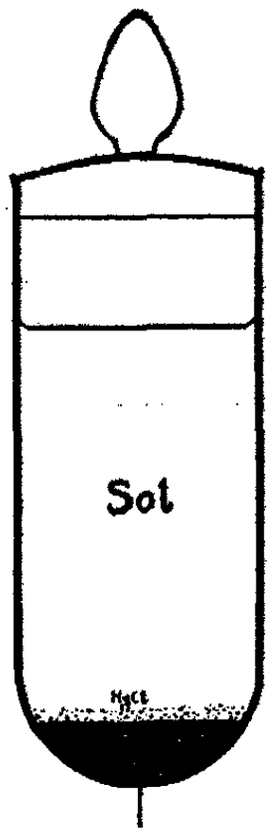

FIG. 2

Potentiometric Measurements. The potentiometric measurements were made by means of a N/10 calomel electrode prepared in the usual way from highly purified potassium chloride, calomel, and mercury. Contact between the standard electrode vessel and the "unknown" was made directly by the aid of a glass tube filled with the N/10 KCl and drawn down to a fine capillary to minimize diffusion. A type K Leeds and Northrop potentiometer was used in conjunction with a Hartman and Braun moving coil galvanometer sensitive to less than 0.1 millivolt.

Calculations. From the observed potential the molar concentration of chloride as potassium chloride was obtained by the use of the modified Nernst equation substituting activities for concentrations. At 25° the activity coefficient of N/10 KCl is 0.749[1] and the equation takes the form $\pi = 0.0591 \log 0.0794/\alpha$. The calculated value of α is converted into molar concentration by dividing it by the corresponding activity coefficient as read off from a graph prepared from data given by Lewis and Randall.[2]

In this connection, attention should be called to an apparent error in the calculations of Rabinowitsch and Kargan. For example, a potential of 0.1589 volts at 19° using a saturated calomel electrode as a standard was calculated to give a chloride ion concentration of 0.00794 mol per liter. The activity coefficient of such a solution is 0.933 and the activity is thus 0.00741. Substituting this value in the Nernst formula at 19° and solving for the activity of the chloride in saturated KCl at 19°, one gets:

$$0.1589 = 0.0579 \log \frac{\alpha_{KCl\ Sat.}}{0.0074}$$

from which, $\alpha_{KCl\ Sat.} = 4.11$.

Now the difference between the potential of the saturated and N/10 calomel electrode at 19° is approximately 0.0874 volt.[3] To give this potential

[1] Lewis and Randall: "Thermodynamics," 362 (1923).
[2] "Thermodynamics," 344 (1923).
[3] Clark: "The Determination of Hydrogen Ions," 200 (1927).

the activity of the chloride in the saturated half element is given by the equation

$$0.880 = 0.0579 \log \frac{\alpha_{KCl\ Sat.}}{9.0794}$$

from which $\alpha_{KCl\ Sat.} = 2.63$. Since the value for α which Rabinowitsch and Kargan must have used is more than 60 per cent higher than the above, their concentrations calculated from the observed potentials would appear to be erroneous.

In this connection Rabinowitsch and Kargan report the same value for the total chlorine in the sol by gravimetric analysis as silver chloride after dissolving the precipitate in nitric acid, and by potentiometric analysis of the supernatant solution after adding a precipitating electrolyte. Since ferric oxide sol prepared according to the procedure employed by Rabinowitsch and Kargan contains chlorine that is not displaced by a coagulating electrolyte, the two methods should not yield the same results. That they did is most likely the result of some compensating error in the potentiometric procedure.

Observations on Ferric Oxide Sol I

Titration with K_2SO_4. After a number of preliminary experiments which led to the procedure described above, the following observations were made of the change in chloride concentration on adding varying amounts of N/25 K_2SO_4 to the sol. Above the precipitation value of the salt, the suspended calomel was carried down completely by the agglomerating oxide. In order to make certain that the supernatant solution was saturated with Hg_2Cl_2 a small amount of calomel paste was added after the coagulation had taken place. The results of the titration are given in Table II and shown graphically in Fig. 3.

TABLE II

Titration of Fe_2O_3 Sol I with K_2SO_4

Cc of N/25 K_2SO_4 added to 20 cc of sol. Total volume 25 cc.	π volts	α Cl^- $\times 10^3$	[Cl] $\times 10^3$	[Cl] displaced $\times 10^3$	[Cl] equivalent to [SO_4] added $\times 10^3$
0.0	0.0857	2.82	2.93	0	0
0.5	0.0834	3.08	3.20	0.27	0.80
1.0	0.0800	3.52	3.68	0.75	1.60
1.5	0.0768	4.00	4.20	1.27	2.40
2.0	0.0746	4.34	4.57	1.64	3.20
2.5	0.0725	4.71	4.96	2.03	4.00
2.0	0.0707	5.05	5.34	2.41	4.80
3.5	0.0686	5.48	5.81	2.88	5.60
4.0	0.0674	5.75	6.10	3.17	6.40
4.5	0.0616	7.11	7.60	4.67	7.20
4.75	0.0608	7.43	7.95	5.02	7.60
5.00	0.0592	7.91	8.47	5.54	8.00
2.5 of N/10	0.0582	8.22	8.82	5.89	10.00

Referring to the data and the accompanying curve, it is obvious that the chloride displaced during the titration follows a regular course. Particularly significant is the fact that the amount of chloride displaced is always appreciably less than the amount of sulfate added, contrary to the observation of Rabinowitsch and Kargan. Since the sol was prepared by essentially the

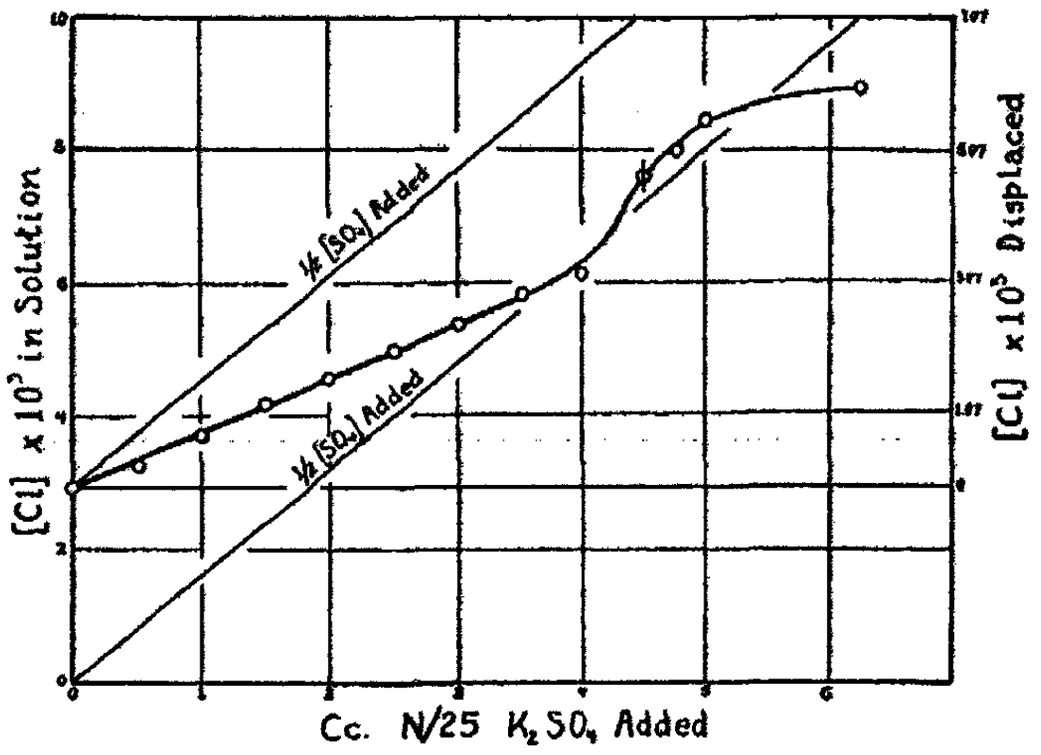

FIG. 3
Titration curve of Fe_2O_3 Sol I with K_2SO_4

same procedure and was similar in oxide and chloride content to the one used by them, it seems probable that their experimental method led to erroneous observations. Attention has already been called to possible errors in their calculations.

It is of interest to note that the curve for chloride displaced follows a nearly linear course until the precipitation concentration is approached when it increases rapidly. Above the precipitation concentration, indicated by a vertical line cutting the curve, the chloride displaced follows the usual adsorption type of curve.

The precipitation concentration 4.5 cc of N/25 K_2SO_4 in 25 cc was the smallest amount of electrolyte which would just cause complete coagulation in three days.

At the precipitation concentration, the supernatant solution gave no test for sulfate with barium chloride even after several days. Since the "sulfate added" comes quite close to the "chloride" curve at the precipitation value, it is clear that the amount of sulfate adsorbed is approximately equivalent to the chloride in the supernatant solution, as Pauli has demonstrated.

Since all the added sulfate is taken up at the precipitation value, it is reasonable to conclude that all of it is taken up below the precipitation value. It is of particular importance to note that at the precipitation value as well

as at all points above and below the precipitation value, the chloride equivalent to the sulfate added is derived in part from the chloride originally present in the intermicellar solution and in part is displaced from the micelles. This behavior will be considered in detail in a later section.

The marked increase in the chloride displaced as the precipitation concentration is approached is undoubtedly the result of partial agglomeration of

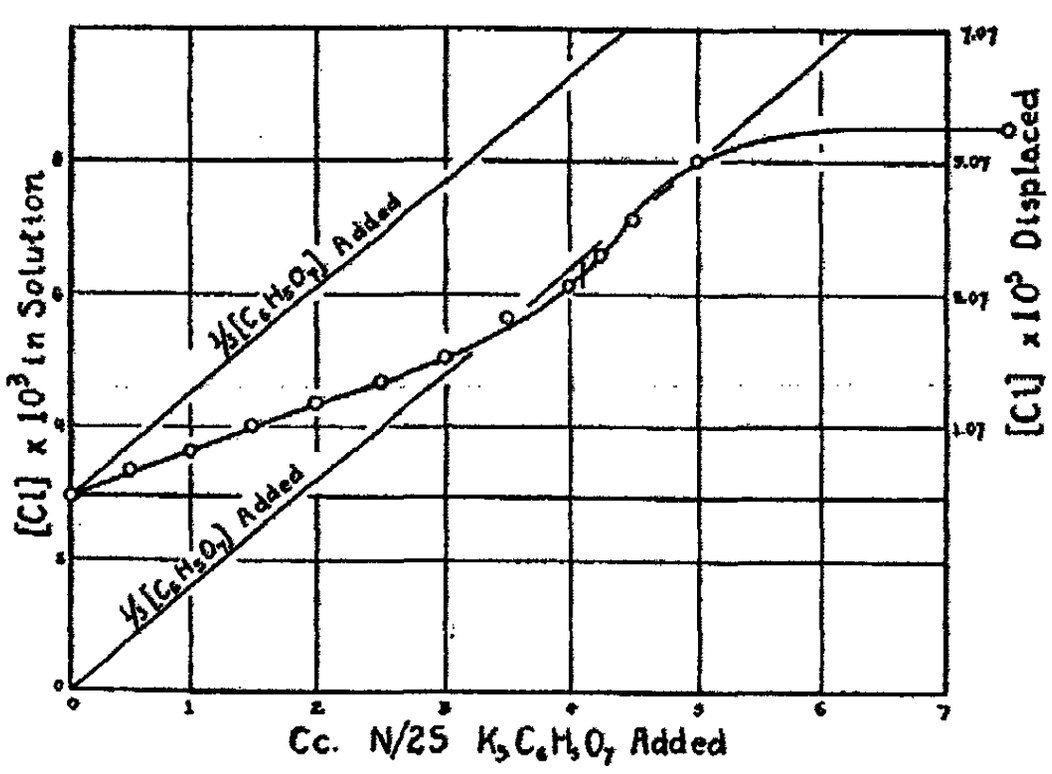

FIG. 4
Titration curve Fe_2O_3 Sol I with potassium citrate

particles with the consequent decrease in specific surface as the charge approaches the critical value below which complete flocculation takes place.

Finally, the form of the upper portion of the "chloride" curve represents the adsorption of sulfate by precipitated ferric oxide in concentrations above the precipitation value, since the sulfate taken up is approximately equivalent to the chloride in solution. Attention has been called to this behavior in earlier communications.[1]

Titration with $K_3C_6H_5O_7$. Experiments with N/25 potassium citrate were carried out by the same procedure used for potassium sulfate. The data are recorded in Table II and shown graphically in Fig. 4. It is evident that the displacement of chloride by citrate follows a course strikingly similar to that for sulfate. The only difference is the earlier upward turn in the curve and the lower precipitation concentration of the salt as indicated in the figure. The maximum amount of chloride displaced above the precipitation value is almost identical in the two cases.

Titration with $K_3Fe(CN)_6$. Since $K_3Fe(CN)_6$ which is the salt of a strong acid might be expected to give largely trivalent anions, it was of interest to compare the behavior of the sol during the stepwise addition of this salt

[1] Weiser: J. Phys. Chem., 25, 299 (1921); Weiser and Middleton: 24, 30, 630 (1920).

TABLE III

Titration of Fe_2O_3 Sol I with Potassium Citrate

Cc of N/25 $K_3C_6H_5C_7$ added to 20 cc of sol. Total volume 25 cc.	π volts	α Cl^- $\times 10^3$	[Cl] $\times 10^3$	[Cl] displaced $\times 10^3$	[Cl] equivalent to $[C_6H_5O_7]$ added $\times 10^3$
0.0	0.0857	2.82	2.93	0.0	0.0
0.5	0.0823	3.22	3.36	0.43	0.80
1.0	0.0805	3.45	3.61	0.68	1.60
1.5	0.0777	3.85	4.04	1.11	2.40
2.0	0.0758	4.16	4.38	1.45	3.20
2.5	0.0740	4.44	4.68	1.75	4.00
3.0	0.0723	4.75	5.01	2.08	4.80
3.5	0.0692	5.36	5.69	2.76	5.60
4.0	0.0674	5.75	6.10	3.17	6.40
4.25	0.0655	6.19	6.58	3.65	6.80
4.50	0.0636	6.66	7.10	4.10	7.20
4.00[1]	0.0606	7.49	8.01	5.08	8.00
7.50[1]	0.0592	7.91	8.48	5.55	10.91

[1] Sol repeptized, with negative charge.

with that of citrate which doubtless gives some trivalent anions but divalent and monovalent anions as well. The titration data are given in Table IV and the curve in Fig. 5. The potentiometric measurements for chloride are very satisfactory so long as practically all of the added salt is adsorbed, but the measurements are uncertain as soon as an appreciable amount of ferricyanide remains in the supernatant solution.

The curve for displacement of chloride by ferricyanide is characterized by the earlier upward bend and the distinctly lower precipitation value as

TABLE IV

Titration of Fe_2O_3 Sol I with $K_3Fe(CN)_6$

Cc of N/25 $K_3Fe(CN)_6$ added to 20 cc of sol. Total volume 25 cc.	π volts	α Cl^- $\times 10^3$	[Cl] $\times 10^3$	[Cl] displaced $\times 10^3$	[Cl] equivalent to $[Fe(CN)_6]$ added $\times 10^3$
0.0	0.0857	2.82	2.93	0.0	0.0
0.5	0.0828	3.17	3.31	0.38	0.80
1.0	0.0801	3.50	3.66	0.73	1.60
1.5	0.0777	3.85	4.04	1.11	2.40
2.0	0.0742	4.41	4.65	1.72	3.20
2.5	0.0717	4.86	5.13	2.20	4.00
3.0	0.0693	5.34	5.66	2.73	4.80
3.25	0.0674	5.75	6.10	3.17	5.20
3.50	0.0655	6.19	6.58	3.65	5.60
4.00	0.0630	6.82	7.27	4.34	6.40
5.00	Uncertain				

compared with both sulfate and citrate. Since all the ferricyanide and sulfate are carried down at the respective precipitation values and since the precipitation value in equivalents of the former is appreciably lower than that of the later, it is obvious that Freundlich's assumption that equivalent amounts of all ions are carried down at the precipitation value cannot be right. My later assumption that the adsorption of equivalent amounts is

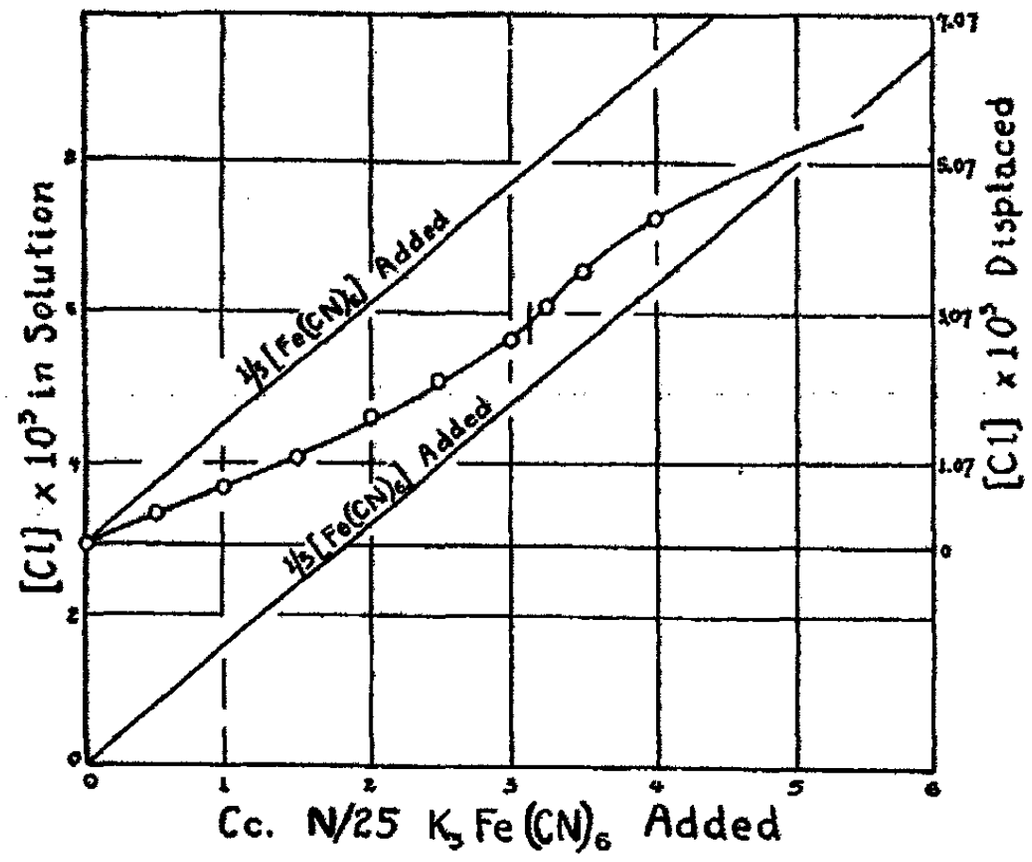

FIG. 5
Titration curve of Fe_2O_3 Sol I with $K_3Fe(CN)_6$

necessary to lower the charge to the coagulation point, likewise is not generally true. The total chloride in the intermicellar liquid near the precipitation value and after coagulation, appears somewhat greater than the ferricyanide added. This is because coagulation with consequent decrease in specific surface starts at very low concentrations and so the displaced chloride is relatively greater for ferricyanide than for other salts at the same concentration. At the same time, it should be noted that there is appreciably less chloride displaced and total chloride in the supernatant solution at the lower precipitation value of $K_3Fe(CN)_6$ than at the higher value for K_2SO_4.

Titration with KNO_3. Since univalent anions in general precipitate positive sols only in relatively high concentration, it was necessary to use a normal solution of KNO_3 to effect the coagulation within 5 cc of electrolyte in 25 cc of mixture. In the interest of accuracy N/10 solutions were used for lower concentrations. The titration data given in Table V are plotted in Fig. 6. The form of the curve is distinctly different from that for salts with multivalent precipitating ions. The amount of chloride displaced for the same concentration is very much less for the univalent ion. Moreover the

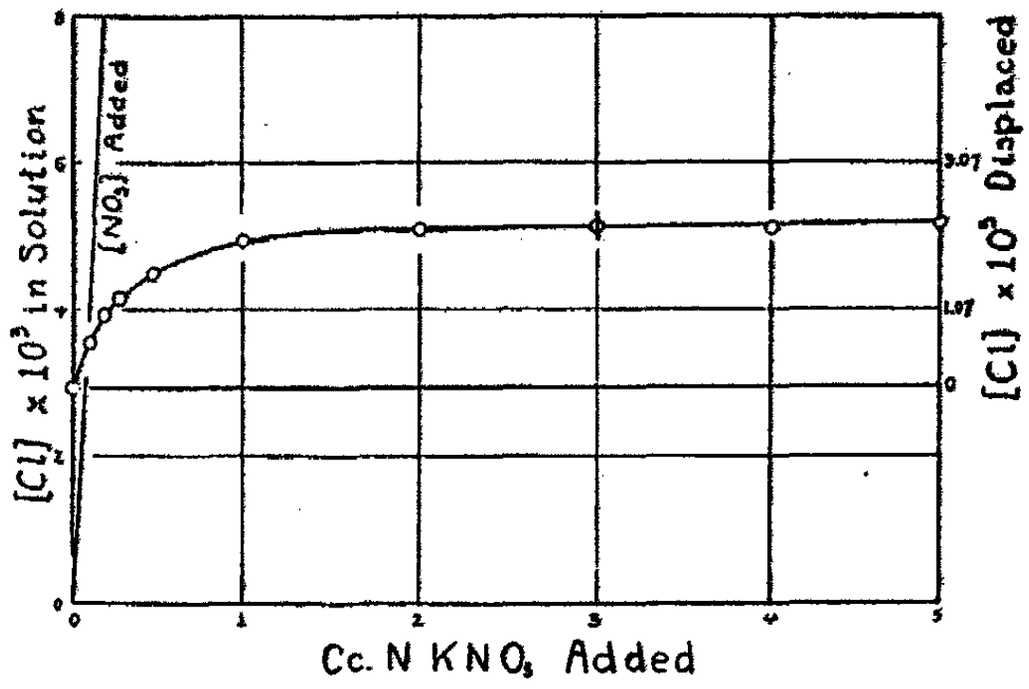

FIG. 6

Titration curve of Fe_2O_3 Sol I with KNO_3

amount of chloride displaced goes up fairly rapidly at relatively low concentrations but soon attains a practically constant value or even decreases slightly. The latter observation may be the result of a salt error introduced with relatively high concentrations of KNO_3. In any event, the maximum amount of chloride displaced is appreciably less for nitrate than for the multivalent ions.

The variation in the chloride displacing power of equivalent amounts of potassium salts of mono-, di-, and trivalent anions is clearly indicated in the composite diagram Fig. 7.

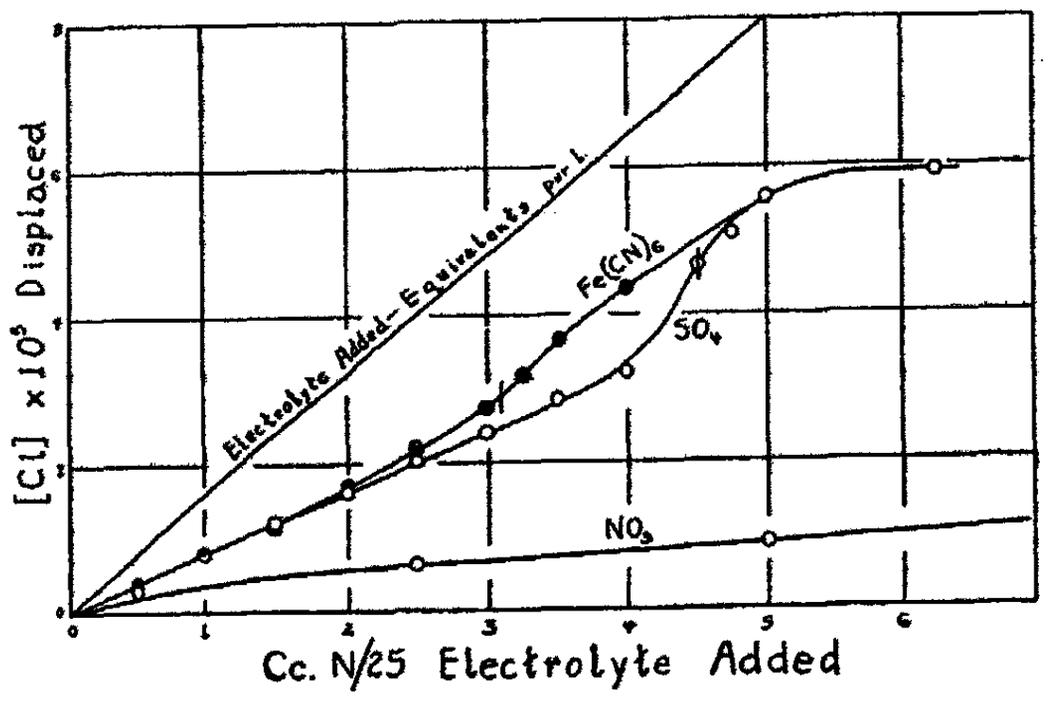

FIG. 7

Titration curves of Fe_2O_3 Sol I with different types of electrolytes

TABLE V

Titration of Fe_2O_3 Sol I with KNO_3

Cc of KNO_3 added to 20 cc of Sol. Total volume 25 cc.	π volts	α Cl^- $\times 10^3$	[Cl] $\times 10^3$	[Cl] displaced $\times 10^3$	[Cl] equivalent to $[NO_3]$ added $\times 10^3$
0	0.0857	2.82	2.93	0.0	0.0
1 of N/10	0.0812	3.37	3.53	0.60	4.0
2 of N/10	0.0785	3.73	3.91	0.98	8.0
3 of N/10	0.0772	3.92	4.12	1.19	12.0
5 of N/10	0.0750	4.27	4.49	1.53	20.0
1 of N	0.0728	4.66	4.92	1.99	40.0
2 of N	0.0720	4.81	5.08	2.15	80.0
3 of N	0.0718	4.84	5.11	2.18	120.0
4 of N	0.0722	4.76	5.03	2.10	160.0
5 of N					200.0

Experiments with Ferric Oxide Sol II

Sol II was prepared in much the same way as Sol I but was aged by heating instead of by long standing. The results with the former merely confirm and extend those with the latter.

Titration with K_2SO_4. The data for the titration with potassium sulfate is given in Table VI and shown graphically in Fig. 8. As compared with Sol I, it will be noted that the curve starts to bend upward at a lower concentration and the precipitation value is somewhat lower. As was to be expected the general form of the curve is the same as with Sol I.

TABLE VI

Titration of Fe_2O_3 Sol II with K_2SO_4

Cc of K_2SO_4 added to 20 cc. of Sol. Total volume 25 cc.	π volts	α Cl^- $\times 10^3$	[Cl] $\times 10^3$	[Cl] displaced $\times 10^3$	[Cl] equivalent to $[SO_4]$ added $\times 10^3$
0.0	0.0910	2.29	2.37	0.0	0.0
0.5	0.0880	2.58	2.69	0.32	0.80
1.0	0.0843	2.98	3.11	0.74	1.60
1.5	0.0804	3.48	3.64	1.27	2.40
2.0	0.0778	3.83	4.02	1.65	3.20
2.5	0.0748	4.31	4.54	2.17	4.00
3.0	0.0727	4.67	4.93	2.56	4.80
3.5	0.0700	5.19	5.49	3.12	5.60
4.0	0.0675	5.73	6.07	3.70	6.40
4.25	0.0647	6.38	6.68	4.31	6.80
4.50	0.0626	6.93	7.40	5.03	7.20
5.00	0.0605	7.52	8.04	5.67	8.00
6.25	0.0597	7.76	8.31	5.94	10.00

In order to test the accuracy of the experimental procedure for determining chloride potentiometrically, an analysis was made of the supernatant solution after precipitation. This was done by precipitating 40 cc of sol with 10 cc of N/25 K_2SO_4 and analyzing an aliquot part of the supernatant solution for chloride by titrating with silver nitrate. The silver nitrate was standardized against N/50 silver chloride and the titrations were made to the same end-point. The results given in Table VII show the potentiometric procedure to be quite accurate.

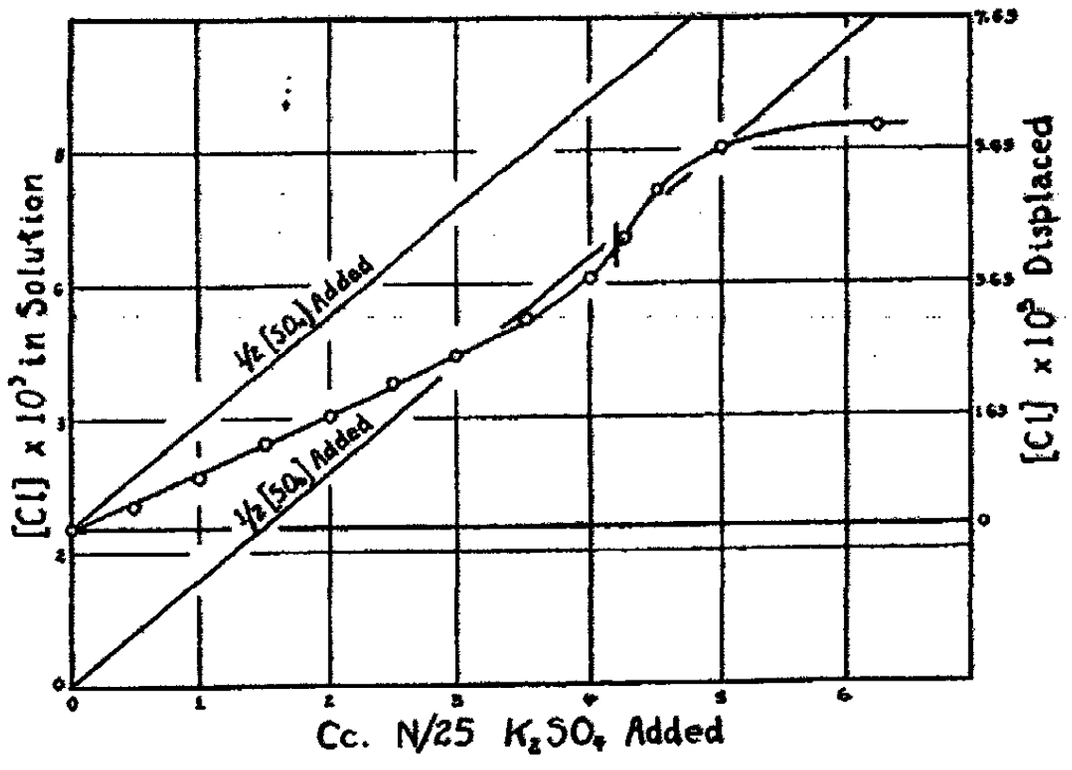

FIG. 8
Titration curve of Fe_2O_3 Sol II with K_2SO_4

TABLE VII
Analysis of Supernatant Solution for Chloride after Precipitation Fe_2O_3 Sol II

Substances mixed		0.001934 N $AgNO_3$ to titrate 25 cc	[Cl] × 10³	
Fe_2O_3 Sol cc	N/25 K_2SO_4 cc	cc	volumetric method	potentiometric method
40	10	10.48	8.16	8.10
40	10	10.45	8.08	8.04
Fe_2O_3 Sol	N/25 K_2CrO_4			
40	10	10.80	8.40	
40	10	10.80	8.40	

Titration with $K_2C_2O_4$. The data and corresponding curves with $K_2C_2O_4$ as precipitating electrolyte are given in Table VIII and Fig. 9, respectively. The upper portion of the curve with $K_2C_2O_4$ runs slightly above that with K_2SO_4 and the precipitation concentration of the former is slightly lower than the latter. As in the case of sulfate, all of the oxalate is adsorbed at the precipitation value.

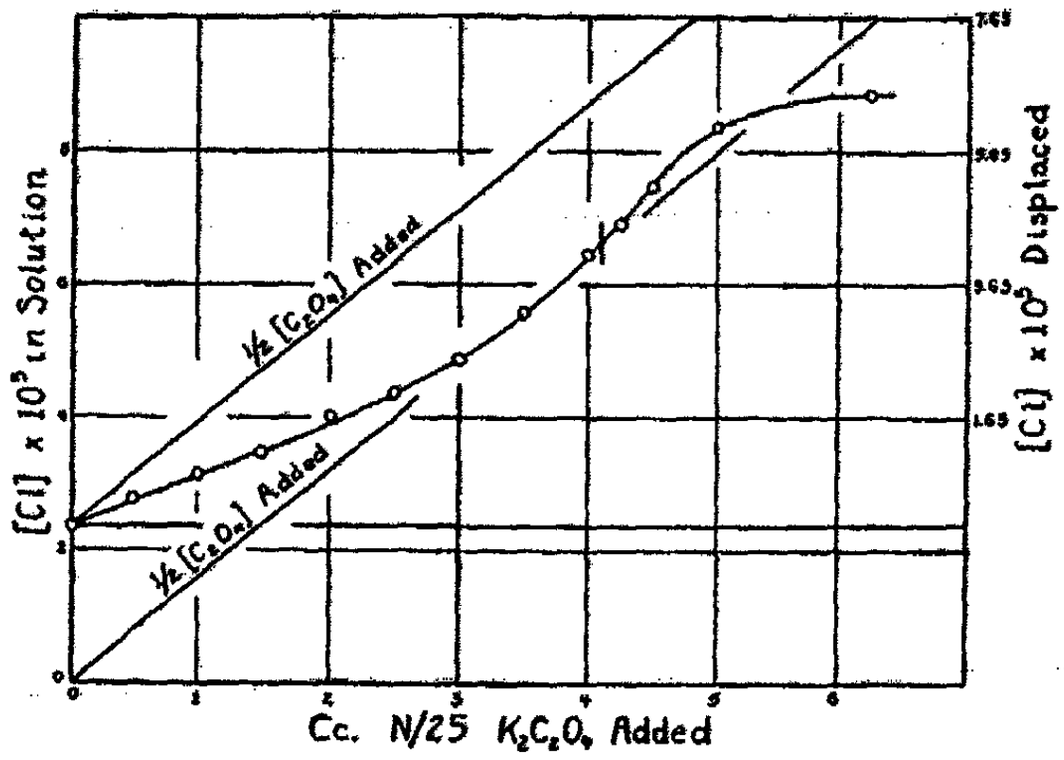

FIG. 9
Titration curve of Fe_2O_3 Sol II with $K_2C_2O_4$

TABLE VIII

Titration of Fe_2O_3 Sol II with $K_2C_2O_4$

Cc of N/25 $K_2C_2O_4$ added to 20 cc of Sol. Total volume 25 cc.	π volts	$a\ Cl^-$ $\times 10^3$	[Cl] $\times 10^3$	[Cl] displaced $\times 10^5$	[Cl] equivalent to $[C_2O_4]$ added $\times 10^5$
0.0	0.0910	2.29	2.37	0.0	0.0
0.5	0.0875	2.66	2.77	0.40	0.80
1.0	0.0840	3.01	3.14	0.77	1.60
1.5	0.0815	3.32	3.47	1.10	2.40
2.0	0.0778	3.83	4.02	1.65	3.20
2.5	0.0758	4.15	4.36	1.99	4.00
3.0	0.0730	4.62	4.87	2.50	4.80
3.5	0.0697	5.25	5.56	3.19	5.60
4.0	0.0660	6.07	6.45	4.08	6.40
4.25	0.0643	6.48	6.90	4.53	6.80
4.50	0.0623	7.01	7.47	5.10	7.20
5.00	0.0595	7.81	8.36	5.99	8.00
6.25	0.0583	8.22	8.82	6.45	10.00

Titration with K_2CrO_4. The data using K_2CrO_4 as precipitating electrolyte and the corresponding curve are given in Table IX and Fig. 10. The curve parallels that obtained with $K_2C_2O_4$ almost throughout the entire range and the observed precipitation concentration lies between the values for oxalate and sulfate. All of the chromate is carried down at the precipitation value. Satisfactory potentiometric measurements were not obtained with appreciable concentrations of K_2CrO_4 in the supernatant solution above

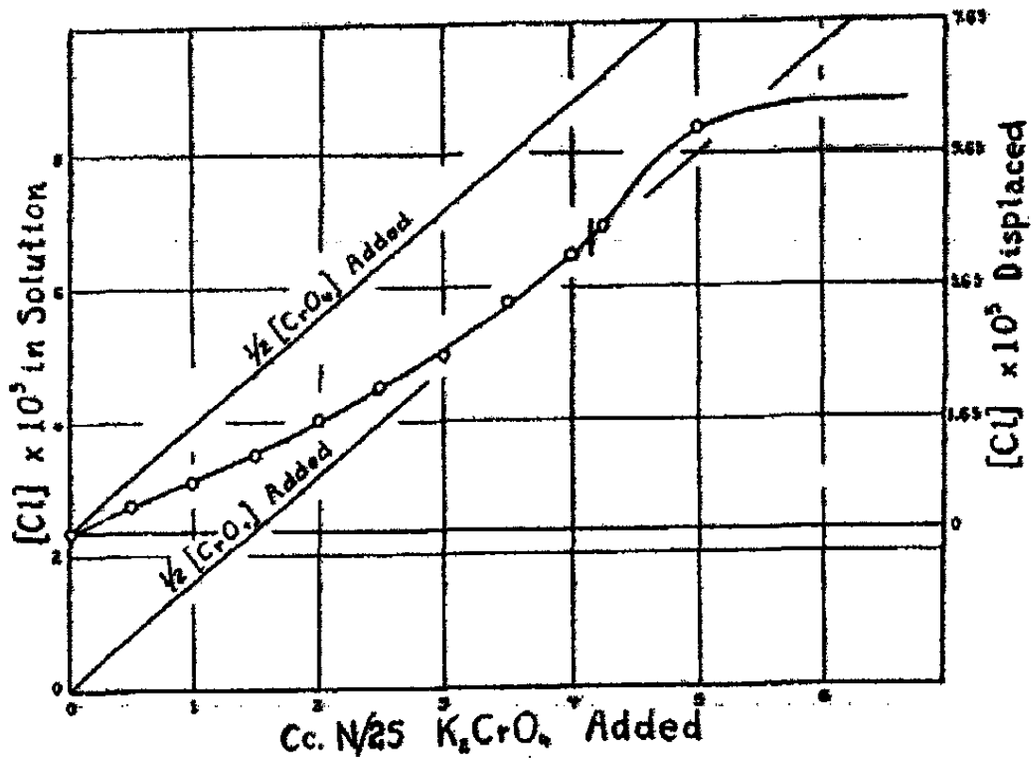

FIG. 10
Titration curve of Fe_2O_3 Sol II with K_2CrO_4

the precipitation value. The point for 5 cc N/25 K_2CrO_4 with 20 cc of sol was obtained by volumetric analysis of the supernatant solution with the results as given in the second part of Table VII. The value 8.40×10^{-3} mols per liter corresponds with 8.36×10^{-3} obtained potentiometrically with oxalate as precipitating electrolyte.

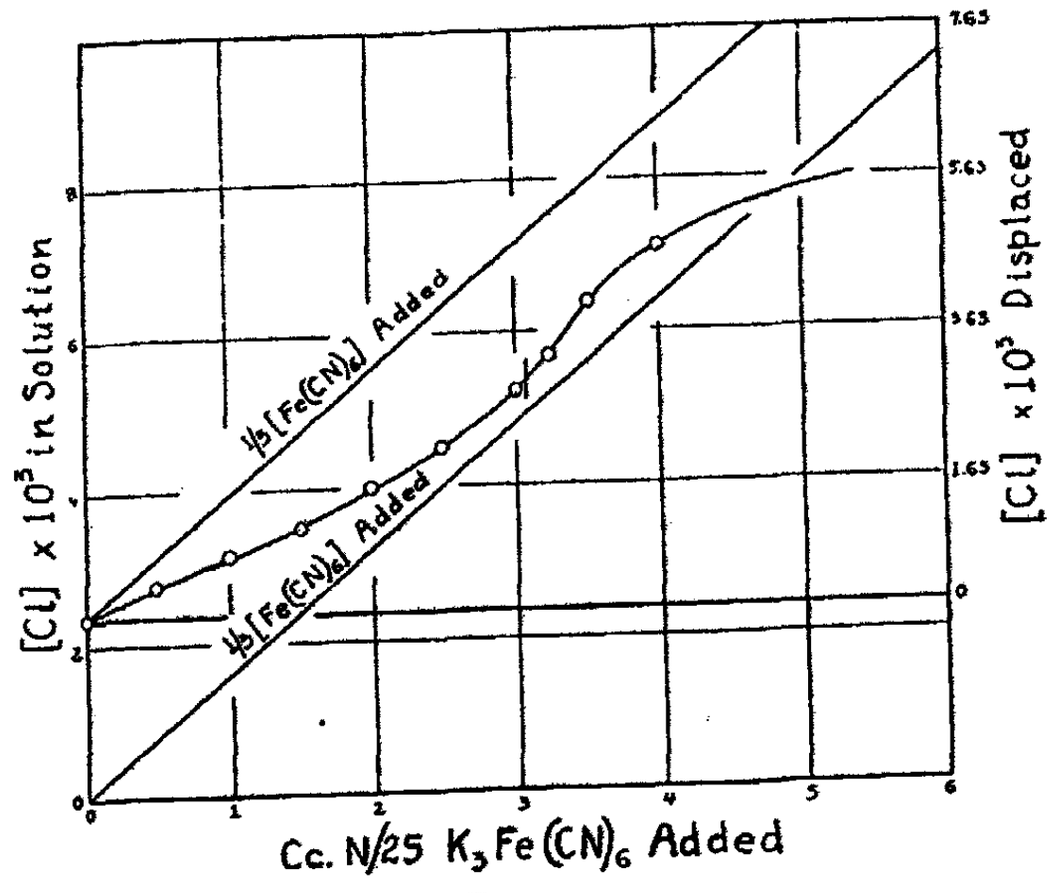

FIG. 11
Titration curve of Fe_2O_3 Sol II with $K_3Fe(CN)_6$

TABLE IX

Titrations of Fe_2O_3 Sol II with K_3CrO_4

Cc of N/25 K_3CrO_4 added to 20 cc. Sol. Total volume 25 cc.	π volts	α Cl^- $\times 10^3$	[Cl] $\times 10^3$	[Cl] displaced $\times 10^3$	[Cl] equivalent to [CrO_4] added $\times 10^3$
0.0	0.0910	2.29	2.37	0.0	0.0
0.5	0.0875	2.66	2.77	0.40	0.80
1.0	0.0845	2.95	3.08	0.71	1.60
1.5	0.0812	3.35	3.50	1.13	2.40
2.0	0.0775	3.87	4.07	1.70	3.20
2.5	0.0746	4.34	4.55	2.18	4.00
3.0	0.0725	4.71	4.97	2.60	4.80
3.5	0.0686	5.49	5.81	3.44	5.60
4.0	0.0658	6.12	6.50	4.13	6.40
4.25	0.0643	6.48	6.90	4.53	6.80
5.00	—	—	8.40[1]	6.03	8.00

[1] Determined analytically, (See Table VII).

Titration with $K_3Fe(CN)_6$. The observations with $K_3Fe(CN)_6$ as precipitating electrolyte merely confirm those obtained with Sol I. The data are given in Table X and shown graphically in Fig. 11.

TABLE X

Titrations of Fe_2O_3 Sol II with $K_3Fe(CN)_6$

Cc of N/25 $K_3Fe(CN)_6$ added to 20 cc. of Sol. Total volume 25 cc.	π volts	α Cl^- $\times 10^3$	[Cl] $\times 10^3$	[Cl] displaced $\times 10^3$	[Cl] equivalent to [$Fe(CN)_6$] added $\times 10^3$
0.0	0.0910	2.29	2.37	0.0	0.0
0.5	0.0870	2.68	2.79	0.42	0.80
1.0	0.0842	2.99	3.12	0.75	1.60
1.5	0.0815	3.32	3.47	1.10	2.40
2.0	0.0778	3.83	4.02	1.65	3.20
2.5	0.0750	4.27	4.50	2.13	4.00
3.0	0.0712	4.96	5.24	2.87	4.80
3.25	0.0692	5.36	5.68	3.31	5.20
3.50	0.0662	6.02	6.40	4.03	5.60
4.00	0.0637	6.65	7.09	4.72	6.40
5.00	Uncertain				8.00

The results of the observations on Sol II are collected in Fig. 12. It is of interest to note the marked similarity in the behavior of the salts with divalent anions. The precipitation concentrations are quite close together and the chloride concentrations of the respective supernatant solutions are almost identical. Since the adsorption of the multivalent anions observed is complete at the precipitation value, Freundlich's assumption that equivalent amounts of ions are adsorbed at the precipitation concentration holds almost

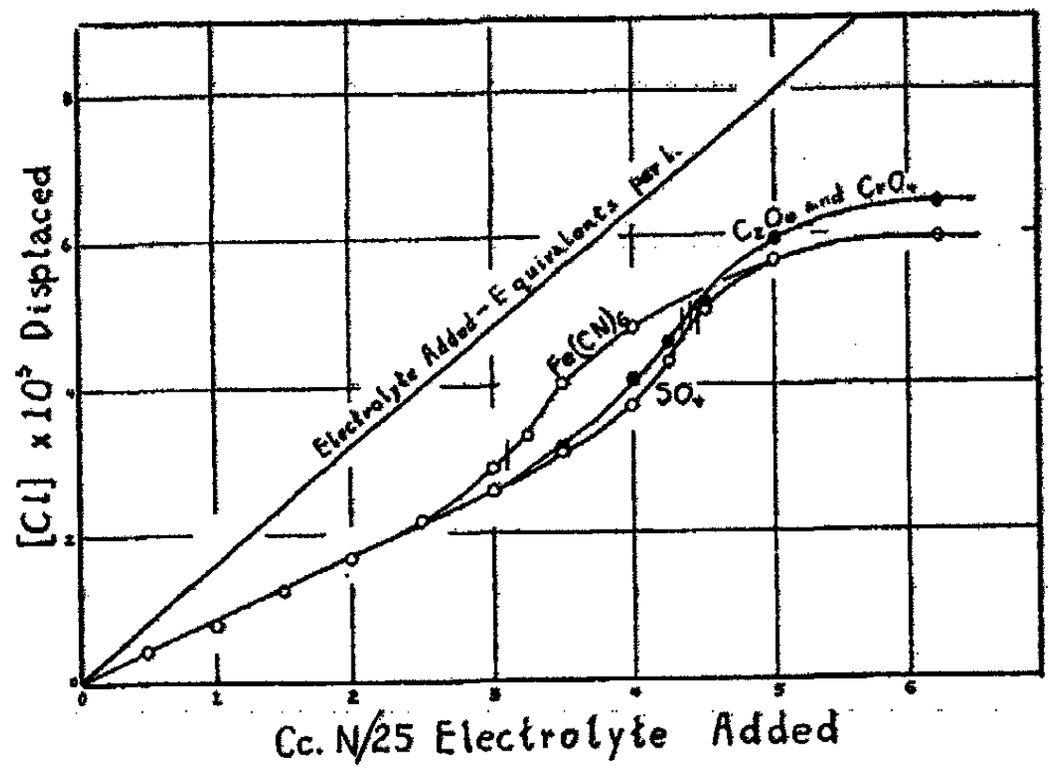

FIG. 12
Titration curves of Fe_2O_3 Sol II with different types of electrolytes

quantitatively for the three ions under consideration. But when one turns to trivalent ferricyanide, one encounters a distinctly lower equivalent precipitation value and correspondingly lower adsorption at the precipitation value, confirming the observation with Sol I.

Observations with Ferric Oxide Sol III

Sol III prepared by hydrolysis of $FeCl_3$ in hot water and dialyzed in the hot was much freer from chloride than either Sol I or II. Moreover, since no ammonia was added, the sol contained simply the hydrolysis products of $FeCl_3$, hydrous Fe_2O_3 and HCl. That its behavior on titrating with K_2SO_4

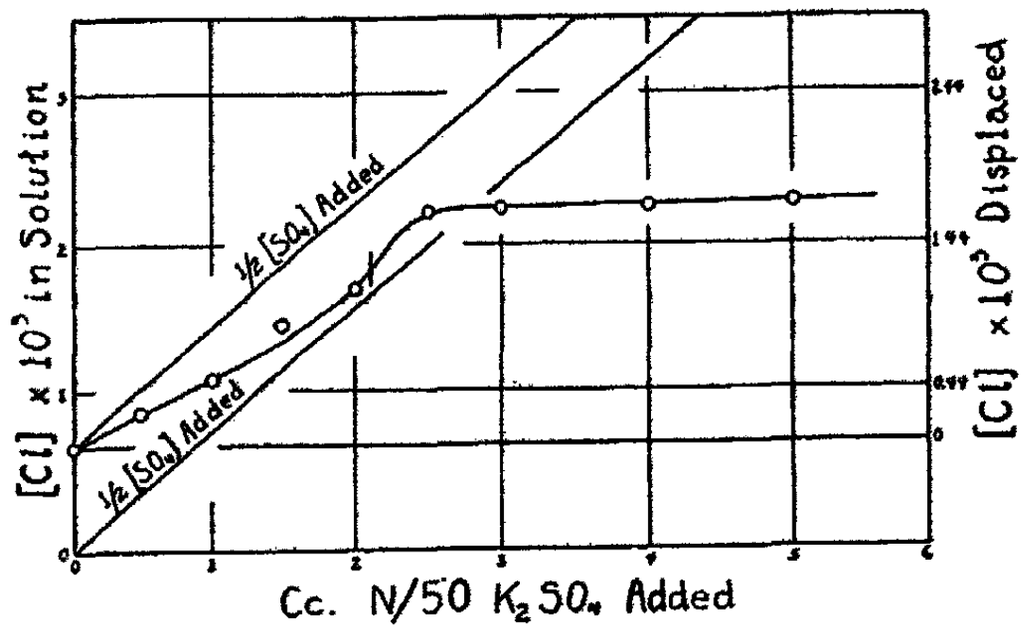

FIG. 13
Titration curves of Fe_2O_3 Sol III with K_2SO_4

is similar in all respects to that observed with less pure sols obtained by somewhat different procedures, is shown by the data given in Table XI and plotted in Fig. 13.

TABLE XI

Titration of Fe_2O_3 Sol III with K_2SO_4

Cc of N/50 K_2SO_4 added to 20 cc. of Sol. Total volume 25 cc.	π volts	α Cl^- $\times 10^3$	[Cl] $\times 10^3$	[Cl] displaced $\times 10^3$	[Cl] equivalent to [SO_4] added $\times 10^3$
0.0	0.1220	0.69	0.70	0.0	0.0
0.5	0.1154	0.91	0.93	0.23	0.40
1.0	0.1097	1.11	1.14	0.44	0.80
1.5	0.1025	1.47	1.51	0.81	1.20
2.0	0.0994	1.66	1.71	1.01	1.60
2.5	0.0926	2.15	2.23	1.53	2.00
3.0	0.0925	2.16	2.24	1.54	2.40
4.0	0.0924	2.17	2.25	1.55	3.20
5.0	0.0922	2.19	2.27	1.57	4.00

Discussion of Results

A theory of the mechanism of the coagulation of colloidal ferric oxide must explain the following facts reported in the preceding section:

1. At the precipitation value of potassium salts of multivalent ions the chloride in the supernatant solution is equivalent to or but little greater than the amount of added electrolyte.

2. Only a part of the chloride that is found in the supernatant solutions after precipitation, can be detected potentiometrically in the original sol before adding electrolyte. Not all of the chloride in the micelles is displaced by a large excess of precipitating electrolyte.

3. The chloride measured potentiometrically following the stepwise addition of electrolyte, consists of the chloride in the sol originally, together with an additional amount that is displaced when the added anion is taken up.

4. The multivalent ions investigated are taken up practically completely by the sol particles in concentrations up to and including the precipitation concentration. The chloride displaced so that it can be detected potentiometrically, is less than half the amount equivalent to the multivalent ion taken up.

5. The amount of chloride displaced follows nearly a linear course at the outset of the stepwise addition of multivalent ions but becomes proportionately greater as the precipitation concentration is approached.

6. The chloride displacement curves for multivalent ions of varying valence follow an almost identical course until the precipitation concentration is approached when there is a marked divergence for ions of different valence.

7. The three salts of divalent anions exhibit a strikingly similar behavior as regards the entire course of the chloride displacement curves and the precipitating power.

8. The trivalent ferricyanide coagulates at a distinctly lower concentration than the divalent ions and the chloride displaced at the precipitation value is proportionately less with the former than with the latter.

9. The chloride displacement curve with potassium salts of univalent ions such as nitrate, follows a course distinctly lower than that for the multivalent ions.

The solubility theory of Pauli would attempt to explain all of these facts on the basis of metathetical reactions with the formation of insoluble salts of the added electrolytes. Even if one disregards the objections to the theory which have been referred to already, the Pauli mechanism appears inadequate to account for the observations. A few cases may be mentioned. First of all, it seems altogether improbable that the alleged complex salts of such widely varying anions as sulfate, oxalate, and chromate should all possess practically the same solubility and so precipitate at the same concentration of added electrolyte. Nor is there any reason for supposing that the solubility of the alleged complex trivalent ferricyanide and citrate should be appreciably less than that of the divalent complexes. Moreover, it is difficult to explain on the basis of solubility relationships, why potassium oxalate and potassium ferricyanide, say, which must be assumed to form salts of widely varying solubility, should give chloride displacement curves which follow an almost identical course until the precipitation concentration of the trivalent ion is approached. Finally, I do not think that the time has yet arrived when anything can be gained by applying the term salt to a complex formed when a positively charged particle of variable composition takes up a given negative ion in varying amounts depending upon the conditions of preparation of the particle.

An adsorption mechanism which will now be outlined appears to offer a more rational interpretation of the facts: When ferric chloride is hydrolyzed there are formed positively charged micelles which vary in size, composition, and charge, depending on the conditions of the hydrolysis. In general, the colloidal particle exclusive of the outer layer has a composition represented by some point in the three-component diagram, Fe_2O_3-HCl-H_2O which may be represented symbolically [$xFe_2O_3.yHCl.zH_2O$]. This indicates the observed fact that there is chloride within the micelle which is not displaced even by high concentrations of precipitating electrolytes. It also indicates what is well known, that the actual composition of the particle is determined by its method of formation and the subsequent history.

Assume for the sake of simplicity that the hydrolysis has taken place to the point where the electrolyte active in sol formation is HCl and not $FeCl_3$. Now the finely divided solid particles of $xFe_2O_3.yHCl.zH_2O$ exhibit such a marked tendency to adsorb hydrogen ion as compared with chloride that the sols prepared as described above are almost neutral having a pH value of 6 to 6.5 whereas an appreciable concentration of chloride ion is observed potentiometrically. If n represents the number of hydrogen ions adsorbed by the micelle and q equals the chloride concentration of the sol that can be measured potentiometrically, the composition of the sol may be formulated as follows:

$[xFe_2O_3.yHCl.zH_2O]H_n^+.n\text{-}qCl^- + qCl^-$. This is represented diagrammatically in Fig. 14 in which the inner layer of the double layer surrounding the particle is composed of the adsorbed hydrogen ions. The outer portion of the double layer is a diffuse layer[1] consisting of an equivalent amount of chloride ions as shown. Some of the chloride ions because of their relatively higher kinetic energy exert sufficient osmotic repulsive force against the electrical attraction

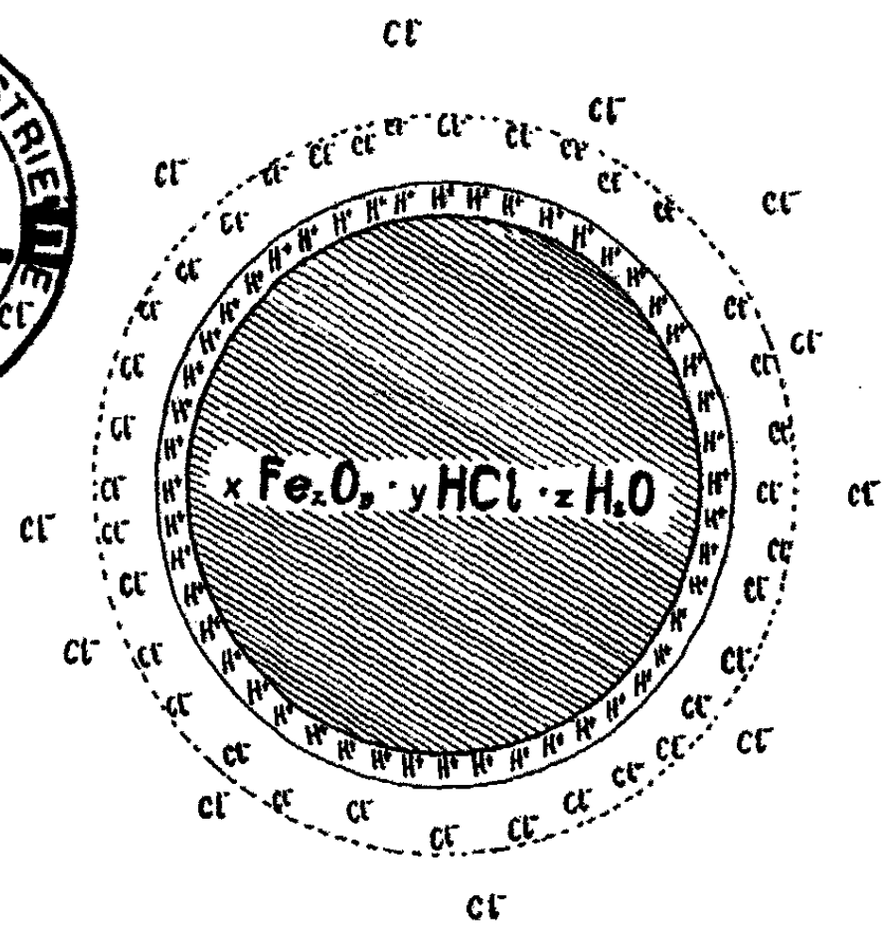

FIG. 14
Diagrammatic representation of the structure of the micelle in a ferric oxide sol.

of the H^+ ion layer, to influence the calomel electrode and are therefore detected potentiometrically. Such ions are represented in the diagram beyond the dotted circle.

When potassium sulfate is added to the sol, the more strongly adsorbed divalent sulfate ion forces itself into the double layer closer to the adsorbed hydrogen ion and displaces chloride as indicated diagrammatically in Fig. 15. Potentiometric analysis enables one to determine the chloride which has been displaced. The difference between the chloride in the sol originally and that after the addition of sulfate, in other words, the displaced chloride is not equivalent to the adsorbed sulfate since a part of the sulfate which enters the layer corresponds to chloride measurable potentiometrically in the original sol.

The adsorbed sulfate lowers the charge on the particle in the following way: A sulfate ion possesses the same average kinetic energy as a chloride ion but it possesses double the charge. Accordingly, if one assumes for the moment

[1] Gouy: J. Phys., (4) 9, 457 (1910).

that the valence only determines the adsorbability, the divalent particles in the outer layer would be drawn closer to the inner layer and the thickness of the double layer would be decreased. Since the potential difference between two layers of opposite sign with constant charge density is directly proportional to the distance between them, it follows that the reduced thickness of the layer will be accompanied by a decrease in charge on the particle.

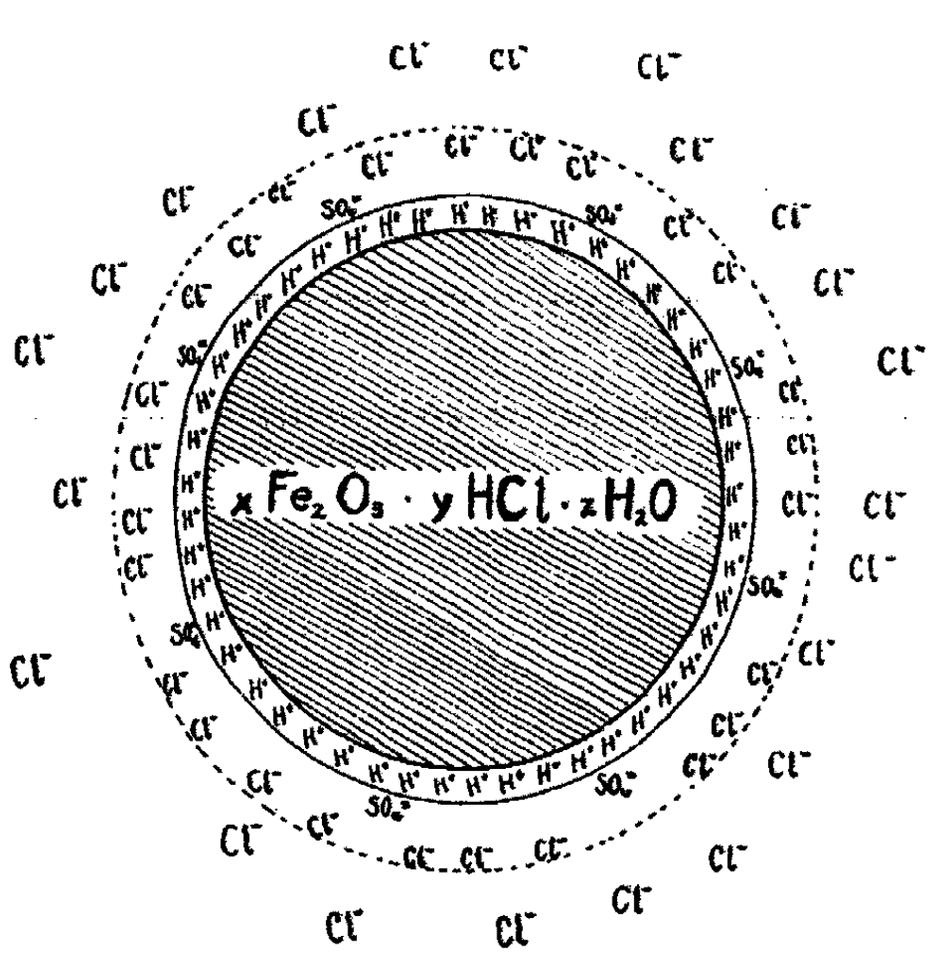

FIG. 15

Diagrammatic representation of the structure of the micelle in a ferric oxide sol after adding some K_2SO_4

Since the three divalent ions sulfate, oxalate, and chromate exhibit such a strikingly similar behavior in displacing chloride and in reducing the charge to the critical coagulation value, it follows that in the case of these three ions the valence is the most important factor determining the adsorbability.

The behavior of trivalent ions such as ferricyanide would follow from what has been said. The ions having the same average kinetic energy but with three charges will be drawn closer to the inner layer than the divalent ions and the further reduction in thickness of the double layer manifests itself in a lower precipitation value. The chloride ion displaced is obviously less since less ferricyanide needs to be adsorbed to lower the charge on the particles to the critical coagulation value.

The adsorption of both the divalent and trivalent ions is sufficiently great that the amount added to cause coagulation is practically completely adsorbed. The adsorption at this concentration is not completely irreversible

however, since shaking the precipitated gel with water results in partial repeptization of the sol owing to some of the precipitating ions breaking away from the close adsorption layer.

The increase in the chloride displaced for a given increment in the multivalent ion added in the region of the precipitation value, is the result of agglomeration and partial coalescence of the colloidal particles into micelles having a lower specific surface for a given mass.

The behavior of nitrate ion as compared with multivalent ions might be inferred from what has gone before. A much higher concentration of the univalent ions is necessary to produce the same effect as the multivalent ions since the latter are attracted so much more strongly toward the adsorbed hydrogen ion and so would be expected to effect the necessary lowering of charge in much lower concentration. The smaller amount of chloride displaced by nitrate as compared with the multivalent ions is not surprising in view of the fact that chloride is quite as effective as nitrate in lowering the charge. There is some chloride displaced because the higher concentration of nitrate causes some of the latter to enter the double layer and force out an equivalent amount of chloride.

Summary

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

1. A procedure is described for accurate potentiometric determination of the change in chloride concentration on adding electrolytes stepwise to hydrous oxide sols containing a slight excess of hydrochloric acid or ferric chloride as stabilizing electrolyte.

2. Only a part of the chloride that is found in the supernatant solution after coagulation can be detected potentiometrically in the original sol before adding electrolyte. The chloride measured potentiometrically following the stepwise addition of electrolyte, consists of the chloride in the sol originally together with an additional amount that is displaced when the added anion is taken up.

3. Titration curves are given which show the increase in chloride ion concentration on adding potassium sulfate, chromate, oxalate, ferricyanide, and nitrate stepwise to different ferric oxide sols.

4. The multivalent anions are taken up practically completely by the sol particles in concentrations up to and including the precipitation concentration. The chloride displaced so that it can be detected potentiometrically is less than half the amount equivalent to the multivalent ion taken up. At the precipitation value, the chloride in the supernatant solution is equivalent to or but little greater than the amount of multivalent ion added.

5. The titration curves follow a nearly linear course at the outset of the stepwise addition of multivalent anions but the amount of chloride displaced for a given increment of precipitating ion is relatively greater as the precipitation concentration is approached. Above the precipitation concentration, the curves take the form of an adsorption isotherm.

6. For simple multivalent ions of the same valence, the titration curves are strikingly similar. For multivalent ions of varying valence there is a marked divergence. Thus trivalent ferricyanide coagulates at a distinctly lower concentration than divalent sulfate and the chloride displaced at the precipitation value is proportionately less with the former than with the latter. The titration curve with a univalent precipitating ion such as nitrate follows a course distinctly lower than that for the multivalent ions.

7. In ferric oxide sols such as those under consideration the composition of the micelle exclusive of the outer layer is given by some point in the three component diagram Fe_2O_3-HCl-H_2O which may be represented symbolically as $xFe_2O_3.yHCl.zH_2O$. This indicates the observed facts that there is chloride within the micelle which is not displaced by electrolytes and that the composition varies with the conditions of preparation and the subsequent history of the sample.

8. The outer capsule of the micelle which largely determines its colloidal properties consists of an ionic double layer. The inner portion is adsorbed hydrogen or ferric ions; the outer portion is a diffuse layer consisting of chloride ions most of which are held by the electrical attraction of the adsorbed positive layer while others because of relatively higher kinetic energy exert sufficient osmotic repulsive force against the inner layer, to influence the calomel electrode and are therefore detected potentiometrically.

9. An adsorption mechanism is outlined to account for the change in composition and nature of the double layer which results in a decrease in charge on the micelle when electrolytes are added to the sol. At the same time, the proposed mechanism accounts for the form of the chloride displacement curve with different electrolytes.

10. The mechanism outlined accounts for the observed fact that relatively less of a trivalent ion must be adsorbed than of a divalent ion in order to lower the charge on a particle to the critical coagulation potential.

11. The relative merits of the proposed adsorption mechanism of the coagulation process and the solubility theory of Pauli are discussed.

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ION INTERCHANGES IN ALUMINUM OXYCHLORIDE HYDROSOLS*

BY ARTHUR W. THOMAS AND THOMAS H. WHITEHEAD

The behavior in solution of many complex inorganic salts (particularly those of cobalt, nickel, chromium, and aluminum) is such that the application of hydrolytic dissociation formulae does not successfully account for this behavior in most instances. Among the several hypotheses formulated to account for the experimental facts, the Werner theory has been successful and consistent in accounting for results obtained and for the prediction of probable behavior of related salts in solution.

The original classical postulates of Werner made in 1893 have since been extended by Pfeiffer, Bjerrum, and Stiasny. The explanation of hydrolysis in Werner terms was made by Pfeiffer shortly after Werner published his first papers.

Bjerrum,[1] in 1907, found it impossible to interpret the results obtained by heating basic chromic sulfate solutions by hydrolytic dissociation formulae. In addition to this, he found that the molecular weight of these salts had increased in some cases to as high as 750. He therefore postulated that perhaps the hydroxo groups in the complex ions were becoming more firmly bound to form larger complexes, such as,—

$$\begin{bmatrix} H_2O & & OH \\ H_2O & Cr & H_2O \\ H_2O & & H_2O \end{bmatrix}^{++} {}_2Cl^{-+} \quad \begin{bmatrix} HO & & H_2O \\ H_2O & Cr & H_2O \\ H_2O & & H_2O \end{bmatrix}^{++} {}_2Cl^{-} \rightleftarrows$$

$$\begin{bmatrix} & OH & \\ (H_2O)_4\,Cr & & Cr(H_2O)_4 \\ & HO & \end{bmatrix}^{++} {}_4Cl^{-} + {}_2H_2O$$

Bjerrum called this process "olation." It accounts for decreased activity of hydroxo groups toward neutral salts and sluggishness of attaining equilibrium.

Stiasny,[2] in order to account for decreased activity of basic chromic salts toward neutral salt solutions and decreased solubility of basic chromic salts when they were heated for long periods of time, further extended the idea of Bjerrum to include the conversion of hydroxo groups to oxygen bridges in the complex ion with formation of acid. This process is called "oxolation,"—

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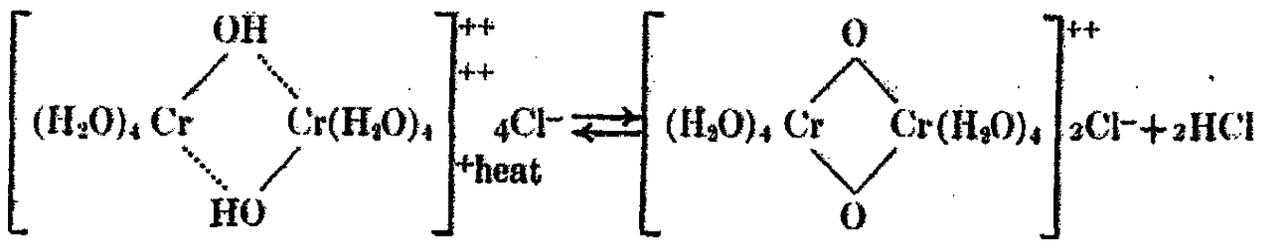
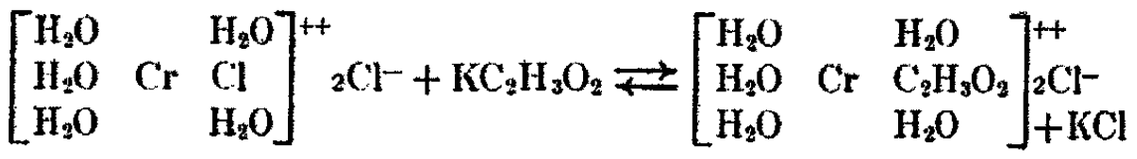
* Contribution from the Department of Chemistry, Columbia University, No. 637.

[1] Bjerrum: Z. physik. Chem., 59, 336 (1907); "Studier over Basike Kromiforbindelser," Kopenhagen (1908), through Stiasny and Grimm: Collegium 691, 505 (1927); Z. physik. Chem., 73, 724 (1910).

[2] Stiasny and Grimm: Collegium, 691, 505 (1927).



Stiasny[3] also found that the addition of neutral sodium sulfate to basic chromic sulfate solutions decreased the hydrogen ion activity and analysis of the resulting salts showed that the anion of the added sodium sulfate had become a part of the basic chromium salt. He found also that different anions had different degrees of effectiveness in decreasing hydrogen ion activity but in each case the added anion was found in the complex chromium salt. He therefore postulated an equilibrium between basic chromium salt ion and anion, being different for each particular anion and shifted by increasing the concentration of anion with respect to concentration of complex basic ion. This process he called "anion penetration," for example,—



An outstanding extension of these hypotheses is to be found in the papers by Gustavson[4] on the elucidation of the complex process of tanning leather by chrome liquors.

The large molecular aggregates obtained by Bjerrum with basic chromic salts led the authors to believe that perhaps particles of colloidal size might be built up in this manner, and, if so, they should act similarly to the basic chromic salts toward heating, aging, and neutral salt solutions.

The object of the present investigation was to apply the above mentioned hypotheses to the explanation of the behavior of aluminum oxychloride hydrosols made in the hot (80°-70°C) toward ageing and neutral salts and to attempt to give some picture of these hydrosols in terms of these hypotheses.

Materials

The C P aluminum chloride hexahydrate used yielded the following results upon analysis: Al = 99.50 per cent of theoretical; Cl = 99.40 per cent of theoretical; Fe = 0.01 per cent; Sulfate = Less than 0.002 per cent.

Ammonium hydroxide, C P.

Sodium hydroxide, C P,—a saturated solution was prepared and let stand for one month. Aliquots were siphoned from this and diluted.

The distilled water was always boiled just previous to use. All reagents after being prepared were kept in "NonSol" glass bottles. Pyrex ware was used in preparation of reagents.

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[3] Stiasny and Szego: Collegium, 670, 41 (1926).

[4] J. Am. Leather Chem. Assocn., 18, 568 (1923); 21, 22, 53 (1926); 22, 68 (1927); Collegium, 672, 153 (1926).

The potassium chloride, bromide, iodide, nitrate, and sulfate were twice recrystallized from boiling distilled water and dried at 110°C for twelve hours.

Potassium oxalate was dried at 110°C for three hours. It was tested for chlorides, sulfates, and heavy metals according to Murray[5] and found to be satisfactory. Its oxalate content was tested by titration against a standard solution of potassium permanganate which had been standardized the day before against sodium oxalate from the Bureau of Standards. Calculated on the basis of the formula $K_2C_2O_4.H_2O$ the oxalate content was 99.90 per cent of the theoretical.

Ammonium acetate was tested according to Murray[5] for chlorides, sulfates, and heavy metals. None was found, so the salt was simply dried over calcium chloride in a desiccator for two weeks.

Preparation of Sols

The general method of preparation was to dissolve 10 grams of aluminum chloride hexahydrate in two liters of water at 20°C. Alumina hydrate was then precipitated by addition of ammonium or sodium hydroxide at 20°C and the whole immediately heated to the desired temperature. (This must not exceed 80°C because it was found that above 80°C the alumina hydrate changes from its greyish color to a white color and becomes very much less soluble.) The mixture was kept hot for two hours and then allowed to cool to 20°C. The alumina hydrate settled out. The supernatant liquor was siphoned off and the precipitate washed with hot distilled water (70°C). After washing, the desired amount of distilled water was added and whole mechanically stirred while the minimum amount of hydrochloric acid necessary to peptize was added. (This amount was determined by preliminary preparation of similar sols.) The mixture was again heated (to same temperature as at first) for two hours, put in a "NonSol" bottle and allowed to stand for 24 hours, after which it was centrifuged for one hour at 1500 r.p.m. (Rotating radius to middle of tube was 42 cm) The supernatant liquor was carefully siphoned off (if any sediment had formed) after standing for 24 hours, and again centrifuged at 1500 r.p. m. for one hour. When nothing was thrown out after one hour centrifuging at 1500 r.p.m., the sol was considered peptized.

This method gave results which were reproducible and offered a means of making aluminum oxychloride hydrosols of a wide range of alumina hydrate concentration.

Four sols were selected varying in concentration of alumina hydrate content, in the temperature at which they were prepared, and in the precipitating reagent. These preparations were considered colloidal because they conformed to criteria which have been cited as being characteristic of the colloidal state; that is

(a) They did not dialyze through nitrocellulose membranes either at 20°C or at 80°C over a period of three days, although HCl in them did.

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[5] "Standards and Tests for Reagent Chemicals," 276 (1920).

(b) They exhibited a Tyndall cone in the carbon arc slit ultra-microscope.

(c) They appeared turbid but did not settle out under gravity over a period of six months or in a centrifuge at 840 times gravity in one hour.

(d) The adition of various salt solutions resulted in precipitation of the dispersed phase.

Analyses of Sols

Aluminum[6], *Total.* Since there were no other interfering elements present except a slight trace of iron, aluminum could be precipitated as the hydrate with ammonium hydroxide, filtered off, and ignited to the oxide.

To 100 cc of sol, 10 cc of glacial acetic acid were added and the whole left on the steam plate until solution was effected, usually about two hours. This solution was then made faintly alkaline with ammonium hydroxide (to methyl red) and allowed to digest over night at 20°C. It was filtered through Whatman No. 44 filter paper, washed twice with distilled water, and filter paper with precipitate transferred to a previously ignited quartz crucible, heated on an air bath till paper was completely charred, then ignited over a Meker flame for one hour, cooled in desiccator and weighed to the nearest 0.5 milligram.

Aluminum, Ionic. No evidence of any aluminum ion was obtained by use of the aluminon test[7] for which a sensitivity of 10^{-5} mol/l aluminum ion is claimed.

Chlorine, Total.[8] One hundred cc of sol and 10 cc of 18 M nitric acid with not more than 10 per cent excess over calculated amount of 0.1 M solution of silver nitrate solution were put on steam plate, covered with watch glass, and allowed to stand for 10 hours in a dark room. After cooling, the silver chloride was filtered off by means of a porous bottom Gooch crucible and heated in an oven at 115°C for three hours. This method had previously been verified in this laboratory by Hamburger in the analysis of ferric oxybromide hydrosols.[9]

Chlorine, Ionic. Chloride ion was determined directly on the sol by taking 100 cc of sol, adding 25 cc of distilled water and 3 cc of 0.1 M potassium chromate. Tenth molar nitric acid was added dropwise till the orange color of bichromate ion was seen, then 1 gram of powdered calcium carbonate[10] was added followed by titration with 0.1 M silver nitrate solution.

Ammonia, Total. The standard Kjeldahl method for nitrogen as ammonia was used to determine total ammonia in the sols.

Ammonium Ion. After solution of the sol has been effected, ammonium ion was determined by use of the Nessler reagent, as prescribed by the American Public Health Association method.[11]

To do this, 2 cc of 0.5 M potassium oxalate solution were added to 50 cc of sol and it was allowed to stand over night and filtered through Whatman

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[6] Hillebrand and Lundell: "Applied Inorganic Analysis," 389 (1929).
[7] Hammett and Sottery: J. Am. Chem. Soc., 47, 142 (1925).
[8] Fales: "Inorganic Quantitative Analysis," 196 (1924).
[9] Hamburger: Dissertation, "A Study of Ferric Oxybromide Hydrosols," Columbia University (1926).
[10] Hillebrand and Lundell: Loc. cit., 590.
[11] "Standard Methods of Water Analysis," 16, 17.

No. 44 filter paper. The precipitate was washed carefully with ten portions of 5 cc each of distilled water, allowing the washings to go into the filtrate. Aliquots of 5 cc each were pipetted out, diluted to 100 cc, 2 cc Nessler reagent added and the color compared with a standard solution by means of a Duboscq type colorimeter. Determinations were run in triplicate and results checked to 0.5 milli-equivalent.

Measurement of Hydrogen Ion Activity

Since it has been established[12] that the quinhydrone electrode gives reliable results between pH 2 and 7.5, this electrode was chosen for use in this investigation. It is interesting to note also that Pelling[13] found the quinhydrone electrode valid for measuring the pH values of aluminum sulfate solutions (0.001 M to 0.4 M).

Electrode Vessel. This was a 125 cc glass, wide mouth, bottle fitted with a rubber stopper admitting electrode, salt bridge, and air stirrer.

Platinum Electrodes. The electrodes were made of bright platinum wire sealed into a glass tube and the tube filled with redistilled mercury. Two were made and constantly checked against each other. It was necessary often to leave them over night in 18 M nitric acid to get consistent and reliable results.

Salt Bridge. The salt bridge was a glass U-tube with stop-cock in the center. The side arms were of equal length and plugged with cotton to prevent diffusion of sol into salt solution, which occurred unless this precaution was taken. The bridge was filled with saturated potassium chloride solution (at 25°C) and the stop-cock kept closed. The stop-cock was well covered with graphite.

Air Stirrer. This was simply a glass tube tapered off to small opening at one end and connected through a calcium chloride tube to the source of compressed air by rubber tubing.

Calomel Half-cell. Two saturated KCl calomel cells were made according to Findlay.[14] They were checked against each other constantly and against a standard cadmium cell at intervals.

The electrode vessels were immersed in a water thermostat at 25°C ±0.1°C and the potentiometric readings were taken to the nearest millivolt which was deemed sufficiently accurate for the purpose of this investigation.

Measurement of the Sign of the Electric Charge

The apparatus used was the same as that used by Sherman, Thomas, and Caldwell[15] for measuring the iso-electric point of malt amylase. A diagram with detailed description of parts is given in that paper.

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[12] LaMer and Parsons: J. Biol. Chem., 57, 613 (1923); Biilmann: Ann. chim., 15, 109 (1921).

[13] J. Chem. Met. Mining Soc. S. Africa, 26, 88 (1925).

[14] "Practical Physical Chemistry," 200 (1928).

[15] J. Am. Chem. Soc., 46, 1711 (1924).

The bottom of the U-tube was filled with sol, the stop-cocks closed and the side arms washed out with distilled water, drained thoroughly, and filled with 0.01 M KCl solution. The electrode vessels were then inserted, the leveling stop-cock opened and the level of the potassium chloride solution allowed to adjust itself; then the leveling stop-cock was closed. The current, 110 volts DC, was then turned on and both large stop-cocks opened simultaneously. The current was allowed to stay on for 24 hours, after which both large stop-cocks were simultaneously closed, the current cut off and the electrode vessels removed. The contents of each side arm were transferred to clean dry beakers, thoroughly stirred and 20 cc portion pipetted out of each and analysed for aluminum.

The colloidal aluminum micelles migrated to the cathode in each case.

Summary of the Properties of Sols

The data concerning the four aluminum oxychloride hydrosols are given in Table I. All figures are in milli-equivalents per liter.

TABLE I

1 Sol*	2 Temp. of prepn.	3 Total Al	4 Total Cl	5 Cl ion	6 Total NH_3	7 NH_4 ion	8 pH
A	80°	44	1.2	1.22	1.0	1	4.51
B	80°	70	54.90	53.04	...	48	4.50
C	70°	44	8.67	8.56	8.15	8	4.68
D	70°	62	13.40	13.30	...	0	4.39

* In the cases of sols A, B, and C ammonium hydroxide was used to precipitate the hydrous alumina from the original aluminum chloride solution, while sodium hydroxide was employed in the case of the alumina formed for the preparation of sol D.

None of the hydrosols gave any reaction for aluminum ion so that the amounts of aluminum given in column three of Table I were bound up in the complex ionic micelle, which as previously mentioned was cationic in each sol.

It may be seen from columns four and five that nearly all of the chlorine present was in the form of chloride ion, the difference being the amount in the complex aluminum ionic micelle. The analytical methods used were equally precise, and the authors think the differences are significant and not the result of different methods of analysis. In the case of ammonia, however, the slight differences shown in columns six and seven are perhaps due to difference in methods and the authors believe that all of the ammonia was present as ammonium ion.

The results in column eight of the table show slight differences in acidity. This is to be expected because the pH depends upon so many factors, *e.g.*, temperature of preparation, age of the sol, aluminum salt concentration, amount of hydrochloric acid used in peptization of the sol, etc., and since no final state of equilibrium had been reached in any case, no definite relation between the pH and other values was expected.

TABLE II

Effect of Ageing at 20°C on pH of Sols

Time	Sol A	Sol B	Sol C	Sol D	Solution $AlCl_3$*
1 hour					4.44
24 hours	4.54	4.56		4.39	4.42
7 days	4.54	4.59		4.41	4.39
14 days				4.41	4.37
30 days	4.63		5.39		
45 days	4.75	5.42	5.49		

* $AlCl_3$ solution—5 grams $AlCl_3.6H_2O$ per liter solution.

The results listed in Table II show that in all cases the hydrogen ion activity of the sols was decreased upon aging at 20°C. This was found to be the case also for chromium salt solutions which had been heated, but those which had not been heated increased in hydrogen ion activity.[16] The last column in Table II shows that the aluminum chloride solution which had not been heated increased in hydrogen ion activity upon ageing. Thomas and Baldwin[17] found similar results with chromium salt solutions at 20°C.

The decrease in hydrogen ion activity of the sols is therefore significant because all the factors involved would apparently lead to increased hydrogen ion activity; namely, loss of water due to slow evaporation, and slow hydrolysis of the aluminum salt.[18]

An explanation for this phenomenon is given later.

Effect of Heat on pH of the Sols

Fifty cubic centimeters of each sol were put in "NonSol" bottles[19] and left in an oven at 80°C for four days, when they were removed, cooled to 25°C, and the pH measured. There was no loss of volume of the sols during this treatment. The results are given in Table III.

TABLE III

Sol	Original pH	After 3 hours	After 4 days
A	4.75	No change	4.65
B	4.61	No change	4.15
C	5.39	No change	5.22
D	4.39	No change	4.09

These results are very significant. They show obviously that heating increases the hydrogen ion activity, but the greater significance is that upon cooling back to 25°C, the hydrogen ion activity did not decrease to its former

[16] Stiasny and Grimm: Collegium, 694, 49 (1928).
[17] J. Am. Leather Chem. Assocn., 13, 192 (1918).
[18] Tian: Compt. rend., 172, 1179 (1921).
[19] Sols heated at 80° for four days in ordinary glass reagent bottles became alkaline to phenolphthalein.

value as do salt solutions which undergo hydrolytic dissociation. Hydrolytic dissociation alone then will not account for these results. It should also be noted that heating for only three hours had no measurable effect. This again indicates that hydrolysis is not all that is involved inasmuch as heat increases the hydrolytic dissociation of salts. This behavior of the sols will be explained later.

Effect of Neutral Salts on pH of the Sols

All salt solutions were made up just prior to use. Solutions were all at 1 normal concentration.

In the case of potassium oxalate which was alkaline, sufficient 0.5 molar oxalic acid was added to make the solution slightly acid. This did not, however, alter the concentration of oxalate ion available for reaction, as the solution was maintained 0.5 molar with respect to oxalate ion.

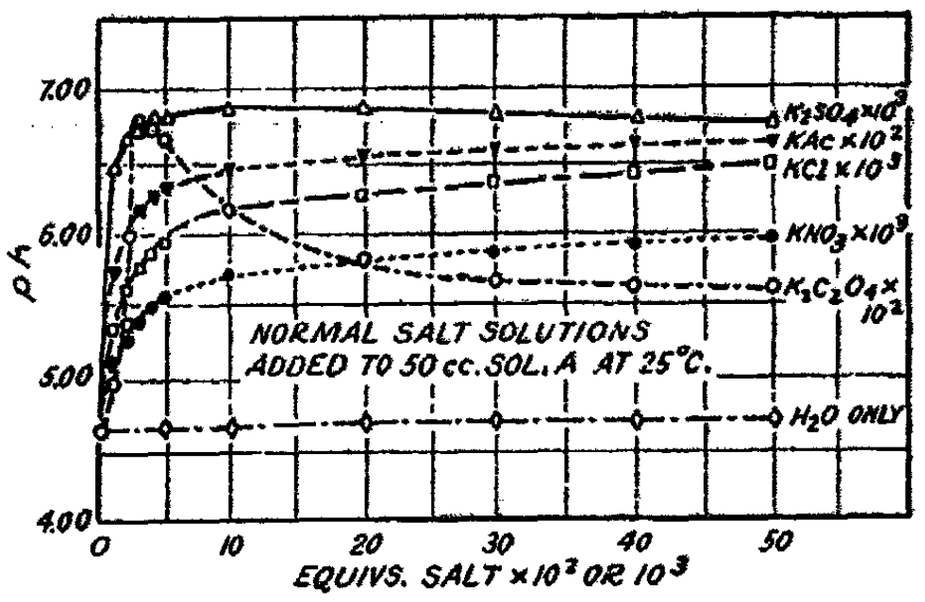

FIG. 1

The pH of the salts solutions at 25°C was:

Salt	KCl	KBr	KI	KNO_3	K_2SO_4	NH_4OOCCH_3	Oxalate
pH	5.44	6.71	7.00	5.86	5.55	7.10	5.07

Technique. The electrode vessel was rinsed with the sol, then 50 cc added with pipette. Half an hour was allowed for saturation by the quinhydrone; readings on the potentiometer taken every five minutes until constant. Usually they became constant in fifteen minutes. Then the salt solution was delivered into the electrode vessel by burette in 1 cc portions (except acetate and oxalate) and potentiometer readings taken after each addition until constant. After 10 cc had been added in this way, the size of portions was increased to 5 cc and added to a total of 50 cc. In the case of acetate and oxalate solutions, the portions were one-tenth the size of the other salt solutions. All solutions except oxalate gave constant readings on the potentiometer within five minutes, so that the readings reported for oxalate are those

taken exactly five minutes after its addition. The drift was probably due to some oxidation-reduction reaction in which oxalate ion is notoriously sensitive.

Several facts are evident from the results shown in Table IV and plotted in Fig. 1.

In the first place, it will be seen that all salt solutions increased the pH of sol A, but their magnitudes are different, oxalate and acetate having a ten times greater effect than the other salt solutions. This suggests a chemical reaction between the sol and salt solutions. This is further borne out by the fact that water alone had practically no effect on pH; the effect of the salt solutions then was not due to dilution of the sol by addition of dilute salt solution.

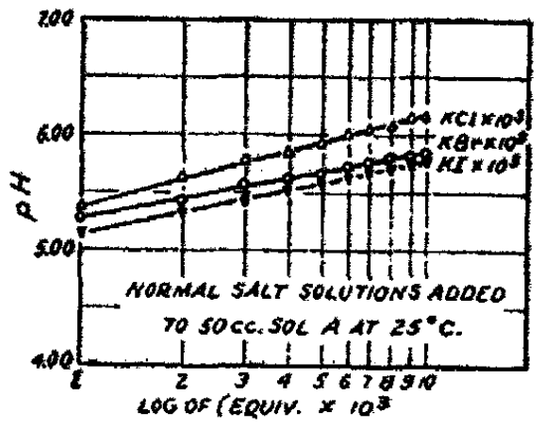

FIG. 2

The question might arise as to whether this effect is due to the action of salt on the hydrogen ion activity shown by Harned[20] for solutions of hydrochloric acid. In the case above described, the effect is too great to be accounted for in such a manner.

It is significant that in no case did the pH go above 7. A maximum was reached with oxalate, acetate, and sulfate after which the pH increased because the salt solutions had a pH of 5.22, 7.02, and 5.55 respectively. This maximum is thought to mark the end of the chemical reaction.

That there was no salt effect on the quinhydrone which could be measured was shown by the fact that the pH of the salt solutions was independent of the volume measured. The authors believe that the pH changes obtained upon titration of the sol with the salt solutions are real and not due to "salt effects" upon the quinone-hydroquinone ratio.

It should be noticed that the order of effectiveness of the anions is :

Nitrate < chloride < sulfate < acetate < oxalate.

In Fig. 2 the concentration of salt solution is plotted logarithmically and the slopes of the lines represent the effectiveness of each salt in decreasing the hydrogen ion concentration. It is obvious that all three salts are of very nearly the same effectiveness. For this reason, potassium chloride is taken as typical of the halogen salts and used as such in comparisons with other salts.

The pH changes upon titration of the four sols and of aluminum chloride solution are shown in Table VI and in Fig. 3.

This graph shows first of all that potassium chloride increased the pH of all four sols in a similar manner, but had greater effect upon the sols of low aluminum content (A and C) than upon the sols of high aluminum content

[20] J. Am. Chem. Soc., 44, 2729 (1922).

(B and D). A similar trend will be noticed with other salts. It is of more than passing interest to point out that sol D was made with sodium hydroxide while B was made with ammonium hydroxide, yet they act alike, indicating that a decrease in hydrogen ion activity is not the result of ammino groups reacting with hydrogen ion. This is further confirmed by the fact that sol A contained only 1 milli-equivalent of ammonia, while sol C contained 26, yet they acted alike.

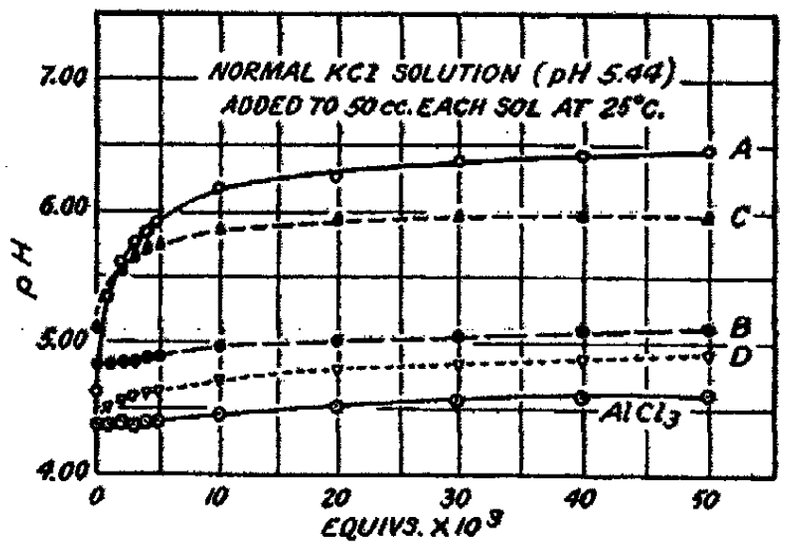

FIG. 3

TABLE IV

50 cc Sol A and 1 Normal Salt Solutions
(Figures are pH values at 25°C)

Cc added	H_2O only	KNO_3	KCl	K_2SO_4	Cc	NH_4Ac	$K_2C_2O_4$
0	4.75	4.75	4.75	4.75	0.0	4.75	4.75
1	4.77	5.13	5.39	6.47	0.1	5.75	4.99
2	4.78	5.28	5.63	6.69	0.2	6.00	5.39
3	4.78	5.42	5.80	6.73	0.3	6.19	6.77
4	4.78	5.51	5.87	6.78	0.4	6.25	6.73
5	4.78	5.57	5.95	6.81	0.5	6.32	6.67
10	4.78	5.71	6.17	6.87	1.0	6.44	6.16
15	4.80	5.76	6.24	6.88	..	...	...
20	4.80	5.81	6.28	6.88	2.0	6.54	5.83
25	4.80	5.84	6.34	6.88	..	...	...
30	4.80	5.88	6.37	6.85	3.0	6.58	5.67
35	4.80	5.91	6.39	6.81	..	...	...
40	4.81	5.93	6.41	6.79	4.0	6.60	5.63
45	4.81	5.93	6.42	6.78	..	...	...
50	4.81	5.95	6.44	6.75	5.0	6.60	5.59

TABLE V

Normal Potassium Halide Solutions added to 50 cc Sol A
(Figures given are pH values at 25°C)

Cc. added	KCl	KBr	KI
0	4.75	4.75	4.75
1	5.39	5.28	5.20
2	5.63	5.45	5.33
3	5.80	5.54	5.44
4	5.87	5.61	5.53
5	5.95	5.67	5.59
10	6.17	5.85	5.79
15	6.24	5.96	5.91
20	6.28	6.01	6.00
25	6.34	6.07	6.05
30	6.37	6.12	6.15
35	6.39	6.15	6.22
40	6.41	6.18	6.27
45	6.42	6.22	6.29
50	6.44	6.22	6.32

TABLE VI

Normal Potassium Chloride added to 50 cc each Sol
(Figures are pH units at 25°C)

Cc added	Sol A	Sol B	Sol C	Sol D	$AlCl_3.6H_2O$*
0	4.75	4.81	5.10	4.39	4.36
1	5.39	4.83	5.39	4.51	4.36
2	5.63	4.85	5.56	4.58	4.37
3	5.80	4.87	5.65	4.59	4.39
4	5.87	4.88	5.71	4.62	4.41
5	5.95	4.89	5.74	4.64	4.43
10	6.17	4.97	5.85	4.72	4.47
15	6.24	5.01	5.91	4.78	4.52
20	6.28	5.02	5.93	4.81	4.54
25	6.34	5.05	5.95	4.82	4.56
30	6.37	5.07	5.96	4.85	4.58
35	6.39	5.08	5.96	4.85	4.60
40	6.41.	5.10	5.96	4.88	4.61
45	6.42	5.12	5.96	4.89	4.62
50	6.44	5.14	5.96	4.91	4.62

* 5 g per liter.

These results seem to conflict with results reported in the literature by Thomas and Baldwin[17] and Wilson and Kuan,[21] but it should be noted that in their work, large quantities of solid salt were added (3 gram mols per 100 cc) while here the total quantity added was between 0.001 and 0.05 mols per 100 cc. The work of Wilson and Kuan was repeated by the authors, and it was shown[22] that when dilute solutions are used a single effect is noted, but if solid salt is used, the factor of hydration of the ions of the salt enters and tends to mask the chemical effect. This is confirmed by the work of Harned[23] who found that small quantities (0.01-0.05 M) of sodium chloride increased the dissociation constant of water at 25°C, but in greater concentration than 1 molar with respect to the solution, it decreased the dissociation constant.

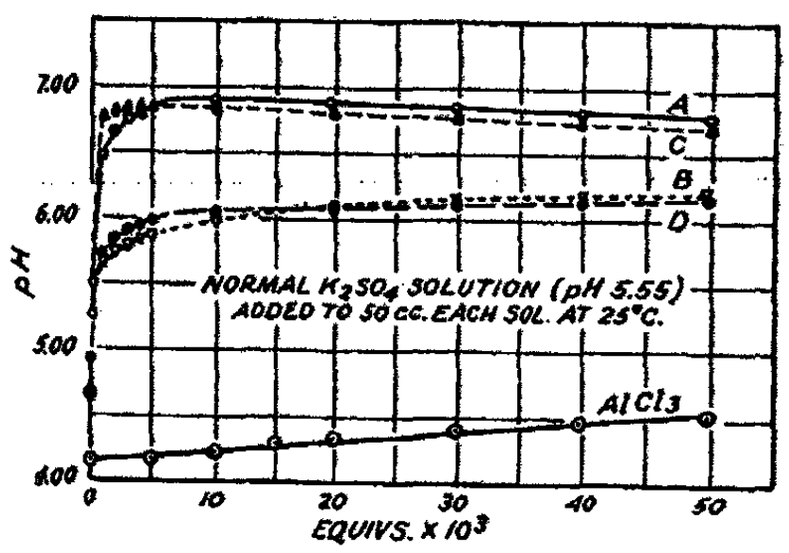

FIG. 4

It will be noted that aluminum chloride solution of the same aluminum content as sol A and C, while showing increased pH values did so to a far less extent than the sols.

Fig. 4 shows that potassium sulfate solution also increased the pH of all sols and reference to Fig. 1 will show that it does so more effectively than potassium chloride solution of same equivalent concentration. Here again it should be noted that the sols A and C acted alike and so did sols B and D.

The authors hope by this time to have shown that one must look for something else to explain the results other than dilution, salt effect on quinhydrone, and hydration of ions. The results with ammonium acetate and potassium oxalate will be even more convincing.

The titration of the sols with ammonium acetate solution is given in Table VIII and in Fig. 5.

The outstanding fact in Fig. 5 is that the effect of acetate ion is ten times greater in increasing the pH of the sols than are nitrate, chloride, and sulfate ions (cf., Fig. 1). It is also shown that the order of reaction was proportional to the aluminum content of the sols (cf., Figs. 3 and 4).

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[21] J. Am. Leather Chem. Assocn., 25, 15 (1930).
[22] Thomas and Whitehead: J. Am. Leather Chem. Assocn., 25, 127 (1930).
[23] J. Am. Chem. Soc., 47, 930 (1925).

It is again emphasized that no maximum was shown by the curves for B and D; that is, the curves approached pH 7 on the vertical axis with increasing salt concentration. But the curves for C and A are parallel to the horizontal axis from 40 to 50, indicating that no change in pH occurred with increase in salt concentration after 40 × 10^2 milli-equivalents were added.

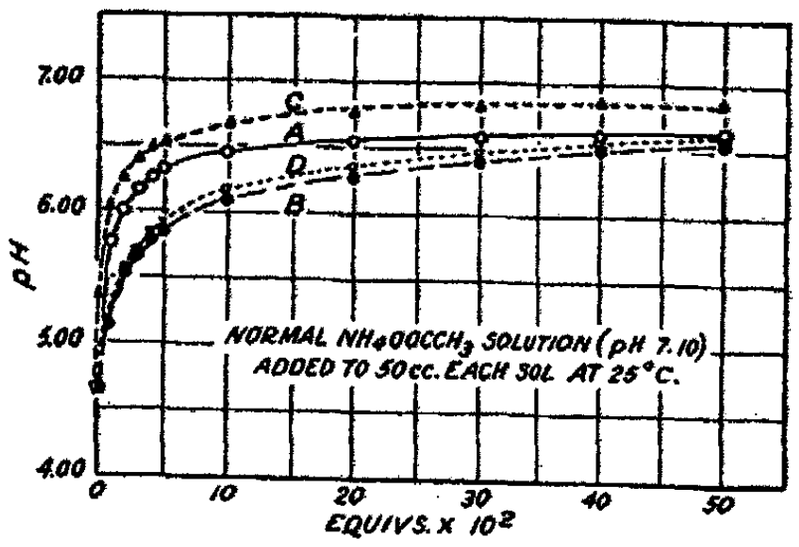


FIG. 5

TABLE VII

Normal Potassium Sulfate Solution added to 50 cc each Sol at 25°C

(Figures are pH values at 25°C)

Cc added	Sol A	Sol B	Sol C	Sol D	$AlCl_3.6H_2O$*
0	4.75	5.42	5.49	4.39	4.14
1	6.47	5.66	6.75	5.73	...
2	6.69	5.75	6.80	5.84	...
3	6.73	5.79	6.81	5.89	...
4	6.78	5.83	6.82	5.94	...
5	6.81	5.86	6.83	5.96	4.16
10	6.87	5.98	6.85	6.03	4.22
15	6.88	6.03	6.82	6.08	4.30
20	6.88	6.07	6.81	6.10	4.35
25	6.88	6.10	6.80	6.10	4.41
30	6.85	6.14	6.78	6.12	4.43
35	6.81	6.17	6.76	6.14	4.44
40	6.79	6.18	6.75	6.15	4.47
45	6.78	6.20	6.73	6.16	4.51
50	6.75	6.22	6.71	6.16	4.53

* 10 g per liter.

Table IX and Fig. 6 reveal the effects of titration of the sols with oxalate. It will be recalled that the oxalate solution consisted of potassium oxalate slightly acidified with oxalic acid.

It will be noticed at once that oxalate ion is very active. The pH of the sols was immediately increased to about pH 7, and except for B, the pH then markedly decreased, gradually approaching the pH of the oxalate solution (5.07). This suggests that a reaction took place with A, C, and D; was completed, and the solution became more acid again. In the case of sol B, the second effect was much less readily executed. This sol contained more aluminum micelle than the others.

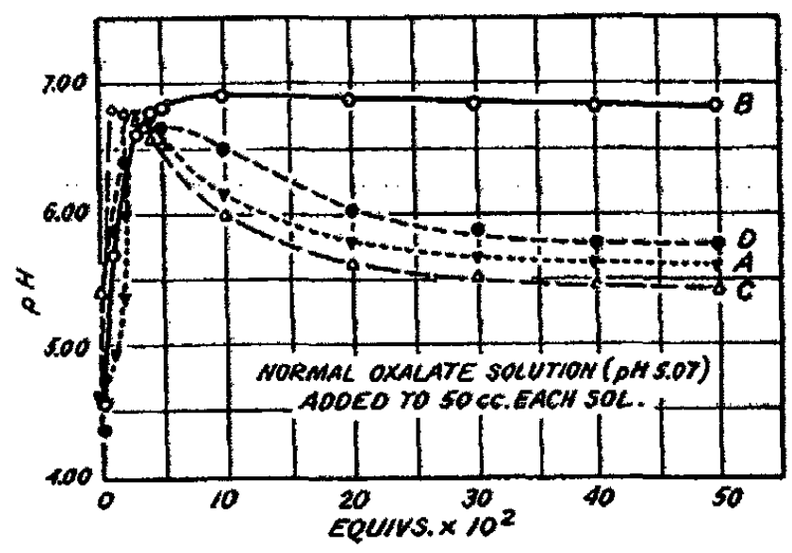


FIG. 6

TABLE VIII

Normal Ammonium Acetate added to 50 cc of each Sol at 25°C
(Figures are pH values at 25°C)

Cc added	Sol A	Sol B	Sol C	Sol D
0.0	4.75	4.59	5.39	4.39
0.1	5.75	5.18	6.01	5.18
0.2	6.00	5.53	6.25	5.51
0.3	6.19	5.66	6.38	5.69
0.4	6.25	5.78	6.47	5.81
0.5	6.32	5.85	6.54	5.89
1.0	6.44	6.08	6.67	6.14
2.0	6.54	6.29	6.79	6.34
3.0	6.58	6.42	6.85	6.47
4.0	6.60	6.51	6.88	6.58
5.0	6.60	6.56	6.88	6.64

Table IX

Normal Potassium Oxalate Solution added to 50 cc each Sol
(Figures are pH values at 25°C)

Cc added	Sol A	Sol B	Sol C	Sol D
0.0	4.75	4.56	5.41	4.37
0.1	4.99	5.69	6.82	4.88
0.2	5.39	6.39	6.77	6.41
0.3	6.77	6.62	6.71	6.56
0.4	6.73	6.78	6.59	6.64
0.5	6.67	6.82	6.54	6.67
1.0	6.16	6.91	6.00	6.50
2.0	5.83	6.89	5.63	6.03
3.0	5.67	6.85	5.51	5.88
4.0	5.63	6.78	5.46	5.76
5.0	5.59	6.77	5.42	5.76

Resumé of Results between Sols and Salt Solutions

Figure 1 showed the order of the effectiveness of the salt solutions in increasing the pH of sol A to be:

Nitrate < Chloride < Sulfate < Acetate < Oxalate.

Figures 3, 4, 5, and 6, showed all sols acted similarly to sol A, so we can say that the same order would apply to the other sols. Figure 2 showed the similarity of the halogens, so that it may be said that the order of anion effect on pH of positively charged aluminum oxychloride hydrosols is:

Nitrate < Halides < Sulfate < Acetate < Oxalate.

This order was found for aqueous solutions of chromic salts by Gustavson,[4] and by Stiasny[24] for solutions of chromic salts that had previously been heated.

All results showed that sols B and D acted similarly despite the fact that ammonium ion was present in B while absent in D as a result of the initial preparation of the hydrous alumina.

Neutral Salt Titration of Aluminum Chloride Solutions of Different Basicities

After the titrations of the sols with the salt solutions had been completed it was considered advisable to include in this paper a few similar measurements made upon crystalloidal aluminum chloride solutions. Selecting sol D for comparison, a solution of aluminum chloride hexahydrate (5 gm $AlCl_3.6H_6O$ per liter) was made containing the same amount of aluminum as sol D. Then a potentiometric titration of the aluminum chloride solution

[24] Stiasny and Balanyi: Collegium, **694**, 72 (1928).

with 0.1 N NaOH was carried out at 25°C, using the quinhydrone electrode, to determine the exact stoichiometric relation, this was found to agree with the calculated amount, *i.e.*, 30.50 cc of 0.1 N NaOH for 50 cc of aluminum chloride solution. To make the basic solutions, 25 cc portions of aluminum chloride solution (containing 10 grams $AlCl_3.6H_2O$ per liter) were mixed with 10.17 cc and 20.34 cc respectively of 0.1 N NaOH mentioned above and the

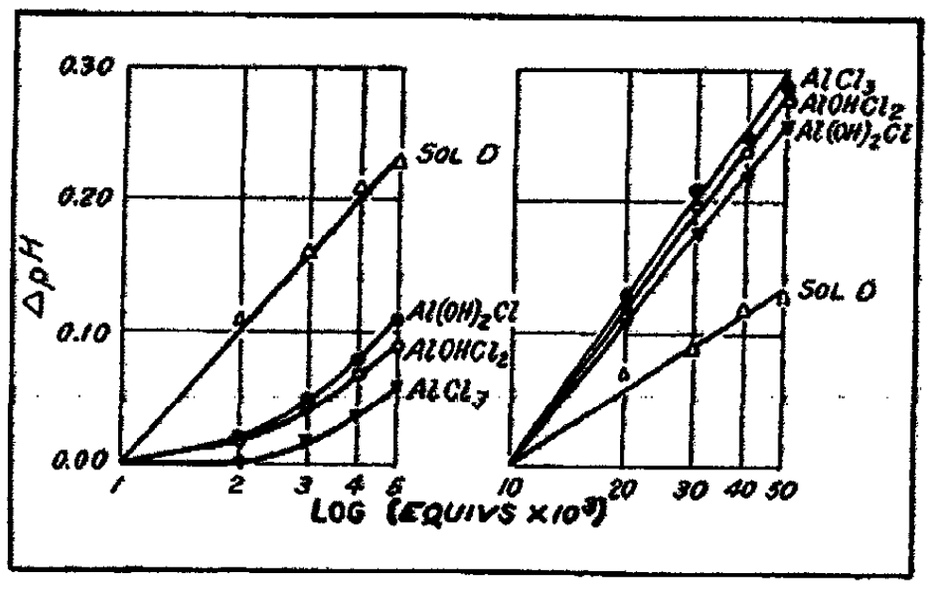


FIG. 7

final volume made up to 50 cc with previously boiled and cooled distilled water. Thus 50 cc portions of $AlCl_3$, $AlOHCl_2$, and $Al(OH)_2Cl$, were obtained all containing the same aluminum content.

Each of these portions was then titrated with the same 1 N potassium sulfate solution at 25°C according to the technique previously described.

TABLE X

Normal Potassium Sulfate Solution added to 50 cc Portions of Each Aluminum Salt Solution at 25°C.

*(Figures are differences in pH units; 25°C)

K_2SO_4	$AlCl_3$		$AlOHCl_2$		$Al(OH)_2Cl$		Sol D	
Cc	pH	ΔpH*	pH	ΔpH*	pH	ΔpH*	pH	ΔpH*
1.0	3.77		3.88		4.14		5.73	
2.0	3.77	0.00	3.90	0.02	4.16	0.02	5.84	0.11
3.0	3.79	0.02	3.93	0.05	4.19	0.05	5.89	0.16
4.0	3.81	0.04	3.95	0.07	4.22	0.08	5.94	0.21
5.0	3.83	0.06	3.97	0.09	4.25	0.11	5.96	0.23
10.0	3.91		4.06		4.34		6.03	
20.0	4.04	0.13	4.19	0.13	4.45	0.11	6.10	0.07
30.0	4.12	0.21	4.26	0.20	4.52	0.18	6.12	0.09
40.0	4.17	0.25	4.30	0.24	4.56	0.22	6.15	0.12
50.0	4.19	0.29	4.39	0.28	4.60	0.26	6.16	0.13

The potentiometer readings were made until constant over a fifteen minute period to plus or minus 0.5 millivolt but are recorded only to the nearest millivolt in Table X. The results are plotted in Fig. 7.

It is evident that potassium sulfate decreased the hydrogen ion activity of all the aluminum solutions and of the sol. It is also seen that the rate of change of pH with respect to change in concentration of K_2SO_4 is not the same in any two cases but is greatest for sol D and least for $AlCl_3$ with the addition of K_2SO_4 solution up to and including 5 cc. The addition of from 10 to 50 cc of K_2SO_4 solution caused a reversal of this order but again there is a progression from sol D through the $Al(OH)_2Cl$ and the $AlOHCl_2$ to the $AlCl_3$ state.

This suggests then that the rate of change of pH with respect to change in concentration of potassium sulfate is a function of the hydroxo groups contained in the basic complex aluminum ion since practically every other condition was held constant. (It should be remarked that the sol was *made up originally* at 70°C, and cooled to 25°C, while the aluminum salt solutions were made and maintained at 25°C, throughout. This was the factor that was not constant in the comparison between sol and solutions and the numerical difference in change of pH with increased concentration of potassium sulfate, although one of degree only, suggests that a closer analogy would have been obtained if this factor, too, were constant.)

Discussion of Results obtained

In attempting to account for the results reported, the same difficulty is encountered that Werner, Pfeiffer, Bjerrum, Gustavson, and Stiasny encountered in working with other complex basic salts; namely, the difficulty of applying the laws of hydrolytic dissociation and the various hypotheses of salt effects.

Hydrolytic equilibria as obtained with simple crystalloidal solutions, such as of potassium cyanide, are not shown by aluminum oxychloride hydrosols. Table III showed that the equilibrium was not immediately disturbed by heat, but on prolonged heating it was disturbed. It likewise showed that upon cooling back, the equilibrium was not shifted back to the original stage.

Tian[19] has suggested that a system like aluminum oxychloride hydrosol may be considered as a heterogeneous system in which the basic salt ion is the dispersed phase. This would explain why upon ageing at 20°C, the hydrogen ion activity increases because the assumption of a dispersed phase introduces a surface phenomenon which would, of course, decrease the original surface exposed by the ions and cause the equilibrium to be disturbed, for example:

$$AlCl_3 + HOH \leftrightarrows AlOHCl_2 + HCl$$

In this case, $AlOHCl_2$ is the supposed dispersed phase, whose formation decreases the surface, and causes a shift in equilibrium to the right; and this results also in hydrogen ion being increased. But if the temperature of such a system should be increased, the degree of dispersity would increase,[25] this

[25] March: Ann. Physik, 84, 605 (1927).

would increase the surface and so should shift the equilibrium to the left; *i.e.*, decrease the hydrogen ion activity. Table IV shows that the opposite is true. This was also found to be the case for ferric salts[26] and by Stiasny[27] for chromic salts.

To explain the effect of ageing and heat, then, one must look to some other source. The Werner-Co-ordination Theory[28] offers a consistent explanation for these results.

The aluminum chloride hexahydrate used precipitated three mols of silver chloride per mol of aluminum salt with silver nitrate. Therefore the following structure can be assigned:—

$$\begin{bmatrix} H_2O & & H_2O \\ H_2O & Al & H_2O \\ H_2O & & H_2O \end{bmatrix}^{+++} Cl^-_3$$

Its hydrolysis according to the $CrCl_36H_2O$ analogue is:—

$$\begin{bmatrix} H_2O & & H_2O \\ H_2O & Al & H_2O \\ H_2O & & H_2O \end{bmatrix}^{+++} Cl^-_3 \leftrightarrows \begin{bmatrix} H_2O & & OH \\ H_2O & Al & H_2O \\ H_2O & & H_2O \end{bmatrix}^{++} Cl^-_2 + HCl \qquad (1)$$

To account for lack of mobility in the shift of equilibrium, we can picture the aluminum oxychloride sol as resembling the polyol basic chromic salts reported by Bjerrum.[1] Bjerrum working with chromic sulfate, found that if he heated his salt solutions to boiling that their molecular weights as determined by freezing point method had values around 750. Stiasny[27] working with the same salt, found that heat decreased pH and that on cooling the pH did not return to its original value. Substituting Al for the Cr of Bjerrum's picture, we have:

$$\begin{bmatrix} H_2O & & OH \\ H_2O & Al & H_2O \\ H_2O & & H_2O \end{bmatrix}^{++} 2Cl^- + \begin{bmatrix} HO & & H_2O \\ H_2O & Al & H_2O \\ H_2O & & H_2O \end{bmatrix}^{++} 2Cl^- \rightleftharpoons$$

$$\begin{bmatrix} & OH & \\ (H_2O)_4\,Al & & Al\,(H_2O)_4 \\ & HO & \end{bmatrix}^{++++} 4Cl^- + 2H_2O \qquad (2)$$

In the above picture it is postulated that the hydroxo groups become more firmly bound which diminishes their tendency to unit with H^+ ion to form aquo groups. Thus the tendency for reversal of the hydrolysis equation by heating is lessened.

The authors present the point of view that the colloidal aggregates are formed according to the mechanisms of equations (1) and (2). That is, heating caused two things to take place:

[26] Thomas and Frieden: J. Am. Chem. Soc., 45, 22 (1923).
[27] Stiasny and Grimm: Collegium, 694, 53 (1928).
[28] Thomas: "Inorganic Complex Salts" (1924).

1. Aquo groups gave up hydrogen ions, leaving hydroxo groups in place of aquo groups.

2. The hydroxo groups then "olated," resulting in the formation of large aggregates, eventually reaching colloidal size.

The Werner Theory as extended by Bjerrum and by Stiasny, therefore, offers a consistent explanation for the formation of the sols, for their decrease in acidity upon ageing and increase on heating, for their sluggishness in readjustment of equilibrium, and for effect of heat upon solubility of aluminum hydrates.

The explanation of the results obtained with salt solutions will now be attempted. It is probable that the more aluminum atoms present in the original aluminum chloride solution, the more olated hydroxo groups there were in the sol produced. (Washing removed the hydrochloric acid of hydrolysis.) It would be expected, then, that the greater the degree of olation, the more sluggish would be the reaction of the complex olated ion. Since in every case this complex ion was positively charged, it suggests that not more than two hydroxo groups were present per atom of aluminum. Now when a salt such as potassium sulfate was added to a sol, the hydrogen ion activity decreased, suggesting that sulfate ion was replacing hydroxo groups in the Werner complex. The hydroxo uniting with hydrogen ion to form water would decrease the hydrogen ion activity. Stiasny[3] analyzed basic chromic salt complexes before and after the addition of sulfate solution, and found that sulfate did go to the chromic complex. This is obviously the case with oxalate ion, because the addition of much oxalate changes the chromium from the cation to the anion.[3] This offers a simple explanation for the results shown in Figs. 1 to 4, inclusive.

The anion order, then represents the "penetration power" of the several anions toward the complex basic aluminum ion. On this basis, oxalato complexes are least dissociated, and nitrato complexes most dissociated. Gustavson[4] found this to be true in chrome tanning.

The anion penetration order explains why Lamb[29] got complete precipitation of chloride ions from green $CrCl_3$ with silver acetate, but not with silver nitrate. Some chloride was in the complex with chromium. Nitrate is below chloride in the penetration order, but acetate is above it and the latter then possesses the property of replacing chloride in the "nucleus" forcing it into the "outer solution."

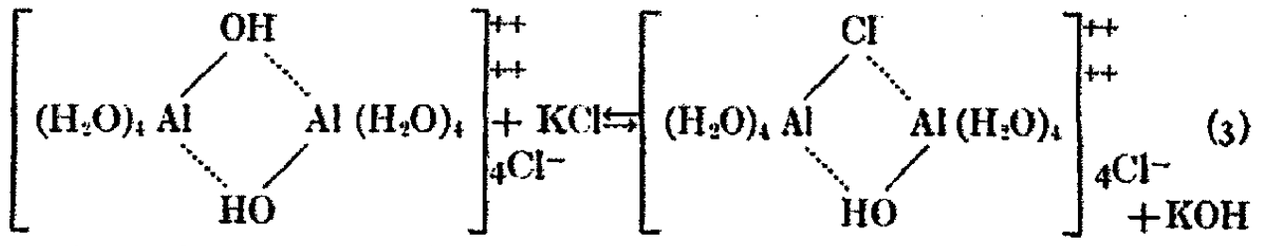
The agreement among the basic aluminum salt solutions (Fig. 7) indicated that their behavior is a function of the hydroxo groups present in the basic aluminum ion and that an aluminum oxychloride sol is a very large basic aluminum ion carrying a positive charge and in equilibrium with chloride ion.

The difference in behavior with respect to small amounts of K_2SO_4, and to larger amounts suggests that hydrolytic dissociation in addition to anion penetration took place at first and when no further hydrolytic dissociation was possible, only the factor of anion penetration was involved. The curves

[29] J. Am. Chem. Soc., 28, 1710 (1906).

in the first half of the figure are in contrast to the almost perfect straight lines in the second half of the figure and suggest a net effect of two unequal factors while the straight lines suggest only one factor producing a linear relation.

Using potassium chloride as a typical example to show the anion effect we have:—

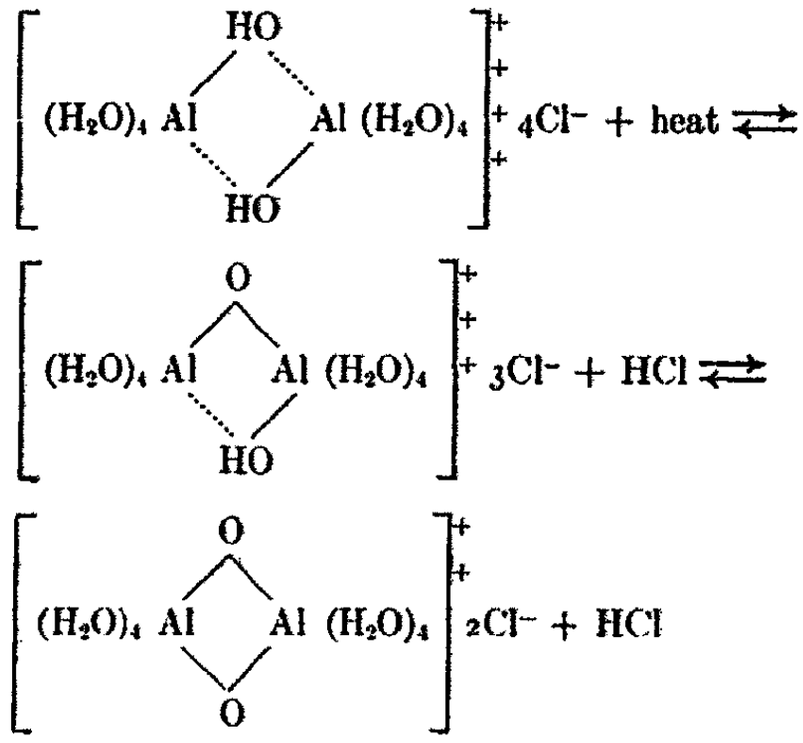


(3)

Since there are many hydroxo groups in a large poly-ol complex ion, the replacement of hydroxo groups will be a function of the concentration of anion added until the maximum penetration for each anion has occurred. This accounts for the maxima in several of salt titration cruves. (Fig. 4, for example.)

On the basis of the evidence submitted the authors present Fig. 8 as representing qualitatively their concept of an aluminum oxychloride hydrosol.

If in Fig. 8 Cr is substituted for Al it becomes the Bjerrum formulation of a poly-ol chromium complex. As stated, this figure is a mere qualitative picture of a simple ol compound since the authors do not know how many aluminum atoms are contained in the colloidal ionic micelle. It is possible. for such an ionic micelle to contain "oxo" groups as well as hydroxo groups. The idea of "oxo-lation" originated by Stiasny is shown in equation (4), which illustrates the conversion of one mole of hypothetical octa-aquo-diol-dialumini tetrachloride to the final product of one mol of the dioxo compound plus two mols of HCl.



(4)

With the conversion of hydroxo groups to ol groups to oxo groups there results inereasing resistance to the action of acids. It may be that one of the differences between aluminum oxide hydrosols made by peptization of freshly

precipitated hydrous alumina and made by the Crum[39] method of boiling a solution of aluminum acetate is that the latter is more oxolated than the former. The authors hazard the guess that the oxolation of ol complexes would result in a loss of the reaction with neutral salts described in this paper.

It is seen that oxolation results in a diminished charge on the ionic micelle. The Crum aluminum oxide sols are less stable than those made by peptization by acids of freshly precipitated hydrous alumina.

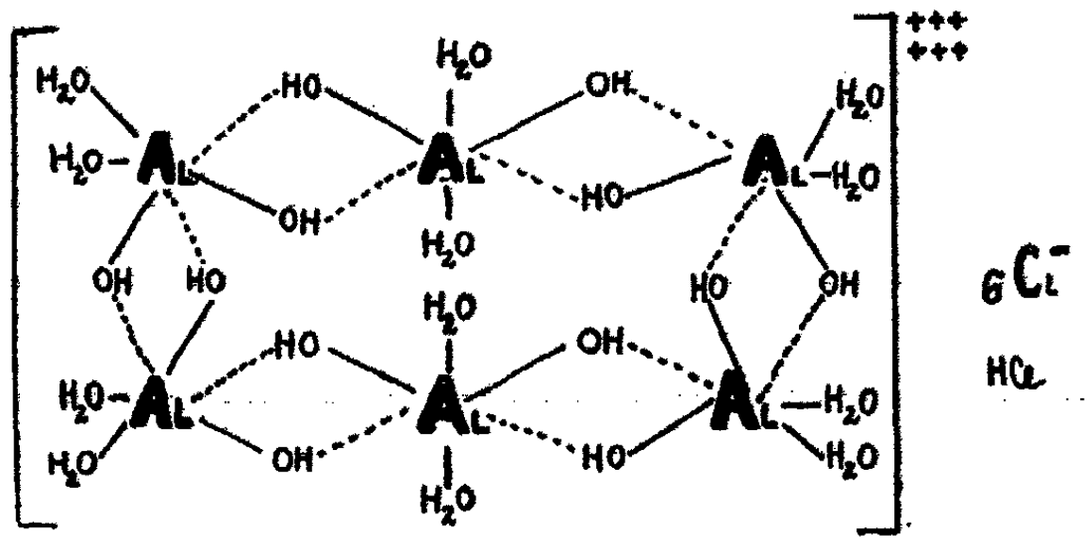


FIG. 8

The ideas submitted by the authors concerning the structure of aluminum oxychloride sols, olation and oxolation were suggested by identical postulates for basic chromium salts made by Bjerrum and by Stiasny and his co-workers.

The postulate that the alkalinity resulting upon the addition of neutral salts is due to replacement of hydroxo (or ol) groups is new in this paper.

The Werner theory with the extensions by Bjerrum and Stiasny so consistently account for the results obtained that the writers believe its application to other similar colloids will be fertile.

Summary

1. Ageing of aluminum oxychloride sols, prepared as described in this paper, at 20°C, resulted in decreased hydrogen ion activity.

2. Heating of such sols resulted in increased hydrogen ion activity and subsequent cooling did not immediately decrease it.

3. The addition of neutral salts to the sols produced a decrease in the hydrogen ion activity.

4. An anion order was established, namely:—oxalate > acetate > sulfate > halides > nitrate which is identical to the "anion penetration" order of Stiasny.

5. Explanations for these results and a suggestion for the constitution of such sols have been offered on the basis of the Werner theory and its extension by Bjerrum and Stiasny.

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[39] Ann. Chim. Phys., (3) 41, 185 (1854); Ann. Chem., 89, 156 (1854).

EQUILIBRIUM PHENOMENA IN COAGULATION OF COLLOIDS[1]

BY E. F. BURTON AND MAY ANNETTS

I. Introduction

The study of phenomena observed in the light scattered from liquids has resulted in bringing the technique of these observations into a high state of perfection.[2] As a consequence this method has already been applied by various workers to follow changes taking place during coagulation of colloidal solutions. The original intention in the present experiments was to use the changes in scattered light to follow changes in samples of colloid to which extremely small amounts of various electrolytes had been added. These results led to the complementary experiment of testing the effects of the coagulation process on the light transmitted by a sample of colloid. The latter in turn led to the discovery of the existence of apparently permanent stages of partial coagulation which do not appear to have been accentuated before. The following account consequently consists of four different parts, *viz.*,

1. Light scattered by aqueous sols of gum mastic and arsenious sulphide during coagulation.
2. Energy transmitted by the above sols during coagulation.
3. Stages of partial coagulation of various sols by small traces of electrolytes.
4. Observations on the structure of arsenious sulphide.

II. Light scattered by Sols during Coagulation

Light scattered by a sample of colloid was studied by the use of a pyrex glass cross similar to that used by Martin in the study of pure liquids. The intensity of the scattered light was compared with that of the incident light by the method fully described by Martin and by Sweitzer.[3]

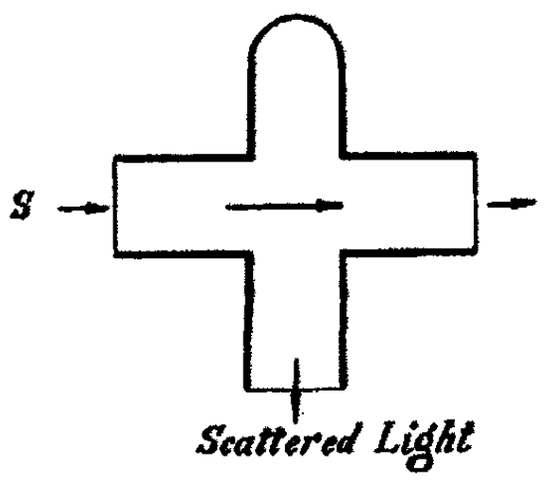

FIG. 1

(i) *Mastic Sol.* This sol was prepared by dissolving gum mastic in absolute alcohol and adding a small quantity of the alcoholic solution to a large amount of water. Small quantities of electrolyte were added to various 100 cc samples and the variation in the intensity of the scattered light was observed. In every

[1] This work was carried out in part with the aid of a Scholarship from the National Research Council of Canada.

[2] Martin: Alexander's "Colloid Chemistry," 1, 340 (1926).

[3] J. Phys. Chem., 31, 1150 (1927).

case this intensity decreased to a value which remained constant until the particles began to settle visibly. The time required for the intensity to reach this steady value depended on the amount of electrolyte added, but in a curious manner. Table I and Fig. 2 record this action for the salts N/5 aluminium nitrate, N/5 aluminum sulfate and N magnesium sulfate.

TABLE I

Cc. of Elect. added to 100 cc Mastic	Time in minutes necessary to reach Steady Value		
	N/5 $Al(NO_3)_3.9H_2O$	N/5 $Al_2(SO_4)_3.8H_2O$	N $MgSO_4.7H_2O$
0.25	53.5		
0.5	20.3		
0.75	14.0		
1.0	8.7	38	
1.5	8.0	22	
2.0	9.3	6	
2.5		8	
3.0	12.0	9	
3.5	18.0	12	36
4.0	23.0	16	24
4.5		21	
5.0	23.7	23	18
5.5		22	
6.0	20.0	18	16
6.5	9.0	11	
7.0	11.0	8	15
7.5		9.5	18
8.0	15.0	13	21
8.5		16	30
9.0	19.0	7	34
9.5	8.0		23
10.0	4.7	4	12
11.0			7
15.0	4.0	4	4

Fig. 2 shews the existence in this case of a curious zonal effect during the process of coagulation, which would be missed entirely by any less sensitive method. At first sight one might think this effect spurious; with the aluminum nitrate curve, the observation was repeated after an interval of some weeks, the two separate observations being indicated by the points distinguished by circles and squares respectively. It is to be noted in addition, that whereas the trivalent ion (Al) gives two maxima and minima, the di-

valent coagulating ion (Mg) shews only one maximum and minimum. Apparently here we have some antagonizing effect of the positive and negative ions.

(ii) *Arsenious Sulphide.* This sol was prepared by the ordinary method of bubbling hydrogen sulphide gas through a solution of arsenious acid and clearing of excess hydrogen sulfide by extended bubbling of hydrogen gas

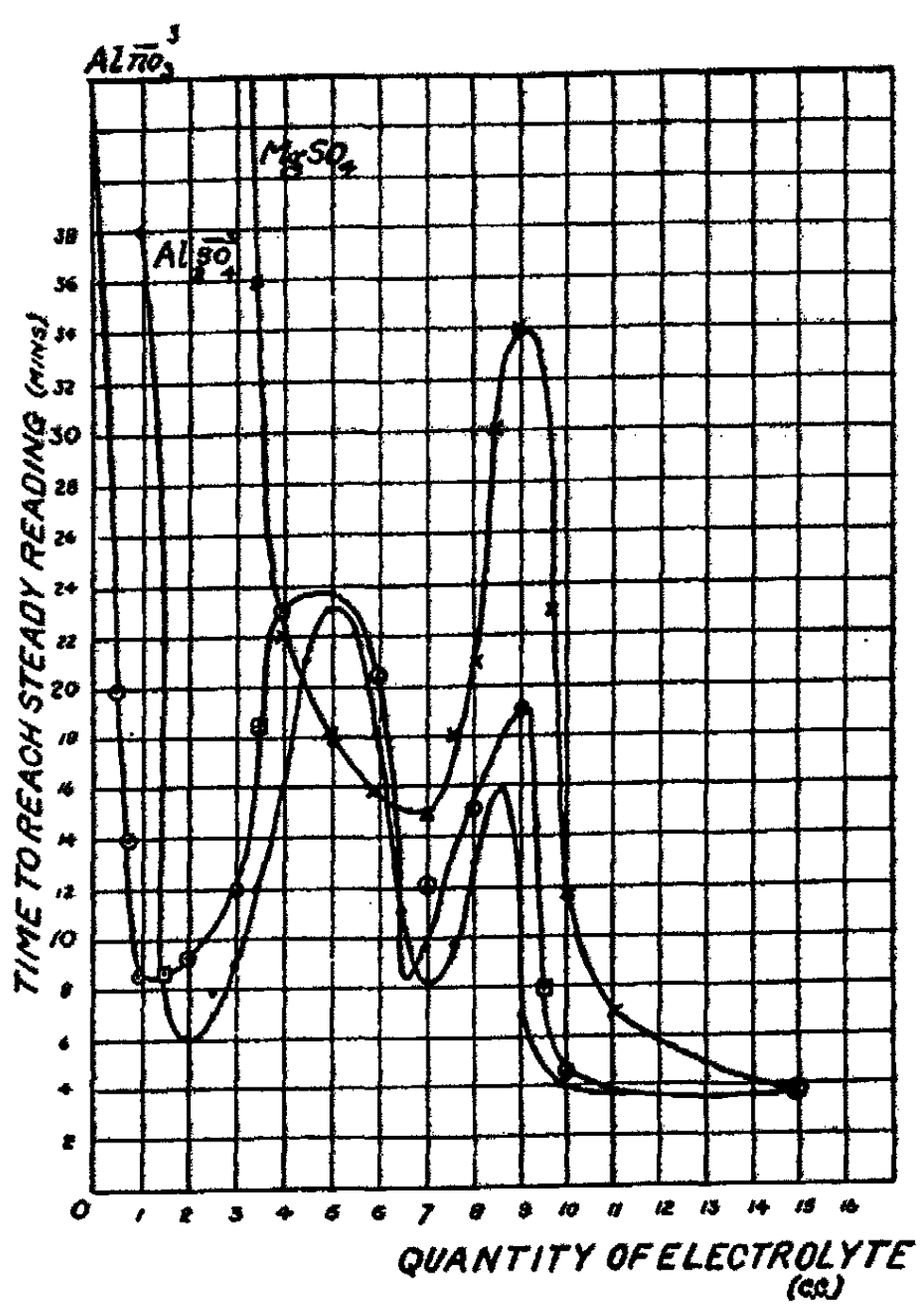

FIG. 2

through the sol. The addition of electrolyte not sufficient to bring about immediate flocculation (about 1 to 5 cc N/1000 aluminum nitrate per 100 cc As_2S_3 sol.) at once caused the particles to scatter much more light—a change of the order of five times the total change recorded in the mastic experiments. After the sudden increase, a further very gradual increase in the intensity of the scattered light continued until the sol was obviously coagulated, at which time the amount of scattered light rapidly decreased. Fig. 3 illustrates this phenomenon. There was no indication of the zonal effect such as given by *mastic*.

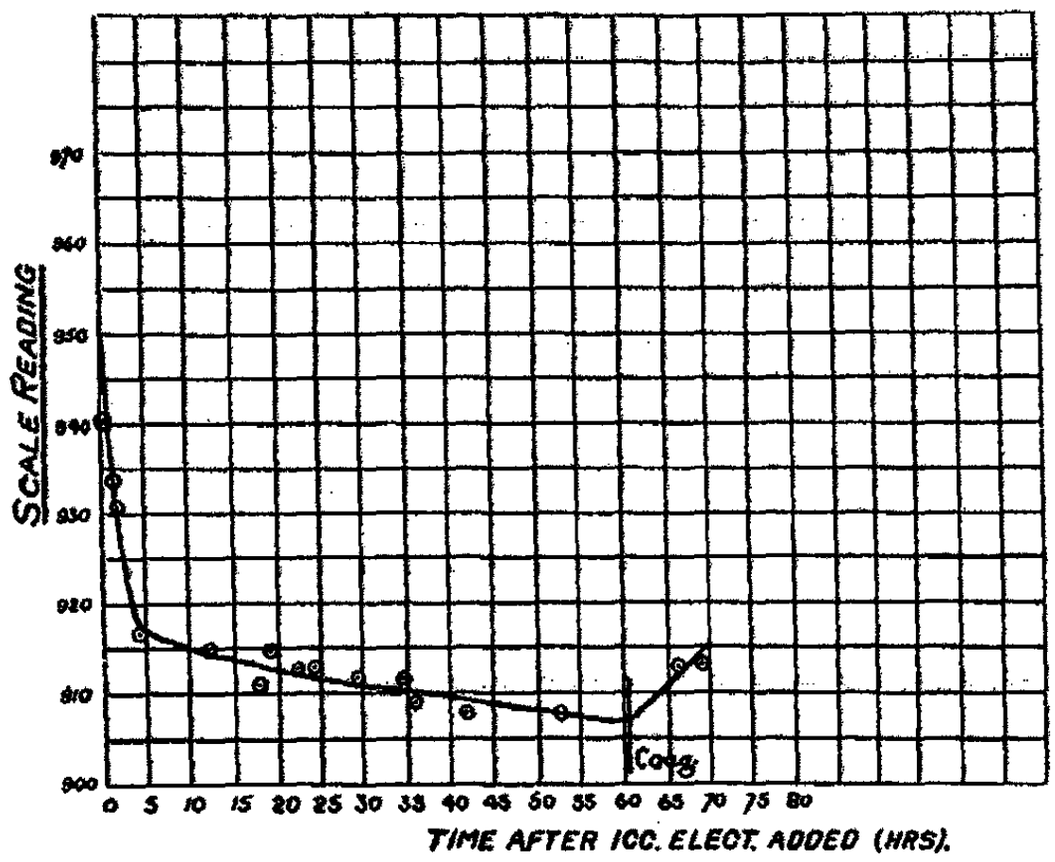

FIG. 3

III. Energy transmitted by Sols during Coagulation

Having made some observations on the scattered light it was natural to follow up with measurements of transmitted energy of radiation on similar sols under similar conditions of coagulation. The simple method of measuring the transmitted energy by means of a sensitive thermocouple was used; the E.M.F. of the thermocouple was measured by a Wolff potentiometer capable of measuring to 0.00001 volt. In essence these measurements are not nearly as sensitive as the measurement of scattered light. The arrangement of

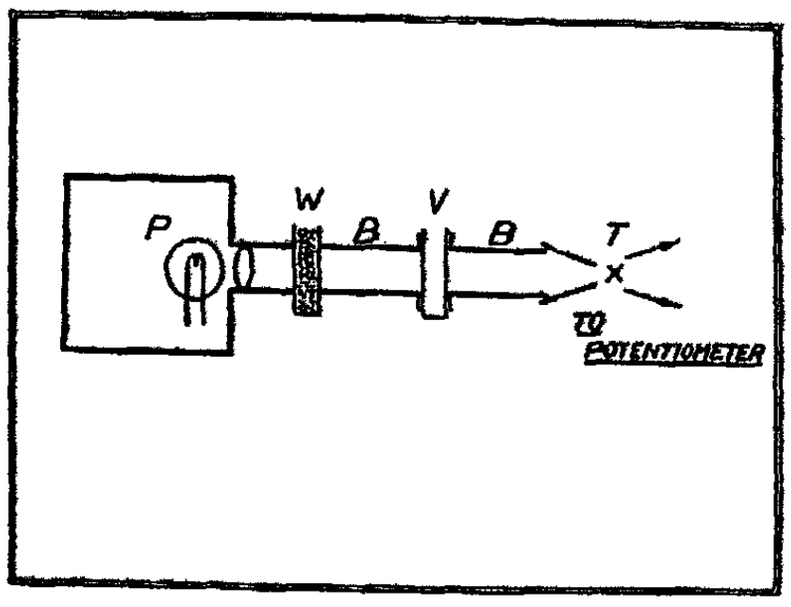

FIG. 4

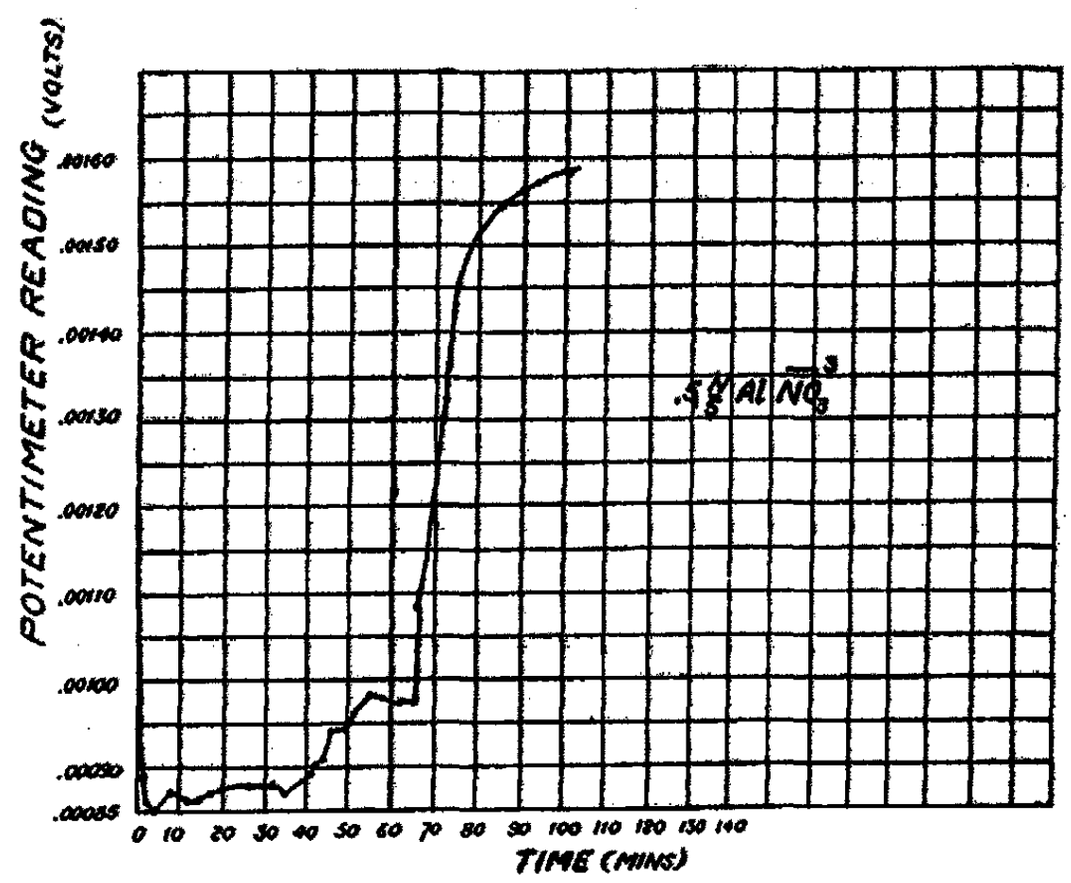
POTENTIMETER READING (VOLTS)
.00160
.00150
.00140
.00130
.00120
.00110
.00100
.00090
.00085
0 10 20 30 40 50 60 70 80 90 100 110 120 130 140
TIME (MINS)
.5 N/5 Al(NO3)3

FIG. 5

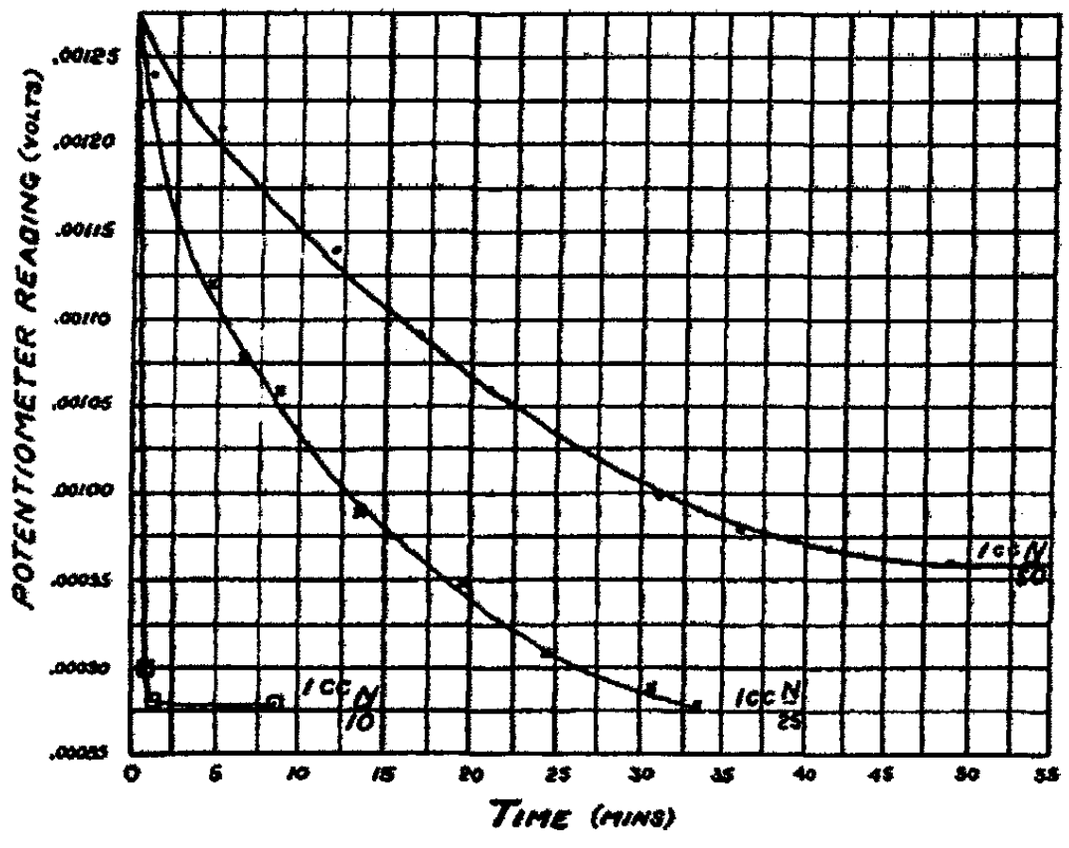
POTENTIOMETER READING (VOLTS)
.00125
.00120
.00115
.00110
.00105
.00100
.00095
.00090
.00085
0 5 10 15 20 25 30 35 40 45 50 55
TIME (MINS)
1 CC N/10
1 CC N/25
1 CC N/50

FIG. 6

apparatus is shewn in Fig. 4, where P indicates a 1000-watt lamp, T the thermocouple, and V the parallel-sided cell of glass containing the sample of sol. B is blackened pipe for protection. W is a water filter to absorb the long heat rays.

A typical set of readings is shewn graphically in Fig. 5, where the thermocouple E.M.F. is plotted against the time elapsed since the addition of the electrolyte. It is apparent that there is a rather sudden drop in the E.M.F. to a minimum in about four minutes, corresponding to a decrease in the transmitted radiation. In the case illustrated, which is the effect of adding 0.5 cc N/5 aluminum nitrate to 70 cc mastic sol, the transmitted radiation then increases rather irregularly until t equals 65 min., when a very sudden increase in the transmission takes place showing a clearing of the sol and a return to practically the value of the transmission of pure water.

Further experiments were carried out to learn how the phenomena occurring in the initial period varied as varying amounts of electrolyte were added. The details are given in Table II and illustrated in Fig. 6, where again the E.M.F. of the thermocouple is plotted against the time in minutes.

TABLE II

Elect. in 70 cc sol.	Time after Elect. added (min.)	Pot. reading (volts)	Elect. in 70 cc. sol.	Time after Elect. added (min.)	Pot. reading (volts)
0.1 cc N/10	0.0	0.00129	0.1 cc N/50	0.0	0.00128
	1.0	0.00090		1.0	0.00124
	2.0	0.00088		5.0	0.00121
	4.0	0.00088		12.0	0.00114
	8.5	0.00088		17.0	0.00109
0.1 cc N/25	0.0	0.00127		21.0	0.00106
	2.5	0.00115		31.0	0.00100
	4.5	0.00112		36.0	0.00098
	6.5	0.00108		43.0	0.00097
	8.5	0.00106		48.0	0.00096
	13.5	0.00099		51.0	0.00094
	19.5	0.00095		71.0	0.00092
	24.5	0.00091			
	30.5	0.00089			
	33.5	0.00088			

They shew that with smaller amounts of electrolyte not only is a longer time required to reach the steady reading (at which the colloid remains until settling out commences) but that this steady state is different. With very small quantities of electrolyte, the sol reaches a steady state for which transmission is higher than for larger quantities of electrolyte; from this condition one gets only partial coagulation.

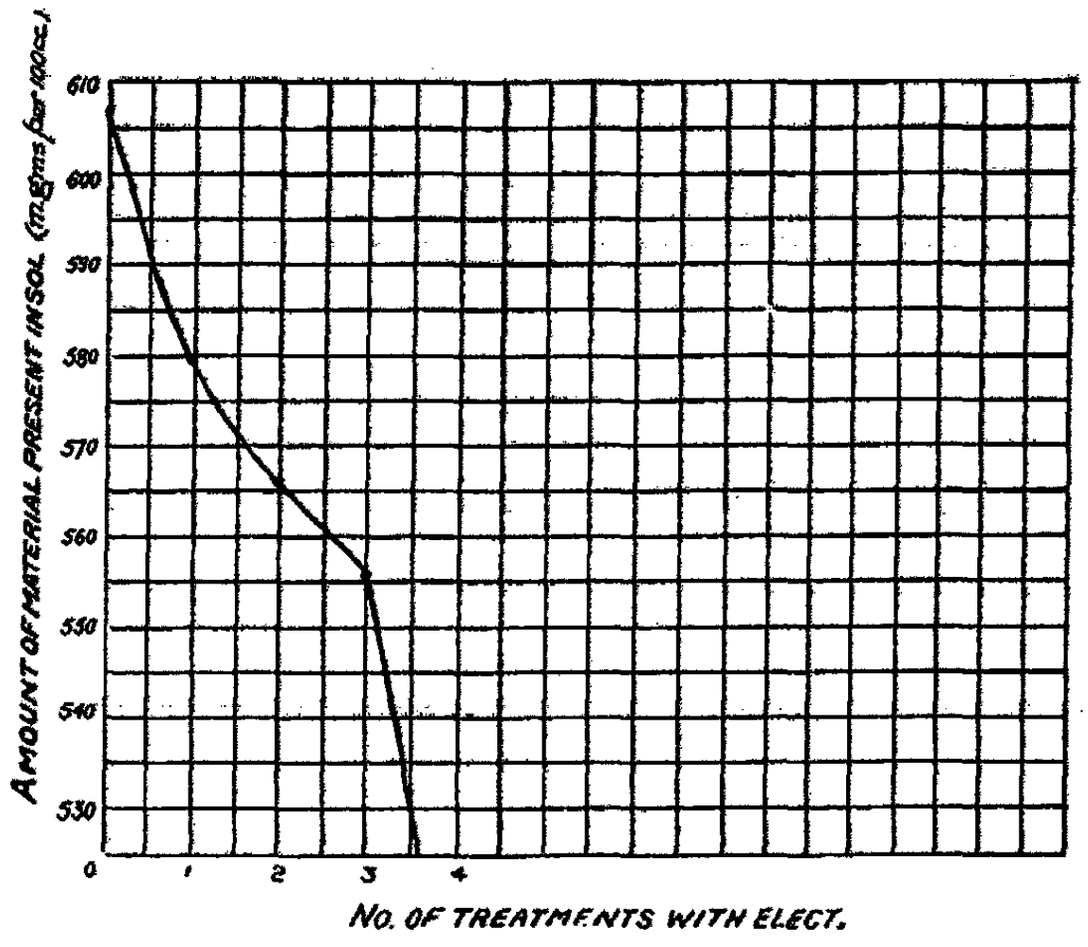
AMOUNT OF MATERIAL PRESENT INSOL. (mgms per 100cc.)
610
600
590
580
570
560
550
540
530
0
1
2
3
4
NO. OF TREATMENTS WITH ELECT.

FIG. 7

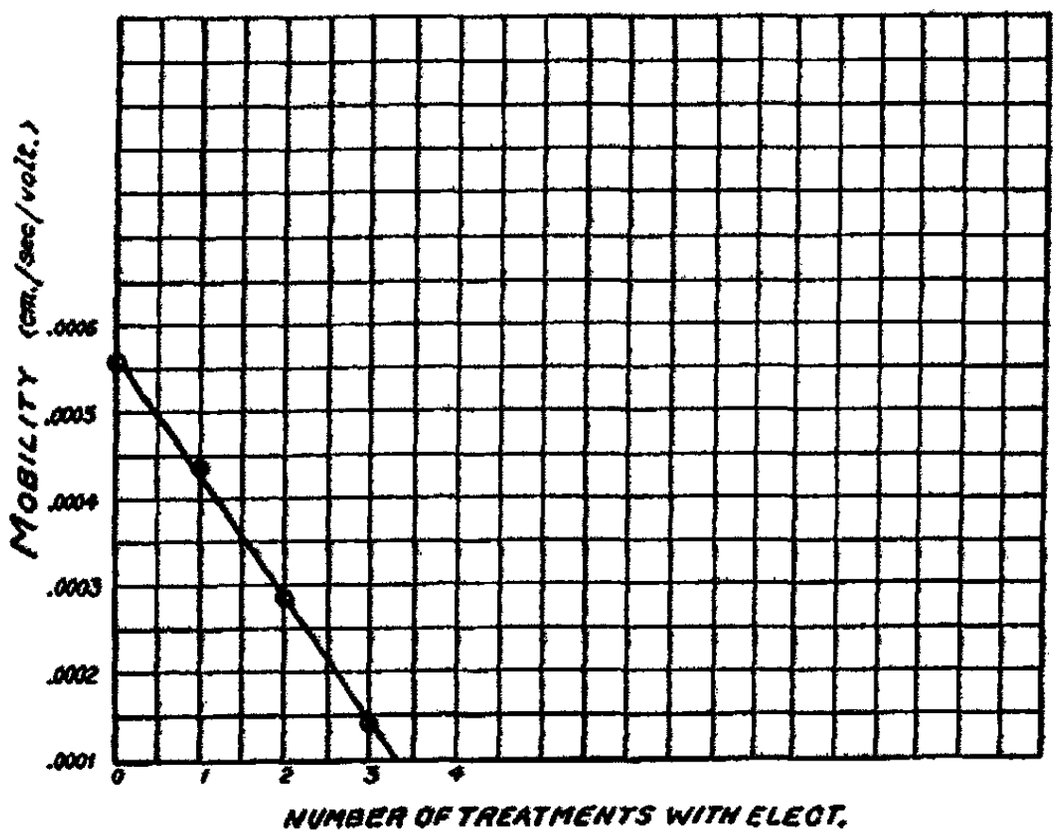
MOBILITY (CM./SEC/volt.)
.0006
.0005
.0004
.0003
.0002
.0001
0
1
2
3
4
NUMBER OF TREATMENTS WITH ELECT.

FIG. 8

IV. Coagulation by Stages

During the course of the preceding experiments it was noticed, first with arsenious sulphide, that, when very small traces of electrolyte were added to a given sample of sol, some of the colloidal material was precipitated, but by no means all. Such a state of affairs is suggested, for example, by the curves in Fig. 6. It was thought at first that this partial coagulation might be due to the presence of various sized particles, *i.e.*, that the first amount of electrolyte carried down only the particles above a certain size. But it was found that centrifuging (at 2000 r.p.m.) when continued several hours, so that an appreciable number of particles were thrown out of suspension, did not alter the phenomenon. A series of experiments was carried out with samples of mastic, gold, and arsenious sulfide. To a comparatively large amount of the original sol a small trace of the precipitating electrolyte was added and partial coagulation completed in the course of a few hours; the uncoagulated supernatant portion was drawn off and additional traces of electrolyte added, causing a second partial coagulation. These stages of partial coagulation actually represented states of equilibrium, as such samples shewed no indication of progressive coagulation when kept even for months. In the case of the arsenious sulphide, partial coagulation was repeated until four or five stages were completed. At each stage the concentration of the supernatant sol was measured by weighing the dry residue left after heating samples in an oven at 110° for three hours. Measurements were also made of the cataphoretic mobility of the particles in the sol at each stage. A typical set of results with arsenious sulfide is recorded in Table III and illustrated by the curves in Figs. 7 and 8.

TABLE III

No. of treatments with Elect. (0.1 cc N/100 $Al(NO_3)_3$	Amt. of Material present in sol 100 cc (mgms)	Cataphoretic mobility cm/sec/volt
0	607	0.00056
1	580	0.00044
2	566	0.00029
3	556	0.00014
4	260	
5	0	

The phenomena recorded above afford conclusive evidence that as regards concentration, electric charge, etc., the colloid is in a state of equilibrium with the surrounding medium, particularly in relation to the amount of electrolyte present. The question at once arose as to whether or not the partial coagulation was due to the complete absorption of the precipitating ion by the colloidal material in the precipitated portion. In order to test this, the precipitation was carried out with small quantities of ferric chloride, as iron lends itself to qualitative estimation in very small proportions. The ferric chloride was added and after the partial precipitation was complete,

the supernatant colloid was tested for iron, which was found to be present in distinctly definite quantities. The decrease in the cataphoretic mobility of the particles as stage after stage of precipitation occurs shews that the charge on the colloidal particle is reduced step by step as the coagulation proceeds.

V. The Constitution of Arsenious Sulfide Sol

It is generally accepted that the charge on the particles of the sulphide sol is primarily due to the hydrogen sulphide which has been adsorbed by the particles during preparation. The particle may be schematically represented[4] as follows:

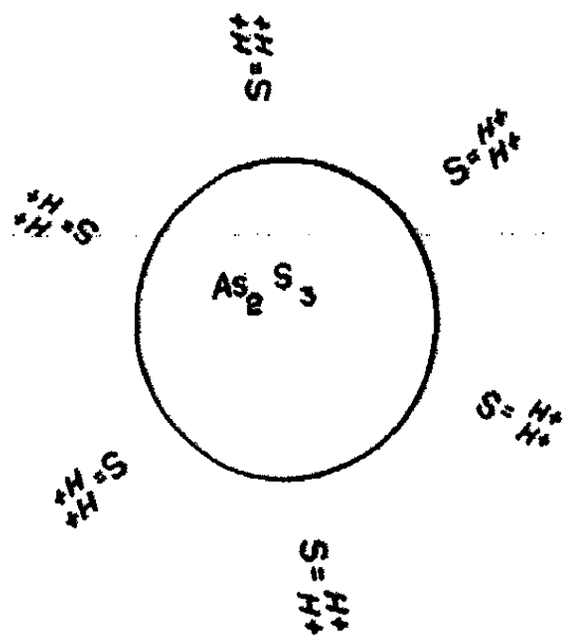

FIG. 9

As pointed out already by Weiser,[5] there is very little to be gained by trying to give a specific formula to any particular sol as the composition varies with preparation, age, etc., We may indicate the composition by the adjustable formula:

$$(nAs_2S_3.mHS)^- + mH^+$$

This suggests that hydrogen sulphide after being intimately adsorbed by the colloidal particle at least partially dissociates leaving the ions HS^- as the charge on the surface if the particle and the H^+ ions as the diffuse outer layer of the Helmholtz double layer.

This theory affords a possible explanation of a strange phenomenon observed during this work. A sample of arsenic trisulphide sol (200 cc) was left standing in a loosely covered graduate. After a few days the upper portion of the sol began to lose its colour dividing the liquid into distinct levels near the top. As time went on the levels gradually merged into one, dividing the liquid very sharply into two sections: the upper one a very pale yellow, almost colourless, the lower one a very dark orange. This level continued to fall with time but no sediment appeared in the bottom of the vessel, and,

[4] Kruyt: "Colloids," 74.
[5] Weiser: "The Colloidal Salts," 24-25 (1928).

when viewed both in the microscope and the ultramicroscope a large number of particles could be seen in samples taken from both layers.

This phenomenon has been repeated with samples of four different arsenic trisulphide solutions including one stabilised by driving off the excess H_2S by bubbling oxygen through. Further it has been shewn that this phenomenon is dependent on exposure to the air, for no settling has been observed in

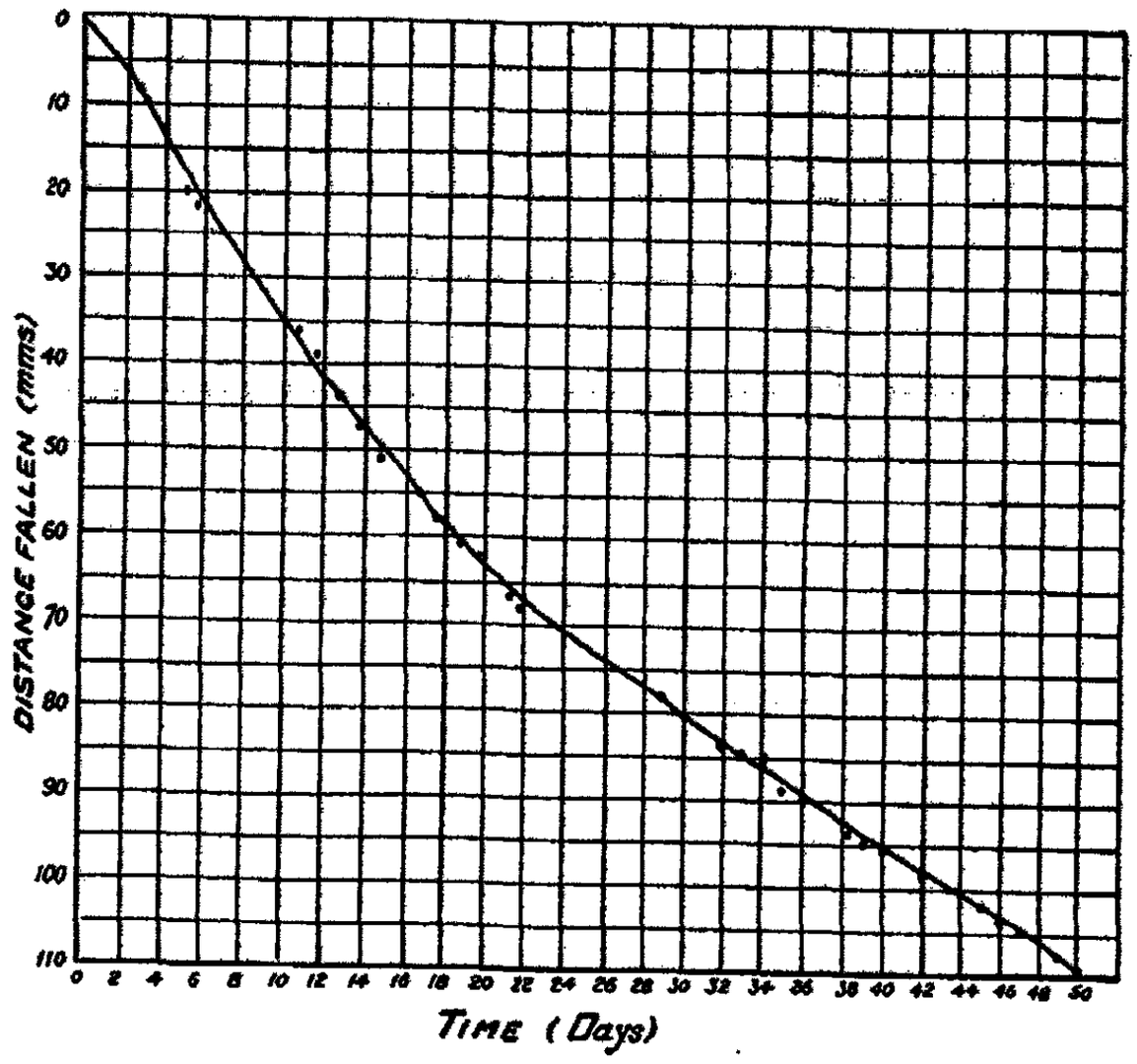

FIG. 10

any sample of sol set up in a tube of the same diameter as used above, but having the top sealed off. In one case a sample of sol which had stood two weeks thus without shewing any trace of settling was set up in air in an open tube and shewed a definite settling level in three days. If we suppose that we have complex polysulphide particles in equilibrium with adsorbed ions, ions in the solution, and H_2S, then some of the H_2S will gradually escape to the air, displacing the equilibrium in the direction causing more ions to go into solution and the particles to break down into simple sulphides. Thus arbitrarily designating the particles by $(n\ As_2S_3)mHS^-$ the equations representing the reactions are

$$(nAs_2S_3)mHS^- \rightleftharpoons (n\ As_2S_3)\ (m-1)HS^- + HS^- \quad HS^- + H^+ \rightleftharpoons H_2S$$

In the case of coagulation (previously referred to) with ferric chloride, it was found that shortly after coagulation the colloid gave the test for iron

in the ferric form, but after a few hours it responded only to the test for the ferrous form. This is in agreement with the above theory of ionisation at the surface of the particle, for in the presence of HS^- ions we would expect the reaction

$$_2Fe^{+++} + HS^- \longrightarrow {}_2Fe^{++} + S_1 + H^+$$

The change of the particles from complex polysulphides to simple sulphides may be regarded as releasing hydrogen sulphide which diffuses up

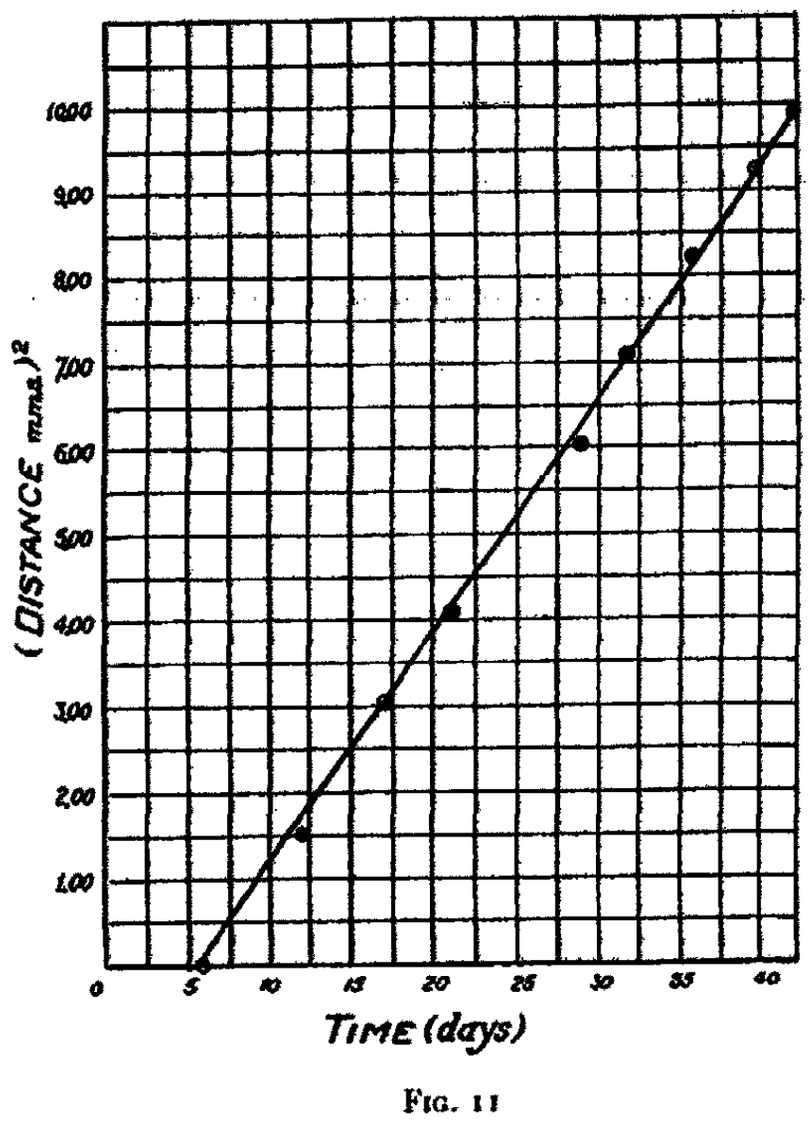

FIG. 11

through the solution. The slow fall of the sharp level separating the two layers is determined by the rate of diffusion of gas through the liquid column above.

Suppose the concentration of hydrogen sulphide just at the surface of separation of the two layers is C, and that that at the air-liquid surface is zero. Then if y is the depth of the "pale" layer and D is the diffusion constant, Q the quantity of hydrogen sulphide passing in unit time through unit area perpendicular to the direction of flow, is equal to $\frac{D(C-o)}{y}$ (approx.)

so that $Q\,dt = Q\,D\,C/y\,dt$

This hydrogen sulphide must come from the "dark" layer and is the difference between M, the total quantity of material given off in time dt, and the amount used to raise the concentration of this newly formed layer (depth dy) to C.

$$(M-C)dy = D\,C/y\,dt$$

$$y\,dy = \frac{DC}{M-C}\,dt$$

$$t = k_1y^2 + k_2$$

One set of such observations is shewn in Table IV while in Figs. 10 and 11, t has been plotted against y and against y^2. (for nine random values of y and t.)

TABLE IV

Time in days	Distance fallen (mms)	Time in days	Distance fallen (mms)	Time in days	Distance fallen (mms)
3.0	8	17.0	55	36.0	90
3.5	10	18.0	58	38.25	94
4.25	13	19.0	61	39.0	95
5.25	20	20.0	62	40.0	96
6.0	22	21.25	67	42.0	99
11.0	36	22.0	68	45.0	102
12.0	39	29.0	78	46.0	104
13.0	44	32.0	84	47.0	105
14.0	47.5	33.0	85	49.0	108
15.0	51	35.0	89	50.0	110

Summary

1. Experiments have been carried out on the measurement of scattered light and transmitted light from samples of colloidal solutions. These give indication of distinct changes in the colloid on the addition of very small traces of electrolyte even before coagulation sets in.

2. By adding successively very small traces of electrolyte to solutions of gold, mastic, and arsenious sulphide, the existence of stages of partial coagulation has been demonstrated.

3. Suggestions are made as to the constitution of the arsenious sulphide particle.

THE STABILIZATION OF BLUE CUPRIC HYDROXIDE

BY HARVEY A. NEVILLE AND CHARLES T. OSWALD

Introduction

Analyses of the voluminous, gelatinous precipitates which are produced by mixing an alkaline solution with solutions of the salts of iron, chromium, aluminum, and many other metals show a high but variable molecular ratio of water to basic oxide. The water is presumably held by adsorption or loose chemical combination and is gradually lost as the product is dried. The composition of the dried precipitate is thus largely fortuitous and, in general, definite hydrates of the metallic oxides are not formed under such conditions. The so-called hydroxides of these metals are, therefore, more correctly described by the term *hydrous oxides*. In the case of the precipitate formed by the action of an alkali with cupric salts the evidence has been inconclusive and opinion has been divided as to the existence of a definite compound corresponding to the composition $CuO.H_2O$ or $Cu(OH)_2$.

The literature with regard to this question is extensive and has been summarized by Mellor[1] and by Weiser[2]. Both of these authors furnish excellent bibliographies of this subject, so only articles which have a direct bearing upon the present discussion will be listed here.

Many authors refer to the blue precipitate as copper hydroxide while others consider it a finely divided form of hydrous copper oxide which darkens upon dehydration and agglomeration. After reviewing the evidence, Weiser concluded, "The gelatinous body must be looked upon as hydrous cupric oxide rather than hydrous hydrated cupric oxide." The view that blue and black cupric oxides differ principally in particle size is consistent with the general observation that the depth of color of a material decreases with decreasing particle size. It has been stated by some authorities that cupric oxide should be blue since the cupric ion is blue in solution and in most cupric salts, and since this ion and the colorless oxygen ion constitute the cupric oxide crystal lattice. This reasoning is open to criticism since Fajans[3] has clearly shown that the color of an ion depends largely upon the amount of deformation of its electron sheath and that when ions combine to form a crystal the electrons do not remain as they were before combination. For example, he cites the case of yellow lead iodide which is formed from two colorless ions.

The Preparation and Properties of Cupric Hydroxide

The gelatinous blue precipitate obtained by adding a solution of NaOH or KOH in slight excess to a solution of cupric salt will, under ordinary circumstances, quickly turn black. This change in the color of the precipitate

[1] "Treatise on Inorganic Chemistry," 3, 142 (1923).
[2] "The Hydrous Oxides," (1926).
[3] Physik. Z., 25, 596 (1924).

will occur while the latter is in contact with the supernatant liquid or while it is being filtered and washed. However, if the precipitation is brought about in dilute solution and at a temperature of about 0°C, the precipitate may be washed with iced water and carefully dried without losing its blue color.

The freshly made gelatinous precipitate is highly hydrous, containing according to van Bemmelen,[4] more than 20 mols of water to 1 mol of cupric oxide even after pressing between porous earthenware for two hours. This material loses water continuously in a dry atmosphere until its composition corresponds to the monohydrate, $CuO.H_2O$ or $Cu(OH)_2$. This last molecule of water is held rather tenaciously and certain carefully dried or stabilized preparations have been heated to 100°C without further loss in water or change in color.

In addition to the gelatinous form, blue hydrous cupric oxide has also been prepared as a granular or crystalline material by a number of investigators, principally by the action of an alkali on a basic cupric salt. It seems probable, however, that these "crystals" of blue cupric oxide are pseudomorphic transformations of the solid cupric salts. Kohlschütter and Tüscher[5] have shown that transformation products of a given salt crystal retain the shape of the original crystal. This change constitutes what they term a *topochemical* reaction—that is, the replacement of one solid by another.

It is claimed that the crystalline blue monohydrate is more stable than the gelatinous form and the latter is said to change to the crystalline material on standing or under certain treatment. This distinction between the two forms does not seem appropriate since, as our results show, even the highly hydrous blue precipitate is crystalline in nature.

Various substances accelerate and other substances retard the change in color of the gelatinous blue precipitate. The change from blue to black is notably accelerated by small quantities of hydrogen peroxide in alkaline solution. This action is stated by Quartaroli[6] to be still perceptible with 1 part of hydrogen peroxide in 200 million parts of water. Ordinary distilled water contains traces of hydrogen peroxide, formed in the process of distillation, but below the sensitivity of the common reagents for hydrogen peroxide. Such traces are, according to Quartaroli, sufficient to act upon copper hydroxide and cause its alteration or at least accelerate the process. In another article Quartaroli[7] states that copper oxide reacts with hydrogen peroxide to form a suboxide of copper and free oxygen and that the suboxide then reacts with hydrogen peroxide to form the normal oxide. It is interesting to observe how quickly blue copper hydroxide turns black when a solution of hydrogen peroxide is added; at the same time, one may note a marked acceleration of the decomposition of hydrogen peroxide as indicated by the evolution of oxygen.

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[4] Z. anorg. Chem., 5, 466 (1894).
[5] Z. anorg. Chem., 111, 193 (1920).
[6] Gazz., 55, 264 (1925).
[7] Gazz., 54, 713 (1924).

Weiser[8] found that while dilute solutions of some salts prevent the blackening of the gelatinous blue precipitate, other salts have no effect or accelerate the change. He noticed that those salts which acted as stabilizers have an acidic reaction due to hydrolysis. He first attributed their effect to a slight solvent action on the copper hydroxide converting it into denser clumps which do not change to the black form so readily. The explanation previously offered by Bancroft,[9] that the oxide of the added salt was adsorbed and acted as a protective colloid was discarded because the addition of such hydrous oxides did not result in stabilization and because copper sulfate could be used as the stabilizing salt. As Weiser remarks, "It is inconceivable that the adsorption of blue hydrous cupric oxide should stabilize blue hydrous cupric oxide."

Fowles[10] concludes that the stabilizing effect of such salts as the sulfates of copper, manganese, and chromium results from the removal of adsorbed alkali (an accelerator) and the formation of basic cupric salts which are very stable. He rejects the idea of solvent action since he found that freshly prepared blue cupric hydroxide, when added to a boiling dilute solution of copper sulfate, instantly turned pale green owing to the formation of a basic salt of the reputed composition $3\,Cu(OH)_2.CuSO_4$. On filtering the liquid immediately no copper could be detected in the filtrate by means of potassium ferrocyanide. From this experiment he concludes that no such solvent action as Weiser postulates can possibly occur since after the first second his material was merely heated in water.

Chatterji and Dhar[11] state that blue cupric hydroxide containing a trace of undecomposed copper salt is stabilized by the latter and does not turn black on boiling as would otherwise be the case. With apparent inconsistency, however, they report that the protective adsorbed cupric salt may be washed out by hot water so that the precipitate turns black, but the black product may be rendered blue by boiling it with a solution containing a trace of cupric salt. In testing this statement we have been unable to remove the protective copper salt by means of hot water, but hydrous black cupric oxide is readily converted to a greenish blue product by boiling it with a dilute solution of copper sulfate. It seems clear that we are dealing here with a basic cupric salt. The investigations of Pickering[12] would indicate that a number of basic cupric salts exist in which the oxide or hydroxide is present in a high ratio relative to the anion. He states that when cold dilute sodium hydroxide is added to a solution of copper sulfate, the basic salt, $CuSO_4.3Cu(OH)_2$ is first precipitated and is only slowly converted by dilute alkali to $CuSO_4.9Cu(OH)_2$ and finally to the normal hydroxide. Mehrotra and Dhar[13] have found that all the copper is precipitated from a solution of a cupric salt by less than the equivalent quantity of sodium hydroxide, that either a basic salt is formed

[8] J. Phys. Chem., **27**, 501 (1923).
[9] J. Phys. Chem., **18**, 118 (1914).
[10] Chem. News, **128**, 2 (1924).
[11] Chem. News, **121**, 253 (1920).
[12] J. Chem. Soc., **91**, 1982 (1907); **95**, 1417 (1909).
[13] J. Phys. Chem., **33**, 216 (1929).

or the cupric and sulfate ions are adsorbed in equivalent quantities by the precipitate giving a product of the approximate composition $CuSO_4.3Cu(OH)_2$ or $CuSO_4.6Cu(OH)_2$. It is, therefore, apparent that in order to prepare the blue precipitate free from basic salts or adsorbed copper salts it is necessary to add excess alkali beyond that point at which the supernatant liquid is neutral to litmus or gives no test for the cupric ion.

Effect of Alkalinity.—If an excess of alkali is added to convert the basic cupric salts into the hydroxide, the precipitate quickly turns black, the more rapidly the higher the temperature. As has been indicated above, when less than the equivalent of alkali is added, the precipitate is blue and stable. As shown by the following data, increasing the alkalinity of the solution up to a certain concentration accelerates the blackening of the precipitate but further increase in the alkalinity of the supernatant liquid seems to delay the transformation:

pH of supernatant liquid	color of precipitate
4.57	blue
7.11	blue, black particles
7.28	black
>9.0	dark blue, black particles
>12.0	blue, black particles.

These results were obtained at room temperature by adding various quantities of 2.5 *N* sodium hydroxide solution to separate, 100-cc portions of 0.5 N solution of copper nitrate. All of the precipitates were blue at first and the change from blue to black required some time. The colors indicated above represent the conditions after about 30 minutes and show the relative rates of change.

Preparation at Low Temperature.—Solutions of cupric nitrate (1.0 N) and sodium hydroxide (1.25 N) were cooled to 0°C and equal volumes of the two solutions were mixed in a chilled vessel with thorough stirring. Freshly boiled distilled water which had been cooled almost to 0° was used to wash the precipitate by decantation and on a suction filter until the washings showed no alkalinity to litmus. This precipitate slowly turns black under water at room temperature but remains blue under water if placed in a refrigerator.

Portions of this precipitate which were dried at room temperature in the atmosphere and in a desiccator over sulfuric acid gradually turned black. A portion which was permitted to dry slowly in an electric refrigerator remained light blue and is now stable at room temperature.

Stabilization with Gelatin.—It is apparent that if, in preparing copper hydroxide, sufficient alkali is added to avoid the presence of basic salts, either an inconveniently low temperature must be employed throughout or some stabilizing agent must be used at room temperature. The well-known protective properties of gelatin suggested its use for this purpose.

Equal volumes of solutions of copper nitrate (1.0 N) and sodium hydroxide (1.25 N) were used as in the previous case. Before precipitation a sufficient quantity of 5 per cent gelatin solution was added to the solution of copper nitrate so that the concentration of gelatin was 0.025 per cent by weight of the combined solutions. The precipitate was washed with freshly boiled distilled water by decantation and suction until the washings were neutral to litmus. This precipitate was then dried in an oven at 55°C where it attained a constant weight in 24 hours. Samples of this blue product were powdered and left in the oven at this temperature for a week without any further loss in weight or indication of darkening. This material is rather hygroscopic and absorbs moisture when permitted to cool in contact with the atmosphere.

A sample of the blue powder which had been brought to a constant weight at 55°C was then heated for 20 hours at 105°C. It turned black and lost 16.96 per cent in weight. This sample was then heated over a Bunsen flame and a further loss of 2.95 per cent occurred, making a total loss in weight of 19.91 per cent. The percentage of water by formula in $Cu(OH)_2$ or $CuO.H_2O$ is 18.55 per cent. The loss in weight by our experiments is thus 1.36 per cent greater than the theoretical water content, but this may be accounted for at least in part as due to the decomposition of the adsorbed gelatin at the high temperature and perhaps some reduction of the copper oxide by these decomposition products.

It can be found by calculation that if all the gelatin present in the original solution were adsorbed and carried down by the precipitate, the quantity of gelatin present in the blue product dried to the composition $CuO.H_2O$ would be slightly over one per cent. Determinations by the Kjeldahl method of the nitrogen content of the blue precipitate dried at 55°C and of the original gelatin, dried at the same temperature, show that the quantity of gelatin present in the blue precipitate dried at 55°C is 1.1 per cent. This result shows that, within the experimental error, the gelatin is completely removed from the solution by adsorption on the precipitate.

A sample of this blue product was heated to constant weight at 55°C and was then heated for periods of 24 hours at higher temperatures until the weight was apparently constant at each temperature. As the following data show, a slight additional loss in weight occurred at each temperature up to 95°; above this temperature the loss was much greater:

Temperature °C	Weight of Sample	Per cent Loss	Color of Sample
55	1.9910 g	——	Light blue
65	1.9728	0.92	" "
80	1.9676	1.18	" "
90	1.9622	1.45	Light green
95	1.9498	2.07	Green
105	1.6533	16.96	Black

The nature of the green material obtained at 95°C, as disclosed by X-ray examination, will be referred to later.

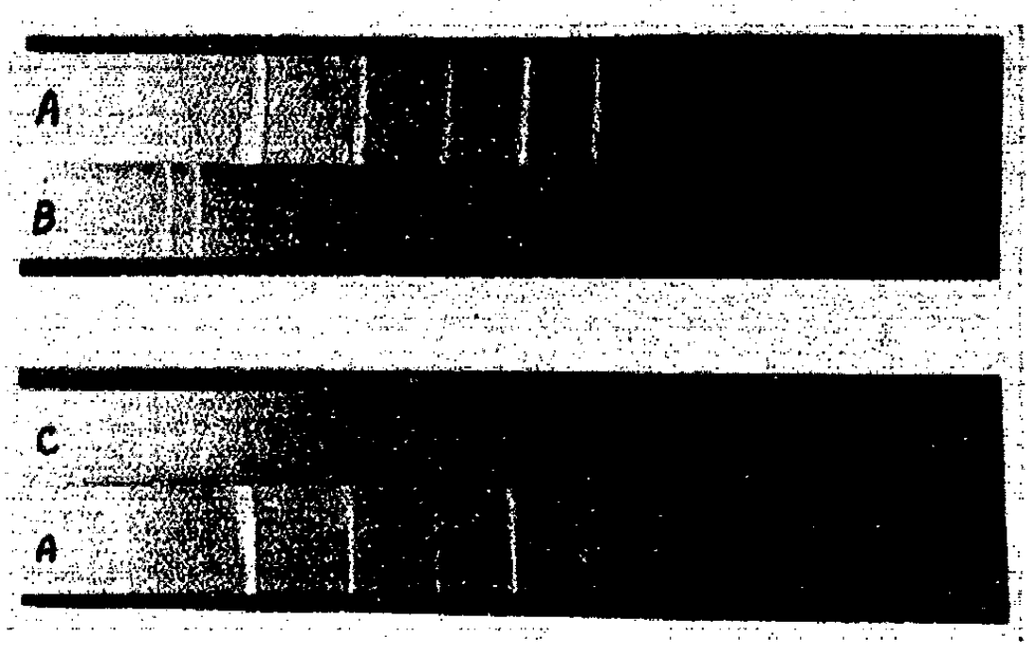


FIG. 1
X-ray diffraction patterns: (A) NaCl; (B) Black CuO; (C) Blue $Cu(OH)_2$.

X-Ray Examination

Materials—Analyses by means of X-rays were made of blue copper hydroxide and black copper oxide to compare them with respect to crystal structure and particle size. The samples used for this purpose were as follows:

1. The blue precipitate prepared at 0° and dried at low temperature as previously described.
2. The blue precipitate obtained at room temperature using 0.025 per cent gelatin and dried at 55°C.
3. The gelatinous blue precipitate prepared as in (2) but used while moist in a cellophane envelope.
4. The black product obtained by heating the dry blue powder at 105°.
5. The black product obtained by heating the blue powder over a Bunsen flame.

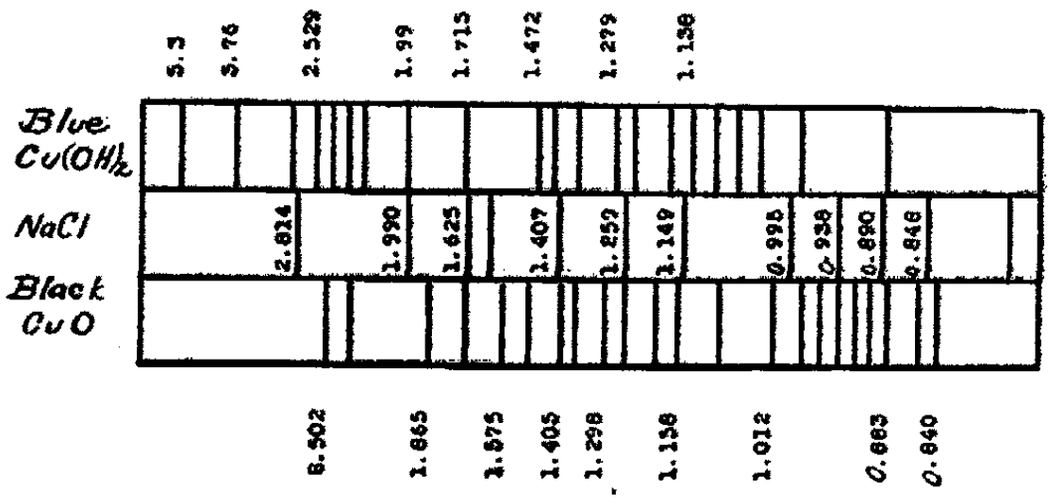


FIG. 2
Inter-planar spacings in Ångström units of the crystals of blue $Cu(OH)_2$, NaCl and black CuO.

6. The hydrous black precipitate obtained at room temperature and used while moist in a cellophane envelope.

7. The green powder obtained by heating the blue material at 95°C as described above.

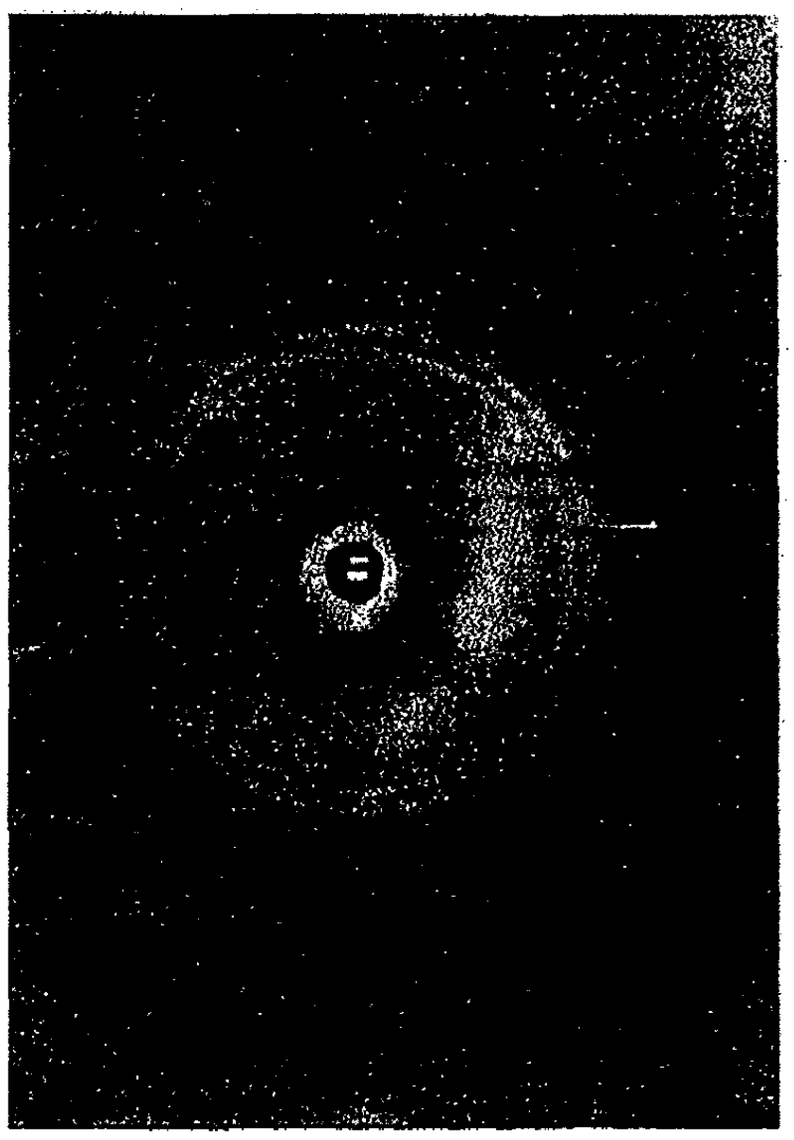


FIG. 3
Monochromatic pin-hole diffraction pattern of black CuO.

Apparatus and Technique—The X-ray outfit used was the General Electric crystal diffraction unit. A Coolidge X-ray tube, operating at 21 milliamperes and 30,000 volts, was employed with a filter which furnished monochromatic molybdenum X-rays ($\lambda_{K\alpha}$ = 0.7212Å.)

X-ray diffraction patterns were obtained by two methods: A. The Hull-Debye-Scherrer powder method, using a quadrant cassette. The distance from specimen to plate was 8 inches and the time of exposure was 66 hours; B. The monochromatic pin-hole method with the specimen contained in a cellophane envelope. The distance from specimen to plate was 11 cm and the time of exposure was 66 hours.

Results—Specimens 1 and 2 by method A and specimens 1, 2, and 3 by method B give identical diffraction patterns. Specimens 4 and 5 by method

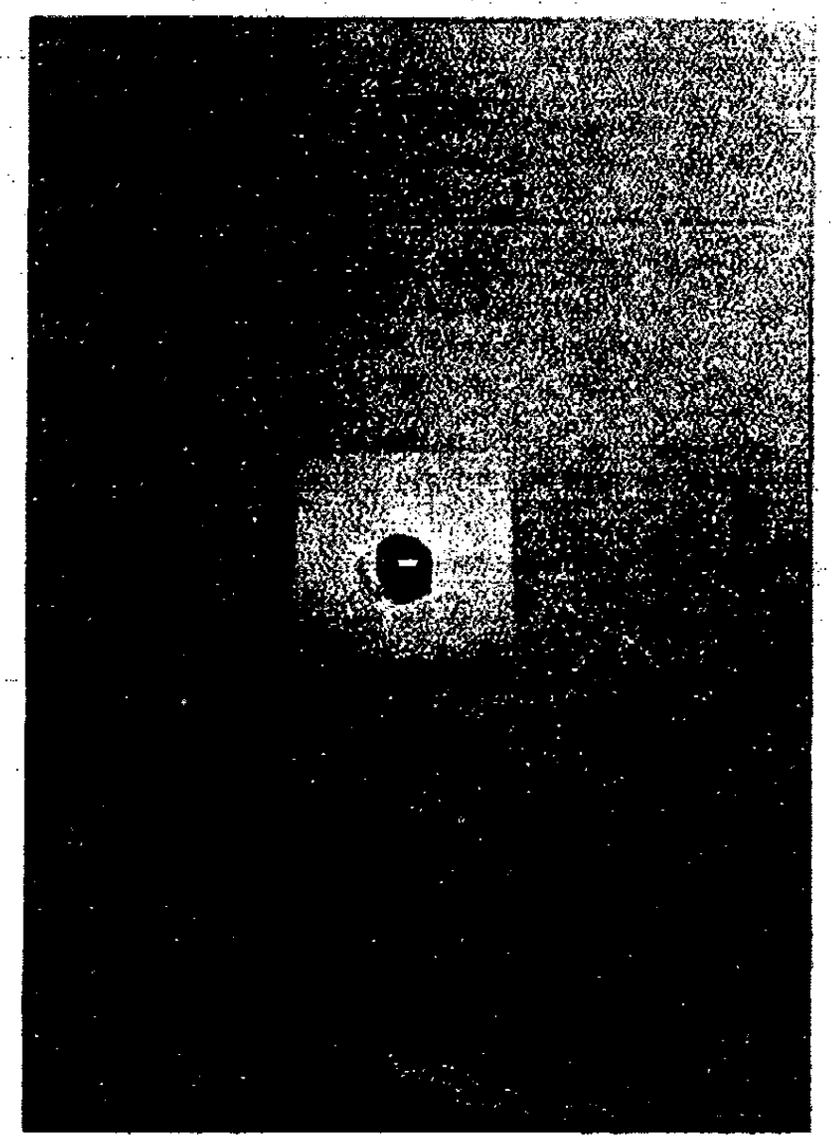
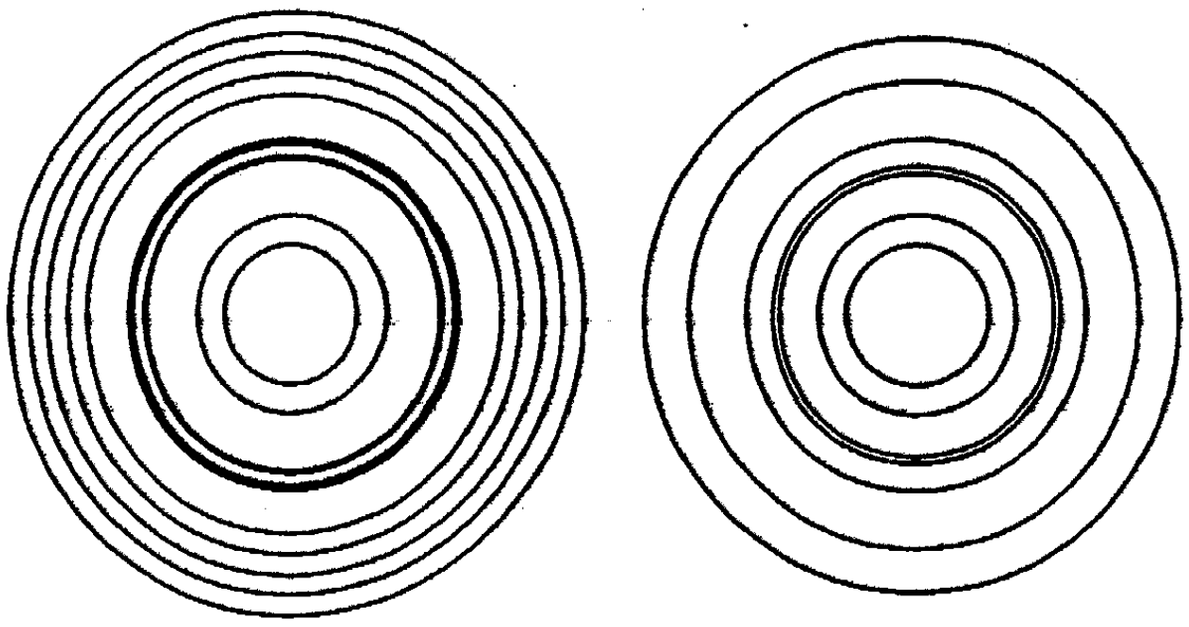


FIG. 4
Monochromatic pin-hole diffraction pattern of blue $Cu(OH)_2$.



Black CuO **Blue $Cu(OH)_2$**

FIG. 5
Pin-hole diffraction patterns of black CuO and blue $Cu(OH)_2$.

A and specimens 4, 5, and 6 by method B give the same pattern which is, however, quite different from the pattern given by the blue specimens 1, 2, and 3. The comparison of these two patterns by method A is shown in Fig. 1 and is more clearly demonstrated in Fig. 2 which was drawn from the negatives of the strip films. The interplanar distances recorded in Ångstrom units in Fig. 2 were likewise measured on these negatives. The comparison by method B of the blue and black forms is shown in Figs. 3 and 4 and the contrast is again more clearly brought out in Fig. 5 which was drawn to scale from these photographs.

Specimen 7 when X-rayed by method A gave a pattern which contained the lines corresponding to both the blue and the black substances, and the green material is therefore a mixture of blue copper hydroxide and black copper oxide resulting from a partial decomposition of the former.

Discussion

The X-ray evidence just presented indicates that the blue and the black substances have a distinctly different crystal structure and hence the blue substance is not simply hydrous cupric oxide in finely divided form but is a definite chemical compound, either $Cu(OH)_2$ or $CuO.H_2O$. In this respect our results agree with those of Posnjak,[14] as yet unpublished, but of which he provides the following abstract: "By means of the X-ray powder method the existence of a definite hydrated cupric oxide has been established. Its composition is that of a monohydrate. The blue gelatinous precipitate usually obtained is crystalline, and is identical with the microscopically crystalline preparations. The optical properties of the latter have been determined. It is erroneous to regard the effect of alkalies and various salts on the stability of the gelatinous hydrated cupric oxide as colloidal phenomena, as the changes brought about by such additions are due to interaction accompanied by the formation of some other substance."

In our experiments it was observed in all cases that the diffraction bands or rings obtained by X-raying blue copper hydroxide were much more diffuse than those from the black oxide. This indicates that the ultimate particles of the blue material are much smaller than those of black copper oxide, regardless of whether the comparison is made with the dry powders or with the hydrous precipitates. It would seem then that three factors may be involved in the transformation of the blue gelatinous precipitate to the black oxide. These factors are:

1. Change in chemical composition involving the release of a molecule of water.
2. Change in crystal structure.
3. Increase in the size of the primary particles.

With regard to the first factor, the loss of water by the blue substance does not appear to be a matter of simple dissociation of a hydrate and we therefore

[14] Reported at the 78th meeting of the American Chemical Society, Minneapolis, Minn., Sept., 1929.

conclude that the molecule has the constitution $Cu(OH)_2$ rather than $CuO.H_2O$ Bancroft[15] has pointed out that if a definite hydrate of the composition $CuO.H_2O$ exists with a practically zero vapor pressure it should form from cupric oxide in the presence of water, but the reverse process actually takes place. We have noticed that this change in the color of the precipitate from blue to black in contact with its mother liquor, or under water after thorough washing, or when filtered but still moist, begins at certain nuclei and spreads in all directions. That is, black particles appear at first in the blue mass and these gradually enlarge until the entire precipitate is black. Even the insoluble particles, presumably copper oxide, which may be observed in a solution of commercial copper nitrate will act as centers for this transformation. This difficulty may be avoided by filtering the solution of the copper salt before the precipitation is made. The effect just noted is an illustration of a reaction occurring at the interface between two solid phases, in this case the phases are copper oxide and copper hydroxide. This is a very general phenomenon and has been observed, for example, by Pease and Taylor[16] in the reduction of copper oxide to copper by means of hydrogen and by Jones and Taylor[17] in the same reduction brought about by carbon monoxide.

Kohlschütter and Tüscher[5] have likewise expressed the view that the blue compound is copper hydroxide and that its change to the black oxide is not simply a molecular splitting off of water but involves the internal neutralization of the ions resulting from the amphoteric dissociation of copper hydroxide. The mechanism is illustrated as follows:

$$Cu^{++} + 2\,OH^- \rightleftarrows Cu(OH)_2 \rightleftarrows CuO^-_2 + 2H^+$$

$$2\,H^+ + 2\,OH^- \longrightarrow 2\,H_2O$$

$$Cu^{++} + CuO^-_2 \longrightarrow 2\,CuO.$$

They maintain that this inner neutralization takes place between molecular complexes of colloidal dimensions and that a definite degree of dispersity is required to facilitate this change. Very high or very low dispersity represses the reaction; between these extremes the stability decreases with increasing dispersion. Equal primary particles may build up larger individuals of looser or more compact structure, the former favoring dehydration and the latter opposing it. If this be the true mechanism of the darkening of blue copper hydroxide, the stabilizing action of gelatin and of low temperature may be understood as inhibiting the agglomeration of the primary particles as they change while drying into a more compact and stable structure. It is well known that gelatin exhibits such protective action both in preventing the agglomeration of fine particles and in interfering with crystal growth.

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[15] "Applied Colloid Chemistry," 246 (1921).
[16] J. Am. Chem. Soc., 43, 2179 (1921).
[17] J. Phys. Chem., 27, 623 (1923).

The properties of copper hydroxide are reported by Müller[18] in a series of papers in which he demonstrates its amphoteric nature. He states that $Cu(OH)_2$ dissolves in solutions of NaOH stronger than 12 M, that its solubility is considerably greater than that of CuO in concentrated alkaline solutions, and that the solubility is due to the formation of the cuprate ion rather than to colloidal phenomena. He prepared by crystallization from alkaline solution a cuprate of the probable formula Na_2CuO_2 which was cobalt-blue in color. Müller states that the dehydration of $Cu(OH)_2$ takes place gradually but the product is not water-free CuO.

Creighton[19] has also studied the solutions of copper hydroxide and copper oxide in concentrated alkalies and states that these solutions do not exhibit characteristic colloidal properties. He presents evidence to show that their blue color is due to the cuprate anion.

Further evidence that blue cupric hydroxide is distinctly different from cupric oxide was obtained by Veil[20] who found that the blue compound has a molecular coefficient of magnetization which is approximately three times as great as that of brown or black cupric oxide.

The conclusion that the blue compound is copper hydroxide and not finely divided copper oxide admittedly does not explain the results of Schenck[21] who found that the hydroxides of copper and aluminum when coprecipitated could be heated in the blast lamp without blackening, provided the ratio of copper oxide in the mixture did not exceed 5 per cent. His analysis of the product which remained blue after ignition showed that no water was present so the blue substance in that case was not copper hydroxide. He argues that the blue substance is not an aluminate of copper but concludes that it is finely divided copper oxide stabilized against agglomeration by means of the alumina. Our results do not deny the possibility that cupric oxide may be blue if sufficiently dispersed; in fact they indicate that increase in particle size is one of the factors involved in the color change. It would seem that X-ray analysis might provide decisive evidence as to the nature of the product obtained by Schenck.

Colloidal Copper Hydroxide

In precipitating copper hydroxide in the presence of a considerable quantity of gelatin and with an excess of alkali, it was noted that the supernatant liquid possessed a purple tint. The depth of color of this solution increases with increasing concentration of gelatin or of alkali. These solutions after filtering were examined in the ultra-microscope and the presence of colloidal particles was evident.

Similar sols were also produced by the peptizing action of gelatin and excess alkali upon the blue precipitate, upon hydrous black copper oxide and

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[18] Z. angew Chem., **33**, 303 (1920); **34**, 371 (1921); Z. physik. Chem., **105**, 73 (1923).
[19] J. Am. Chem. Soc., **45**, 1237 (1923).
[20] Compt. rend., **178**, 329 (1924).
[21] J. Phys. Chem., **23**, 283 (1919).

even by permitting a solution of gelatin (for example, 1 per cent) in dilute sodium hydroxide to stand in contact with commercial copper oxide. In every case it was necessary to have present both gelatin and excess alkali in order to obtain peptization.

A sample of the purple sol was placed in a collodion membrane and dialyzed against distilled water. The sol was first partially neutralized with hydrochloric acid to prevent the alkali from damaging the membrane. The presence of the chloride ions also furnished a convenient means of testing the rate of dialysis. Tests with silver nitrate showed that practically all of the sodium chloride had diffused through the membrane at the end of 15 hours. The distilled water was changed daily and at the end of 4 days a blue precipitate of copper hydroxide appeared in the dialyzate. This precipitate when dried remained light blue but was horny in nature due to the large proportion of gelatin present. This experiment confirms the observation that gelatin alone is unable to peptize copper hydroxide; when the alkali is sufficiently removed by dialysis the copper hydroxide precipitates.

When an acid is added gradually to the purple sol, copper hydroxide first precipitates at the neutral point and this precipitate dissolves as more acid is added. Sols of copper hydroxide or copper oxide in alkaline solution are negatively charged and the peptizing ion is either the hydroxyl ion or possibly the cuprate ion; gelatin in alkaline solution is also negatively charged so that its efficient aid in forming these sols may be understood. Judging by the depth of color produced in the supernatant liquid, powdered cupric oxide is much more readily peptized in a normal solution of sodium hydroxide containing 1 per cent of gelatin than it is in normal sodium hydroxide containing 5 per cent of glycerol, while a 5 per cent solution of sucrose in normal alkali produces only a faint blue tint after a week in contact with copper oxide. The reddish-purple sols produced with gelatin are quite distinct in color from the familiar blue sols in which copper hydroxide is peptized in alkaline solution with the aid of sugars, glycerol, etc. These latter usually show a precipitation of cuprous oxide on standing, whereas the sols containing gelatin appear to be more stable.

Summary

The blue gelatinous precipitate obtained by the action of an alkali with a cupric salt is variously described as cupric hydroxide and hydrous cupric oxide. The literature relative to the preparation and properties of this substance is reviewed with particular reference to the conditions which retard or accelerate its change to black cupric oxide.

It is shown that the blue compound may be stabilized by precipitating it in the presence of gelatin which is completely removed from solution by adsorption on the precipitate.

By means of X-ray diffraction patterns the blue preparations, both moist and dry, are shown to have a distinct crystal structure which differs from

that of black copper oxide. From this and other evidence it is concluded that the blue substance is cupric hydroxide rather than hydrous cupric oxide.

The ultimate particle size of the blue hydroxide is shown to be smaller than that of the black oxide, and the factors involved in the transformation of hydroxide to oxide are discussed.

A colloidal solution of copper hydroxide peptized by the combined effect of alkali and gelatin is described.

Acknowledgment

The writers are grateful to Professor H. V. Anderson of this university for his valuable assistance in the X-ray analyses described in this paper.

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TRANSMITTED STRUCTURAL BLUE IN MICROSCOPIC OBJECTS

BY CLYDE W. MASON

In the microscopical examination of precipitates, emulsions, sublimates, and other finely divided material, which is known to be colorless, a distinct blue transmission color is sometimes encountered. Although this phenomenon is obviously a case of structural color, it has apparently been noted by few observers, and the conditions governing its appearance have not been formulated. The recognition of the nature of such anomalous color, when it occurs, is of interest in chemical microscopy, and the realization that it may exist should serve as a caution whenever the color of fine structures is studied.

The conditions under which structural transmitted blue is observable are as follows:

1. A fine structure substantially in one plane and possessing uniform dimensions must exist. It may consist of particles distributed irregularly but all of substantially equal diameters, such as may be produced when solids or liquids (silver chloride, sulphur, organic bases) are precipitated from solution, or sublimates (sulphur, arsenic trioxide) are collected on a cool surface. As a simpler case, the structure may be made up of more or less parallel and evenly spaced striations, such as are found on butterfly scales or diatoms.

2. The boundaries of the structural details (particles or striations) must make a "contrasty" image in the microscope. Dry mounted structures, in the form of spherical particles, and deeply incised grooves or ridges in very high relief give the strongest blues.

3. Substantially axial or only slightly convergent brightfield illumination is necessary. The aperture of the illuminating cone should be markedly less than that of the objective. This would ordinarily be the case when the iris diaphragm of the substage condenser is closed as far as possible; opening the diaphragm, so as to flood the object with convergent light, destroys the color.

4. The aperture of the microscope objective must not be too great. The blue color is exhibited best with an objective of aperture barely sufficient to resolve the structure. A given structure may therefore appear blue with a low power objective and colorless with a higher power.

It is evident that the above conditions of microscopical observation are far from impossible of occurrence in ordinary studies.

General Phenomena of Diffraction

The explanation of the origin of transmitted blue must lie in diffraction, for the color disappears in uniform light, as no other type of structural color does, and requires substantially uni-directional light for its observation. Let us consider the diffraction phenomena exhibited by structures of varying fineness.

When a fine structure is illuminated by a narrow pencil of light, secondary radiation is set up from each point on its bounding surface. If the structure is approximately spherical or has some other systematic arrangement of surfaces the diffracted radiations will tend to reinforce each other in certain directions depending on the dimensions and the wave length. With multiple structures, such as particles of uniform size or gratings, these diffraction effects are proportionately enhanced. The minimum dimension which will produce diffraction maxima in a definite direction is equal to the wave length of the light used; the diffracted light is then emitted perpendicular to the illuminating beam. With coarser structures the angle of diffraction is less than 90°.

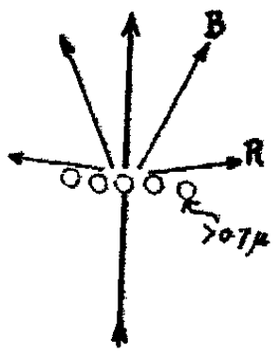

FIG. 1

Diffraction of light by uniformly sized particles, resolvable with all wave lengths of light. Transmitted blue if the aperture of the objective is reduced.

So with a 0.75 μ structure, illuminated with white light, red light ($\lambda = 0.75\mu$) will be diffracted at an angle of 90° from the direct beam. The shorter wave lengths will be diffracted at less angles. For a structure of dimensions d the angle α between the diffracted ray and the axis of the illuminating beam is given by $\sin \alpha = \lambda/(n \cdot d)$. The structure will be at the limit of the resolving power of the microscope using axial red illumination, and will be well within the limit for blue light. When a grating (14,000 lines per inch) or As_2O_3 sublimed on a slide is illuminated with a substage condenser diaphragmed as much as possible, and an objective of 0.6-0.9 N. A. is focussed on the preparation, the diffracted rays are clearly visible at the back aperture of the objective when the eyepiece is removed. The axial (unidiffracted) maximum appears as a bright spot of light in the center of the aperture. If the structure is a grating, diffraction spectra are seen on either side of the central beam, transverse of the rulings. If the structure consists of fine uniformly sized particles, these spectra exist as concentric zones of color, the blue end being innermost and the red nearer the periphery of the objective opening. The numerical aperture of the objective required to resolve such structures with axial illumination is given by the formula N. A. $= \lambda/d$.

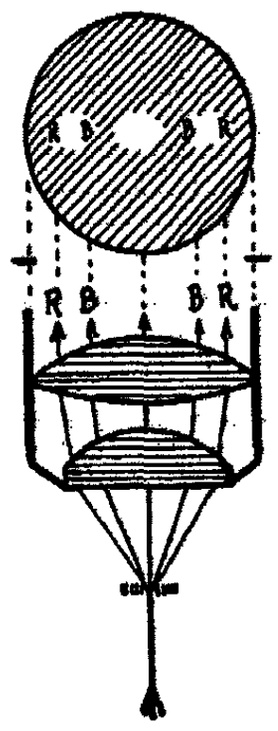

FIG. 2

Diffraction spectra from a grating, as seen at the back aperture of the objective.

If the structure is distinctly smaller than the wave length of red light, resolution with all wave lengths is impossible if axial illumination is used. For example, structures having dimensions of 0.4 μ are only barely resolvable with blue light ($\lambda = 0.4^{+}\mu$), the diffracted rays making an angle of nearly 180° with each other. With red light and structures of this size, lateral diffraction maxima are impossible, because light emanating from two points λ apart will be out of phase in any direction except forward along the axis of

the beam. As a consequence the structure will tend to transmit preferentially the longer wave lengths, when illuminated with white light.

The diffraction of the shorter wave lengths laterally, out of the path of the direct beam, also follows from the fact that secondary radiations emanating from two points λ apart will be in phase along a direction perpendicular to the axis of illumination. This agrees with the well-known behavior of Tyndall blue media, which ideally have as their maximum particle size about $0.4^{+}\mu$. Still smaller particles will tend to scatter blue more strongly than red, in accordance with Rayleigh's calculations, the intensity being inversely as λ^4.

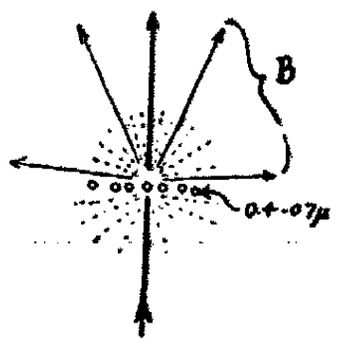

FIG. 3
Diffraction of blue light by particles not resolvable with red axial light. Transmitted blue; longer wave lengths scattered.

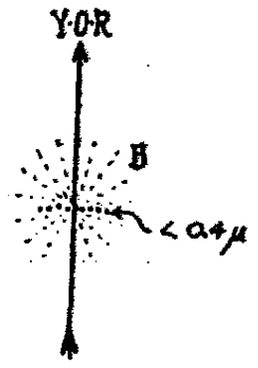

FIG. 4
Scattering of light by particles not resolvable with blue axial light. Tyndall blue scattered; longer wave lengths transmitted.

A single isolated particle (ZnO pigment) of diameter less than 0.4μ can be seen to scatter a clear blue light when illuminated orthogonally in a slit ultramicroscope; such particles are deep orange by transmitted light. Similar phenomena are observable with aggregates of fine needle-like crystals as well as in the case of numerous other examples of Tyndall blue. The scattered blues are better if the particles are in a thin layer, and the red or orange transmission color is stronger the thicker the layer of particles traversed. In general, smaller particles give a deeper blue, and the blues become paler and whitish if the particles grow larger.

In connection with the scattering of blue and the transmission of red by structures 0.4μ or smaller, it is of interest to consider how coarser structures may effect light of longer wave length. By using red light (0.75μ) and a 0.7μ structure, the system is in effect almost doubled in scale. Laterally diffracted radiations will be in phase, and therefore red light will tend to be scattered. Blue light will be diffracted at a lesser angle, and hence will travel in a general forward direction through the system. In general, since the longer wave lengths are diffracted more than the shorter ones, there will be a tendency for red to be deviated out of the path of the illumination beam, and for blue to pass through the system more nearly parallel to this path.

In addition to the above points regarding diffraction, which are also the basis of Abbe's theory of microscopic resolution, the character of the diffracting structure is of great importance in the production of the various color

phenomena. The intensity of the diffracted light depends to a large extent on whether the refractive indices of the structure and its surrounding medium are markedly different or nearly identical. In the latter case a large proportion of the light passes through the system without diffraction, and if the illumination is white, simply serves to mask the effect of removal of certain wave lengths by deviation from the direct beam. The brilliancy of the diffraction spectra and of the scattered light is very greatly reduced under these conditions.

The shape of the diffracting structure likewise governs its effects. A grating having faint or shallow rulings (as most artificial gratings do) will allow a large proportion of the light to pass through it undiffracted, and will yield relatively faint colors. Wood[1] emphasizes the importance of the depth of the rulings in intensifying the brilliancy of the diffracted light at the expense of that directly transmitted.

Experiments with Microscopical Structures

In applying the principles of diffraction to explain the colors of microscopic objects, it is to be expected that such boldly contoured objects as fine particles of solids or liquids, perforated or embossed diatom valves, or deeply grooved butterfly scales, will show more striking color effects than can be expected from artificial gratings. Such objects, when mounted dry, exhibit relatively strong diffraction which may be related to their color phenomena by rather simple experiments.

A "natural diffraction grating" may be taken as the first and least complicated case.

The unpigmented scales of the common "Silverspot" (*Argynnis*) butterfly are deeply striated, and under ordinary conditions appear colorless. Under the microscope with a 5.4 mm, 0.74 N. A. objective the striae are easily resolved. The image is black and white with axial illumination. At the back aperture of the objective two orders of diffraction spectra are brilliantly visible on either side of the colorless axial beam from the diaphragm opening of the condenser. These spectra are crosswise of the striae, with their red ends outermost. The purity of the spectra is greatly enhanced by narrowing the illuminating beam, and they are lost due to overlapping when the condenser is increased.

On reducing the aperture of the objective, by means of an iris diaphragm near its back focal plane, to about N. A. 0.50, only one pair of spectra (first order) is included by the objective. The image is black and white and the striae are easily resolved. Further reduction of the aperture produces a succession of colors in the image: yellow green, blue green, blue, and violet. Correspondingly, the red, orange, and yellow portions of the diffraction spectra are cut off by the diaphragm. When the objective is diaphragmed to N. A. 0.25, the structure is barely resolvable and is a strong blue by transmitted light. At the back aperture of the objective only the white axial

[1] "Physical Optics," 219 (1919).

beam and the intense blue inner portions of the two diffracted spectra are visible. The structure is not resolvable by red light, with this numerical aperture.

If the opening of the objective is reduced below 0.25 N. A. the structure is not resolvable even with blue light, and its transmission color goes from blue or violet to dark brownish orange or yellow. No diffraction spectra are visible at the back of the objective.

On rendering the illumination slightly oblique instead of axial, by displacing the condenser diaphragm laterally of the striations, the transmitted blue is perfectly restored, together with the resolution, and correspondingly the blue end of one of the diffracted spectra is seen to enter the aperture of the objective.

The dark-brownish transmission color, observed when the objective is diaphragmed so that no part of the diffraction spectra is included by its aperture, is due to the fact that there is some scattering of light in addition to the diffraction in definite maxima. The shorter wave lengths are scattered more, leaving the longer ones to be transmitted along the axial beam; the brownish color is therefore the complement of Tyndall blue from a coarse structure.

The relationship between resolution and numerical aperture is strictly in accordance with the theory of diffraction, so that the dimensions of the structure may be determined from the numerical aperture of the objective which barely resolves it. The measured distance between striae, 1.6μ, is the same as the calculated limit of resolution, for axial blue light, of a 0.25 N. A. objective.

These experiments on butterfly scales deal with a diffracting system of a very simple sort. When an artificial grating is used, the results are analogous as regards the diffraction spectra, but the transmission colors are practically lacking. This is due to the shallowness of the rulings, and the consequent lessened intensity of the diffracted spectra. The weak transmitted blue from the first order spectra is masked by the intensity of the axial beam.

When the butterfly scale is surrounded by liquid instead of air, a similar loss of transmitted blue occurs, due to the decrease in diffraction and increase in intensity of the axial beam. When diffraction is thus minimized, only a faint brownish yellow transmission color (the complement of Tyndall blue) is observed.

A somewhat more complicated case is afforded by the diatom *Pleurosigma angulatum*, which possesses a very fine pattern of dots in rows 120° to each other and about 0.5μ apart. Instead of two diffraction spectra at the back aperture of the objective, at 180°, it shows six, at 60° intervals. These are not included by a 0.7 N. A. objective, and the structure is unresolvable and faintly yellow by axial transmitted light(complement of Tyndall blue). With a 0.95 N. A. objective the diatoms are bluish by transmitted light, and at the back aperture of the objective the blue ends of the six spectra are visible.

Particles of uniform diameter but not arranged in an orderly pattern constitute a more common type of diffracting system. A film of particles of

sublimed As_2O_3 or sulphur may be collected on a microscope slide by the ordinary methods of micro-sublimation. Areas of several square millimeters (more than sufficient to fill the field of a moderate or high power objective) having substantially uniform-sized particles, are readily obtained.

When such a preparation is illuminated by a very narrow pencil of axial light, such as may be obtained by inserting a pinhole diaphragm below the substage condenser the beam is diffracted by the particles to give concentric zones of spectral colors at the back aperture of the objective; blue is innermost and nearest the axial beam, which itself is practically colorless. The spectra and transmission colors of such a system are less pure than those of diatoms or butterfly scales, because the particles are not so perfectly uniform in size.

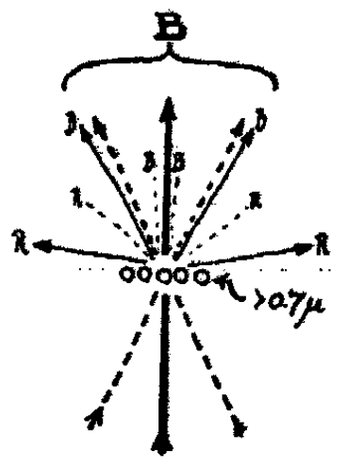

FIG. 5
Diffraction with convergent light. Blue rays overlap through a considerable angle, giving transmitted blue.

On diaphragming the objective so as to exclude successively the various colors of the diffraction spectra, beginning with the red, the transmission color, as seen in the microscopic image, varies just as in the case of the butterfly scale. As soon as the red is cut off, the particles become bluish green by transmitted light; when only the blue diffracted rays and the axial beam are allowed to pass through the aperture of the objective, transmitted blue is observed, and the structure is barely resolvable. Further diaphragming of the objective destroys the resolution. If the objective diaphragm is reduced to the point where the direct axial (undiffracted) beam fills its aperture, a distinct decrease in brightness and purity of the color results, and the transmitted blue may even be destroyed. If the structure is so fine as to cause "scattering" of blue (Tyndall blue) then the direct beam and the final transmission color will be yellow.

An illuminating beam which is somewhat less narrow, and therefore equivalent to slightly convergent or diffuse transmitted light, may be obtained by using the ordinary condenser diaphragm, closed nearly as far as possible. With such illumination the above diffraction phenomena, especially the zones of spectral colors, are much less well defined, because each "ray" of the illuminating beam follows a different path, and has its annular diffration spectrum in a different position, so as to cause them to overlap.

Within a small cone however, which is numerically somewhat less than that which just includes the blue diffracted rays with strictly axial light, only the inner blue portions of the spectra overlap. At the back aperture of the objective this is manifest as a pale blue central beam of light, which corresponds to the opening of the condenser diaphragm. If the diaphragm of the condenser is opened still further, the overlapping of diffracted spectra is still greater and the blue color of the rays within the narrow cone is masked.

With the full aperture of the objective and illumination of the degree of convergence just described, transmitted blue is not observable, because all

the diffracted light is admitted by the objective to form the image. But if the objective is diaphragmed until only the blue central beam is included (that is, until its aperture is no greater than that of the condenser) the transmitted blue is strikingly evident.

The effect of particles or structures of various sizes is demonstrable by means of particles from different portions of the film of sublimate; those which have condensed at the edge of the patch of particles are finer than those nearer the material to be sublimed, which have probably grown by "digestion" after they first condensed on the slide. The finer particles, practically unresolvable except by blue light, show only a transmitted yellow, at any aperture. Where they are slightly coarser, the transmission color is orange; where still coarser, it varies through purple to blue.

When films of sublimed particles are examined by dark-field illumination, those portions which are yellow by transmitted light (finer particles) scatter blue light and appear blue against the dark ground. The areas with coarser particles (blue by transmitted light) scatter yellow. Still coarser particles (neutral gray by transmitted light) scatter white. The lack of perfect uniformity of size is more manifest in the areas of coarser particles, and the transmission color tends to be grayish and indistinct, while the color zones at the back aperture of the objective become ill-defined.

Diatoms having much more highly uniform structure (from "Celite"; unidentified) show simple perforations or markings. The transmission colors vary with the size, just as in the case of the sublimed particles, but are more distinct.

When any of the above diffracting structures are immersed in liquid, the color phenomena which depend on diffraction practically vanish, though the finer structures still show a faint yellowish transmission color (complement of Tyndall blue).

The destruction of transmitted blue when markedly convergent instead of unidirectional illumination is obtained by opening the condenser diaphragm, and the necessity for a narrow aperture objective, both confirm the character of the color as a diffraction phenomenon rather than "scattering." The relationship of the aperture of objective and condenser in order to obtain a transmitted blue when slightly convergent light is used, is also a check on this theory.

The above phenomena indicate that the appearance of transmitted blue in microscopic objects is a function of the numerical apertures of the objective and of the condenser, and that it depends on the exclusion of all diffracted spectra except first order blue. Furthermore, since transmitted blue only occurs in "contrasty" objects, it is evident that it also depends on the intensity of the diffracted spectra as compared with the axial undiffracted beam.

There appears to be no necessary reason why transmitted blue cannot be observed in relatively coarse structures, provided the aperture of the objective bears the proper relationship to that of the illumination, the dimen-

sions are uniform, and the diffracting power is high. However, since the aperture of the objective would have to be adjusted more precisely for the "compressed" diffraction spectra from coarse structures, and since non-uniformity is more common, such cases have not as yet been observed. Probably special coarse, very deeply ruled gratings, if such were available, would serve to demonstrate the phenomenon over a wider range of sizes. The minimum dimension for transmitted blue is about 0.4μ; below this extends the range of Tyndall blue. The maximum dimension is probably about 1μ.

Transmitted Blue as seen with the Naked Eye

The explanation of transmitted blue and yellow, as produced with microscopic objects and observation, throws some light on the transmission colors of fine particles as seen with the naked eye. The sublimates of fine particles which exhibit areas of blue and of yellow by transmitted light, when viewed under the microscope, show these same areas colored to the naked eye. The colors are not noticeable, with the exception of Tyndall blue as seen against a dark background, unless the illumination is practically unidirectional. With diffuse light, as in close proximity to a white background, the transmission colors are not visible.

The yellow transmission color may be explained as simply the complement of Tyndall blue, since it occurs in the areas which show a good Tyndall blue to the naked eye. The color disappears in diffuse illumination because the particles receive light from a wide angular range, hence their transmission color, yellow, and the blue which they scatter are superposed and more or less nullify each other. Furthermore, there is not the cumulative action of superposed particles such as would be the case in a suspension of some thickness. This same reasoning applies to the disappearance of transmitted blue, and indeed to all diffraction colors.

Transmitted blue is visible to the naked eye partly because the particles may be of such a size that they actually tend to scatter yellow light fairly effectively, as shown under dark-field illumination. The complementary color, blue, is therefore transmitted. The general explanation in terms of diffraction is also applicable, for if the numerical aperture of the eye is reduced by means of a pinhole diaphragm placed close to it, the color becomes much grayer and may be destroyed just as when the objective aperture is reduced below that of the condenser. Furthermore, if the illumination is much more diffuse than would correspond to an angular aperture equal to that of the angle between the blue diffracted rays with axial light, the blue color is obscured.

Although the present paper deals only with a thin layer of particles, it is probable that the qualitative reasoning employed may be applied to relatively thick systems of particles in suspension. These are known[2] to show a similar series of transmission colors (yellow, orange, blue) when the size of

[2] Keen and Porter: Proc. Roy. Soc., 89A, 370 (1914); Raman: 100A, 102 (1921); Ostwald and Auerbach: Kolloid-Z., 38, 336 (1926).

the particles is approximately that which gives these colors under the microscope. There is also the cumulative effect of many layers, which, even if each particle only deviated a small intensity of light through a small angle, would tend to enhance the transmission color.

Summary

On the basis of direct qualitative experimental evidence, rather than computations which of necessity would demand even more assumptions, the conclusions of this paper may be summarized as follows.:

1. Uniformly sized particles of structures finer than *ca* 0.4μ scatter light inversely as λ^4, and are not resolvable with axial illumination. They exhibit Tyndall blue and transmit yellow or orange, even with relatively diffuse illuminations.

2. Uniformly sized particles or structures between *ca* 0.4μ and *ca* 0.7μ scatter red light and diffract blue in maxima at such angles as to be resolvable with blue light and axial illumination. If they are of bold outlines or surrounded by a medium widely different refractive index, they exhibit transmitted blue and scatter yellow or orange, even with slightly diffuse illumination.

3. Uniformly sized particles or structures coarser than *ca*. 0.7μ diffract all wave lengths, the red more than the blue. If of good contrast, they exhibit transmitted blue, provided the numerical aperture of the objective is such as to include only the blue end of the diffracted spectra obtained with a narrow axial illuminating cone.

4. Transmitted blue, which is lost in diffuse light, is apparent to the naked eye with specimens or coarser than 0.4μ. It is due to the greater deviation of red than blue, either by scattering or by diffraction.

5. Transmitted blue, visible to the naked eye, exhibited by suspensions of fine particles, is probably explainable by the above reasoning.

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THE VAPOR-ADSORPTION CAPACITY OF SILICA GELS AS AFFECTED BY EXTENT OF DRYING BEFORE WET-HEAT TREATMENT AND BY TEMPERATURE OF ACID TREATMENT AND ACTIVATION

BY HARRY N. HOLMES AND A. L. ELDER

During the past few years a great increase in the use of porous silica gel has been noted. It has found its way into such industrial processes as the removal of sulfur compounds (and colored material) from petroleum; the recovery of gasoline from still gases, and of benzene from coke oven gases; and the drying of air, oxygen, chlorine, acetylene, ethylene, carbon dioxide, and sulfur dioxide. It is also an excellent carrier for catalysts, and is a good adsorbent in refrigeration.

Silica gel is usually prepared by mixing a dilute solution of sodium or potassium silicate with a suitable acid. Patrick[1] prepared a hard glassy silica gel by mixing hot sodium silicate of 1.185 sp. gr. with an equal volume of 10 per cent solution of hydrochloric acid. After the gel had set, it was broken into pieces and the salt and excess acid were washed out with water. The gel was then air dried. The porosity of the gel depends upon degree and rate of drying. Holmes[2] and his co-workers[3] prepared porous silica gels by first adding such salts as ferric chloride to sodium silicate solution, drying the gel thus formed to a moisture content of 55-60 per cent, and removing the iron oxide from the firm solid by treating with acid. It was noted that the porosity of the gel depended upon its moisture content before acid treatment, the acid used, and the temperature at which it was given the acid treatment. It is of interest to note that silica gels produced by Ray[4] in 1923 adsorbed only 23 percent of their weight of benzene. Wet heat-treated gels prepared by Holmes[5] have adsorbed 140 per cent of their own weight of benzene from air saturated at 30°C.

Inasmuch as the adsorption capacity of a gel is a function of temperature and extent of drying before the wet-heat treatment, the rate of drying, and the temperature and method of removing some of the constituents of the gel, it was thought that a detailed study of these factors would be worth while.

Patrick, Frazer, and Rush[6] have studied the effect of activation temperature on the adsorption capacity of pure silica gel and silica gel soaked in sodium sulfate. They found that the pure gel did not lose seriously in porosity

[1] U. S. Pat., 1,297,724.

[2] The preparation of silica gels and their use as catalyst supports are covered in U.S. Pats., 1,739,305; 1,739,306; 1,739,307; 1,665,264; and others pending.

[3] Holmes and Anderson: Ind. Eng. Chem., 17, 28 (1925); Holmes, Sullivan, and Metcalf: 18, 386 (1926).

[4] Chem. Met. Eng. 29, 354 (1923).

[5] "Laboratory Manual of Colloid Chemistry," 195 (1928).

[6] J. Phys. Chem., 31, 1510 (1927).

until heated above 750°C. At 1100°C the amorphous silica gel changed to the crystalline form; due, they believe, to the atoms acquiring sufficient mobility to produce a new orientation. The gel containing sodium sulfate lost in adsorption efficiency at a lower temperature. The use of silica gel in adsorbing substances which later are removed by burning made it advisable to extend this study to include other types of silica gels.

It has been noted that there is a tendency for the more porous gels to decrease in adsorption capacity on standing a few years. The benzene-adsorption capacities of some gels, prepared and tested years ago, were redetermined.

Apparatus

A diagram of the apparatus used in this investigation to determine the benzene-adsorption capacity of silica gel is shown in Fig. 1. Air from the

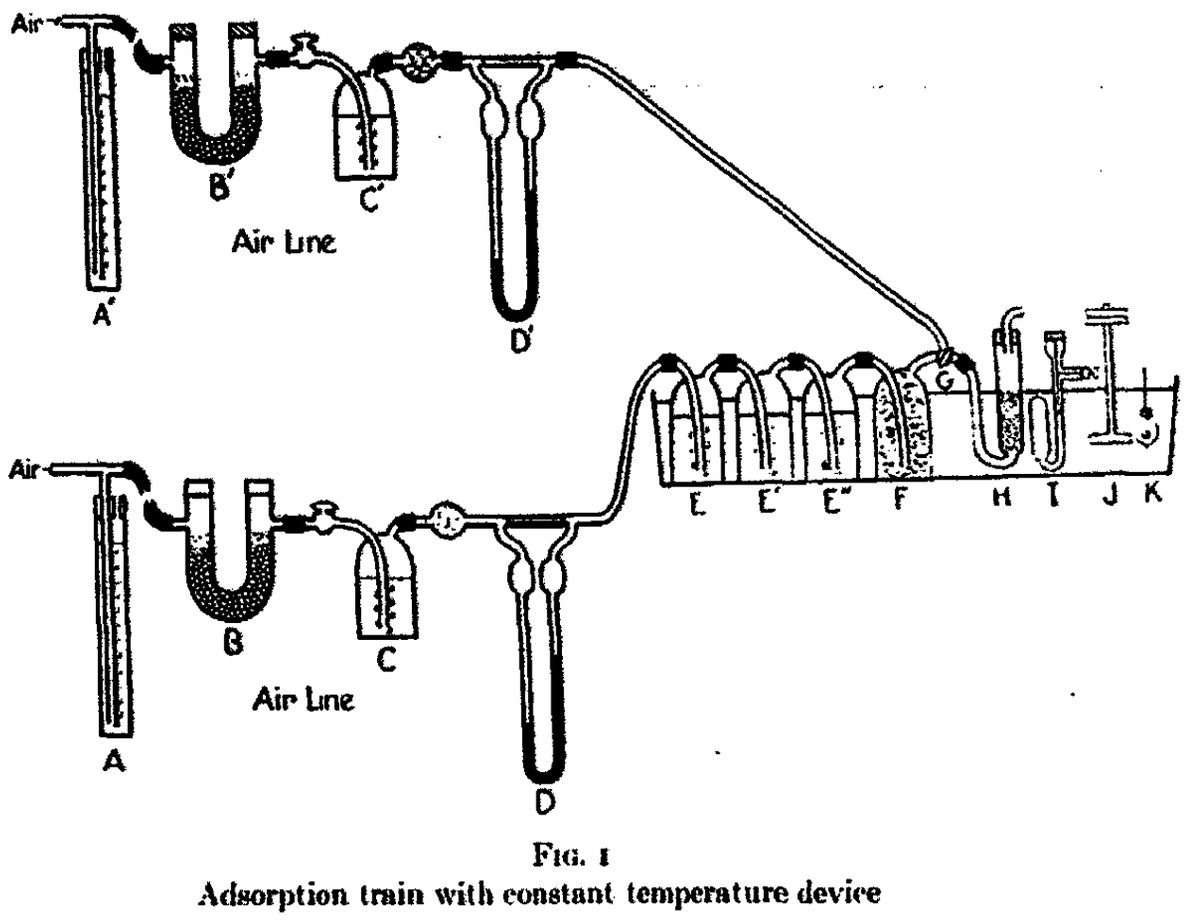

FIG. 1
Adsorption train with constant temperature device

compressed air tank was forced through the air-pressure regulator A, a calcium chloride drying tube B, a bottle C of concentrated sulfuric acid, a flowmeter D and through three bottles of benzene, E. E', E'' as saturators, and a fourth bottle F containing glass wool to catch any spray. In those experiments in which the benzene-adsorption capacity of gels was measured with air saturated with benzene, the saturated air passed directly through the three-way stopcock into the adsorption tube H which contained the silica gel. In experiments in which the benzene saturated air was diluted with air containing no benzene, air was passed through a second system, A', B', C', D', (A' B' C' D' are units similar to A, B, C, D) into the first adsorption train through the stopcock G. The bottles containing the benzene and the ad-

sorption tube were placed in a water bath which was kept at 30°C by the thermoregulator I. A stirrer J was used to decrease temperature fluctuations of the water bath. K is an electric bulb used for heating the water bath to 30°C. The electrical connections are not shown in the drawing. To further decrease temperature fluctuations the water bath was enclosed in a glass case so that the air above the bath could be kept at 30°C.

In making a measurement, the sample of gel to be tested was ground to between 10 and 20 mesh, and activated by passing a stream of dried air at 140-200°C at the rate of 100 cc per minute through the gel until it reached constant weight. The activating tube consisted of a piece of pyrex tubing 2 cm in diameter and 50 cm in length, surrounded with nichrome wire the surface of which was well insulated with asbestos. The activation process required from one to two hours. After activation the gel was placed in the adsorption tube H, which was then stoppered, cooled, weighed and attached to the adsorption train. The air stream saturated with benzene was run through the tube at the rate of 100 cc per minute until the adsorption tube ceased to gain in weight. Adsorption under the given conditions by this dynamic method is calculated as per cent weight of the gel samples. Those gels which were used in the study of the effect of activation temperature on benzene-adsorption capacity were activated in a quartz tube placed in a Hoskins furnace. The activation temperature was determined by use of a thermocouple.

Effect of the Age of a Gel on Its Benzene-Adsorption Capacity

Some gels which had been bottled and kept around the laboratory for several years were used for these experiments. When the gels were first made, their benzene-adsorption capacities were determined at 30°C. These values were redetermined at a later date. The results are given in Table I for eleven different gels. These data show that as the gels age, there is a tendency for their benzene-adsorption capacity to decrease.

TABLE I

Effect of the Age of a Gel on its Benzene-Adsorption Capacity

Gel number	First Date	Per cent Benzene adsorbed	Second Date	Per cent Benzene adsorbed	Per cent Decrease
1	4/–/28	115	10/1/29	111	3.5
2	1/1/27	140	10/2/29	118	15.7
3	1/–/28	49	10/4/29	48	2.0
4	5/26/25	90	10/5/29	72	20.0
5	5/16/25	120	10/7/29	86	28.3
6	1/–/26	44	10/8/29	39	11.3
7	1/–/27	62	10/9/29	41	33.8
8	1/–/28	77	10/10/29	63	18.1
9	1/–/28	50	10/12/29	44	12.0
10	1/–/27	105	10/15/29	103	1.9
11	1/–/27	116	10/16/29	109	6.0

Sufficient information is not available to indicate the cause of the decrease in benzene-adsorption capacity. It is possible that a new orientation of the silica takes place, aided, no doubt by the water films present.

Effect of the Activation Temperature on the Benzene-Adsorption Capacity of Silica Gel

In this investigation five different gels were studied. The gels were activated at temperatures varying from 100°/1000°C for four hours and their benzene-adsorption capacities then determined. Gel 1 was known as the

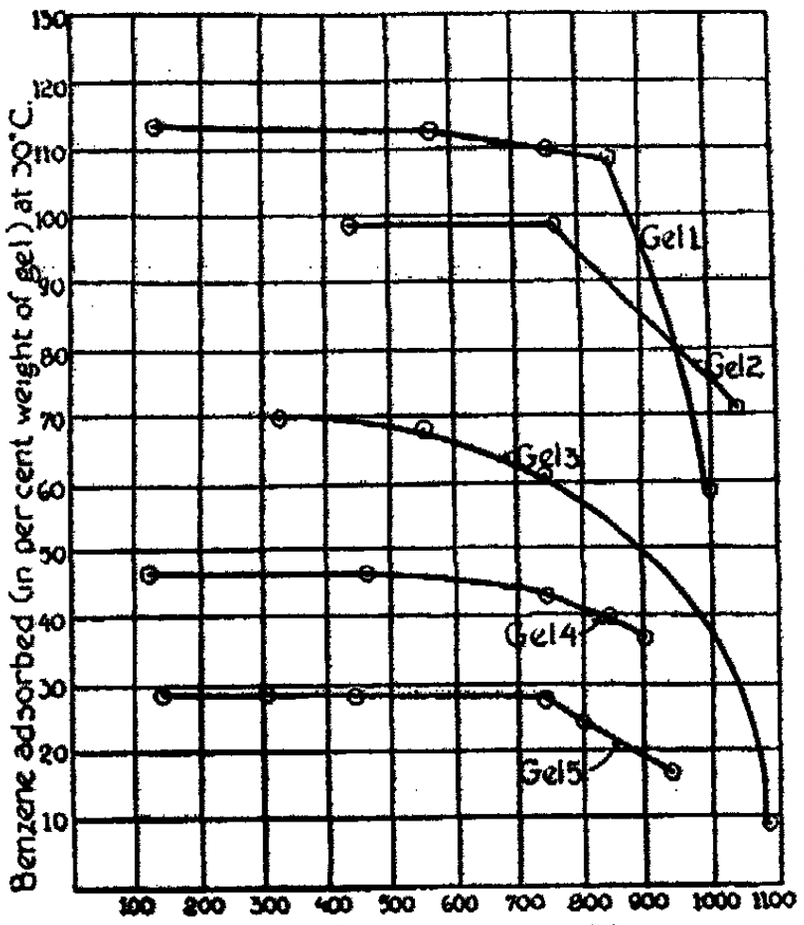

FIG. 2
Effect of activation temperature on the adsorption of benzene by silica gel from an air stream saturated at 30°C.

Holmes chalky gel. Gel 2 was prepared by treating a nickel salt with sodium silicate solution. The soluble constituents, (nickel salts, etc.) were then removed by acid treatment. Gel 3 was prepared by treating an aluminum salt with sodium silicate solution. The dried gel was then given the acid treatment. Gel 4 was prepared by mixing solutions of ferric chloride and sodium silicate. The gel was then given the wet-heat treatment to set the structure and to wash out the by-product, sodium chloride, but was not given an acid treatment. It therefore consisted of $xFe_2O_3ySiO_2.zH_2O$. Gel 5 was Patrick's commercial silica gel. The results of this investigation are given in Table II, and represented graphically in Fig. 2. These curves are similar to those reported by Patrick, Frazer and Rush[6] showing that with

four of the five gels studied activation temperatures up to 800°C do not materially decrease the benzene-adsorption capacity of the gel. Any of these gels might therefore be used with safety in adsorbing material to be burned out later, or in supporting catalysts for reactions in which the temperature would not exceed 800°C. Large drops in the benzene-adsorption capacity of these gels are noted if the activation temperature is raised to 1000°C.

TABLE II

Effect of Activation Temperature on Benzene-Adsorption Capacity of Silica Gel

Gel number	Activation temperature	Adsorption in percent at 30°C	Gel number	Activation temperature	Adsorption in per cent at 30°C
1	130°	114	4	120	47
1	570	113	4	460	47
1	750	110	4	740	43
1	850	109	4	840	40
1	1000	59	4	900	37
2	440	99	5	140	29
2	760	99	5	300	29
2	1040	71	5	440	28
3	320	70	5	740	28
3	550	68	5	800	24
3	740	61	5	940	17
3	1090	9			

Effect of Variation in Extent of Drying before Wet-Heat Treatment and of Temperature of Acid Treatment on the Benzene-Adsorption Capacity of Silica Gel

The first porous gels prepared in this laboratory were made by mixing together such quantities of ferric chloride and sodium silicate solutions that the resulting filtrate was neutral to litmus. The precipitated gels were dried and given acid treatment to remove ferric oxide and then washed with water to remove the resulting soluble ferric salts and excess acid. It had been noted that if the gels were not dried to at least 60 per cent moisture content they broke into very small particles when given the acid treatment. If, however, they were dried to below 40 per cent moisture content the final gel was very hard and had lower benzene-adsorption capacity.

The "wet-heat treatment" described in a previous paper[3] depended upon the fact that gels dried to less than 70 per cent water content were so firmly set in structure by heating to approximately 100°C under water (to prevent evaporation and shrinkage) that later drying caused relatively little shrinkage. Consequently a greater porosity was secured.

To test the effect of variations in moisture content before wet-heat treatment and of temperature of acid treatment, six types of gel were made.

The first gel contained a larger proportion of ferric chloride mixed with sodium silicate than had been used previously in making the Holmes chalky gel. The second gel was prepared according to the procedure of Holmes' Laboratory Manual of Colloid Chemistry, page 193, and was practically a neutral gel. The third gel contained an excess of sodium silicate. In the other gels, copper sulfate was used in place of ferric chloride, the solution above the fourth gel being acidic, the fifth neutral, and the sixth basic.

In Table III are given the quantities of reagents used in preparing these gels.

TABLE III

Quantities of Reagents used in preparing Acid, Neutral, and Basic Silica Gels

Gel number	2 N $FeCl_3$ in cc	N/3 $CuSO_4$ in cc	cc Sodium Silicate, Density 1.37	cc Water	Reaction to Litmus
1	15,495		3,250	75,000	Acid
2	8,000		2,500	47,500	Neutral
3	8,520		4,000	80,000	Basic
4		2,880	200	6,120	Acid
5		2,400	220	6,580	Neutral
6		2,400	320	6,480	Basic

The quantities of reagents as tabulated in Table III were mixed to make six gels which were allowed to stand 60 hours and then filtered through fine cheesecloth supported on coarse galvanized wire. The layers of fresh gel on the filter racks were about 7 cm in depth. As soon as the masses could be handled they were broken up into large lumps, dried on screens, and then broken into smaller lumps about 2 cm in diameter. Determinations of the water content of the gels were made from day to day and samples bottled at different moisture contents varying from about 40 to 60 per cent. The bottles were sealed and allowed to "sweat" or synerize for a week. Drops of solution appeared on the outside of the lumps while the gels were forming a better structure. The samples were then treated with 9N H_2SO_4 at different temperatures, washed free from the ferric sulfate formed and other soluble constituents, dried, activated, and used for benzene-adsorption experiments at 30°C. As shown in a previous paper,[3] removal of soluble iron or copper salts from a soft gel would merely mean a collapse of the gel, filling the spaces previously occupied by ferric oxide, etc. It is essential here that the gel be dried to a firm, non-collapsing condition before acid treatment, so that the space previously occupied by ferric oxide is obtained as increased porosity. The benzene-adsorption determinations are given in Table IV. The results from iron gels prepared by mixing ferric chloride with sodium silicate solution, given in Fig. 3, show that the benzene-adsorption capacity of a gel depends not only upon the ratio of ferric chloride to sodium silicate used in the preparation of the gel, but also upon the moisture content of the gel before acid

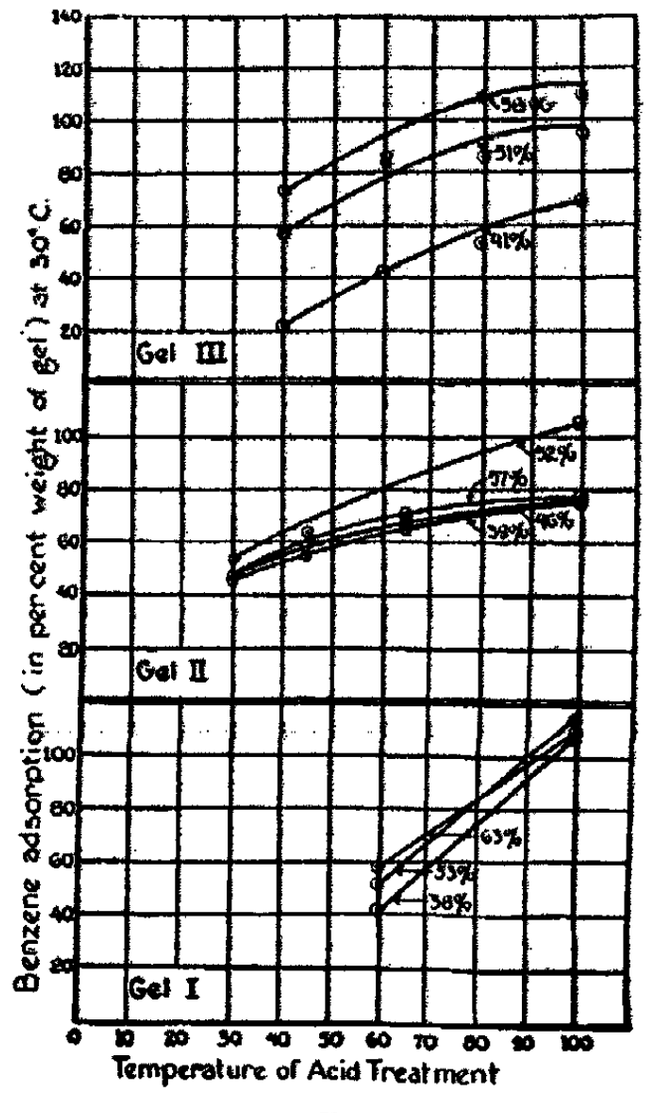

FIG. 3

The effect on adsorption of variations in the moisture-content before wet-heat treatment and temperature of acid-treatment of silica gels made from the product of mixing ferric chloride with sodium silicate. (Adsorption was from an air stream saturated with benzene at 30°.)

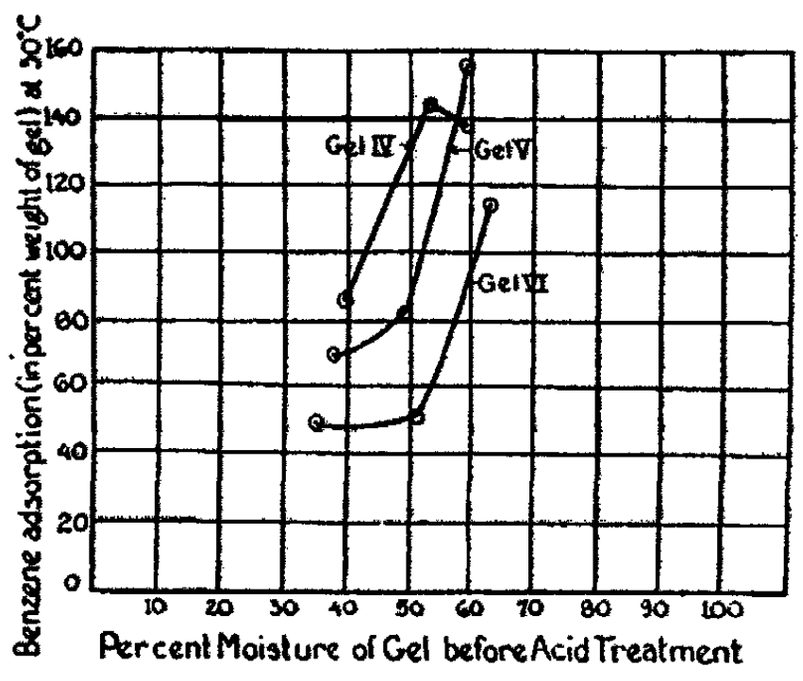

FIG. 4

The effect on adsorption of variations in the moisture content before wet-heat treatment (at 100°) of silica gels made from the product of mixing copper sulfate with sodium silicate. (Adsorption was from an air stream saturated with benzene at 30°.)

treatment and upon the temperature at which the acid treatment is applied. An increase in the temperature of acid treatment from 30°C to 100°C increases the benzene-adsorption capacity of the gel.

TABLE IV

Effect of Variation of Moisture Content before Wet-Heat Treatment and Temperature of Acid Treatment on Benzene-Adsorption Capacity of Silica Gel

Gel number	Per cent moisture content	Temperature of treatment with 9N H_2SO_4	Per cent C_6H_6 adsorbed by the gel at 30°C
1	38	60	42
1	38	100	107
1	53	60	54
1	53	100	114
1	63	60	59
1	63	100	109
2	39	30	47
2	39	45	55
2	39	65	65
2	39	100	76
2	46	30	43
2	46	45	58
2	46	65	70
2	46	100	78
2	52	30	55
2	52	45	64
2	52	65	—
2	52	100	105
2	57	30	48
2	57	45	59
2	57	65	71
2	57	100	77
3	41	40	23
3	41	60	42
3	41	80	55
3	41	100	71
3	51	40	59
3	51	60	84
3	51	80	87
3	51	100	96
3	58	40	73
3	58	60	86
3	58	80	110
3	58	100	111
4	40	100	87
4	53.5	100	144
4	59	100	140
5	38	100	71
5	49	100	82
5	59	100	156
6	35	100	50
6	51	100	52
6	63	100	115

For gels which were precipitated from acid, neutral, and alkaline solutions the highest benzene adsorptions were obtained from gels which contained 53, 52, and 58 per cent moisture respectively at the time of acid treatment.. Gel 2 was the usual type while Gel 1 was prepared with an excess of ferric chloride (acidic) and Gel 3 with an excess of sodium silicate (basic).

The data for the benzene capacity of gels made by mixing copper sulfate with sodium silicate and then removing certain constituents by acid treatment, are shown in Fig. 4. A new record for adsorption capacity of a gel

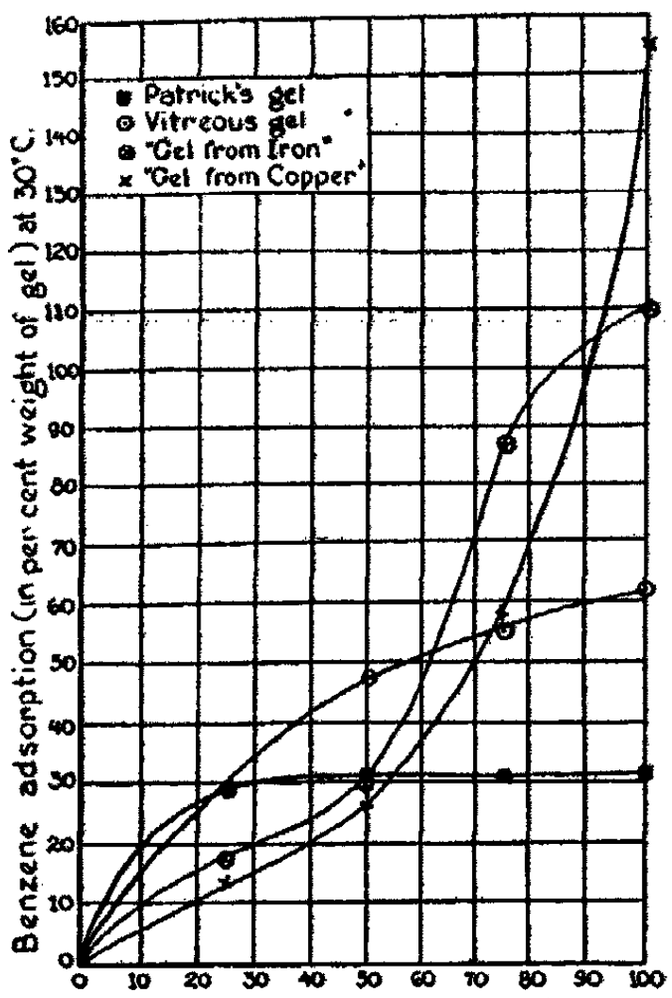

Fig. 5
Adsorption of benzene by silica gels under different partial pressures

was obtained with gel 5, which contained 59 per cent moisture at the time of acid treatment. This gel adsorbed 156 per cent of its own weight of benzene. The most porous gels were obtained from precipitates dried to 50/60 per cent moisture.

Relation of the Porosity of Silica Gels and Their Adsorption Isotherms

Demonstration of the great increase in the adsorption capacity of silica gel due to certain variations in its preparation indicates the superior quality of the more porous gel where the volume of gel to be used must be minimized. The adsorption capacity of Patrick's gel under low partial pressures had been shown, but no comparison of the relative merits of different gels under varying partial pressures was known. To determine this factor adsorption isotherms

for four typical gels were obtained. These were Patrick's glassy gel, a vitreous gel prepared by the method of Holmes and Anderson, a chalky "gel from iron" (see Table IV, gel 58 per cent water, acid treated at 100°C), and a chalky "gel from copper" (see Table IV, gel 59 per cent water, acid treated at 100°C). Adsorption curves were obtained for these four gels by measuring their capacity for adsorbing benzene from air, 25, 50, 75, and 100 per cent saturated with benzene. The data are recorded in Table V and shown graphically in Fig. 5. Patrick's gel and the hard vitreous gel were equally efficient at the lower partial pressures of benzene. The total capacity of the hard vitreous gel was double that of Patrick's. The two chalky gels are not efficient at low partial pressures. Their large internal volume indicates usefulness in economically removing most of a vapor to be adsorbed from a gas if followed in series with some hard gel with which to remove the last traces of it.

TABLE V

Adsorption of Benzene by Silica Gels under Different Partial Pressures

Gel	Per cent saturation of air with benzene at 30°C	Benzene adsorbed in per cent weight of the gel
Patrick's gel	25	29
" "	50	31
" "	75	32
" "	100	32
Hard vitreous gel	25	28
" " "	50	48
" " "	75	56
" " "	100	63
Chalky gel from iron	25	17
" " " "	50	30
" " " "	75	88
" " " "	100	111
" " " copper	25	13
" " " "	50	26
" " " "	75	59
" " " "	100	156

Summary

(1) Eleven silica gels studied showed a decrease in benzene-adsorption capacity on ageing for a few years.

(2) Four of the five silica gels examined were heated above 900°C without causing serious decreases in their benzene-adsorption capacities.

(3) Increase in the temperature of the acid treatment of a gel from 30° to 100°C increases the porosity of the gel.

(4) A gel capable of adsorbing 156 per cent of its own weight of benzene from an air stream saturated with benzene at 30°C was obtained.

(5) The most porous gels which still showed good firm structure were prepared from gels dried to 50-60 per cent moisture content before acid treatment. Useful gels may be made by first drying to a water content as low as 30 per cent.

(6) The Holmes' chalky gels have large capacities for adsorbing benzene under high partial pressures but are not efficient under low partial pressures. The Holmes' vitreous gels are practically equal to the hard glassy type at low partial pressures yet have double the total capacity of the latter at high partial pressures.

(7) Increase in efficiency of vapor adsorption by utilizing chalky to remove most of the vapor, followed by the use of vitreous or glassy gels to remove the last trace is suggested.

Acknowledgment

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THE RELATION BETWEEN PHOTOGRAPHIC REVERSAL AND THE SENSITIVITY OF THE SILVER HALIDE GRAIN

BY FRANK E. E. GERMANN AND D. K. SHEN

The use of photography as an aid to research is possibly unsurpassed by any other scientific tool. Its nearest competitor, the X-ray, would be of considerably less value if it were not possible to leave a permanent record on the photographic plate. The universal appeal of photography to both scientist and layman has brought it about that many persons have tried to explain the numerous secrets of nature associated with the making of pictures. As a result there is probably no field of science in which more amateurs are working or in which the literature is more filled with contradictory theories. However, the reason for confusion is even deeper seated than this, and may be found in large part to be due to the particular character of the science. Here if ever we deal with the chemistry of the infinitely small, and as a consequence, mere traces of chemicals which easily escape the scrutiny of the most careful analyst, may completely change the character of the results. Then again failure to realize that something added for a special purpose may have far reaching results of an altogether unexpected nature, has led to much confusion.

Our study of the grain sensitiveness of silver iodide in photographic emulsions illustrates how easily one may be led astray.[1]

The most apparent difference between silver bromide and silver iodide grains is their reducibility by means of chemical developers, a fact to which Lüppo-Cramer[2] attributes the apparent insensitivity of silver iodide.

The silver bromide emulsion, when coated in a single grain layer, usually develops very quickly with the unbromided developer, even without having received an exposure; in other words, it fogs very readily. Work carried out by previous investigators has been confined mostly to silver bromide grains, and the developers used contained a large amount of potassium bromide to suppress the development. In order to show the development centers, the development had to be stopped at the end of about a minute. We have shown that in the case of silver iodide grains in a one grain layer emulsion the development goes on very slowly; even at the end of fifteen minutes in a developer containing no soluble halide, some grains are still incompletely developed. The fact that a grain will be either completely developed or not at all was confirmed by developing the slides of an evenly exposed plate different lengths of time and counting the percentage number of grains developed, assuming a grain would be completely developed if it contained one or more centers. The plate and the exposure were so chosen that only a small

[1] Germann and Shen: J. Phys. Chem., 33, 864 1583 (1929).
[2] Lüppo-Craner: Eder's Jahrb., 40, (1903).

fraction of the grains would be made developable, in order that fog correction, if any, could be made by having an unexposed plate developed along with it. In the short development the centers were so small that they could easily escape observation, but as the development went on, the centers increased in size until the whole grain was developed. Fig. 1 shows that the percentage number of developable grains made visible increases with time of development and becomes practically constant after about ten minutes. The values plotted have been corrected for fog, which, even after thirty minutes of development is less than one per cent. This is a very striking characteristic of

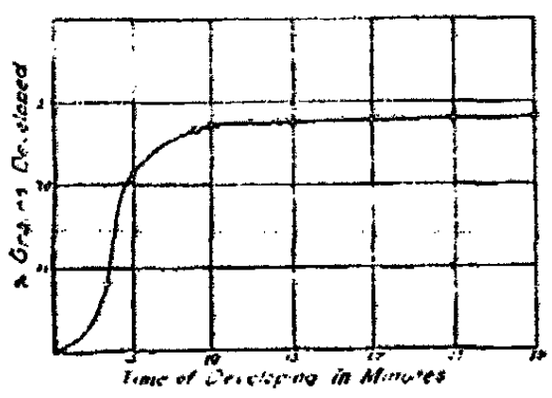

FIG. 1

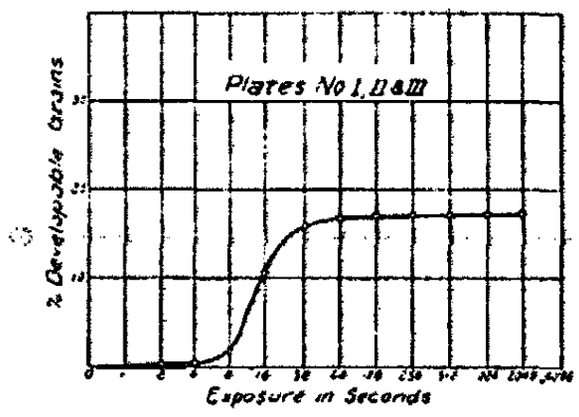

FIG. 2

silver iodide emulsions. Since prolonged developing does not increase fogging appreciably, fifteen minutes was adopted in all cases for the complete revelation of the centers. Fig. 2 shows the relation between time of exposure and percentage number of developable grains when a one grain layer silver iodide plate is exposed, developed, and examined as detailed above. It is to be noted that the maximum developability is almost reached at the exposure of 64 seconds, and that only 17 per cent of the total silver iodide grains are ever made developable. Further increase in exposure decreases the number of developable grains, that is, the period of reversal is entered.

The relationship between sensitivity and grain size has been realized since the early days of photography. Fast emulsions usually consist of large grains, but it is not at all true that the sensitivity of any large-grained emulsion exceeds that of any small-grained one.[3] Furthermore, emulsions having identical grain characteristics may differ considerably in sensitiveness. The fact that only in one and the same emulsion,[4] are the large grains more sensitive than the small ones, makes it apparent that grain size is not the sole factor determining high sensitivity.[5] We still do not know what causes sensitivity; we know, however, that the sensitivity of an emulsion can be increased through processes which simultaneously increase the size of grains. We do not know the mechanism by which the sensitivity is increased; it seems justifiable to believe that the factors which govern the increase in

[3] Renwick: Phot. J., 61, 333 (1921).
[4] Sheppard: Colloid Symposium Monograph, 1, 346 (1921).
[5] Svedberg: Z. wiss. Phot., 20, 36 (1920); Phot. J., 61, 325 (1921); 62, 183, 186, 210 (1922); 64, 272 (1924); Renwick: 64, 360 (1924); 66, 163 (1926); Sheppard: J. Franklin Inst., 203, 829 (1927).

sensitivity coincidently favor the growth of grains. In one and the same emulsion, the conditions under which the large grains are produced are decidedly different from those in the formation of the small-grain fraction; a difference in sensitiveness between these two classes of grains should not be surprising.

If the sensitivity is due to the presence of some impurity in the gelatin, allyl thiocarbamide, according to Sheppard,[6] and the degree of sensitivity depends upon the size of the sensitive specks situated on or in the silver halide grains,[7] the large grains would be more sensitive because the sensitive specks on the large grains are likely to be larger. If we assume that the amount of the sensitive material is limited in the gelatin, the amount adsorbed on the silver halide grain would be greater in the earlier stages of precipitation when the concentration of the sensitive material is the greatest. When an emulsion is made by pouring a silver nitrate solution into the soluble halide solution to which gelatin is added, it is obvious that at the earliest stage of precipitation, the concentration of the soluble halide is also the greatest, which favors the so-called Ostwald ripening, *i.e.*, the grains produced will attain the largest size. From these considerations, therefore, the large grains which are more sensitive are produced during the earlier stages of precipitation, during which time the concentration of both soluble halide and sensitizing material is greatest.

The insensitiveness of the silver iodide emulsion cannot be explained to be merely due to the incapability of the normal developers to reduce the silver iodide grains, as suggested by Lüppo-Cramer, because such explanation cannot satisfy the fact that seventeen per cent of the total grains are developable, unless the assumption is made that the rest of the grains are materially different and entirely lacking in sensitivity. If sensitivity is due to the presence in the grain of some foreign material derived from gelatin, then only this seventeen per cent of the total grains is supplied with such material, and the lack of sensitivity of the rest of the grains would be due to deficiency of the sensitivity material on account of the fact that they are formed during the latter stage of precipitation in which the sensitivity material is practically exhausted. If this were the case, the developable grains would have been those formed at the earlier stage of precipitation, *i.e.*, those of the largest size.

In order to test the above conclusions, two extreme fractions containing the largest and smallest grains of an emulsion were obtained by repeated centrifuging, and coated on separate glass plates. Both plates were exposed and developed in exactly the same manner; it was found that the developability-exposure curves for the large- and small-grained fractions coincided with that of the uncentrifuged emulsion. This is shown in Fig. 2, plates I, II, and III representing the uncentrifuged, large- and small-grained emulsions respectively, all of which coincide. This would indicate that the undevelopability

[6] Sheppard: Phot. J., 65, 380 (1925).

[7] Sheppard: J. Franklin Inst., 200, 51 (1925); Colloid Symposium Monograph, 3, 86 (1925).

of eighty-three per cent of the grains cannot be due to the depletion of the sensitivity promoting material in the solution. It would, furthermore, indicate that there is no appreciable difference in sensitivity between the large and small grains of the same emulsion.

When one of these plates consisting of grains which were only 17 per cent developable, was bathed in a one per cent solution of either hydroquinone or pyrogallol, prior to exposure, it was found that the number of developable grains increased with time of bathing until 100 per cent was reached. Prolonged bathing in the sensitizer produced no further effect. The sensitized plate, after being thoroughly washed in running water, does not resume its initial state of low percentage developability, a fact confirming Lüppo-Cramer's early observations.[8] Metol, glycin, and amidol were also tried as sensitizers, and were found to act the same as pyrogallol and hydroquinone. Fig. 3 is a composite of many curves and shows their interrelationship better than would be possible with single ones. In cases where the same curve has various numbers, not all points are given, as there would be too much overlapping. With the scale used, practically all of the points fall on the curves, and the various curves represented by one are identical. Thus Plates I, II, and III all yield identical curves, giving a maximum developability of about 17 per cent. Plates IV and V were sensitized for ten minutes with 1 per cent hydroquinone and pyrogallol respectively, and dried without washing. The points at 4096, and 8192 seconds showing reversal, belong only to IV, the maximum time of 2048 seconds having been adopted for all other experiments. Plates VI and VII were sensitized for ten minutes in 1 per cent pyrogallol, the one being dried and then washed in running water for two hours and again dried, the other having been washed for two hours immediately after sensitizing and then dried.

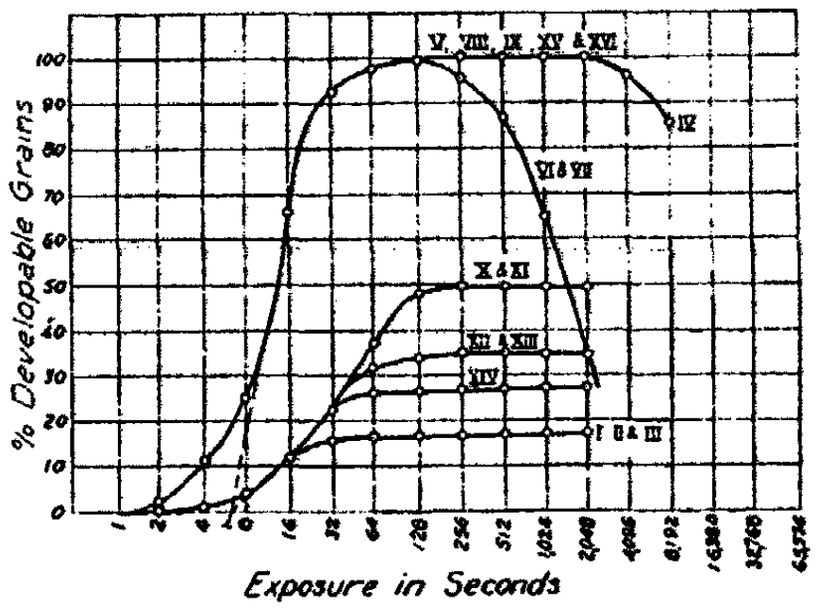

FIG. 3

[8] Lüppo-Cramer: Phot. Korr., 38, 158 (1901); 40, 25 (1903).

In order to find the relative effect of sensitizers on large and small grains, Plates VIII and IX were prepared. Plate VIII consisted of the large-grain fraction prepared by centrifuging the emulsion as previously described, and Plate IX the small-grained fraction. Both were sensitized with a 1 per cent pyrogallol solution for ten minutes, and dried without washing. Thus Plate II before sensitizing corresponds to VIII after sensitizing, and similarly Plate III corresponds to Plate IX.

The power of sensitizing silver iodide plates is not limited to the usual developers, as is shown by Plates X to XV inclusive. Plates X and XI were sensitized for ten minutes with 0.2 and 0.5 per cent solutions of acetone semicarbazone respectively, and dried without washing. Plates XII and XIII were sensitized for ten minutes with 1 and 5 per cent solutions of sodium nitrite respectively, and dried without washing. Plate XIV was sensitized for ten minutes in a 1 per cent solution of sodium sulphite and dried without washing. Sodium nitrite and sodium sulphite, although much stronger halogen absorbers than the usual developers are not such good sensitizers. Plate XV was sensitized for ten minutes with a 1 per cent solution of sodium bisulphite and dried without washing. It is seen to be as effective a sensitizer as are the usual developers.

Sensitivity and Speed. The curves in Fig. 3 are similar to the characteristic curves for the various emulsions, since the percentage of developable grains is proportional to the density of the plate. When the middle, or straight line, portions of these curves, which represent the range of correct exposure, are projected until they cut the exposure axis, it is seen that they intersect at a common point marked (i). This point has been called the inertia of the emulsion by Hurter and Driffield, and may be taken as a measure of the speed. Obviously, the greater the inertia the less the speed of the emulsion. Since all these curves intersect at one point, it is obvious that the sensitizers have had no effect on the speed, but have merely increased the developability of the grains. Sensitivity is measured in terms of the amount of light that will make the grain developable. A change in sensitivity involves, therefore, a vertical displacement of the curve without changing the value of the inertia (i), while a change in speed involves a horizontal shift in (i). By sensitivity of a grain we mean that the grain is developable if a sufficient exposure is given. Speed represents the degree of sensitiveness. Obviously we cannot state that all the grains of a given emulsion have the same speed, but the average of all speeds is proportional to the reciprocal of the inertia.

The terms sensitizers and desensitizers should, therefore, be assigned to those substances which increase or decrease the developability of the grains. Substances which increase or decrease the speed should be called accelerators and retarders respectively.

The Rôle of Sensitizers. Assuming that in a given emulsion we have a wide range of speeds of the various grains, it is obvious that the grains possessing the highest speeds would be developable after a very short exposure. If the

exposure is prolonged, then we enter the period of reversal for the fast grains, while at the same time making some of the slower grains developable. A wide range of speeds would accordingly yield a plate of low maximum percentage developable grains. If something can be added to such an emulsion which will prevent the reversal of those grains which have become developable, without interfering with those which have not become developable, then it should be theoretically possible to make all the grains in an emulsion developable if given a long enough exposure. This apparently is actually what happens when a sensitizer is added. When the sensitizer is not washed off, but allowed to dry in excess on the plate, the percentage number of developable grains increases to 100 per cent in some cases and remains at that value for a considerable overexposure. Finally, when the exposure is very long, the sensitizer seems to be exhausted, and the period of reversal is entered. When excess sensitizer is washed off, reversal comes quickly. *The rôle of a sensitizer thus appears to be that of preventing or delaying reversal.* If, therefore, sensitivity is merely a case of inhibited reversal, it is very possible that many substances which are at present regarded as insensitive to light may be made sensitive when suitable substances are found to prevent their rapid reversal.

The insensitivity of pure silver iodide emulsions is probably due to the existence of a wide range of speeds among the grains, combined with the phenomena of quick reversal. There might not be any inherent difference in sensitivity between grains, but we must admit that grains in a given emulsion possess different speeds. The constancy of the percentage number of developable grains in the normal unsensitized silver iodide emulsion throughout a wide range of exposures may be explained by assuming that by a given exposure those which have higher speeds may be reversed, while others are just made developable. Equilibrium may finally be reached when the number reversed per unit of exposure equals the number made developable and the horizontal portion of the curve results. If a certain critical amount of light energy is required to make a grain developable, and a definite small increment of that amount would make it reverse, the curve of the reversal should exactly repeat the curve of developability, but in a reverse direction. This is most probably the case as indicated by Curves VI and VII, Fig. 3. This simply means that the course of reversal follows exactly the rule that governs the developability of the grains.

Since the phenomenon of reversal actually takes part even in a normal exposure of a modern fast plate,[9] it becomes evident that such a phenomenon cannot be neglected in the study of photographic processes. The failure of the reciprocity law seems very likely to be due, among other factors, to the intervention of reversal.

Solarization or Reversal. Numerous theories have been offered to explain the phenomenon of reversal; the question still remains unsettled. If the action of light is to affect the grains in such a way as to initiate development, it is

[9] Svedberg: Phot. J., **64**, 272 (1924).

rather difficult to see how excessive exposure could destroy the effect already produced. The solarization cannot be the reversed reaction of that producing the latent image, because reversible reactions would come to an equilibrium as their ultimate stage. It is thermodynamically impossible that a reaction goes to completion in one direction and then completely reverses to its original state under the same external conditions. The view that the chemical composition of the solarized image is different from that of the normal latent image and that the silver halide grains having received a solarizing exposure are chemically different from the normal unexposed grains, is a very debatable assumption. Arguments of this nature will ultimately lead to the ever-present controversy over the chemical or physical nature of the latent image. In fact, we have proven experimentally that solarized grains are practically identical to the normal unexposed grains in the case of silver iodide emulsions so far as their behavior towards sensitizers is concerned. When a silver iodide one-grain layer plate which has been exposed to complete solarization is sensitized with a 1 per cent pyrogallol solution, the exposure-developability curve falls exactly on that of the similarly sensitized normal plate. This is shown by Plate XVI of Fig. 3 which was a one-layer silver iodide emulsion exposed twenty minutes to a 150-watt incandescent lamp at a distance of 0.5 meter, then sensitized with a 1 per cent pyrogallol solution for ten minutes, and dried without washing.

Photo-Retrogression. Another interesting characteristic of the silver iodide plate is its rapid photo-retrogression. On one occasion, a silver iodide plate was exposed and left undeveloped for twelve hours. On developing, the maximum percentage developable grains was reduced to half of what it would have been had the plate been developed immediately after exposure. The nature of photo-retrogression, though very little understood, is probably due to the same causes as reversal.

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THE THERMOELASTIC EFFECT IN CELLULOSE ESTER FILMS[1]

BY J. G. McNALLY AND S. E. SHEPPARD

In general, metals, as well as many other materials, are cooled, *i.e.*, *absorb* heat, when stretched.[2] The relationship of the elastic and thermal properties of such normal materials may be summed up in the statements[3] that with increasing temperature, (a) the modulus of elasticity decreases, (b) the elasticity number or deformation increases, *i.e.*, the cross-sectional alteration increases more rapidly than the elongation; however, (c) the volume alteration decreases. This behavior indicates a relation of the elastic properties to the coefficient of thermal expansion, in fact this coefficient depends upon the stress on the material in question. From thermodynamic reasoning it follows that the temperature coefficients of thermal expansion and of elastic deformation (or of the modulus of elasticity) must have opposite signs.

Accordingly, with normal materials, *e.g.*, metals, the thermal expansion coefficient increases with increasing stress, while the modulus of stretch (Young's modulus) decreases with rising temperature.

Apparently quite contradictory is the behavior of rubber. Early observations by Gough,[4] rediscovered by Page[5] and Joule[2] showed that rubber is warmed, or develops heat, on stretching. In agreement with the previously sketched reciprocal relations of the thermal and elastic properties, and more generally, with the Braun-LeChatelier rule, Kelvin[6] predicted that stretched rubber would contract if heated; this was experimentally confirmed by Joule.

Since then a large number of investigations of the Joule effect with rubber have been made, and numerous explanations offered. A review of these researches has been made by Whitby.[7] The phenomena are complicated, and point to transitions between metal-like and rubber-like solids. The main results for rubber may be summarized as follows:

(1) Some samples of rubber show an initial cooling on stretching followed by a rise in temperature.[8] Other experimenters find only the heating effect.[9] The rate of extension has a marked effect on the thermal change: a high rate causes the disappearance of the initial cooling and an increase in the amount of heating at any extension.[10] At a given rate of elongation, a critical temperature exists above which the negative (cooling) effect is not apparent.[9]

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[1] Communication No. 445 from the Kodak Research Laboratories.

[2] Joule: Proc. Roy. Soc., London, 8, 335 (1857); Phil. Mag., 14, 226 (1857).

[3] Cf. Auerbach: Winkelmann's "Handbuch der Physik," I (1), 584 (1908).

[4] Mem. Proc. Manchester Lit. Phil. Soc., 1 (2), 228 (1805); Nicholson's J., 13, 305 (1886).

[5] Silliman's J., (2), 4, 341 (1847).

[6] Cf. Joule: Proc. Roy. Soc., 8, 335 (1857); Phil. Mag., 14, 226 (1857).

[7] "Plantation Rubber and the Testing of Rubber," 453 (1920).

[8] Villari: Ann. Physik, 144 274 (1872).

[9] Schwartz and Kemp: Mem. Proc. Manchester Lit. Phil. Soc., 55 (12), 9 (1911).

[10] Chauveaux: Compt. rend., 128, 388, 479 (1899).

(2) Rubber under low stresses expands longitudinally on heating but contracts when heated under a high stress.[11] The contraction caused by an increase in temperature is greater at a low temperature than at a high temperature and if the temperature is raised sufficiently, no contraction takes place. The temperature at which the change of sign occurs is higher the greater the load.[12] It may be mentioned that muscle fibers show many points of resemblance to rubber on thermoelastic relations,[13] but, so far as we are aware, no investigation of these has been made with synthetic organic colloids. Investigations on the birefringence of cellulose ester films under stress[14] as well as the change in X-ray diagram of these materials under stress[15] show them to have certain similarities to rubber in structure and behavior. On the other hand, it has been pointed out that their elastic behavior in some respects approaches that of metals more nearly than that of rubber.[16] We have made a study of the thermoelastic relations of cellulose nitrate and cellulose acetate films, covering both the heat changes taking place when the films are stretched, and measurement of the coefficient of thermal expansion at different temperatures and stresses.

I. Heat Changes of Cellulose Ester Films when stretched

Experimental Method

Test pieces of cellulose acetate and nitrate films were placed in a dynamometer that made a record of the stress-strain curve of the material. A multiple junction Moll thermopile was clamped to the lower jaw of the dynamometer in such a manner that the opening of the instrument was kept in contact with the flat surface of the film during the stretching. The leads from the thermocouple were attached to a Leeds and Northrup high sensitivity galvanometer, the deflections of which were read on a scale 1 meter distant while the film was stretched. By noting the time at which the stress-strain data were recorded by the dynamometer and the time at which the galvanometer was read, the thermal effect during any part of the stress-strain curve could be determined.

All test pieces were 15 cm long, 1 cm wide, and very close to 0.014 cm thick.

Experimental Results

Cellulose Nitrate: Figure 1 shows the stress-strain curve for a sample of cellulose nitrate at 18.6°C and R.H. = 55 per cent. The three curves are check runs and indicate the degree of reproducibility of the experiments. The numbers along the curves give the scale deflections in millimeters of the

[11] Van Bjerken: Ann. Physik, 43, 817 (1891).
[12] Lundal: Ann. Physik, 66, 741 (1898).
[13] Engelmann: "Ueber den Ursprung der Muskelkraft," 2nd Ed. (1893); McCallum: J. Biol. Chem., 14, 96 (1913).
[14] McNally and Sheppard: J. Phys. Chem., 34, 165 (1930).
[15] Trillat: J. phys. radium, 10, 370 (1929).
[16] Sheppard and Carver: J. Phys. Chem., 29, 1244 (1925).

galvanometer at the corresponding elongation and stress. It will be seen that the *cellulose nitrate film cools on stretching up to the yield point, when it starts to warm up* and continues giving off heat until it breaks. The evolution of heat is greater than the absorption during the cooling period. This film was weakly biaxial and the test piece was cut in the direction of the residual extension, as in all of the remaining experiments on biaxial films.[17]

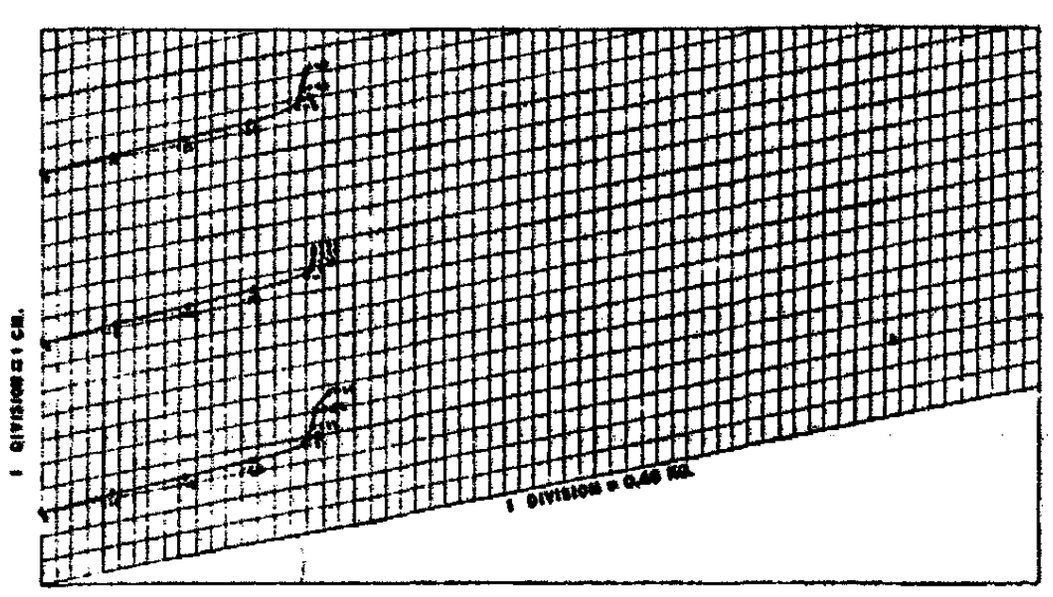

FIG. 1

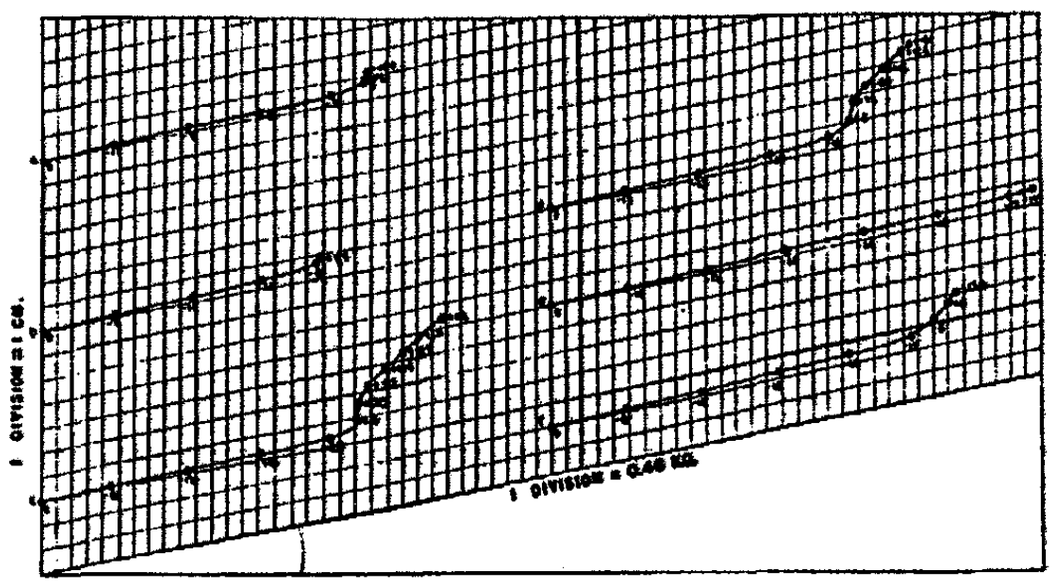

FIG. 2

Cellulose Acetate. Figure 2a shows the thermal changes observed on stretching a biaxial cellulose acetate film at 16.7° and 53 per cent R.H. The curves obtained with a uniaxial plate coated acetate film were very similar (Fig. 2b) and both are nearly identical with the nitrate film.

Elongation at Constant Rate

As mentioned above the negative heat effect changed to a positive one at the yield point. Whether this change was caused by a difference in the re-

[17] For a method of determinmg micellar orientation in films see McNally and Sheppard: J. Phys. Chem., 34, 165 (1930).

action of the internal structure of the film to stress at this point, or whether the inversion was simply connected with the rate of extension of the film, could not be determined. The following experiment was therefore carried out in which the film was stretched at the constant rate of 0.13 cm per second until the film broke. The data from this experiment are presented in Table I. θ is the scale deflection of the galvanometer. The change in sign of the thermal effect came at an elongation of about 7 per cent, which checks very closely with the extension at the yield point for this film (see Fig. 2c).

We conclude, then, that the increased rate of extension after the yield point does not cause the inversion of the thermal effect.

The thermoelastic relations of another mechanically coated film are given in Fig. 2c. The curve is similar to the former. The measurements were made at 18.6° and 55 per cent R.H.

Change in Temperature

Figure 2d is a duplicate of 2c carried out at 22.4°C. This is the greatest variation in temperature it was possible to obtain under our present experimental conditions but it appears that this variation causes little if any change in the thermoelastic relation.

TABLE I

The Thermal Effect on Stretching Cellulose Nitrate Film at a Constant Rate of 0.13 cm/sec at 18.4°C, 50 per cent R.H.

Time sec	L cm	ΔL cm	100 $\Delta L/L_0$	θ
0	15.00	0.0	0.0	0
1	15.13	0.13	0.86	—
2	15.26	0.26	1.72	−0.5
3	15.39	0.39	2.58	—
4	15.52	0.52	3.44	−3.8
5	15.65	0.65	4.30	—
6	15.78	0.78	5.16	−5.5
7	15.91	0.91	6.02	—
8	16.04	1.04	6.88	−1.8
9	16.17	1.17	7.74	—
10	16.30	1.30	8.60	+2.8
11	16.43	1.43	9.26	—
12	16.56	1.56	10.12	+7.8
13	16.79	1.79	10.98	—
14	16.92	1.92	11.84	+11.2
15	17.05	2.05	12.70	—
16	17.18	2.18	13.56	+13.4
17	17.31	2.31	14.42	—
18	17.44	2.44	15.28	+14.0

Coagulated Cellulose Nitrate Films Dried under Varying Tension

Figure 2e indicates the heat effect of stretching a film prepared by setting a collodion solution in water as in preparing membranes and stretching the coagulated film 10 per cent during curing. The period of plastic flow is absent and the heat evolution that accompanies it is also missing. The data from a film prepared in the same way but allowed to shrink 10 per cent on curing are given in Fig. 2f, and it is essentially the same as the air dried film. Both films were biaxial, the former very strongly so and the latter very weakly.

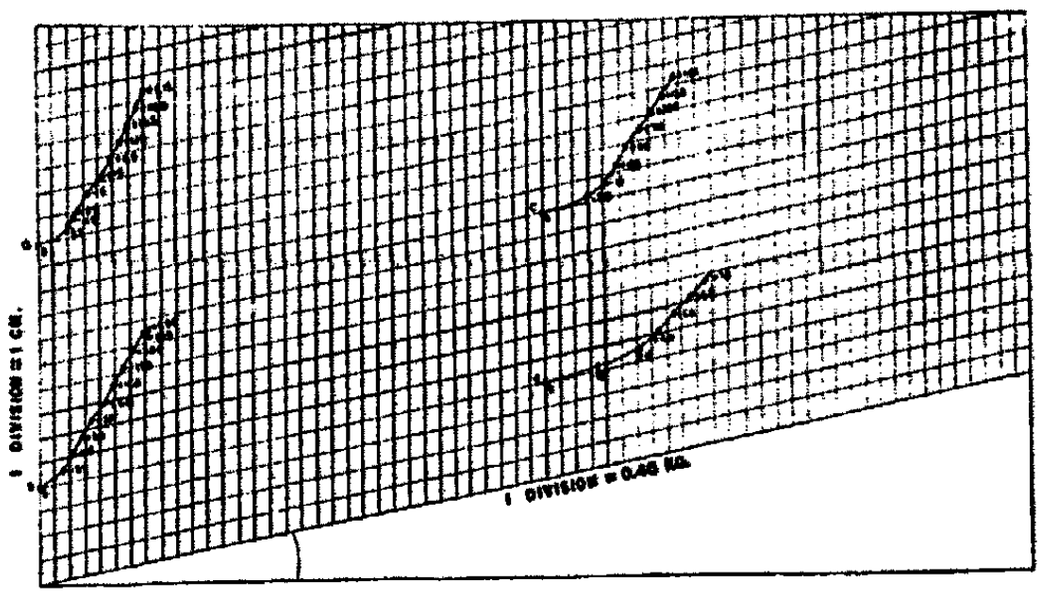

FIG. 3

Coagulated Cellulose Nitrate Films with High Volatile Content

In Fig. 3 the stress-strain curves are given for a number of coagulated films. A was stretched while still containing about 50 per cent of volatile material, b about 30 per cent; c about 15 per cent, and d about 10 per cent. While the shapes of these stress-strain curves are very different, the thermal effect is still the same—cooling at low elongations and heating at higher elongations.

Conclusions as to Thermoelastic Effect

(1) It appears that at ordinary temperatures both cellulose nitrate and cellulose acetate films cool when stretched to small elongations. At higher strains (deformations) an inversion in the thermal effect takes place, and heat is evolved. This result holds both for films formed by air drying (solvent evaporation) and by coagulation (solvent extraction).

(2) If the film is stretched on drying sufficiently to become strongly biaxial, this secondary heating effect disappears.

(3) The thermoelastic properties of coagulated films are independent of their content of volatile solvent.

(4) The thermoelastic effect is the same at constant rate of elongation as under the loading conditions with a dynamometer.

From these results it would appear that cellulose nitrate and acetate films should show lower resistance to a small strain (elongation) but increased

resistance to a large one as the temperature is raised. But if the material is analogous to rubber, the rate of heating and the rate of loading would determine whether or not the films would show increased or decreased resistance to stretch at higher temperatures.

II. The Thermal Expansion of Cellulose Nitrate

To fill out our knowledge of the thermoelastic properties of cellulose esters, a study was made of the thermal expansion of cellulose nitrate.

It is well known that several crystals—silver iodide and calcspar for example—have negative coefficients of thermal expansion along certain crystallographic axes. The phenomenon has also been met with in the case of strained elastic colloids, notably rubber where it has been the subject of a large number of extensive investigations. No data existed on the thermal coefficient of expansion of any of the cellulose esters so the experiments to be described were undertaken to supply this need.

Apparatus

The thermal coefficient of expansion of crystals and metals is a well-defined property of the material that depends on the mean distance between the vibrational centers of the component atoms. In the case of organophilic colloidal materials, however, the measurement of expansion coefficients is complicated by the property which the material possesses of flowing at very low stresses. Further, the rate of flow is increased by a rise of temperature so that the elongation observed on raising the temperature of a test piece is partly caused by thermal expansion and partly by plastic flow.

In constructing an apparatus to measure the thermal expansion coefficient of organic films the rate of heating of the film should be rapid and it should be possible to measure the temperature of the film accurately at any time during the experiment. Further, dimensional changes of the test piece caused by adsorption and desorption of water or solvent vapors by the film should be eliminated. Since it would be extremely difficult to keep the test piece continuously in an atmosphere of constant humidity while the temperature was changing rapidly, it was necessary to carry out all experiments at 0 per cent relative humidity, *i.e.*, with all solvent and water vapor removed from the film.

A diagram of the apparatus used is shown in Fig. 4, and Fig. 4a gives an enlarged view of the arrangement of the interior. The test piece, F, is clamped between the two clamps C_1C_2, the bottom clamp being fixed and the top one being free to slide up and down the guide rails R_1R_2 which are rigidly secured to the heavy base plate B, of the apparatus. Tension is applied to the film by the weights, W, acting over the frictionless pulley P and through the metal rod A. The elongations were measured by means of the traveling microscope M which was fitted with an $\times 7.5$ ocular and a 4 mm objective. The microscope was focused on the micrometer slide S the lines of which were ruled 100 to the millimeter, and was illuminated by a microscope lamp not shown in the diagram. For small rapid changes in the length of the test piece it was found convenient to observe the movement of the scale, leaving the microscope in a fixed position.

The temperature of the test piece was controlled by the use of the cylindrical cooling jacket J and the nichrome wire heating coil N the cork layer I serving as an insulator. The test piece was brought to the lower limit of the temperature interval to be investigated by circulating a cooling liquid through J. Wherever possible, this was done by circulating water from a constant temperature bath by means of a centrifugal pump, the liquid entering through O_1 and being forced out through O_2. During the experiments that were carried out at low temperatures, the circulating liquid was ethyl alcohol and

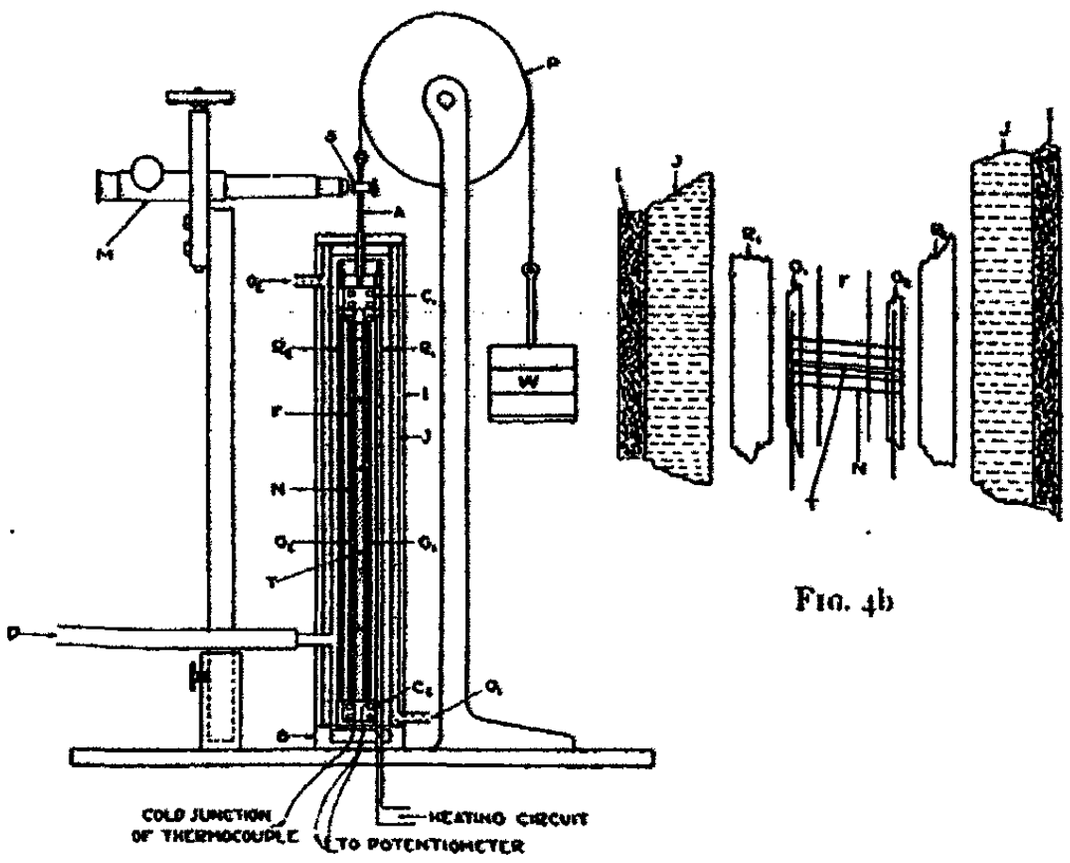

FIG. 4a

FIG. 4b

cooling was effected by passing the liquid through a copper coil immersed in a carbon dioxide-ether eutectic mixture. The temperature of the test piece was raised by passing an electric current through the nichrome coil N which was wound around the glass tubes G_1G_2. These tubes were attached to the inside of the guide rails at either end. The rate of heating could be controlled by a potentiometer in the heating circuit. In all the experiments described in this paper the potentiometer was so set that the temperature of the film was raised from 15 to 45° in 45 seconds. The cooling took somewhat longer, as it required about three minutes for the film to return to its original temperature; but during most of this time the film was only a few degrees above 15°, so the rate of flow was low. The temperature of the film being studied was measured by the five-element copper-constantan thermel T the junctions of which were placed inside the heating coil and were about 0.1 mm away from the film. The thermocouple leads were carried through the glass tubes G_1G_2 and out of the cylinder through a hole in the base. The ends of the thermel were connected to a Leeds and Northrup potentiometer temperature indicat-

ing instrument, and alternate junctions were kept in a tube immersed in an ice-water bath. This temperature measuring system was calibrated against a Bureau of Standards pentane thermometer.

The test piece was thoroughly evacuated at room temperature before being placed in the apparatus. It was then kept in an atmosphere of 0 per cent R.H. for fifteen hours before expansion measurements were attempted. Air was passed through two sulfuric acid scrubbing towers and into the apparatus at D. A constant head of dry air was thus maintained inside the apparatus which prevented the condensation of moisture at low temperatures.

Finally, the whole apparatus was mounted on a spring suspension hung from the roof rafters of the building to eliminate errors caused by vibration. Measurements were read on scales to 0.01 mm and estimated to 0.001 mm so that a change in length of 0.0005 per cent on a 20 cm test piece could be recorded.

Materials

All of the experiments described here were carried out on a single sample of cellulose nitrate film. The film was slightly biaxial[14] and the double refraction measurements made on the film are given in Table II.

TABLE II

Double Refraction of Cellulose Nitrate Test Sample

d = 0.15 mm

C Axis			B Axis		
θ	δ	δ/d	θ	δ	δ/d
0	+5	+13	0	+5	+33
10	+2	+13	10	+5	+33
20	0	0	20	+7	+46
30	−5	−33	30	+13	+87
40	−12	−80	40	+20	+133
50	−24	−160	50	+30	+200
60	−32	−210	60	+40	+266

Test pieces were cut from this film in the direction of coating so that tension was applied along the direction of stretch. The test pieces were cut exactly 0.50 cm wide by means of a slitting tool made with the two knife edges 0.50 cm apart. As mentioned above, the film was 0.15 mm thick and the original length of the unstrained test pieces between the grips was 21.20 cm.

Experimental Results

(1) *The Thermal Expansion of Cellulose Nitrate Film from 15 to 35°.*

A test piece of cellulose nitrate film was prepared and placed in the apparatus as described above. After the film had been in an atmosphere of dry air for fifteen hours, a tension of 200 grams (stress = 0.26 Kg/mm^2) was applied and the test piece was alternately heated to 40° and cooled until the retraction curve showed no hysteresis lag. This reversible effect is shown at

the lowest part of the curve in Figs. 5-7. The film was then judged to be dry and free from volatile solvents. The load was increased to 1000 grams (stress = 1.33 Kg/mm²), when the elongation measured increased by 0.22 per cent of the original length. As indicated by Figs. 5-7, heating and cooling curves show that at this stress, the film support is not perfectly elastic. The cooling curve maintains a very appreciable lag under the heating curve. As the extension and retraction cycle is repeated the difference between the elongation and retraction curves decreases until after the fifth cycle the two

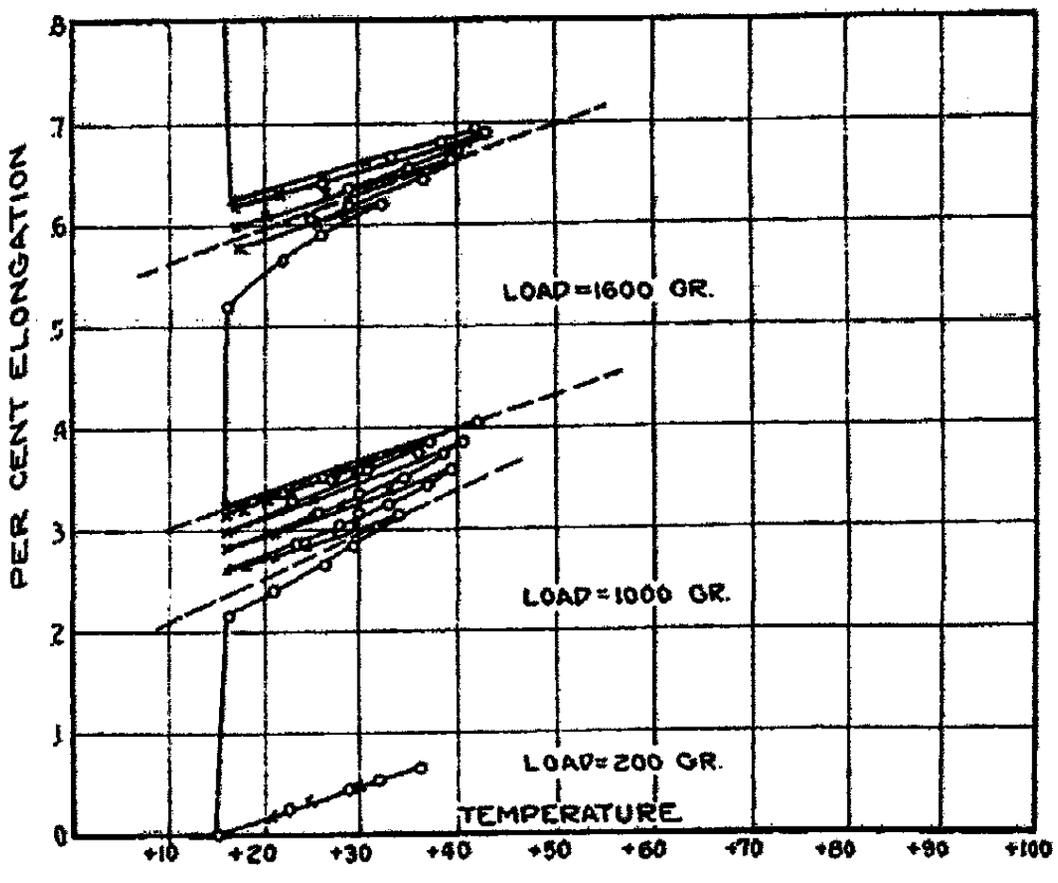

FIG. 5

curves practically coincide. If, now, the load be increased to 1600 grams (2.13 Kg/mm²) the initial hysteresis lag becomes more marked than was the case at lower stress and the form of the initial extension curve becomes concave with respect to the temperature ordinate. The curves again coincide after the cycle of extension and retraction has been repeated several times.

As the tension on the film support is increased, a progressive series of changes takes place in the thermal expansion curves. Referring again to Figs. 5-7, it will be seen that the initial heating curve remains concave with respect to the temperature axis but the successive heating curves become strongly convex in the region where the stress varies from 3.19 to 5.05 Kg/mm². At the same time the retraction curves become markedly convex so that over a large portion of this region of stress, the two sets of curves intersect each other. Above a stress of 2.1 Kg/mm², the divergence between the final lengths reached after extension and retraction does not become appreciably less on repeating the cycle. Finally, at a stress of 7.98 Kg/mm², the rate of plastic flow of the material was so great that it became impossible to measure temperature effects with any accuracy with the present type of apparatus.

The coefficient of thermal expansion of the support is a poorly defined quantity as it depends on the stress acting on the film and the rate at which the heating and cooling operations are carried out. Under the conditions of our experiments the latter factor may be neglected because the error in a single determination attributable to plastic flow is negligible. While the curves are not linear, the coefficient depends on temperature interval over which it is measured and it always depends on whether the extension or re-

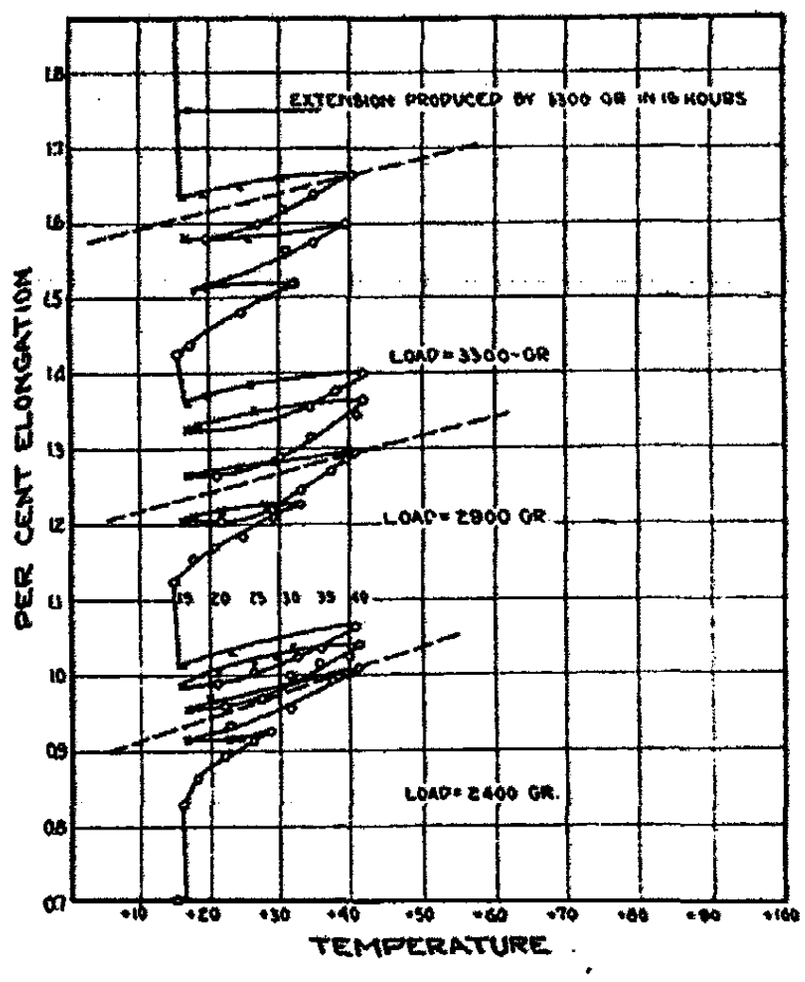

FIG. 6

traction of the film is used for the computation. An average value for the thermal coefficient of expansion for film support may be defined by the equation:

$$\alpha = \frac{L_1 - \frac{1}{2}(L_0 + L_2)}{(L_0)(T_1 - T_0)}$$

where α is coefficient of linear expansion, L_0 is the length of the test piece before expansion at temperature T_0; L_1 is the length to which the film expanded at the higher temperature, T_1, and L_2 is the length to which the test strip contracted at temperature T_0. The slopes from which the values of α were calculated are shown by dotted lines in Figs. 5 and 6. Table III shows the results of such calculations at different stresses.

TABLE III

The Linear Coefficient of Thermal Expansion for Cellulose Nitrate Film between 15 and 35°

Stress—Kg/mm²	$\alpha \times 10^{-5}$
1.33	4.38
2.13	3.43
3.19	3.00
3.86	2.43
4.49	2.20
5.05	2.14

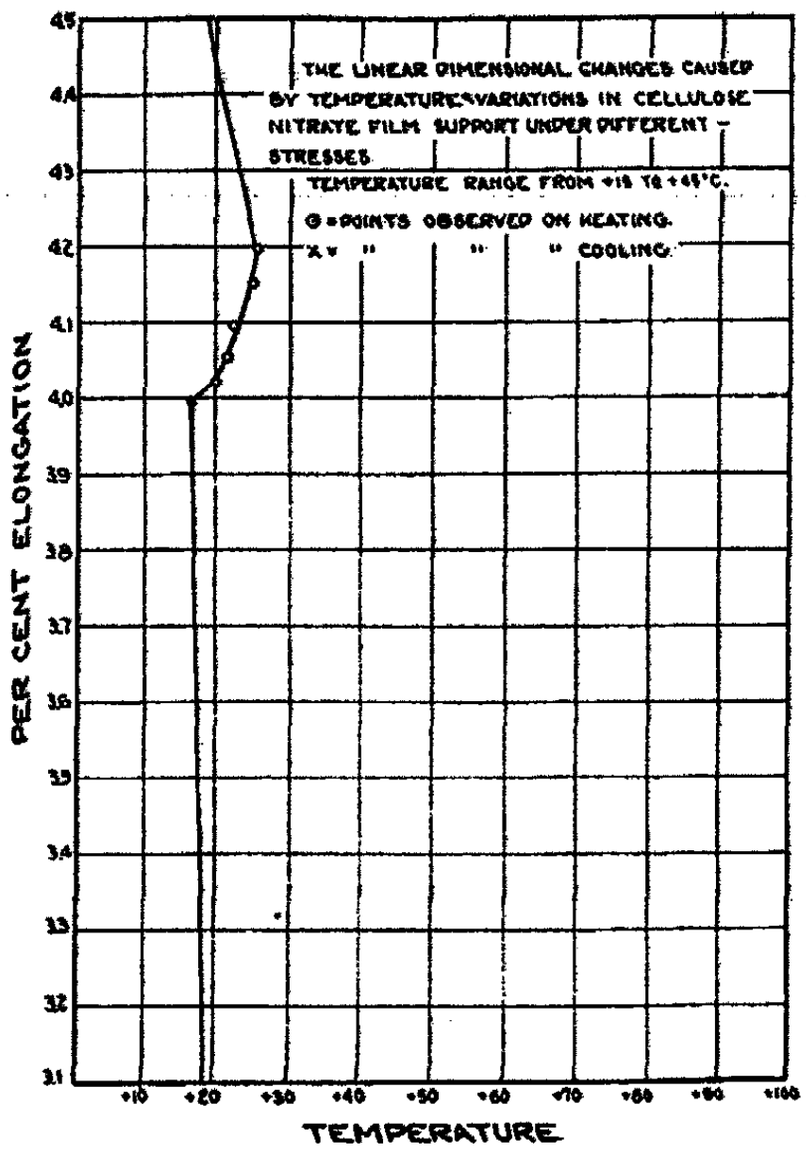

FIG. 7

The coefficient decreases progressively as the stress increases but the rate of decrease as shown by Fig. 8 decreases as the stress increases.

The influence of the previous treatment of the film on its coefficient of thermal expansion is shown in Figs. 5 and 6 by the decrease in the coefficient caused by successive elongations and retractions carried out at a constant stress. For example, at a stress of 1.33 Kg/mm², α equals 4.38×10^{-5} on the first extension-contraction cycle and 4.27×10^{-5} on the fifth. The stresses on the test pieces of the size used throughout these experiments are given on the next page, together with the corresponding load.

TABLE IV

Load—Kg.	Stress Kg/mm²	Load—Kg.	Stress Kg/mm²
0.2	0.266	2.9	3.85
0.4	0.52	3.0	3.99
1.0	1.33	3.3	4.39
1.6	2.33	3.8	5.05
2.0	2.86	6.0	7.98
2.4	3.19		

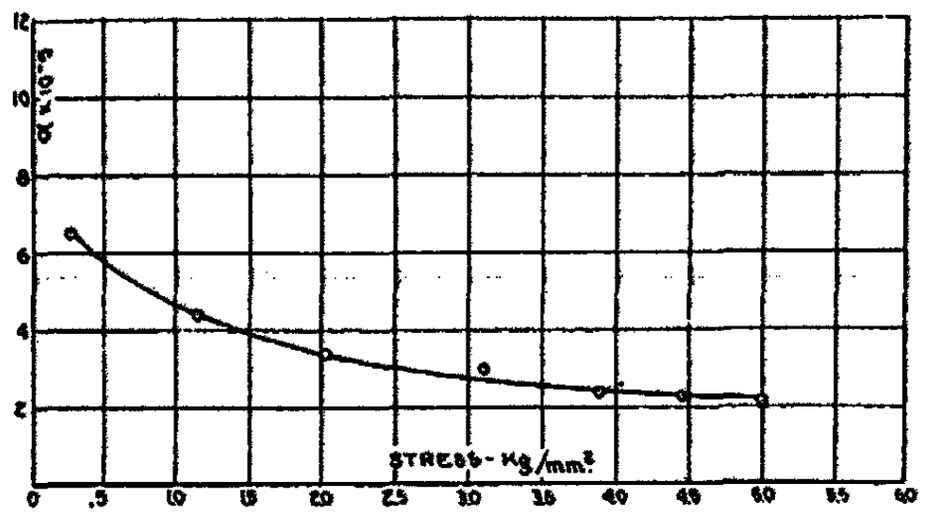

FIG. 8
The coefficient of thermal expansion of cellulose nitrate film support at different stresses. Temperature interval from +15 to +45°C.

(2) *The Thermal Expansion of Cellulose Nitrate from −10 to −35°.*

The above thermoelastic studies led to the conclusion that under the proper conditions, cellulose ester films should contract when heated. The flat portions of the extension curves in Figs. 5 and 6 are probably the resultant of two opposing tendencies of the film to change its length. The first is a plastic flow tending to increase the length of the sample and the second is an elastic contraction. When the two are equal, the net resultant observed is zero.

If the above explanation of the flat portions of the curves were correct, it should be true that at low temperatures, where the rate of plastic flow was decreased, a resultant contraction of film support could be observable when the temperature of the test sample is raised. Figures 9 and 10 show the thermal extension-contraction curves of cellulose nitrate under varying stresses over the temperature range from −10 to −35°. At low tensions while the film has undergone but little strain and is sensibly isotropic with respect to the lengthwise direction, the thermal extension is positive but it has a lower value than at higher temperatures. At a stress of 0.53 Kg/mm² between −27 and −12°, $\alpha = 2.5 \times 10^{-5}$. As the film becomes anisotropic from stretching at higher stresses, the initial effect of a rapid rise in temperature of the film is to cause a contraction of the film. The negative expansion coefficient is of the same order of magnitude as the positive one, being equal to -3.4×10^{-5} at a

stress of 1.33 Kg/mm². The initial contraction of the film support continues up to a stress of 5.0 Kg/mm². At higher stresses, plastic flow becomes rapid so that the effect can no longer be observed.

In the case of crystals belonging to an irregular system, α usually has very different values in different directions, calcite for example having $\alpha = +25 \times 10^{-6}$ parallel to the optic axis and -5×10^{-6} perpendicular to the axis. It seems not improbable, then, that the coefficient along and across an anisotropic film may be quite different. The values of α across certain biaxial films may be many times the values given here.

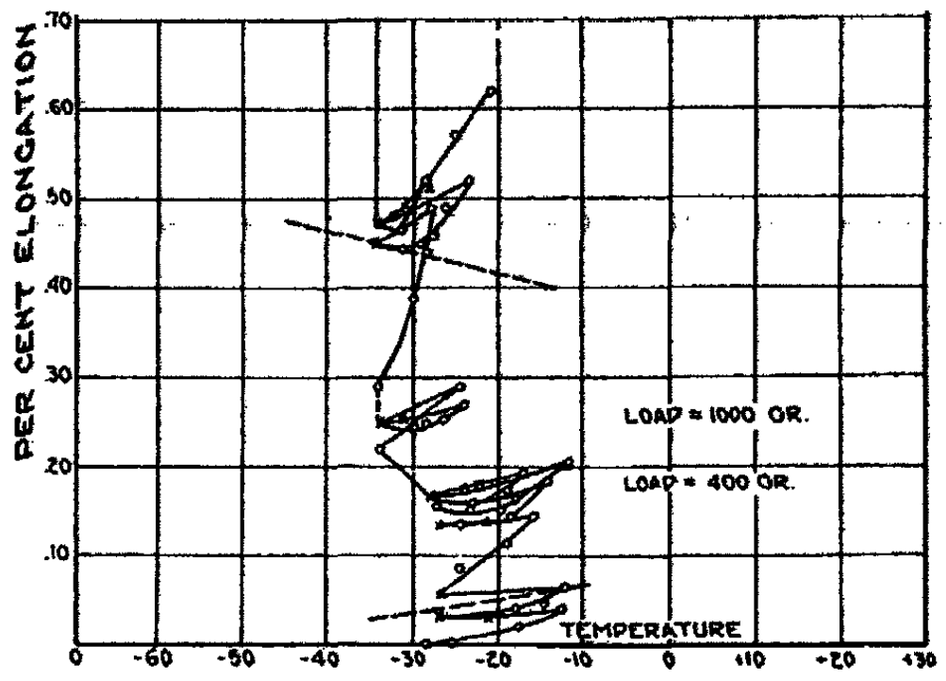

FIG. 9

The linear dimensional changes caused by temperature variations in cellulose nitrate film support under different stresses. Temperature range from −15° to −35°C.
⊙ = points observed on heating
X = points observed on cooling

Summary and Conclusions

Cellulose acetate and nitrate films that have not been subjected to large stresses on drying, cool when extended to small elongations but become warm if the extension is prolonged beyond the yield point of the material. If the structure of the film is altered by drying the film under large stresses, the region of strain corresponding to the exothermic reaction disappears. Coagulated films containing large amounts of solvent showed the same thermal behavior on stretching as the dry film, although the stress-strain relations were totally different.

The thermal coefficient of expansion of cellulose nitrate is a poorly defined quantity which depends on the stress on the material, the previous mechanical and thermal history of the sample and the temperature range over which the thermal expanison is measured. At low temperatures and at moderate stresses a negative thermal expansion was observed which is analagous to the Joule effect in rubber.

From this evidence it may be reasoned that the predominating structural alteration taking place in the film while being stretched is different in the different regions of the stress-strain curve. Possibly the cooling effect is associated with an increase in the potential energy of the micellar structure caused by an increase in the mean distance between attraction centers of the component units, this effect predominating at low strains. The exothermic change may then be evidence of mechanical dissipation of energy by internal

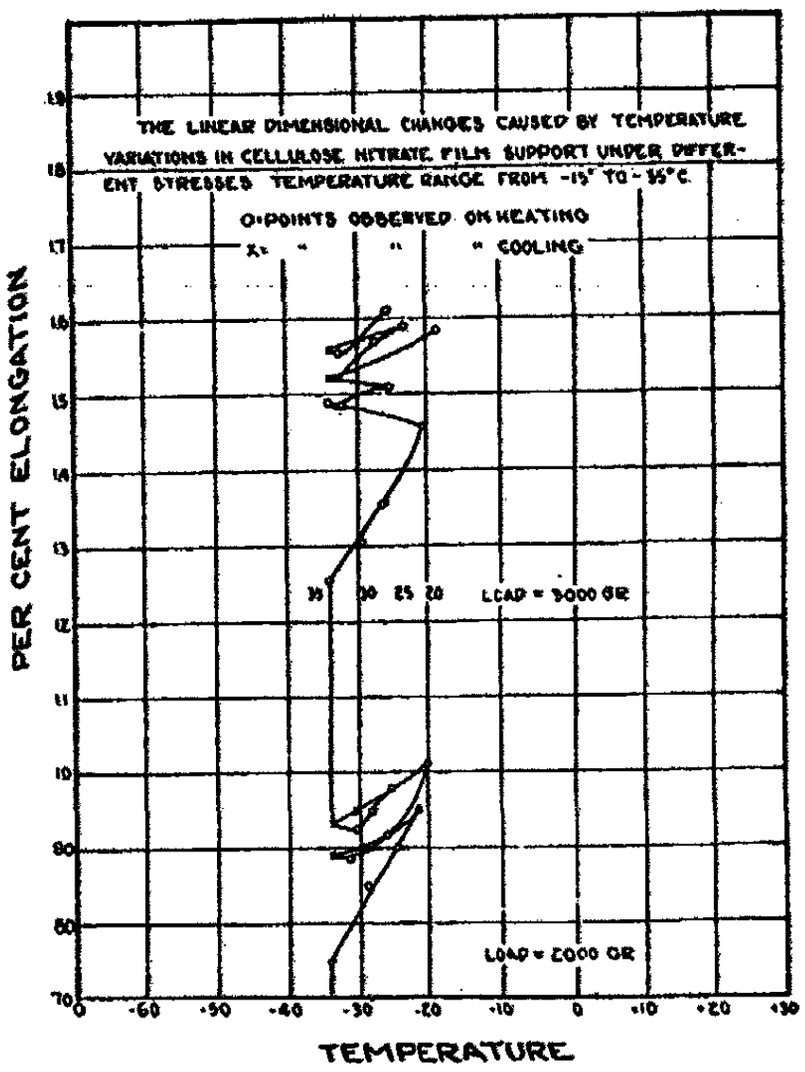

FIG. 10

friction in the film or a further structural change which results in a space lattice arrangement of the cellulose ester molecules and produces a thermal effect akin to a heat of crystallization as has been discussed recently in the case of rubber.[18] At any rate, the existence of the anomalous Joule effect in a dry, solvent-free cellulose ester film proves that the effect is not *a priori* evidence of a two-phase structure of the colloid, as has been suggested in the case of rubber.[19] It is also inconsistent with Wo. Ostwald's[20] explanation of

[18] Hock: Kolloid-Z., 37, 19 (1925); Katz: 36, 300 (1925).
[19] Freundlich and Hauser: Kolloid-Z., 36, 15 (1925).
[20] Kolloid-Z., 40, 58 (1926).

the structural change in rubber on stretching. Ostwald attributes the appearance of a "fiber diagram" to the deformation of a preëxisting mesh or network structure in the sheaths of the latex particles. But, the parallel behavior of gelatin and cellulose esters on stretching, in approaching to or developing "fiber diagrams", makes this hypothesis unnecessary and inadequate, since the gelatin and cellulose ester films may be prepared from solutions containing only amicroscopic particles. And that is also the case with rubber from Feuchter's D-rubber (or diffused rubber sol).

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A METHOD FOR MEASURING AVERAGE PARTICLE SIZE OF EMULSIONS

BY WHEELER P. DAVEY

Experiment shows that if a drop of an oil-in-water emulsion is allowed to fall into clean water with such force as to break through the water surface the original drop of emulsion will retain its identity for some time, diffusing only slowly into the body of the water. If, however, it is deposited gently on the surface of the water without making a splash, it will spread on the water like an oil.[1] The spreading takes place with extreme rapidity and may be considered to be a two-dimensional explosion. If we assume that the layer on the surface is one particle thick and that the droplets of the disperse phase are small enough in diameter to hold a spherical shape, then the average diameter of the droplets may be measured by the apparatus which Langmuir [2] used for measuring the length of oil molecules. Trial shows that, if all other conditions of the experiment are kept constant, successive measurements of the same emulsion at different concentrations which are still of the same order of magnitude are consistent with each other and are independent of the quantity of emulsion used.

The technique of the measurement is obviously as follows. An enamelled iron tray about eight inches wide, thirty inches long and about one-fourth inch deep is filled with water. A piece of paraffined aluminum foil is floated on the surface at one end of the tray and attached to a balance such as was used by Langmuir, or to a torsion wire such as is used in the Du Nouy apparatus. The spaces between the walls of the tray and the ends of the aluminum float are sealed by constant pressure air jets. The rest of the water surface is then swept free of monomolecular layers of grease, oil, etc. by means of glass sweepers, and a drop of the emulsion is spread on this clean surface from a micrometer pipette. The area of the film is determined exactly as in Langmuir's experiments with oil films.

The calculation of particle size requires a knowledge of the total volume of the droplets of the disperse phase *as they exist in the emulsion*. Although in many cases this volume is practically the same as that of the same mass of undispersed material, it cannot be assumed that this must always be the case. The volume may be obtained by curdling a known volume of emulsion with a known volume of a solution of a suitable electrolyte, removing any included water from the curd and adding it to the rest of the water phase. The total volume of the water phase is then measured and the volume of the disperse phase is found by difference. This gives at once the concentration C of the

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[1] Davey: Science, 64, 252 (1926).

[2] Langmuir: Proc. Nat. Acad. Sci., 3, 251 (1917).

emulsion. If V is the volume of the drop of emulsion which was spread on the water, then CV is the volume of the disperse phase in that drop. The mean diameter of the particles of disperse phase is therefore

$$d = \frac{C\,V}{A}$$

where A is the area which was covered.

The method is subject to the following limitations:

(1) The emulsion must not be so concentrated that it cannot be diluted by the simple addition of water at room temperature without vigorous stirring.

(2) The emulsion must not be so dilute that it cannot always present to the water on which it is spread a substantially continuous surface of disperse phase.

(3) The water on which the emulsion is spread must be neutral[3] (pH = 7). This condition should ordinarily be met even if it be necessary to add a buffer to the water and later make the necessary corrections as outlined below.

(4) The restoring force on the aluminum float must be very small if uncertainties in the calculated particle size are to be avoided. These four restrictions will be discussed in order.

(1) This restriction makes it impossible to use the method for determining the size of aggregates of disperse phase in concentrated emulsions which are almost ready to gel. It is obvious that the method requires the emulsion to be dilute enough so that each droplet of disperse phase can float on the water surface without being tied up with any other droplet. The method is, therefore, best adapted to measuing the size of the ultimate droplets of disperse phase. This limitation on concentration is not only due to the properties of the emulsion itself, but is due also to the practical consideration that only a small volume of disperse phase can be spread on a water surface of convenient size. The accurate measurement of the volume of disperse phase requires, of course, considerable dilution.

(2) The probable mechanism of the water-spreading of emulsions is of considerable interest. We are at first sight tempted to consider a hanging drop of an emulsion as being surrounded by a sort of bag of oriented molecules of free emulsifying agent. Such a picture may be true in some cases, but in the cases with which the writer has worked, it is hard to see why, on the basis of such a picture, the drop retains its identity when it hits the water with such force that it goes below the surface. It seems simpler to assume that at least a large part of the surface of the drop is covered with a monoparticle layer of disperse phase. This layer would correspond to the membrane around a living cell. Its existence on the surface of the drop would be consistent with the water-spreading phenomenon of emulsions which forms the basis of the method described in this paper. If such a picture is adopted, it follows that the concentration of the emulsion must be such that, as the drop flattens out on the water surface, there will be a constantly available supply

[3] Weeks: Phys. Rev., 35, 668, (1930); See also Weeks theses for M.S. degree, The Pennsylvania State College.

of disperse phase to keep the surface completely coated. Otherwise, droplets of disperse phase would find their way into the body of the water in the tray and the measurements of particle size would not be substantially independent of concentration. It should be noted that we have dealt with extremes of concentration in (1) and (2). It is not intended to imply that our measurements of average particle size are independent of the tendency for particles of disperse phase to become aggregated as the concentration is increased.

(3) When particle-size measurements are made on water whose pH is kept at 7, the area covered by the emulsion is constant with time. If the pH of the water is greater than 7, the area covered by the emulsion (after subtracting the area covered by buffer in the same time) approaches its final value slowly, and the final value is larger than when it is measured at pH = 7. The effect is what might be expected if we assumed the extra alkali to saponify some free acid in the disperse phase, thus causing the average particle size of the disperse phase to become smaller. Besides, the soap molecules thus formed being smaller than the original particles of disperse phase, would tend to lower the average particle size. When the pH is less than 7, the area covered by the emulsion increases with time without reaching an equilibrium value, so that the disperse phase acts like a two-dimensional gas just above its critical temperature.

(4) The monoparticle layer of disperse phase floating on the surface of the water in the tray can hardly be expected to be as rigid as a corresponding monomolecular layer of a fatty acid. Excessive horizontal pressure on the layer may be expected to crumple the layer rather easily, thus giving a layer which, in some portions at least, would be more than one particle thick. For this reason, the force-area curves for emulsions do not show as sharp a point on inflection (Langmuir's S point) as is shown by fatty acids and soaps. This introduces some error in the final calculated size. Since (3) implies that the restoring force on the aluminum float lies in the optimum range for pH = 7, it is recommended that this pH be used even if it is necessary to add a buffer to the water in the tray and then correct for whatever buffer material may be adsorbed on the water surface.

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THE SPIERER LENS AND WHAT IT REVEALS IN CELLULOSE AND PROTOPLASM

BY WILLIAM SEIFRIZ

The Spierer Lens

Charles Spierer, Swiss physicist, has devised a lens for ultramicroscopic observation[1] which involves the principle that light scattered by colloidal matter is greatest in the direction of the illuminating ray (Fig. 1). It would naturally be of advantage to view matter against a dark field yet toward the source of illumination. It was Spierer's task to accomplish this. He did it by placing a small mirror in the lens system of an oil-immersion objective (Fig. 2). The illuminating rays come directly from below as in an ordinary microscope; consequently, that part of the scattered light which is of greatest intensity is toward the observer. The small mirror in the objective gives the dark field.

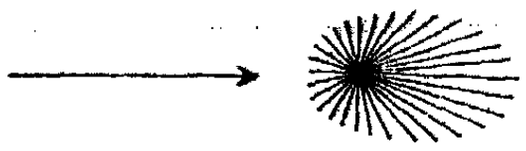

FIG. 1
The ellipse of scattered light from a colloidal particle.

The principle involves two primary prerequisites; first, the mirror must reflect all of the direct light, second; the mirror must be smaller than the lens aperture, in order to leave room for the scattered rays from the object to enter. The first prerequisite is accomplished by having the aperture of the substage diaphragm at least as small as the mirror; in practice this is 1.5 mm.

The mirror may be of gold, silver, platinum, or aluminum. In the experimental stage, and later when Spierer lenses were made by Nachet of Paris, the mirror was a piece of gold or aluminum foil placed between the lenses of the objective. The method now employed, by Zeiss, is that of electric deposition. The lens is placed behind the opening of a screen situated near the anode of a cathode tube at the opposite end of which is a cathode of platinum; the opening in the screen is of the size the mirror is to be. Platinum cathode rays are given off and deposited on the exposed surface of the lens.

Aluminum is fully opaque and gives a perfectly black field. Gold or platinum have some transparency and permit a little of the direct light to pass which is an advantage at times. The gold mirror gives a dark-green field and the platinum mirror a gray field.

The Spierer lens is an oil-immersion objective of 1.25 aperture (1/12 inch = 2.12 mm). It is provided with an adjustable iris which is useful in that it allows the observer to keep off part of the diffracted light when the diffraction phenomena are too intense and give a blurred image. (This intensity depends upon the nature of the object and of the embedding medium.) It is necessary to close this iris partially when using the latteral illumination of a cardioid condenser, otherwise the field is not suffieiently dark.

[1] Arch. sci. phys. nat., 8, 121 (1926).

It is sometimes of advantage to use a cardioid (dark-field) condenser in conjunction with the Spierer lens; this is not, however, necessary since the Spierer lens is itself a "dark-field," and gives very satisfactory results with an Abbe condenser, or none at all. The advantage of a cardioid condenser, when used in addition to the Spierer lens, lies in the fact that it increases the

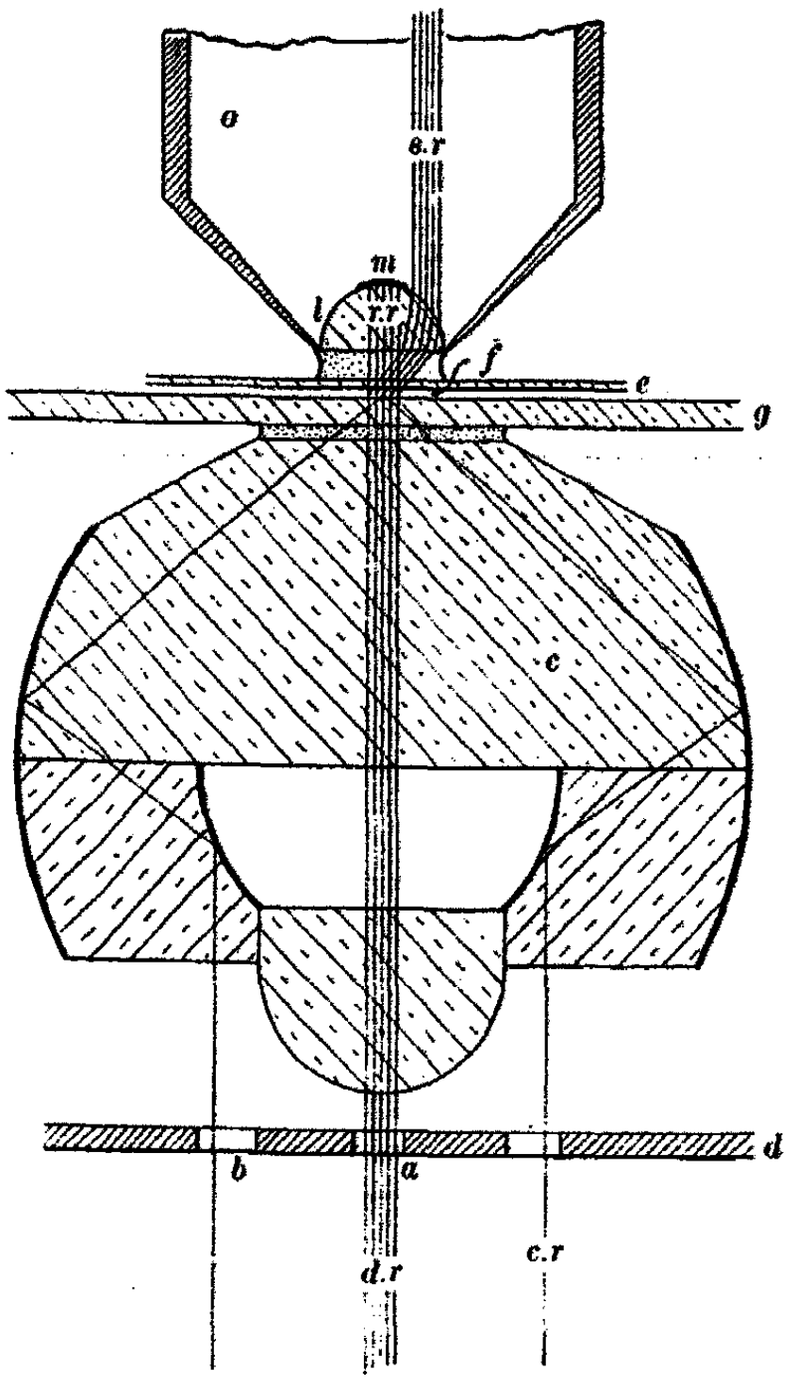

FIG. 2

The Spierer lens and special (Zeiss-Spierer) cardioid condenser: o = microscope objective; l = lower lens of the oil-immersion system; m = platinum (Spierer) mirror; $r.r.$ = reflected rays from the (Spierer) mirror, e = cover-slip, f = colloidal material; g = slide; c = cardioid condenser; d = special fixed diagraphm; a = 1.5 mm aperture for direct light, $d.r.$, to Spierer lens; b = slit for cardioid rays, $c.r.$

illumination of the colloidal structure by adding its share of scattered rays, which help though they do not come from the region of maximum dispersion as do those produced by the Spierer lens.

Spierer has combined in a special condenser the parts necessary for using the cardioid with his lens (Fig. 2). The condenser c contains the usual car-

dioid elements and in addition a fixed diaphragm *d* with a permanent aperture *a* of the desired size. This arrangement also gives perfect alignment of the illuminating ray, an important condition for the Spierer lens. The condenser possesses a movable disk which obstructs or leaves open the aperture. With the disk in the center, *i.e.*, the aperture closed, no direct rays pass through the condenser to the objective; the cardioid alone is then in use and the Spierer lens functions like any oil-immersion objective. With the disk aside, direct rays pass to both the cardioid system and the Spierer lens.

To use the Spierer lens alone, the iris diaphragm, which is part of the microscope substage and is situated below the condenser, must be closed enough to allow no light to strike the reflecting surface of the cardiod system; the small aperture in the fixed diaphragm of the condenser remains open to permit the vertical illumination to reach the Spierer lens. A simpler way, however, to use the Spierer lens alone as a dark-field lens, is to replace the special condenser by an ordinary Abbe one.

The soundness of the theory on which the Spierer lens is built is proven by the results obtained. Spierer[1] has observed a fine granular structure in dry collodion which is not revealed by any other type of optical system. The cellulose and protoplasmic structure to be told of here is also not to be seen except with the Spierer lens.

There can be no doubt that this new optical system of Charles Spierer will bring a finer structure to view than we have yet been able to see in many materials.

There are substances in which no more, in some instances less, can be seen with the Spierer lens than with the ordinary dark-field condenser. This is likely to be true where the index of refraction of the material investigated is sufficiently different from that of the surrounding medium to give pronounced optical contrast; where the surrounding medium is of nearly the same index of refraction as is the object viewed, then the Spierer lens reveals contrast and structure not visible by any other lens or system of illumination. For example, *Pleurosigma angulatum* has an index of refraction of 1.6 (that of silica); when this diatom is mounted in water (index = 1) its structure is fully visible, but when it is mounted in cedar oil, the index of refraction of which is 1.5, nothing is to be seen with ordinary illumination except the periphery. Lateral illumination (cardioid condenser) brings out considerable structure but leaves part of the diatom blank and the rest unclear; the Spierer lens reveals a much clearer structure and shows it throughout the diatom. The index of refraction of water is very close in value to that of cellulose and protoplasm; the Spierer lens should, therefore, show more of the structure of these substances than do other optical systems.

The success of work with the Spierer lens is to a great degree dependent on the nature of the medium in which the material to be studied is mounted. It is well to try air, water, glycerin, balsam, and other media before giving up, though often one is as good as another.

There is another important difference between the Spierer lens and the usual cardioid type of ultramicroscope; this is the distinction between what is light and what is dark in the two cases. If we view a bacterium with a cardioid condenser, only the edges of the minute object are bright; the interior, the bacterium itself, is dark. The same object viewed with the Spierer lens reverses things, the edges are dark and the bacterium light(since the material is transparent); in other words, the Spierer lens gives, in a sense, a "Roentgenogram" of the *interior*, while the cardioid only *illuminates* the object, giving a "photogram" of the whole.

Experimental

The observations to be reported here are restricted to the cellulose walls of the dead pith cells of *Sambucus* (elder), the dead and living epidermal leaf-cells of *Allium* (onion), the stalk of *Apium* (celery), and the protoplasm of

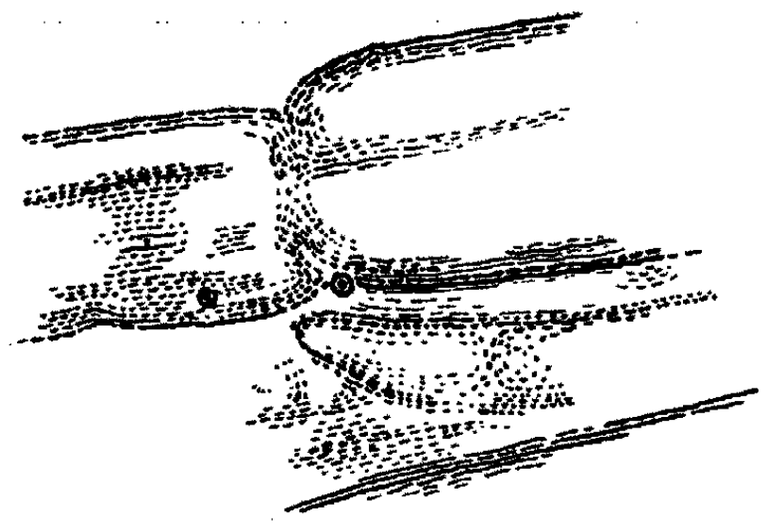

FIG. 3

Cellulose wall of dead elder pith cells showing end-to-end orientation of linear micelles in parallel striae, surface view.

the living cells of *Allium*. Some of the results were obtained in cooperation with Mr. Spierer in his laboratory in Geneva. I am greatly indebted to him for his technical assistance and continued interest in my work which involves the use of his lens.

Since writing the first draft of the manuscript of this article I have learned from Mr. Spierer that he too has continued our first investigations on the cellulose walls of plant cells, and obtains confirming results on such other material as the leaves of *Cichorium* and *Plantago*. With Mr. Spierer's kind permission I shall incorporate some of his findings in with our original and my recent ones.

Cellulose. The ultramicroscopic[2] structure of the cellulose walls of both dead and living plant cells is characterized by linear arrangement and discontinuity (Figs. 3 and 6). The linear arrangement is of parallel striae; the discontinuity is due to the presence of small rod-shaped particles oriented end-to-end (Figs. 3, 5, 6, and 9). The striae usually run parallel to each

[2] In this article I shall use the word ultramicroscopic simply to mean what is seen with the Spierer lens or other dark-field system without reference to size of structural units.

FIG. 4

Cellulose (parallel lines, upper right), protoplasm (broken lines, lower left), and nucleus (spotted circle) of living onion cell (nucleus is 20μ across).

other with only occasional irregularities. The general arrangement of the striae is often strikingly symmetrical (Figs. 7 and 8). At times, the striae run at right angles to or even cut diagonally across each other.

There is little difference to be seen in the ultramicroscopic structure of the epidermal walls of elder, onion, and celery, nor does it matter (as regards structure) whether the material is mounted in balsam (Fig. 3), in water (Fig. 4), or in air (Fig. 7). In some instances, the discontinuity of the striae, *i.e.*,

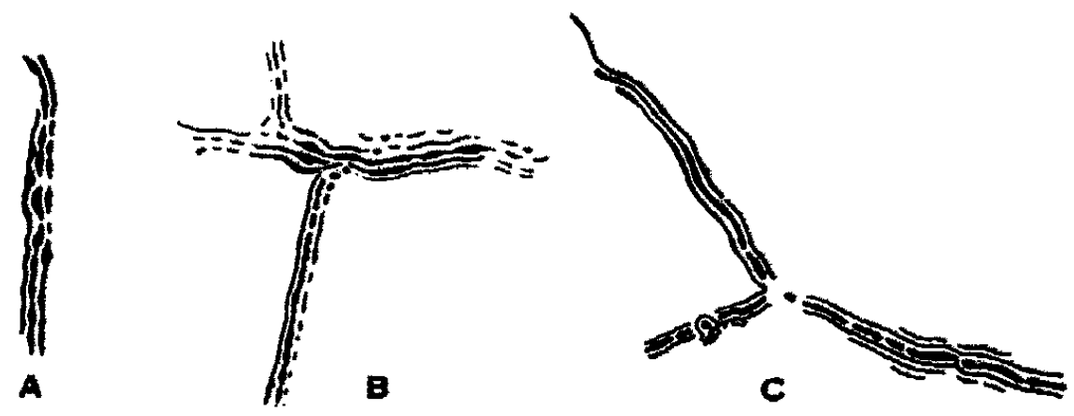

FIG. 5

Detail drawings of cellulose structure showing micelles and striae: A. from cell wall shown in Fig. 3 (elder), B. from cell wall shown in Fig. 4, C. optical transverse section of vertical walls at junction of three cells in onion epidermis (see Photo. 2 for same view with dimensions).

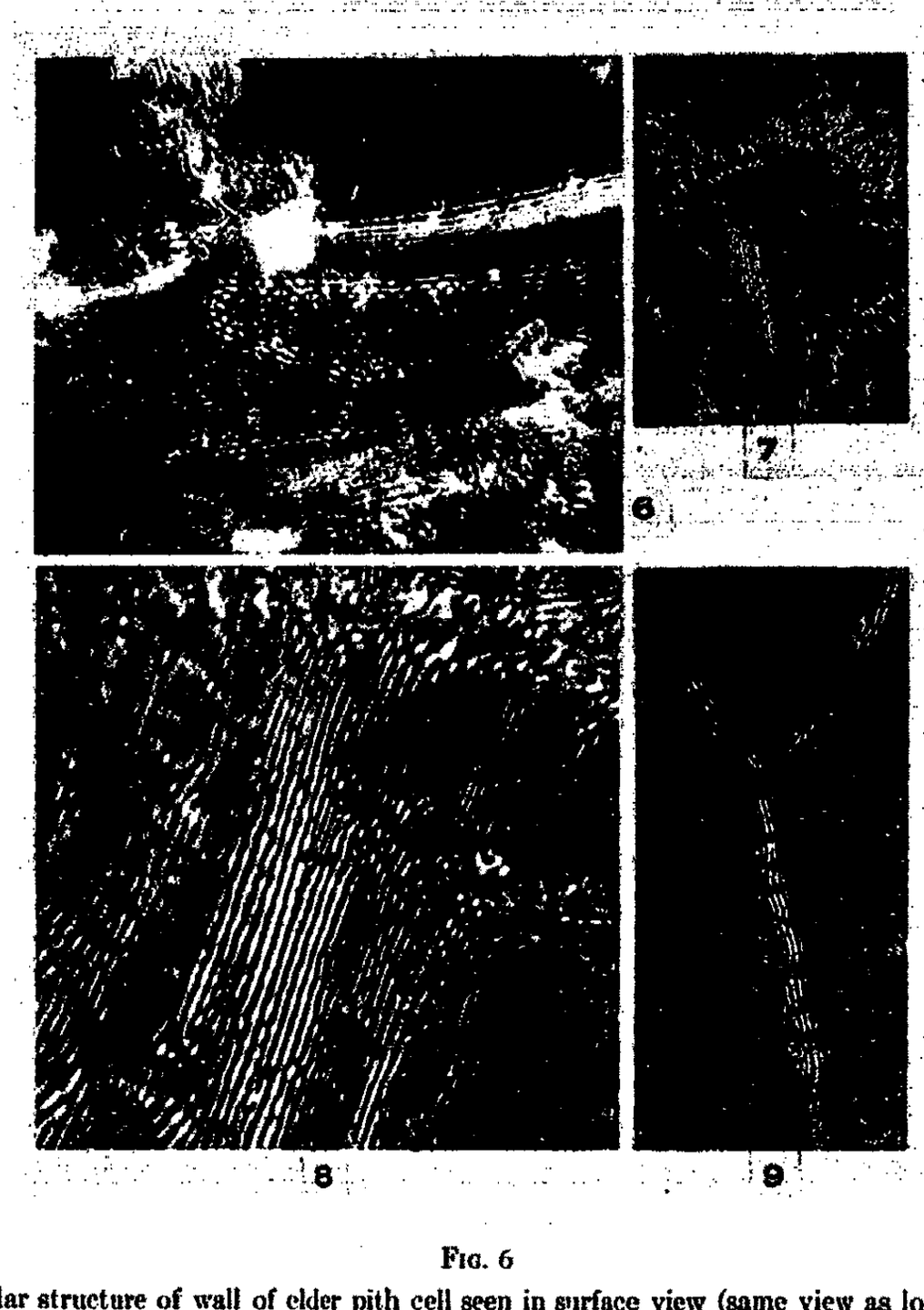

FIG. 6

Micellar structure of wall of elder pith cell seen in surface view (same view as lower half drawing, Fig. 3.)

FIG. 7

Striated structure of the dry cellulose wall of a dead onion cell, surface view.

FIG. 8

Parallel striations of cellulose wall of onion cell, surface view: note lobbed appearance of striae, the result of a micellar structure which is here less marked than in Fig. 6.

FIG. 9

Detail of transverse optical section of vertical walls at junction of three onion cells: the first rod (compound micelle) from the junction in the tail of the "Y", is 5μ, the second, 3μ, and the third 2.3μ long; the total thickness of a vertical wall, consisting of four striae, is 3μ (see Fig. 5c for drawing of this same view)

the presence of short rods in the cellulose, is lacking (Figs. 7 and 8), though often the same cell may show continuous striae in one region (Fig. 4) and discontinuous ones in another region (Fig. 5, c). Furthermore, though separate rods are sometimes not present and the striae are unbroken lines, yet such striae are nearly always lobbed or undulating, as if built of distinct particles (Fig. 8).

The striae average from 0.5 to 0.7μ in thickness. The rod-shaped particles which build up the striae, vary in size, though they average rather close to 1 or 2μ in length; some, however, are two or three times this size, and some are no longer than broad (0.7μ). The longer ones are probably, like the long unbroken striae, built up of several unit particles. The 1μ rod-shaped units are not of the order of magnitude which Nägeli had in mind when he gave us the term micellae. The units of these stiae are super-micelles.

A striated appearance in the cellulose walls of plant cells is no new observation. Strasburger[3] in 1882, pictured fine striations in the walls of plant cells. These markings are visible with an oil-immersion lens and direct illumination. They have long been believed to be due to the rhythmic deposition of cellulose by protoplasm. These linear markings seen by earlier workers may be comparable to the striations described here but they, first, lack the discontinuous feature, and second, have been described for transverse optical sections of *vertical* walls and not for the *surface* view of *horizontal* walls. There are, however, parallel markings to be seen on the surface of cell walls when viewed with ordinary, direct, illumination. These are quite another thing; they are twice as coarse as are the striae seen with the Spierer lens. Spierer, in his continuation of our original joint work, has paid special attention to the distinction between the coarser microscopic striations and the finer "ultramicroscopic" ones. I shall, therefore, quote, in part, from him (which is done with his kind permission).

It is possible to pull the epidermis of plant tissue off in such a way so as to have only a single layer of cellulose, *i.e.*, the upper wall of the epidermal cells. This cellulose membrane Spierer macerated for six months in water, sometimes slightly alkaline, sometimes slightly acid, and sometimes neutral. It was thus freed entirely from cytoplasmic residues. The membrane was also, in some cases, boiled. In every instance a structure composed of long super-micelles was to be seen with the Spierer lens, but with no other system. The markings which are visible with direct illumination have nothing to do with the intimate structure of cellulose. These coarser markings result, apparently, from a very fine folding (undulation) of the membrane. As a rule, they are transversal, (*viz.*, perpendicular to the large axis of the cell), and if a pull is exerted on the membrane, these markings disappear entirely, or take the opposite direction, becoming longitudinal on account of the pull. The true micellar structure does not disappear when the membrane is stretched. When the membrane is examined carefully by changing the adjustment of the Spierer lens, the folds are recognized separately from the micellar striae.

[3] "Zellhäute" (1882).

Question naturally arises over the actuality of these striae and rods, as, indeed, of any structure "seen" with dark-field illumination; thus, Fierz-David[4] working with a cardioid condenser, finds a "parallel" structure in artificial silk (cellulose) and natural silk. He observed a granular appearance in one of his preparations and frankly states that he regards it as not real but as an optical artifact. One cannot get an artifact without something to get it from; while of course, this does not preclude having artifacts, yet one should not be too ready to disregard them but rather be prepared to interpret them.

First, in regard to the striae, the evident criticism here is that these are diffraction lines. Observations on living protoplasm, where the striae are in motion, clearly oppose such a criticism. Furthermore, diffraction rings occur at the edges of objects; the ultramicroscopic striae of cellulose cover the surface. The following test finally eliminates diffraction phenomena as the cause of the observed striae.

The Spierer lens contains an adjustable iris; diffraction lines are eliminated when the iris is closed. In the classical test object, the diatom, *Pleurosigma*, all detailed structure disappears when the iris is closed (the *Pleurosigma* surface and contours remain visible from diffused light); the observable *Pleurosigma* structure depends, therefore, mainly on diffraction effects. The striated cellulose structure in plant cell walls, remains unaffected when the lens iris is closed, proving that this structure is not entirely dependent on diffraction but is and remains visible by diffused light.

As for the structural units of the striae, the super-micelles, continued study of them under differing conditions leaves little doubt of their reality. Cellulose would not show optical discontinuity without a structural background which possesses certain discontinuous features. Also, I find it difficult by any change in illumination to eliminate the very marked broken appearance of the parallel striations; nor does focusing up and down reveal a structure of which the rods might be the "cut" ends. Personally, I do not doubt but that the discontinuity in structure shown by the Spierer lens is a real picture of the ultramicroscopic structure of the cellulose of plant cell walls.

It was my intention to compare photomicrographs of the same material taken, first with direct illumination, then with the cardioid condenser, and then with the Spierer lens, but the picture which direct light gives with an oil-immersion lens is so pale, and the structure to be seen with the cardioid condenser so blurred when compared with the beautifully clear-cut picture given by the Spierer lens, that photographic comparison would be useless. I can, however, state with emphasis that the micellar structure pictured in the illustrations of this article are not to be seen with ordinary (direct) illumination, nor with the cardioid condenser, but only with the Spierer lens.

Protoplasm. While observing the cellulose walls of living plant cells, I often found it difficult to tell whether the lens was focused on wall or inner protoplasm. This was difficult chiefly because the protoplasm seemed to have essentially the same type of structure as the cellulose walls. How

[4] Naturwissenschaften, 17, 703 (1929).

marked the resemblance may be is to be seen from Fig. 3 of cellulose and the lower half of Fig. 4 of protoplasm. The difficulty of distinguishing protoplasm from cellulose can be overcome by macerating the tissue and ridding it of protoplasm, as did Spierer, or by plasmolyzing the cells (protoplasts), that is to say, causing the protoplasm to shrink away from the cell walls by dehydrating it in a hypertonic solution. This will leave part of the cellulose walls free from protoplasm.

Partially surrounding the nucleus (the large sphere in the center of Fig. 4) are concentric layers of cytoplasm, each built up of short rod-shaped particles. This is protoplasmic material. Where the protoplasm is stretched into strands—protoplasm often forms strands within a cell extending from wall to wall or from the nucleus to all the walls—the linear orientation of the rodlets is very pronounced (Fig. 4, below the nucleus), so much so that it is difficult, on the basis of structure alone, to distinguish a protoplasmic strand from cellulose.

The nuclear material (Fig. 4) shows no linear orientation of structural units; we have to do here with a fine emulsion.

The linear arrangement of rods in living protoplasm is, under favorable conditions, very marked. The rods are light gray in color (translucent) and the background black. The linear masses are separated from each other by distances shorter than their length, as in cellulose, and they retain their relative positions, even while the protoplasm is streaming.

The question, What fills the interstices of a group of micelles? has been considered by chemists in relation to cellulose, but, I believe, not definitely answered. The same question arises in the case of protoplasm, but here it is more easily answered, and with more certainty, though perhaps with no more satisfaction to the chemist. The black and optically structureless background, which constitutes, in a sense, the dispersion medium of the visible rod-shaped particles, is one of the constituents of the complex mixture which we call protoplasm. Indeed, of these two main components, the visible gray rods and the invisible black substratum, the latter is probably of primary importance. I believe this to be true because foreign globules (of fat) are carried by the ground substance quite independent of the visible rods. Scarth[5] supports this in stating that only a portion of protoplasm moves (by which he must mean that only a portion exhibits *active* movement). The rods, revealed by the Spierer lens, move, as do foreign globules also, but their motion is a passive one; they are carried by the active component, the black optically empty background.

As in cellulose, the discontinuous character of the protoplasmic striae is not always evident. The parallel lines are often continuous, but only in quiescent protoplasm. Whether this, as in cellulose, is a true structural feature, *i.e.*, the semi-fluid protoplasmic rods have fused, or an optical impression, cannot be definitely said.

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[5] Protoplasma, 2, 189 (1927).

We have, then, two main constituents of protoplasm, when viewed with the Spierer lens, the one, bright illuminated rods, oriented end-to-end in parallel lines; the other, an optically structureless material filling in the interstices of the rods. Perhaps these two materials are comparable to Strasburger's distinction between *trophoplasm*, the less active nutritive component, and *kinoplasm*, the active, irritable component.

We are still much in the dark over the ultramicroscopic structure of protoplasm, and I hesitate to compare too closely the rods seen in protoplasm with those seen in cellulose. In form and general appearance, they are almost identical, but in cellulose they are apparently the primary component (the nature of the intermicellar substance in cellulose being in doubt), while in protoplasm the rods are very likely of secondary importance. We must, however, grant that the remarkable similarity in the structure of protoplasm and of cellulose in living plant cells, as revealed by the Spierer lens, is a very striking one.

Discussion

Historical. Nägeli, in 1864, advanced the hypothesis that the structural units of cellulose cell walls are linear, anisotropic, crystalline micelles. This hypothesis, which was extended to include other colloidal systems of the lyophilic (gelatin) type, has been critized and discarded from time to time; it is probably not applicable to all lyophiles. As for cellulose, the Nägeli hypothesis is substantiated by the investigations presented here.

Full support of both the micellar and the striated structure of the cellulose walls of plant cells as revealed by the Spierer lens, is to be found in a brief survey of the literature.

As for the striae, in addition to the findings of Strasburger[3] and Fierz-David[4] already referred to, Anderson,[6] working more on the chemical side, finds that the outer wall of the epidermis of plant tissues is built up of alternate layers of cellulose and pectin.

The prevailing botanical opinion, that the lamellae of plant cell walls are the result of a rhythmic deposition of cellulose by the protoplasm, may explain the presence of certain layers composing the walls of cells. I would rather not question too critically so old a botanical hypothesis which may be true in part; however, rhythmic deposition is not the cause of the striae illustrated here. It cannot be, since the striated structure is as pronounced when seen in surface view, the plane of the supposed rhythmic deposition, as in traverse view.

As for the micelles, in spite of the severe criticism to which their existence has been subjected in recent years, subsequent work continues to bring substantial support to the micellar hypothesis of the structure of certain lyophilic systems, notably cellulose.

The cellulose "molecule" is a chain of some forty anhydrous glucose rings. Sponsler and Dore[7] were the first to indicate, by X-ray studies, a chain

[6] Jahrb. wiss. Botan., 69, 501 (1928).
[7] Colloid Symposium Monograph, 4, 174 (1926).

structure of cellulose. These chains are bundled together into fascicles, to which Meyer and Mark[8] have given the old Nägeli term "micellae," which may, in cellulose, be regarded as "crystallites" since the internal arrangement of the chains is orderly. We recall that Nägeli found cellulose anisotropic. Frey,[9] working on the submicroscopic structure of the cellulose walls of bast fibers and other plant cells, finds them to consist of distinct micelles which are strongly anisotropic, optically like rhombic crystallites, and seven times as doubly refractive as quartz.

Clark,[10] on the basis of X-ray studies, finds cellulose to be built up of oriented colloidal micelles which are bundles of long primary valence chains. On the basis of such a structure Clark gives a rational interpretation of the physical and chemical properties of cellulose fibers.

The work of Sheppard and McNally,[11] and also that of Hatschek,[12] gives support to the possibility of a micellar structure in gelatin, the substance which has been the center of the micellar controversy. Sheppard concludes that the birefringence of gelatin films is due to the orientation of symmetrical molecules or micelles, but whether the micelles are truly multimolecular or simply macromolecules cannot be stated. Seifriz[13] has carried this conception of a fibrous structure of cellulose and related systems over to living protoplasma.

Size of Micellae. Chemists regard the micelle as a bundle of chain molecules. No limiting size is given to this bundle, nor can this be readily done, any more than one can specify dimensions for a crystal (the micelle of cellulose is a crystallite). Yet, the cellulose micelle is assumed to be of ultramicroscopic dimensions. Biologists, on the other hand, have characterized as micelles particles well above the visual limit of the microscope whether or not they have viewed these particles with an ultramicroscope. It might be well to arrive at some understanding as to what the term micelle shall denote, even though we may be forced to conclude that a micelle is no more capable of precise limitation as to size than is a crystal.

The size of cellulose crystallites varies within limits generally placed at 100—200 A. U. long and 50-75 A. U. thick. An exceptional maximum length is 600 A. U. for the crystallites of ramie fiber. Even this size is much smaller than the 1μ super-micelles visible in the cellulose walls of plant cells. We must, therefore, be dealing with a larger unit in the visible (dark-field) structure of cellulose. These super-micelles are probably aggregates of crystallites. This idea is supported by Herzog[14] who states that a number of micelles may come together to build up larger structural units which he calls secondary particles.

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[8] Ber., 61, 593 (1928); see also Mayer: Naturwissenschaften, 16, 781 (1928).
[9] Jahrb. wiss. Botan., 65, 195 (1926).
[10] Ind. Eng. Chem., 22, 474 (1930).
[11] Colloid Symposium, 7, 17 (1929).
[12] Kolloid-Z., 35, 67 (1924); 36, 202 (1925).
[13] Am. Naturalist, 63, 410 (1929).
[14] Z. angew. Chem., 34, 385 (1921).

It is at present impossible to say whether the "secondary particles" of Herzog and the super-micelles of microscopic dimensions described and pictured here, are aggregates of primary crystallites, or represent the continued growth of a crystallite; in other words, is the inner structure of a super-micelle a continuous and uniform distribution of chain molecules, or is it a larger bundle of primary crystallites? Without answering this question definitely in favor of an intermediate unit, I believe that while our knowledge of cellulose structure is still vague, we should tentatively recognize several possible sizes of micelles, if we wish to use the term in its broadest sense. The true or primary micelle is the crystallite of Meyer and Mark (200 × 50 A.U.); above this there may be a continuous series from the "secondary particle" of Herzog to the microscopic super-micelles described here (1 × 0.5μ).

Summary

1. The Spierer lens is an oil-immersion objective in which is inserted a mirror, smaller than the lens, which reflects all direct light coming into the objective. Scattered light is picked up by the lens around the mirror.

2. The structure of cellulose (and protoplasm) as revealed by the Spierer lens is that of tiny rods or super-micelles, arranged end-to-end to form long and parallel striae.

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ULTRAFILTRATION AS A TEST FOR COLLOIDAL CONSTITUENTS IN AQUEOUS AND NON-AQUEOUS SYSTEMS

BY J. W. McBAIN AND S. S. KISTLER

One of the most important tools in the study of colloids is the ultrafilter devised by Bechhold and developed by later workers.[1] Sometimes it constitutes the only direct proof that certain matter is in the colloidal state. It is not sufficiently realized, for example, that the ultramicroscope is comparatively disappointing, because most of the important stable colloids and all of the jellies may be prepared in such condition that they are invisible even in the best ultramicroscopes.[2]

The usual ultrafilters are in the coarser ranges with pores whose sizes extend from those of bacteriological filters down to moderately small colloidal particles. The ultrafilters in which the writers have been specially interested continue the series down to the dimensions of very small single molecules.[3] McBain and Jenkins[4] found it possible to utilize ultrafiltration for the measurement of osmotic pressure, hydrolysis, determination of the amounts of crystalloidal and colloidal forms, respectively, measurement of the solvation of the colloid, and even for the separation of ordinary soap micelle from ionic micelle. With a membrane such as was used for the last named purpose it should be possible to determine the hydration of each of the colloidal constituents in the solution separately. The writers have used even finer filters which hold back such molecules as sucrose or potassium chloride, while still allowing methyl alcohol and water to pass through freely.

There is a distinct limit to the denseness of membranes made from collodion, and collodion is too reactive for many purposes. It is therefore very fortunate that, as we have repeatedly emphasized, ordinary commercial cellophane provides a convenient and very finely porous ultrafilter. Cellophane is as chemically indifferent as ordinary filter paper. It is made from viscose and consists of cellulose with a trace of glycerine.[5] We have shown that its pores may be made as small as desired by filtering through it viscose cellulose dissolved in Schweitzer's reagent, or collodion dissolved in ether-alcohol. Commercial cellophane[6] is supplied in large sheets with the thickness desig-

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[1] Bechhold: Z. physik. Chem., 60, 257 (1907); 64, 328 (1908); Brown: Biochem J., 9, 320, 591 (1915); 11, 40 (1917); Elford: Brit. J. Exp. Path., 10, 126 (1929); Proc. Roy. Soc., 106B, 216 (1930); Krueger and Schultz: Proc. Soc. Exp. Biol. Med., 26, 600 (1929); Krueger and Ritter: J. Gen. Physiol., 13, 409 (1930).

[2] McBain: Colloid Symposium Monograph, 4, 7 (1926); Kolloid-Z., 40, 1 (1926).

[3] McBain and Kistler: J. Gen. Physiol., 12, 187 (1928); J. Phys. Chem., 33, 1806 (1929); Trans. Faraday Soc., 26, 157 (1930); Brukner [Z. Ver. deut. Zucker-Ind., 76, 3 (1926)], using Zsigmondy's commercial Ultrafein-filter impregnated with copper ferrocyanide, reported that sugar became concentrated in the molasses which they were filtering.

[4] J. Chem. Soc., 121, 2325 (1922). These studies have been much extended by McBain and Kawakami (not yet published).

[5] See, for example, duPont Magazine, December (1923).

[6] We have used some of French manufacture and some made by the duPont Co.

nated by numbers ranging from 250 to 2400. Some of the thicker samples appear to be laminated and tend to separate on soaking in water. Cellophane 600 appears to be the most suitable for general use. It needs only to be swollen in water for filtering aqueous solutions, holding back all but the finest colloidal particles. It may be used with any non-aqueous solvent, but first it is necessary to displace the water by mixtures of mutually miscible solvents until finally only the desired solvent remains in the membrane.

Our special object was to develop this tool for detecting the presence of colloidal constituents in aqueous and, particularly, non-aqueous solutions of electrolytes, where anomalies in osmotic and electrical behavior are so frequent and yet where the possible presence of colloidal electrolytes has been overlooked in all reviews of the electrochemistry of non-aqueous systems. For this purpose it is essential to be satisfied that the membrane is much too coarse[7] to hold back any ordinary molecules, such as sucrose or anthracene. To avoid ambiguity in this respect we have refrained in general from using impregnated membranes.

The result is a demonstration that colloidal constituents are of very common occurrence in non-aqueous solutions of electrolytes that are usually regarded as quite simple, such as silver nitrate, silver bromate, or cadmium iodide.

The most striking result is that in aqueous solutions of certain electrolytes colloidal constituents are present. This is shown to be the case for the uni-univalent electrolyte potassium iodate which therefore is a colloidal electrolyte *in aqueous solution.*

Test of the Membrane with Known Crystalloidal Molecules[8]

It was found that known simple molecules, such as acetic acid, benzene, amyl alcohol, aniline and piperidine, pass freely through cellophane 600. In a previous communication[9] it was found that cellophane 600 has to be considerably thickened before it holds back sucrose at all. Further tests were made with solutions of naphthalene and of anthracene dissolved in benzene.

The membrane was made permeable to benzene by successive immersion in aqueous alcohol of several compositions up to 95 per cent alcohol which was then displaced by benzene. The original solution, the filtrate, and the residual solution above the membrane were each analyzed by measuring the refractive index by a Pulfrich refractometer, the results being compared with a previously established calibration scale. The data in Table I record experiments carried out by M. E. Laing McBain.

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[7] The bubble test of McBain and Kistler (Trans. Faraday Soc., 26, 159 (1930)) showed that the larger pores are from 40-60 A in diameter.

[8] The very convenient form of ultrafilter used is that supplied by Vereinigung Göttinger Werke, Göttingen, with internal electrical stirring, and attachable directly to a cylinder of nitrogen. It is designed for pressures from one atmosphere up to 150 kilograms per square centimeter. All the chemicals (except where otherwise noted) were the purest supplied by Kahlbaum.

[9] McBain and Kistler: J. Gen. Physiol., 12, 187 (1928).

TABLE I

Ultrafiltration of Anthracene and Naphthalene in Benzene

Substance	Expt.	Pressure	% Concentration of Filtrate	% Concentration of Residue	Change in residue, %
Naphthalene	1	10 atms.	14.20	14.10	−0.10
	2	20 atms.	13.67	13.67	0.00
Anthracene	1	5 atms.	0.820	0.782	−0.038
	2	5 atms.	0.715	0.715	0.000

It is clear from Table I that filtration is not holding back any of these known molecules. Had either naphthalene or anthracene been held back by ultrafiltration, there would have been a positive increase in concentration of the residue and hence necessarily a corresponding loss in the ultrafiltrate. It is interesting to note that in an earlier experiment with a sample of "anthracene," which was subsequently found to be very impure, colloidal impurities were concentrated in the residue.

Proof that Colloidal Constituents are present in Solutions of Silver Bromate in Diethylamine

McBain and Coleman in 1913-1914[10] carried through a careful study of solutions of silver bromate in diethylamine. The boiling points and lowerings of vapour pressure calculated in the usual (erroneous) manner indicate association instead of dissociation ranging from 3.4 fold in 0.89 N_w to 2.04 fold in 1.64 N_w solutions. The conductivity shows a maximum of 2.64 mhos at 1.7 N_w, nearly disappearing on dilution to 0.07 N_w. Such behavior is not infrequent in non-aqueous solutions and bears some resemblance to that of aqueous solutions of the soaps which are now accepted as the best studied type of colloidal electrolytes.

For the ultrafiltration experiments,[11] diethylamine (Eastman Kodak Co.) was distilled and that fraction distilling within 0.2° was used. The silver bromate was made by double decomposition of potassium bromate and silver nitrate, the finely crystalline precipitate being washed thoroughly with distilled water and dried at 100°.

The temperature gradient of the solubility curve is particularly steep. Thus at 20°C the saturated solution has a concentration of $0.115N_w$, while at 32° the concentration has risen to $1.3N_w$. At 40° Coleman obtained a 3.12 N_w solution. This is like some of the soaps. If the solvent is distilled after use or after contact with the membrane, the solubility of silver bromate is still higher, moisture perhaps accounting for the increase. All these solutions showed a brown precipitate on longer standing, due probably to silver oxide since its amount was proportional to the moisture content.

[10] Not yet published.

[11] The ultrafilter was heavily plated with silver before use.

Analysis of silver bromate in the presence of diethylamine presents difficulties, since the latter makes it impossible either to determine the silver by the Vollhard method or to determine the bromate ion by oxidation of hydriodic acid and final titration with sodium thiosulfate. The following method gave good results. The solution is added to about 200 cc of water, made alkaline with sodium hydroxide and boiled for about one-half hour. The diethylamine is completely driven off and the silver is precipitated as flocculent Ag_2O which is titrated with ammonium thiocyanate after solution in dilute nitric acid. The bromate ion is reduced with hydriodic acid and the iodine titrated. This method not only gives a double check but shows whether there is a preferential concentration of either ion during the ultrafiltration.

The following table gives the quantitative results obtained after standardizing the method of analysis.

TABLE II

Ultrafiltration of Silver Bromate in Diethylamine

Concentration filtered	Temperature	Increase in concentration of residue
$0.130N_w$	20°	0.0%
$0.960N_w$	40°	12.8%
$1.29\ N_w$	32°	28.1%*
$1.37\ N_w$†	20°	21.0%

* *Concentration of filtrate 1.00 N_w, of residue 1.65 N_w.*
† Moisture present.

It will be seen from Table II that the higher the concentration of the solution, the greater is the proportion of colloid as shown by the per cent increase in the original solution. This is to be expected from Coleman's data and from analogy with soap solutions which are colloidal electrolytes but on sufficient dilution become simple, ordinary electrolytes.

Proof that Colloidal Constituents are present in Solutions of Silver Nitrate in Piperidine

Lincoln[12] found that solutions of silver nitrate in piperidine show a continuous decrease in equivalent conductivity with dilution. The following table gives the data obtained by ultrafiltering silver nitrate solutions in piperidine through cellophane first swollen in piperidine rather than in water, this treatment resulting in the same rate of filtration.

TABLE III

Ultrafiltration of Silver Nitrate in Piperidine

Original Concentration	Membrane	Increase in residue
$0.065\ N_w$	300*	10%
$0.120\ N_w$	600	29%
$0.246\ N_w$	400	40%

* Cellophane 300 is more porous than cellophane 600.

[12] J. Phys. Chem., 3, 470 (1899).

The fact that the percentage of silver nitrate retained upon filtration increases rapidly with increase in concentration of the solution filtered again suggests that in the more concentrated solutions the frequency of larger molecular aggregates is much greater, as would be expected.

The results of further exploration are collected in Table IV which is followed by any necessary supplementary details.

TABLE IV

Ultrafiltration Data for Substances in Non-Aqueous and Aqueous Solution

Solute	Solvent	Original Conc.	Membrane	Per cent Increase in residue
Ammonium iodide	Aniline	0.28 N_w	600	11.4
Barium perchlorate	Amyl alcohol	0.47 N_w	600	13.0
Cadmium iodide	Amyl alcohol	1.083 N_w	600	3.6
Cadmium iodide	Amyl alcohol	1.083 N_w	600†	44.0
Cadmium iodide	Ethyl alcohol	2.76 N_w	600†	**
Potassium acetate	Acetic acid	1.34 N_w	1200	9.0
Pyridine	Acetic acid	10%	600	10.0
Sodium acetate	50% acetic acid	8%	600	3.0
Potassium iodate	Water	0.35 N_w	2400‡	12.0
Potassium iodate	Water	0.333 N_w	1800	16.8φ
Potassium iodate	Water	0.333 N_w	600	7.3φ
Potassium iodate	Water	0.333 N_w	600	13.6φ

Qualitative experiments with acetic acid in isoamyl alcohol, copper acetate in amyl alcohol and mercuric iodide in benzene are not reported since special reasons in each case rendered them inconclusive.

† Swollen in aqueous ethyl alcohol.
** Residue not analyzed; filtrate was 1.02 N_w.
‡ Reinforced.
φ Experiments by Miss W. L. McClatchie. About four-fifths was filtered before analysis. The increase in concentration of the residue was, of course, accompanied by a corresponding decrease in concentration of the filtrate. The ultrafilter used was heavily silver plated throughout. Analysis was made by titration with thiosulfate after addition of potassium iodide.

In the experiments with ammonium iodide in aniline there was much difficulty due to polymerization, or possibly to reaction with the material of the filter, since the residue always developed a brownish precipitate. However, the satisfactory result here recorded was obtained after silver plating the filter. Then there was no residue or decoloration, but after long standing, the silver plating is loosened. The increase in concentration observed, ascribable to colloid constituents, accords well with the observation of Sachanov[13] who obtained a minimum in equivalent conductivity at approximately 0.12 N.

[13] Bull. Acad. Imp. Sci., St. Petersburg, p. 106 (1913).

The results for barium perchlorate in amyl alcohol show a fair proportion of colloid, though there are no conductivity data for comparison. Migration experiments by Hittorf, using cadmium iodide in amyl alcohol, showed a negative migration of cadmium that was so pronounced that the migration number of the iodine attained the extraordinary value, 2.3. Mere complex ions would hardly be expected to give so large a value, and it would appear that we have here a case analogous to that of soap curd in which the anion migration number ranges from 2 to 4 and is explained by the presence of large amounts of neutral colloid. These experiments show very definite evidence of the presence of colloid.

For cadmium iodide in ethyl alcohol, the ultrafiltration, though not complete, supports the suggestion of colloid complexes indicated by the minimum conductivity between 0.01 and 0.02 N as measured by Jones and Mahin.[14]

The filtration of potassium acetate in acetic acid was unusually slow, 10 hours being required for 7 cc of filtrate to collect at a pressure of 75 atmospheres. However, this was possibly due to the extreme fineness of the membrane, number 1200 being used. The increase in concentration is again paralleled by an anomalous conductivity curve. Völmer[15] found a pronounced maximum and minimum in the conductivity curve for this system, potassium acetate and acetic acid.

Pyridine in acetic acid exhibits both a maximum and a minimum in its equivalent conductivity curve.[13] In the ultrafiltration experiment recorded, some difficulty in analysis was experienced, for the pyridine acetate seemed to act as a buffer in the titration with sodium hydroxide. Jones and Carroll[16] found that the equivalent conductivity of sodium acetate in aqueous acetic acid solutions exhibits a minimum. The shape of the curve is greatly influenced by the percentage of acid, showing the greatest abnormality at 50 per cent acid. The solutions were analyzed by density, and there is again an increase in concentration of the residue by filtration.

Potassium Iodate as a Colloidal Electrolyte in Water

0.333 N_w potassium iodate in water when filtered at 50 atmospheres pressure through an unthickened cellophane membrane (number 1800) gave a 16.8 per cent increase in concentration in the residue and a corresponding decrease in the filtrate. Cellophane number 600 exhibited the same unmistakable effect. This confirms the similar result obtained with a thickened membrane and leads to the remarkable conclusion that aqueous potassium iodate contains colloidal constituents.

It is well known (compare International Critical Tables) that, whereas aqueous solutions of iodic acid exhibit excellent conductivity, they give a lowering of freezing point which is far less than that of such an electrolyte as hydrochloric acid. This would be characteristic of a colloidal electrolyte, but

[14] Z. physik. Chem., 69, 389 (1909).
[15] Z. physik. Chem., 29, 187 (1899).
[16] Am. Chem. J., 32, 542 (1904).

no one has cared to give this interpretation to the data, and the matter has not been further tested. Jones and Bury,[17] and Grindley and Bury,[18] have concluded that micelle formation occurs in aqueous solutions of butyric acid. McBain and Van Rysselberge[19] have shown that complex ions are of normal occurrence in aqueous solutions of electrolytes, but this new result from ultrafiltration points to further unsuspected constituents. Needless to say, such results are incompatible with any assumption of complete dissociation of electrolytes save in extreme dilution.

Summary

It is shown that cellophane provides a membrane which holds back all but the smallest colloidal particles and allows all known simple molecules to pass through. It serves as a test to show that colloidal constituents are commonly present in the numerous non-aqueous solutions of electrolytes, such as silver nitrate, ammonium iodide, silver bromate, cadmium iodide, etc., which exhibit anomalies in electrical conductivity and osmotic behavior, and may even occur in aqueous solutions of electrolytes such as potassium iodate. It is pointed out that these membranes may be thickened as desired until they hold back large molecules and ions, such as sucrose and sodium or potassium chlorides, while still allowing the smaller molecules to pass through.

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[17] Phil. Mag., (7), 4, 841 (1927).
[18] J. Chem. Soc., 679 (1929).
[19] J. Am. Chem. Soc., 50, 3009 (1928); 52, 2336 (1930).

A STUDY OF THE BLOCKING EFFECT OF MEMBRANES

BY G. H. BISHOP, FRANK URBAN, AND H. L. WHITE

In connection with a study of the filtration process through the glomerular membrane of the kidney by one of us occasion arose to investigate certain aspects of filtration through supposedly less complex membranes, as cellophane. The results of these experiments being still too complex for analysis, we have been led to an examination of the flow of solutions through glass capillaries of 0.035 to 0.150 mm inside diameter, varying also in length and degree of taper. We believe that certain deviations in our results from the conventional law for the value of streaming potentials may assist in the interpretation of corresponding deviations from simplicity in the behavior of cellophane membranes. It is barely possible that this may in turn contribute to an understanding of the biological process.

Cellophane membranes were tied over thistle tubes and sealed on with collodion, and the volume flow read by means of a microscope on the capillary stem. Volume change due to slow stretch of the membrane was checked by supporting the membranes in certain experiments with perforated plates, and by forming collodion or cellulose acetate membranes on alundum disks. Tapered or straight capillaries were made by drawing out very heavy walled pyrex capillary tubing and employing either the uniform middle section or the rapidly tapering end. These were sealed into larger tubes after measuring the diameters at each end; the outer tube was allowed to fall in upon the middle of the section of capillary used without distorting the lumen, as seen in Fig. 3, U.

Calomel electrodes sealed into the system allowed voltage readings to be taken, and other electrodes permitted application of current across the system. Readings were made by connecting the apparatus in series with a two m.f. condenser to the EMF leads of a Leeds and Northrup type K potentiometer, so that at balance the condenser was uncharged. The condenser charge was detected by a galvanometer of 10^{-10} amp sensitivity used ballistically, 0.1 millivolt discharged from the condenser giving a detectable deflection.[1] Potentials can be read significantly when the source measured has a resistance of 10^9 ohms, with adequate insulation and allowing sufficient time for charging the condenser. Pressure from the air line was regulated by escape from a side tube dipping into an iron pipe A filled with mercury, to an adjustable depth, and read on a mercury manometer B (Fig. 3). All units of the apparatus were mounted separately on ¼ inch plate glass.

Results. When water or dilute KCl solution (0.0005 to 0.005 molar) is forced through cellophane membranes under pressure of 80 mm Hg or less, the streaming potential cannot be detected (less than 0.1 mv). Filtration commences at a maximum rate when the pressure is applied and in the course

[1] Bishop: Proc. Soc. Expt. Biol. Med., 21, 260 2 (1930).

of 15 minutes to 1 hour may fall off to as low as ten per cent of the initial rate. The results of such an experiment are shown in Fig. 1, curve 1, where the slope of the curve represents the rate of filtration. Such blocking has been observed before by various workers on different membranes,[2] With higher salt concentrations this blocking decreases; also, it was not seen when a solution of 0.01 gm $ThCl_4$ per liter was filtered through the same membrane, (Fig. 1, curve 2). Electroendosmose without pressure exhibits the same phenomena, with similar time relations. Application of a constant current

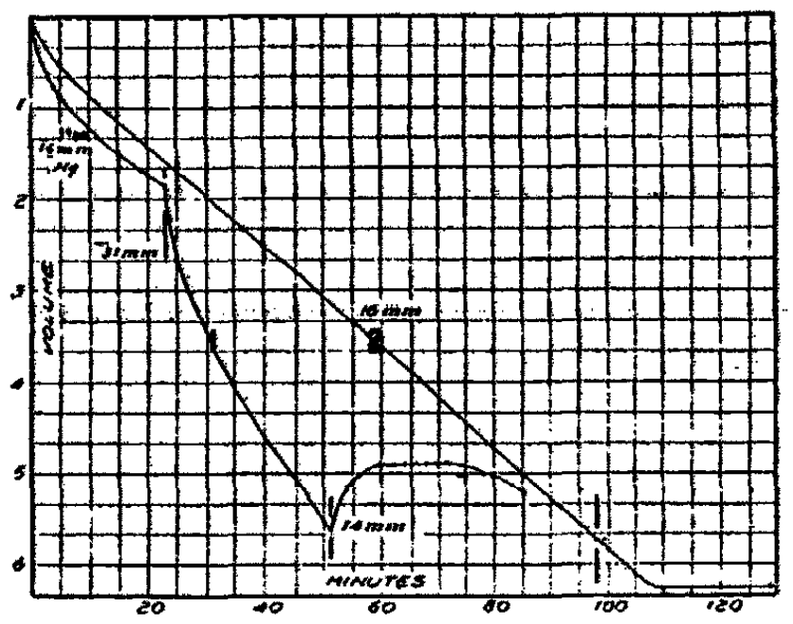


FIG. 1

after equilibrium conditions have been obtained under pressure (two hours' filtration) give the same result. With pressure alone, when this is removed the flow reverses; if only reduced the flow may first reverse and then proceed in the previous direction. The same applies to application of current alone without pressure, thus indicating that stretch of the membrane is not a factor. Upon cessation of applied current, a residual (polarization) EMF persists, and its disappearance has a time course closely parallel to that of the accompanying filtration. It thus appears that the blocking of filtration through these membranes may be correlated with the electrical phenomena of the nature of polarization which are associated with electroendosmose; the difficulty of such an interpretation arises from our inability to detect a potential across the membrane under filtration pressure which should account for the blocking of the filtration process.

It seemed possible that the two phenomena, the gradual falling off in the rate of filtration and the absence of a measurable potential difference (streaming potential) across the membrane might have a common explanation in differences in the behavior of the electrical processes taking place in the various pores of the membrane. Thus, if for any reason the streaming potential be-

[2] Brukner: Z. Ver. deutsch. Zucker Ind., 76, 3 (1926); Simon and Neth: Z. anorg. allgem. Chem., 168, 221 (1928); "Membranefilter, Cella und Ultrafilter," 20 (1920); Manegold and Hofmann: Kolloid-Z., 50, 22 (1930).

tween the ends of the pore AB was greater or developed more rapidly than with the pore CD, a return circuit would be set up through CD. Fig. 2. The point D being negative to the point B, a current would flow as indicated by the curved arrow, constituting essentially a Dolezalek's ring circuit. The plus sign below and the minus sign above the membrane indicate the potential difference which would be set up across the membrane provided the streaming potentials were allowed to develop unhindered. The short circuit through the relatively inactive pore CD would oppose electrosmotically the flow of solution due to the pressure head, resulting in an apparent falling off in the rate of mechanical filtration, and would at the same time discharge the potential difference across the membrane. This hypothesis, offered in explanation of both the falling off in filtration rate and the absence of a measurable potential difference across the membrane, can be defended only if it can be demonstrated that some factor or factors as, for instance, differences in size or shape, *ceteris paribus*, can result in differences in the electrical activity of various capillaries, *i.e.*, can result in a lesser magnitude or a slower development of the streaming potentials of some capillaries as compared with others. Since it is obviously impossible to investigate the behavior of the individual pores in a cellophane membrane we have used glass capillaries as models of these pores.

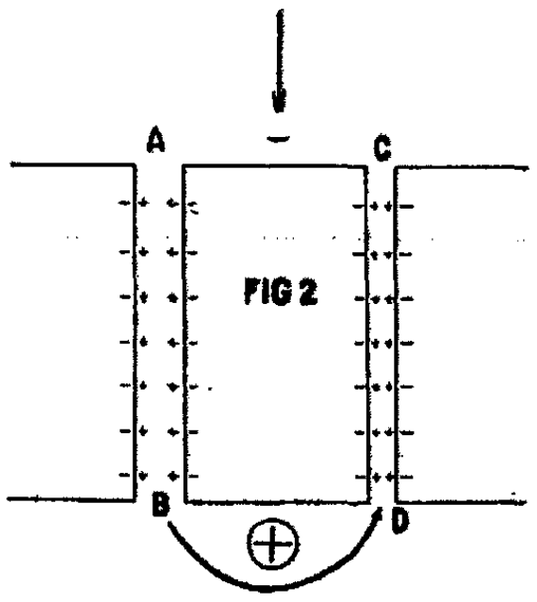


FIG 2

The apparatus diagrammed in Fig. 3 was used. In some of the experiments a single capillary dipped into a beaker E, as shown in the figure, in others the outlet tube from the bottle D was branched and bore on each of its branches a capillary dipping into its own beaker. Great care was taken to prevent contamination of the 0.0005 molar KCl in the capillaries by diffusion of the 0.05 molar KCl in the calomel electrodes, H and F. In all our experiments on glass capillaries 0.0005 molar KCl has been used.

The results of an experiment with a pair of capillaries are given in Fig. 4. The smaller capillary, curve 2, had an inside diameter at the tip of 0.075 mm and passed 0.6 cc of solution per minute at 40 cm Hg pressure; the larger, curve 1, had a diameter of 0.125 mm at the tip and passed 7.2 cc of solution per minute; both of them tapered rapidly to the tip. Thirty runs made over a period of 10 consecutive days at pressures ranging from 20 to 60 cm Hg invariably showed a higher final streaming potential for the larger capillary. Furthermore, the development of the potential was much slower with the small than with the large; the potential of the larger capillary had usually practically reached its maximum before that of the smaller began to show a significant rise. It is obvious that if both these capillaries had had their tips

dipping into the same container, as is of course the case for all the pores traversing a filtering membrane, the conditions diagrammed in Fig. 2 would be realized. In another set of experiments the smaller capillary showed the lower potential at low pressure, up to 40 cm Hg, while at pressures above 40 and up to 80 cm the potential of the smaller capillary was the greater.

In another experiment the effect on the streaming potential of breaking off successive fragments or a tapering capillary was investigated, the pressure remaining constant at 60 cm Hg. The results are shown in Fig. 5; the data

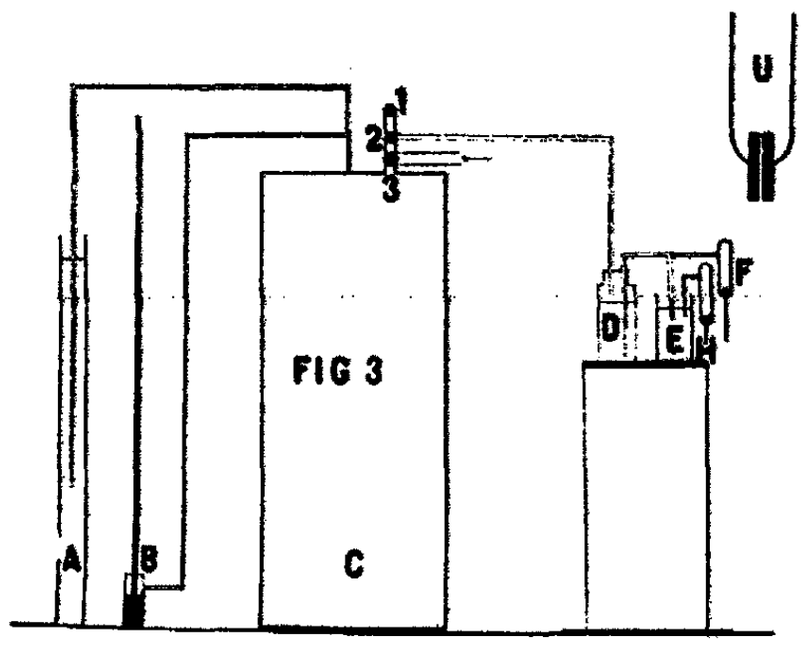
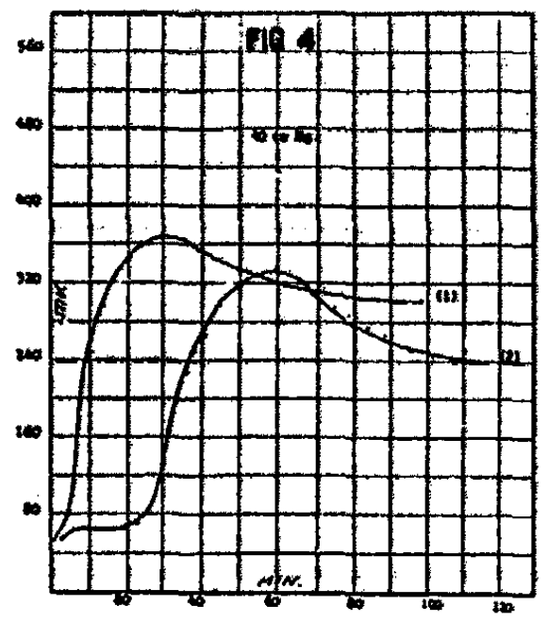


FIG 3

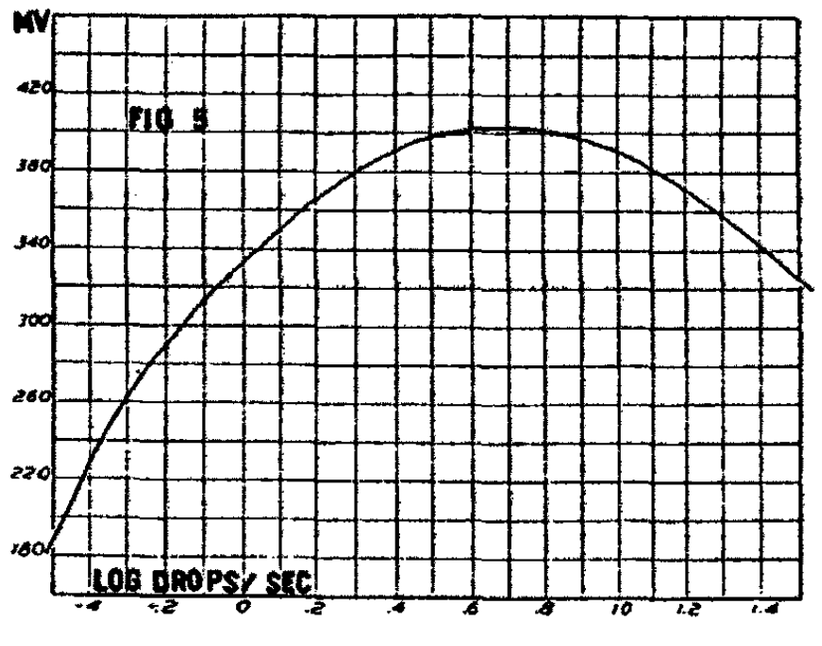
are plotted semilogarithmically merely for convenience. It will be seen that at first the potential rises as the rate of flow, due to decreased resistance, increases; with further increase in the rate of flow the potential falls. This experiment is complicated by the fact that the shape as well as the size of the capillary is being changed. In another experiment with a straight capillary (inside diameter 0.040 mm) 5 cm long the potential was unchanged on reducing the length by one half; the rate of flow was doubled. We believe that the shape (whether straight or tapering) as well as the diameter of capillaries is a factor in determining the magnitude of the streaming potential and its rate of development. The change of potential with time in a single capillary suggests a counter force analogous to a polarization counter EMF. In a tapered capillary there should be forces of different magnitude at the two ends of the capillary. The rise to a maximum with subsequent marked fall shown by the potentials of such capillaries resembles the curve of charge of two condensers of different sizes in series, with suitable leak circuits, such shunted condensers being satisfactory models for polarizable mechanisms[3]. An extended consideration of this question cannot be entered into in the present communication.

In an effort to evaluate the factor of capillary diameter alone, three untapered single capillaries were taken, having inside diameters of 0.040,

[3] Bishop: Am. J. Physiol., 85, 417 (1928).



0.080 and 0.125 mm, respectively; the first was 5 cm long, the others 1 cm long. The fact that one of these capillaries was longer than the others was not considered as invalidating a comparison on the basis of differences in diameter, since the results of a single experiment, referred to above indicated that for straight capillaries the streaming potential was independent of the length. It would seem at first thought a simple matter to take three capillaries of different diameters and compare their streaming potentials. The matter is complicated, however, by the fact that the streaming potential of one and the same capillary has, in many of our experiments, fallen off from day to day. This has not always been the case; thus, with one straight capillary of 0.035 mm inside diameter the streaming potential at 60 cm Hg stayed between 735 and 750 millivolts for 17 consecutive days. In other experiments, where equally strenuous efforts were made to keep conditions constant, the potential showed a progressive fall from day to day. This was the case with all three of the capillaries under consideration here. It was arbitrarily decided to take as the basis of comparison the maximum potential shown by each capillary on



the second day of its use. It was found that the 0.040 mm capillary showed a potential of 392 mv, attained 188 minutes after the pressure of 60 cm Hg was applied, the 0.080 mm capillary showed 681 mv, attained after 190 minutes and the 0.125 mm showed 333 mv after 64 minutes. From this series alone one might conclude that there is an optimum diameter for the development of a stream potential, lying between 0.040 and 0.125 mm. We are not ready to state, however, that this is the case; we can only say that there appears to be a relation between capillary diameter and stream potential but it apparently is not a simple one. It may be noted that earlier workers who have investigated the possibility of an influence of capillary diameter on streaming potential have worked with quite large capillaries. Dorn[4] used capillaries ranging from 0.252 to 4.113 mm in diameter. Their failure to find a relation between capillary diameter and streaming potential may merely mean that the sizes they used were above the range where diameter influences potential, except in so far, as noted by Dorn, the excessively large diameters bring about a departure from Poiseuille's law.

It is evident that the matter of variation in streaming potential of a given capillary from day to day demands further investigation. This has been noted since the earliest reports on the subject; no more definite explanations have been advanced than those of Helmholtz[5] that a part of the active surface of the glass may undergo dissolution, that adhering foreign substances may gradually be washed away or that the negative component of the double layer may penetrate more deeply into the glass, bringing about a redistribution of the pore charge with a resultant change in the steaming potential. Grumbach[6] and Kruyt[7] report only a slight falling off during ten days. In many of our experiments the extent of fall is greater than we have found reported by previous workers. The possibility that this might be due to contamination of the capillaries with the 0.05 molar KCl from the electrodes was considered. We believe for two reasons that this is not a factor. In the first place, some of our capillaries have kept a practically constant potential for many days, although the opportunities for contamination were the same as with those which showed the falls. In the second place, the possibility has been tested directly as follows. The beaker E (Fig. 3) was filled with 0.05 molar KCl at a time when the level of solution in the bottle D was 5 cm below the level in the beaker E; the system was allowed to stand for one hour. The streaming potential before the beaker was filled with 0.05 molar KCl, *i.e.*, when it was filled as usually with 0.0005 molar KCl, had remained steadily at 362 mv for over 30 minutes, the pressure being 60 cm Hg. After the capillary had had its tip in the 0.05 molar KCl with this strong solution siphoning up into the capillary for an hour, the 0.05 molar was replaced by 0.0005 molar KCl. The first reading, made one minute after the replacement, was 65 mv, 2 minutes later was 310 and 2 minutes later was 357. It thus appears that

[4] Wied. Ann., 9, 513 (1880).
[5] Wied Ann., 7, 344 (1879).
[6] Ann. Chim. Phys., 24, 433 (1911).
[7] Kolloid Z., 22, 93 (1918).

the potential is restored even after a known contamination with relatively concentrated KCl solution as soon as the latter is swept out of the capillary. We do not yet know the cause of these drops in potential; they are not due to mechanical plugging of the capillary by foreign particles, as has been established by determinations of the rate of flow.

A systematic investigation of several of the points considered here is in progress but is far from being complete. The exact roles played by differences in diameter and shape and by "spontaneous" changes in the nature of the capillary wall in determining differences in the stream potentials of various capillaries are at present not at all clear. It may again be pointed out, however, that for the statement in a preliminary form of the hypothesis proposed here a complete knowledge of the mechanisms involved is not essential. The conditions diagrammed in Fig. 2 will be realized if for any reason the streaming potential of certain capillaries or pores is different from that of others, either as to magnitude or to rate of development. Even though the pore CD has the potentiality of attaining ultimately a streaming potential equal to that of AB it will not have a chance to develop it if the beginning of its development is tardy. For the return circuit through CD, by opposing electrosmotically the flow due to the head of pressure prevents the normal downward passage of liquid through CD and thus deprives CD of an opportunity to develop any streaming potential. We have established that various capillaries made from the same piece of glass, subjected to the same treatment, left for the same periods of time, having the same solutions forced through them at the same pressures may exhibit significant differences in streaming potential; regardless of the reasons for the differences, the fact constitutes a substantial support to the hypothesis. Since it is only reasonable to assume that there are great variations in the shapes and sizes of the pores traversing a membrane and not unreasonable to assume, in view of experiences with "uniform" sample of glass capillaries, that the ζ potential is not the same in all the pores of the membrane, it seems probable that the conditions established for glass capillaries and diagrammed in Fig. 2 obtain in filtering membranes.

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THE DENATURATION OF ALBUMIN*

BY WILDER D. BANCROFT AND J. E. RUTZLER, JR.

1. Denaturation by Heat

Man is incurably empirical. When a given experiment fails to produce the expected result, he says it will not work. Whereas, were he neither empirical nor dogmatic he would say that it does not work.

When egg albumin or egg white, as the case may be, is heated to a certain temperature, coagulation of the suspended particles takes place. Because people, in the past, failed to repeptize the gel so formed, it has been tacitly assumed that it cannot be restored chemically unaltered, at least, to the original colloidal state. Some profound change has been held responsible for this failure of the albumin to repeptize. This apparent set of circumstances left an opportunity open to coin a word; the term "denaturation" or "denaturization" resulted inevitably.

Much has been written about "denaturation", for instance, the following:[1] "One of the most characteristic properties of the albumins is the physical instability of their solutions and their marked tendency to revert to a solid or semi-solid state. This change may be effected by apparently trivial factors, such as evaporation, contact with porous substances, etc. In this respect also the albumins behave very much like the inorganic colloids. This change (irreversible coagulation) can be brought about at once by the application of heat, and it is important to note that *all true native albumins can be coagulated* in this manner. After coagulation their solution can only be effected by influences which lead to their more or less extensive destruction. They have lost those physical properties which characterized them individually as albumins; they are permanently *denaturized*, as Neumeister expresses it."

On page 32, Simon continues: "Coagulation is not an essential phase of denaturization. Denaturization may indeed become manifest by the non-occurrence of coagulation. Denaturized and coagulated albumins can only be brought into solution by means which will at the same time produce integral changes in their composition, viz: by means of proteolytic ferments, dilute mineral acids or alkalies, concentrated organic acids under the application of heat, etc.

"The nature of the process which determines denaturization is possibly a primary cleavage. Nothing certain, however, is known."

It would seem from this quotation that denaturation is a process occult and more or less unintelligible.

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* This work is part of the programme now being carried out at Cornell University under a grant from the Heckscher Foundation for the Advancement of Research established by August Heckscher at Cornell University.

[1] Simon: "Physiological Chemistry," 30 (1904).

Writing of "Denaturation and Coagulation", Miss Lloyd[1] says: "Coagulation is a physical condition, and by suitable means coagula can be redispersed or dissolved. The solution of coagulated protein, however, differs very definitely from that of the original material from which it came. Coagulation is not in itself an irreversible process, but in all cases is preceded by an *irreversible chemical change in the protein known as denaturation.*[2]

"Under the heading of 'denaturation' can be included a number of reactions, the common features of which are a complete loss of solubility in water and in dilute salt solutions. Denatured proteins, however, are readily dissolved in dilute acids or alkalis, giving viscous colloidal solutions which react towards electrolytes as if they were of the suspensoid type rather than the emulsoid type characteristic of normal proteins. The change involved in denaturation seems to be a structural alteration in the protein molecule, which leads to a re-arrangement of the linkages in the molecule, but not an actual degradation. This change is accompanied by a complete loss of the power of swelling by the imbibition of water. . . . Proteins can be denatured by strong acids or alkalies, by salts of the heavy metals, by heat, by light, by mechanical agitation, by pressure or adsorption on a surface, and by the action of alcohol or acetone. The interrelation between different types of denatured proteins has not yet been worked out.' "

On page 229 Miss Lloyd continues: "The commonest example of this [heat denaturation] is, of course, the setting of the white of an egg which takes place on boiling. Denaturation and coagulation are both influenced by temperature, time, the reaction of the solution, the presence of water and by the nature and concentration of the electrolytes present; but the effect of these factors is different for each of the two processes."

Bechhold[3] also makes the point that when proteins are denatured they lose their capacity to swell. On page 163, Bechhold makes the definite statement that, "reversible coagulation is purely a salting out, whereas one must assume a chemical change with irreversible coagulation."

Young[4] maintains that denaturation is a primary chemical change.

Anson and Mirsky[5] make the statement that, "denaturation is not a general disintegration of the native protein." In a second paper the authors[6] come to the conclusion that denaturation and its reversal are very obscure chemical changes.

We find Robertson[7] on record as follows: ". . . which leads to the apparently irreversible character of the process (dehydrating proteins by heat); *apparently* and not actually irreversible because, as Corin and Ansiaux[8] have

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[1] "Chemistry of the Proteins," 228 (1926).
[2] Hardy: J. Physiol., 24, 158 (1899).
[3] Bechhold: "Die Kolloide in Biologie und Medizin," 161 (1929).
[4] Proc. Roy. Soc., 93B, 235 (1922).
[5] J. Gen. Physiol., 13 II, 121 (1929).
[6] J. Gen. Physiol., 13 II, 133 (1929).
[7] "The Physical Chemistry of the Proteins," 308, 309 (1918).
[8] Bull. Acad. roy. Belg., (3) 21, 321, 345 (1891).

shown, if a solution of protein be cooled and vigorously shaken just as the first traces of heat coagulation appear, the incipient coagula will again pass into solution. The apparent irreversibility of the later stages of heat-coagulation is probably attributable to the high internal friction of the floccula which are formed, leading to extremely slow molecular movement and the introduction of a time element of very considerable magnitude."

Cohnheim[1] says that albumin cannot be put back into solution without extensive changes and splitting; it is permanently denatured.

The denaturation of serum albumin solution by heat can be retarded by adding sucrose or glycerol to the system.[2] The physico-chemical properties of the native proteins are left more or less unchanged as a result. The protective action of the glycerol was found to be less than that of the sucrose. Further, with sufficient concentration of sucrose, rabbit serum proteins were found to be completely thermostable at 62°; while egg albumin, under like conditions, was thermo-stable at 75°.

Albumin is prevented from coagulating[3] even in boiling water by the presence of starch. Coagulated egg albumin was found to redissolve when heated to 148° with a small quantity of water.

Chick,[4] working with pseudo-globulin, derived from horse serum, makes the statement that denaturation cannot be identified with any chemical changes in the material; whereas we find that Wu[5] concludes that the essential step in denaturation is a hydrolytic fission of the protein, and the essential step in coagulation is molecular condensation. Earlier Chick and Martin[6] maintained that the fact that the hydrogen ion concentration diminishes after heat coagulation points to the view that denaturation is a chemical change.

"It is not at present easy to form a satisfactory theory of denaturation," are the words Miss Lloyd[7] uses in launching a discussion of the theories of denaturation. The author then mentions three prevalent theories, the opening up of internal anhydride rings, the closing of rings with the consequent formation of internal anhydrides, and hydrolytic cleavage, none of which are adequate to explain all the facts.

From this short review it becomes obvious that the behavior of albumin, as a result of which it supposedly becomes either irreversibly coagulated or chemically changed, is not clearly understood. People are at variance as to the mechanism; and cause and effect are sometimes apparently confused. The whole problem has been approached from the viewpoint of true solutions, or colloidal ions, or amphoteric electrolytes. The problem has not been considered logically from a strictly colloid chemical viewpoint.

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[1] "Chemie der Eiweisskorper," (1911).
[2] Beilinsson: Biochem. Z., 213, 399 (1929).
[3] Kingzett: "Animal Chemistry," 380 (1878).
[4] Biochem. J., 8, 404 (1914).
[5] H. Wu: Chinese J. Physiol., 3, 1 (1929); Chem. Abs., 23, 4952 (1929).
[6] J. Physiol., 40, 404 (1910).
[7] "Chemistry of the Proteins," 243 (1926).

Bancroft,[1] in discussing the effect of electrolytes on albumin, says: "In other words, we will give up, for the time being, the dogma that albumin is an amphoteric electrolyte." Further, "the precipitation of a colloid is always reversible in case no coalescence or agglomeration takes place, because one of the standard methods of preparing a colloidal solution is to wash out the excess of the precipitating agent. Now the more strongly the precipitating agent is adsorbed, the harder it is to wash it out and consequently the more nearly irreversible the precipitation is."

Electrolyte-free albumin is said to be very stable toward the action of heat,[2] although Pauli[3] disputes this finding. Also, it is well known, that electrolyte-free albumin does not coagulate on standing. Concerning this Bancroft says: "The only way that I see to account for the stability of the electrolyte-free albumin is to postulate that in the absence of salts the peptizing action of water is enough to keep the albumin in colloidal solution.

"It does seem to me, however, that it will be an easier task to account for the properties of electrolyte-free albumin on the basis of varying adsorption than on the basis of an amphoteric electrolyte".

Wo. Ostwald[4] takes a step in the right direction when he says: "Albumin sols are usually amphoteric, that is, they must be either positively or negatively charged, depending upon certain conditions," although the way the word amphoteric is used is somewhat unfortunate.

Kruyt[5] is quite positive in his discussion of proteins as colloids. "There is, however, a special reason which has led many investigators to look upon emulsoids as molecularly dispersed systems, more particularly, as electrolyte solutions; this is the fact that a great many properties of protein solutions may be explained by considering these solutions as systems of *amphoteric electrolytes*. It may be pointed out at this place that a discussion of emulsoids in terms of ionically dispersed systems must necessarily conflict with typically colloidal properties of these systems.

"The main criticism that can be raised against the concept of the electrolyte nature of protein solutions lies in the fact that the division of colloids into suspensoids and emulsoids would then be without continuity. In other words, we should have to ascribe to colloid chemistry a dualistic line of reasoning which is highly unsatisfactory. Whereas, for instance, the electrical properties of suspensoids are to be explained by means of the electroadsorptive phenomena of the peptizing ions which divide themselves between the particles and the medium . . ., we should have to consider for protein solutions an ionic equilibrium of one single kind of molecules dissociated into ions, the degree of dissociation being governed by Ostwald's dilution law."

Denaturation, in review, is defined as the irreversible precipitation of a protein sol. Likewise, coagulation is defined as the reversible precipitation

[1] J. Phys. Chem., 19, 349 (1915).
[2] Schmidt: Pflügers Archiv, 8, 75 (1874); Heynsius: 9, 514.
[3] Beitr. chem. Physiol., 10, 53 (1907).
[4] "Practical Colloid Chemistry," 151 (1924).
[5] "Colloids," 178, 179 (1927).

of a protein sol. There is an experiment which apparently illustrates this difference between denaturation and coagulation. Pauli and Handovsky[1] boiled an egg albumin system which was 2-normal in respect to potassium thiocyanate. There was no coagulation. A control system and a portion of the treated sol were dialyzed against running water. The control system remained clear; whilst, unfortunately, there was extensive flocculation in the treated sol. The boiled, undialyzed system containing potassium thiocyanate is considered to be denatured but not coagulated.

Denatured serum albumin has been reversed by Spiegel-Adolf.[2] The serum albumin was treated with dilute sodium hydroxide solution. "The experiments were carried out thus: Varying quantities of the same heat denatured albumin were dissolved in 100 cc. of 0.01 N NaOH in exactly the same way. It then appeared that the absolute content of the protein of the resulting solutions decreased with the decreasing quantity of the proteins employed, while a constantly decreasing residue of protein remained undissolved. If these liquids were electrodialyzed, the quantity of protein remaining in solution was found to decrease with a decrease in the initial quantity of heat-denatured protein used, and finally to disappear. That is, from the solution of 0.5 gram of heat-denatured albumin in 100 cc. of 0.01 N NaOH, there results a protein solution which is quantitatively precipitated on electrodialysis. There exist, therefore, two limiting cases, within which there are continuous transitions. With a sufficiently large excess of protein, we get only water-soluble protein; with a correspondingly large excess of alkali, only a water-insoluble protein." The water soluble protein was obtained by dissolving 4 grams of serum albumin in 100 cc. of 0.01 N NaOH.

"From this physico-chemical evidence, the product in question (the water-soluble protein) is not distinguishable from true albumin.

"In order, however, to try a further criterion for the characterization of protein X, the highly sensitive immuno-biological methods were employed. The precipitin method was selected." The experimental results show that both horse serum-albumin and the electrodialyzed sample (4 grams of protein dissolved in 100 cc. of 0.01 N NaOH) behave as antigens toward the precipitin up to a dilution of one part of protein to one hundred thousand parts of physiological salt solution. The negative result of the control test demonstrates the specificity of the reaction."

The author then summarizes, p. 311: "Accordingly no essential difference is demonstrable between protein X and its parent material (a true serum albumin) by the physico-chemical and immuno-biological methods here employed. The agreement is so close that, provided no new experimental results arise to contradict it, we are forced to admit an actual identity of the two proteins. Such an identification, however, would imply that the changes produced by heat had been made chemically reversible by the treatment given the heat-coagulated albumin."

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[1] Bechhold: "Die Kolloide in Biologie und Medizin," 170 (1929).

[2] Alexander: "Colloid Chemistry," 2, 309 (1928).

In an attempt to explain the chemical changes which have supposedly taken place, the author says on page 313: "The demonstration that the changes brought about by heat can be reversed by small amounts of alkali or acid, supports the view that ring closure accompanies the heat-change. For, while the action of these added substances, which persists even after their electrodialytic removal, can be interpreted as an hydrolysis, there might possibly have been involved a breaking down of a pre-existing ring structure. On the other hand, it is not obvious how any previously occurring hydrolysis can be completely reversed by an added substance which itself is known to aid hydrolysis. The above findings seem to strengthen the theory that the change appearing upon heat-denaturation of the proteins depends upon a ring closure of the groups involved."

The reversal of denaturation is obviously a paradox. It can be accounted for in two ways. In the first place, the experimental results of Spiegel-Adolf can be discounted. This seems to be highly improbable.

Refusing to challenge these results brings up the question as to whether the term denaturation is really accurate or not. This will be taken up later.

Wilhelm[1] predicted, in 1927, that it should be possible, under the correct conditions, to reverse denaturation. In a later paper[2] he made good on his prediction and reversed heat-denatured serum albumin. The coagulated albumin was prepared by electrodialysis in a hot water bath, or over a free flame. The gel was repeptized by heating it in boiling water containing a definite amount of salt. The salts used were potassium thiocyanate, sodium salicylate, and sodium benzoate. The systems are defined, for example, as follows: 7.2 mg. of albumin, dissolved in enough 2.15 N KCNS solution so that the KCNS content was 1.06 grams; the same amount of albumin was dissolved in enough normal sodium salicylate solution so that the sodium salicylate content was 0.32 gram. In order to obtain a clear solution of the coagulated serum albumin these concentrations (in addition to several other concentrations which the author tabulates) had to be rigidly adhered to; greater or lesser amounts would not accomplish the results.

After dialysis of these systems containing peptized albumin, the albumin was found to be again coagulable by heat. It was found that the same salts which peptize the coagulated albumin also prevent its coagulation, much less salt being necessary for the latter than for the former. It is a noteworthy fact that Wilhelm found that both the total quantity and the concentration of peptizing agent with respect to the albumin must be fixed, as is shown from the data above.

From the results obtained, it was concluded that the peptization of the coagulated protein is influenced by two distinct processes. There is first an imbibition of water by the protein; the swollen protein then adsorbs ions from the solution becoming peptized thereby.

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[1] Biochem. Z., 180, 231 (1927).

[2] Kolloid-Z., 42, 217 (1929).

The results of Wilhelm controvert the conclusion to which Pauli[1] came concerning the two processes, denaturation and coagulation.

Denatured hemoglobin was repeptized by Anson and Mirsky.[2] Horse hemoglobin was used in this work. Either sodium hyposulphite or potassium cyanide was found to be apparently indispensable to the repeptization of the denatured protein. The system was extracted with toluene during the process. Carbonyl hemoglobin was finally crystallized from repeptized systems which were denatured by heat, acid, and urea. The reversed protein was shown to be identical with the original: by crystallizing the carbonyl derivative, by its restored heat coagulability, and by the fact that it denatured again with acids and alkali.

The conclusion is reached that the coagulation of proteins, in general, is a reversible chemical change which is very obscure.

In another paper Anson and Mirsky[3] discuss denaturation at greater length. They state that it has not yet been proved that the various forms of denaturation are due to the same changes in the protein, for concentrated solutions of urea denature proteins but keep the denatured proteins in solution. When the urea is dialyzed out, the protein precipitates completely.

Anson and Mirsky say that the denaturation of hemoglobin is exactly the same process as the denaturation of albumin. They also say that KI, KCNS, and sodium salicylate probably denature proteins in general, when the protein solution is buffered at $[H^+] = 1 \times 10^{-4.7}$, or near the isoelectric point.

Apparently urea can denature egg albumin, and likewise dissolve the denatured albumin. Egg albumin was allowed to stand in a concentrated urea solution for a day. A few drops of this solution were added to 15 cc of water which was buffered at $[H^+] = 1 \times 10^{-4.7}$. This caused a heavy precipitation. Upon dissolving some urea crystals in the water, the protein redissolved.

In these two papers there is no mention of peptization, the view-point being strictly one of chemical reaction.

The problem to repeptize heat-coagulated egg albumin not having been solved, the present work was undertaken with two purposes in view, i.e., to accomplish this repeptization, and to endeavor to show that so-called denaturation is a colloidal phenomenon and not due to a chemical reaction. For the purpose of this investigation the principles of colloid chemistry will be adhered to as rigidly as the subject will permit, and "the dogma that albumin is an amphoteric electrolyte" will be discarded. It has been shown that it is possible to repeptize serum albumin gels by the use of a variety of reagents and to obtain solutions which are identical with the original. Considered as a problem in colloid chemistry, there is no good reason why this should not be so. This theme will be dealt with more completely further on.

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[1] Hofmeister's Beiträge, 9, 415 (1908).
[2] J. Gen. Physiol., 13, II, 133 (1929).
[3] J. Gen. Physiol., 13, II, 121 (1929).

Experimental Study

In order to observe experimentally the manner in which heat-flocculated egg albumin and egg white behave, from the colloidal standpoint, some rough qualitative experiments were undertaken first.

A portion of the white of a hard-boiled egg was ground in a mortar to a fine powder with solid potassium iodide and cane sugar. Distilled water was added to the mixture. A cloudy sol formed which cleared up somewhat upon the addition of more sugar. Upon performing this experiment several times it became apparent that the amount of peptization depended, as one would expect, to a large extent upon the degree of fineness to which the system was reduced upon grinding.

The selective wetting of heat-denatured, globulin-free albumin by several liquids was next determined. Glycerol and water both wet albumin. When dried and finely ground albumin is put in contact with water the particles show a tendency to form lumps, to agglomerate. With glycerol, however, there is apparently little or no agglomeration. Small samples of albumin were put in contact with chloroform, acetone, and benzene. Upon adding glycerol to each of the systems, the albumin immediately passed into the glycerol layer. Thus, glycerol wets egg albumin preferentially to these liquids. In view of this, the heat-coagulated albumin must be considered as still being hydrophylic, although Bechhold[1] states that heat coagulation changes natural proteins, which are hydrophilic, so that they become hydrophobic. What actually happens is that they lose most of their water sheath.

Cold coagulation (Kältefällung) of albumin is said to be irreversible. However, it was found that freezing the white of an egg and then lowering the temperature below minus 10° did not visibly affect the physical condition of the sol when it again comes to room temperature. It will later be shown that this is exactly the behavior that would be expected of such a sol.

Following the lead of Spiegel-Adolf,[2] we tried to repeptize heat-coagulated egg albumin with sodium hydroxide solution. The globulins were precipitated out of an absolutely fresh egg-white sol by the approved method. The globulin-free albumin was coagulated by heating it in boiling water for fifteen minutes. The lumps of coagulated albumin were filtered off and washed several times with boiling distilled water. Five systems were prepared using this sample; 16 grams of the wet sample were put into a flask with 100 cc. of distilled water and 0.7 gram of sodium hydroxide; 10 grams of the wet sample were put with the same amounts of sodium hydroxide and water; five grams of the wet sample were put with one-half the amount of sodium hydroxide and the same amount of water; 0.5 gram of the albumin was put with 5% of the amount of sodium hydroxide in the same amount of water, and finally; 16 grams of the wet albumin were put with 2.1 grams of sodium hydroxide and 100 cc. of water. All of the systems, except the last, were agitated on a shaking machine for 3 days. The last system became clear, with all of the

[1] "Die Kolloide in Biologie und Medizin," 164 (1929).

[2] Alexander: "Colloid Chemistry," 2, 309 ff. (1928).

albumin apparently peptized, in the course of 17 hours. The others failed to peptize to any marked extent. The system containing the peptized albumin was dialyzed against running distilled water for about 30 hours. The sol was then found to have the following physical and chemical characteristics. It was neutral to litmus, alkaline to methyl orange, and slightly alkaline to phenolphthalein. It was odorless, and absolutely clear and colorless. The xanthoproteic and biuret reactions were positive. It coagulated with heat only upon making it acid to phenolphthalein but not adding enough acid to make it acid to methyl orange. Ammonium sulphate was used to change the alkalinity of the sol. The addition of glacial acetic acid caused a heavy precipitation. In the presence of alcohol and sodium chloride, the sol did not coagulate when heated to above 78°. It required less than half-saturation with ammonium sulphate to precipitate large quantities of the colloid.

Because of the slight dissimilarities between this sol and uncoagulated albumin we cannot at the present time conclude that the albumin did not suffer some slight hydrolytic cleavage during repeptization.

The statement[1] has been made that ether denatures egg albumin. Upon investigating this phenomenon quite the reverse was found to be true, under certain conditions. Fresh egg white was diluted with distilled water to form a 10% sol. Globulins, of course, precipitated; they were filtered off as completely as possible. The sol was extracted twice with ether. Quite a stable emulsion persisted at the ether-sol interface. The ether was gently boiled out of the extracted sol. The addition of alcohol to this sol produced no coagulation whatever. Alcohol did precipitate it when enough was added so that the dispersion medium was more than a 50% solution of alcohol. The effect of heat was determined by immersing the sol in a test tube in boiling water for 15 to 20 minutes. The sol remained clear; absolutely no coagulation took place.

This was too good, so that the obvious explanation that most of the albumin had concentrated at the interface was tested. The xanthoproteic reaction was tried on the sol. The addition of nitric acid resulted in heavy coagulation. To check this test, glacial acetic acid was added to the sol; again a large amount of precipitate came down. The whole experiment was repeated several times with the same results. A portion of the sol which was not extracted with ether coagulated normally upon immersing the test tube containing it in boiling water.

This method of preventing coagulation was tried on a 50% egg white sol (50 cc. egg white diluted with 50 cc. of distilled water). The result was the formation, upon heating, of a slight amount of coagulum, which was manifest by the appearance of a heavy cloud in the sol. A far larger amount of precipitation occurred upon the addition of either acetic acid or nitric acid.

A striking difference in properties between the native egg-white coagulum and that produced when an ether-extracted sol was coagulated by heat in the

[1] Lepeschkin: Kolloid-Z., 32, 100 (1923); Hammarsten: "A Textbook of Physiological Chemistry," 107 (1914).

presence of a little acetic acid is observable. The untreated sol coagulates into lumps, or into one solid mass, depending upon the conditions. The ether-treated sol, when coagulated by heat in the presence of a little acetic acid comes down in the form of strings. The dense precipitate is apparently more highly hydrated than the string-like precipitate; its probable classification is as a curdy[1] precipitate. The other precipitate would then be classified as a flocculent precipitate, or as will be shown in a later paper more probably as a jelly. In this case there is apparently a rather sharp line between flocculent and curdy precipitates. The ether under this classification must stand trial for the removal of something which makes the water sheath of the colloidal albumin particles less strongly adsorbed; or else the ether itself is held by the albumin thus making its water sheath less strongly adsorbed. Coagulation, under this last hypothesis, must start before the ether is removed from the albumin particles by the heat.

It has been shown that ether can be used to prevent heat coagulation. If heat coagulation were due to a chemical reaction, it is difficult to see just how the ether extraction of the sol would prevent it. How ether could react with an amino group, an imino group, a carbonyl group, a sulphhydryl group, a carboxyl, or phosphorus group is not at all obvious. Further, how it could, in this case, form a heat-stable addition product, cause hydrolysis, or open an internal anhydride ring is equally hard to see. Also, the ether was free from peroxide by actual test; so that that could not have been responsible for the condition which was brought about. Therefore, the burden of the proof is upon him who claims that this phenomenon is due to a chemical reaction.

The ether removes something from the albumin sol. There was a distinctly measurable amount of residue upon evaporation of the ether which was used for the extraction. The solid material is apparently soluble in ether and peptizes in water; for the solution remained clear until most of the ether was evaporated off. Then, when the water content became greater than the ether content, the system became cloudy. The sol so formed was diluted with water and an electrophoresis experiment performed upon it. The sol was discharged from both electrodes with a greater amount of discharge from the anode than from the cathode. This must mean that there are two substances present, one charged negatively and the other positively, the one charged negatively predominating.

The concentrated extract apparently coagulates a 10% albumin sol, for it became decidedly more turbid upon addition of the extract.

It is interesting to note the results obtained by an electrophoretic study of three lecithin sols. The lecithin was prepared from egg yolk.[2] The first sol was prepared by shaking lecithin with water and drawing the air out of it by means of a vacuum pump. As was expected,[3] the suspended particles travelled toward the anode, showing that they were negatively charged. The second

[1] Bancroft: "Applied Colloid Chemistry," 193 (1926).
[2] Webster and Koch: "Laboratory Manual of Physiological Chemistry," 1 (1903).
[3] Kakiuchi: J. Biochem. (Japan), 1, 165 (1922).

sol was prepared by adding an alcoholic solution of lecithin to about a 20% alcohol-water solution. The suspended particles were apparently discharged at both the anode and the cathode, with the larger amount of discharge at the anode. The third sol was the same as the first; only it was heated to about 90° before the electrophoresis was started. It behaved, not like the first sol, but like the second.

An analysis of egg white[1] shows that the amount of fat, including lecithin, present is 0.25%. From these facts it is obvious that the thing partly responsible for heat coagulation may be a fatty material associated with lecithin, but having under certain conditions an opposite charge. The plus charge that this substance has would then be partly responsible for the flocculation of the protein from suspension upon heating.

When one allows undiluted egg white to stand with enough ether for an appreciable time, it does, as has been maintained, coagulate. This is quite obviously due to the removal of water, not from the albumin molecule, but from the sheath of water surrounding the individual suspended albumin particles.

The white of an egg was diluted 50% with distilled water and coagulated by immersion in boiling water. Part of the substance prepared in this manner was extracted for eight hours with peroxide-free ether, by merely allowing the ether to stand in contact with the egg white, and changing the ether frequently. The ether was drained off of the sample and a portion of it was put in 125 cc. of distilled water containing a fairly large amount of ammonium thiocyanate. The system was agitated on a shaking machine. In about 24 hours the appearance of the sol indicated that considerable peptization had resulted. The ether extraction of a portion of the coagulated egg white was continued until the ether, as a result of many changes, dried the egg white to a hard, transparent mass. Three experiments were performed upon this material. A small amount of it was put into each of the following: 15 cc. of water containing about two grams of ammonium thiocyanate, 15 cc of water containing about two cc. of ammonium phosphate solution (prepared by neutralizing syrupy phosphoric acid with ammonium hydroxide and adding enough base to produce a faint ammoniacal odor). The three test tubes were shaken on a machine for three and a half days. At the end of this time it could be seen that in the case of the latter two experiments peptization occurred, whereas, with the pure water there was no peptization. The three systems were heated to the boiling point. The system containing only albumin and distilled water became quite cloudy during this process; the other two did not change markedly.

Another portion of the coagulated egg white described in the paragraph above was extracted with peroxide-free ether for three days in a Soxhlet extractor. A portion of the albumin thus obtained was placed in water and the system boiled for about ten minutes. A cloudy sol formed. It was further broken up by stirring by means of a high-speed soda mixer. This was

[1] Hutchinson: "Foods and Dietetics," 148 (1900).

followed by shaking for 12 hours on a shaking machine. The result was the formation of a very cloudy albumin sol. Heating separate portions of this sol with ammonium thiocyanate, potassium iodide, and starch revealed the fact that the sol became less cloudy (accompanied by no precipitation) in the case of the first compound but did not change in appearance with the other two. The sol containing ammonium thiocyanate was acid to litmus. Sodium bicarbonate was added to neutralize it. This resulted in the liberation of ammonia and the sol at the same time became quite clear, indicating more or less complete peptization.

When the coagulated and extracted protein was boiled with water in the presence of ammonium thiocyanate there was no visible amount of peptization. The difference between this case and the case above, where the peptizing agent was added after the boiling seems to be concerned with the swelling of the albumin particles. When the electrolyte was present during boiling the amount of swelling appeared to be distinctly less than when it was added after the system was boiled and had cooled to room temperature.

The effect of various reagents which could reasonably be presumed to exert a peptizing action upon coagulated egg white was next studied. The sample was prepared by diluting egg white with an equal volume of water and heating the sol so formed for 15 minutes in boiling water. The coagulum was extracted for 72 consecutive hours with ether. When the extraction was completed the coagulum was found to be very dry. Upon placing a portion of it in boiling water peptization occurred. A large volume of this sol was then prepared. The effect of peptizing agents was tried on separate portions of the sol. Potassium thiocyanate in an amount such that it was very concentrated in respect to the electrolyte was added to 15 cc. of the sol. After shaking by hand for a few minutes and allowing to stand for a day the sol was quite cloudy. The addition of a little glacial acetic acid caused considerable precipitation. This shows us that there was a significant amount of coagulated albumin peptized by the water and the electrolyte. The experiment was repeated using potassium iodide. This time the glacial acetic acid produced a very large amount of coagulation when added to the sol. When the experiment was tried using cane sugar instead of an electrolyte peptization takes place. The sol so produced does not coagulate when glacial acetic acid is added. Nitric acid does, however, cause coagulation. It has been found[1] that both sulphur dioxide and formaldehyde prevent the heat coagulation of albumin sols. It was also found that this property is probably not dependent upon reduction because other reducing agents were without effect. One-half cubic centimeter of formaldehyde was added to 10 cc. of the sol and the system was agitated for a short time. In two days the sol was tested for peptized protein by adding acetic acid. There was no precipitation. However, nitric acid caused a noticeable amount of coagulation. Gortner[2] states

[1] Munaretto: Arch. farm. sper., 14, 460.

[2] "Outlines of Biochemistry," 404 (1929).

that formaldehyde combines with the proteins, whereas there is apparently no evidence, in the case of egg white, that the action is anything other than a peptization.

Because of the utility of a good chemical test for albumin at this stage of the work the sodium nitroprusside ($Na_2Fe(CN)_5NO.5H_2O$) test[1] was examined critically. The test is stated to be for the presence of an SH group. It is performed by adding to one to two cubic centimeters of the substance to be tested an excess of finely powdered ammonium sulphate. This is followed by two to four drops of a freshly prepared 5% sodium nitroprusside solution. The system is made alkaline by the addition of a few drops of ammonium hydroxide. A magenta color indicates the presence of denatured protein. The author states that crystallized egg albumin gives no reaction when this test is applied but that albumin coagulated by heat or acetic acid gives the test immediately. Egg white evaporated on an extensive surface showed only a doubtful nitroprusside reaction, when tried by Harriss.

When dried egg white was suspended in water it was found to give a distinctly positive reaction upon performing this test. The white of an egg was diluted to one half with distilled water and coagulated by heating in boiling water for 14 minutes. The gel was cooled and the nitroprusside reaction tried on a portion of it. No reaction was noticeable. These experiments were repeated with the same results as before. The experiments were then repeated twice again, allowing more time for the reaction to take place and varying the amount of sodium nitroprusside solution used. The results were no different this time. Finally the test was carried out on a sodium thiosulfate solution which was acidified with a little acetic acid. A magenta-colored ring formed where the ammonium hydroxide came in contact with the body of the liquid. From this it would appear that colloidal sulphur also gives the nitroprusside test for denaturation.

These experiments indicate that this test is not to be regarded as reliable enough for our use in studying heat coagulation, for it may fail to work when it should, and it may be positive when it should be negative.

The effect of dextrose upon heat coagulation was studied briefly. A 15% egg white sol was not prevented from coagulating by the addition of 0.25 gm of dextrose to 10 cubic centimeters of the sol. However, when the sol was saturated with respect to dextrose heating in boiling water caused no coagulation. Considering this from the colloidal viewpoint it offers an explanation for the peptizing action of cane sugar upon coagulated albumin. We shall see later just how this ties in.

Having repeptized coagulated egg white, and, further, having prevented the coagulation of egg white sols it now only remains to be shown that the repeptized sols are chemically identical with the original sol. For this purpose the immuno-biological reaction known as the precipitin reaction was chosen.[2]

[1] Harriss: Proc. Roy. Soc., 94B, 426 (1923).

[2] Our thanks are gratefully extended to Professor W. A. Hagan, Head of the Department of Veterinary Bacteriology of the New York State Veterinary College at Cornell University for his supervision of and help with this part of the work.

The protein precipitins are highly specific. They show their characteristic reaction only with the proteins which were used in preparing them.[1] Investigating the effect of chemical and physico-chemical changes of the protein molecule upon its antigenic behavior, Obermayer and Pick[2] state that both types of change prevent its visible reaction with native immune serum. Pick[3] came to the conclusion that agencies which effect, even in the slightest degree, the properties of the proteins lessen or completely prevent their antigenic behavior.

Anson and Mirsky[4] found that upon reversing denatured hemoglobin the specificity, which was lost in the denatured protein, is restored in the regenerated product.

Jordan[5] says: "Particular groups within the protein molecule—the amino-acids—are probably responsible for the specificity of anaphylaxis and other antigen-antibody reactions. Both chemical composition and isomeric arrangement doubtless play a part in the close correspondence that exists between antigen and antibody."

The precipitin reaction, therefore, is an extremely sensitive test for establishing the chemical identity of coagulated, repeptized albumin with native albumin.

Fresh egg white was diluted with distilled water to form a 15% egg white sol. The system was agitated for less than ten seconds under a high speed soda mixer to homogenize it. Globulins precipitated out. They were removed by passing the sol through coarse filter paper three times. It was allowed to stand for two days, during which time incipient precipitation occurred, and then it was filtered three more times using ashless filter paper. The sol so prepared was passed through a sterilized Berkefeld filter.

Five cubic centimeters of the sterile sol was injected intravenously into each of two rabbits. One week later ten cubic centimeters of the sol, which had been kept at 4°, was injected into each rabbit. After a lapse of two weeks ten cubic centimeters of a freshly prepared sol was again injected into each rabbit. Finally, five days later the rabbits were injected with the third ten cubic centimeter dose, this time subcutaneously. Ten days were allowed for the serum to build up its titer. The rabbits were then bled, the blood centrifuged, and the serum recovered. This serum was used for the precipitin reaction.

Two methods for repeptizing heat-coagulated egg white were used in preparing the antigen for the precipitin reaction. The white of an egg was diluted with distilled water to make a 50% homogeneous egg white sol. The system was heated in boiling water for 15 minutes to coagulate the protein. It was brought to room temperature and 85 cc. of distilled water added. Chemically pure urea was added to the system until it was practically sat-

[1] Spiegel-Adolf: Alexander's "Colloid Chemistry," 2, 311 (1928).
[2] Wien. Klin. Rundschr., 1902, No. 15; Wien. Klin. Wochenschr., 1903, 659; 1906, No. 12.
[3] Beitr. Chem. Physiol. Path., 1, 445 (1902.)
[4] J. Gen. Physiol., 9, 169 (1925).
[5] "A Textbook of General Bacteriology" 193 (1929).

urated. The large test tube containing the system was shaken moderately for 24 hours with the addition of small amounts of urea from time to time. The sol so formed was cloudy. A portion of it was dialyzed against running distilled water using a small parchment dialyzing thimble. The size of the dialysate container and the rate of flow of the water were so arranged that there was the equivalent of a complete change of the water every 20 to 30 minutes. The sol was dialyzed for three days; at the end of that time the dialysate showed no residue upon evaporation at room temperature under a vacuum. The sol so produced was cloudy, but contained invisible particles as proved by the precipitation with acetic acid. The other sample was prepared from a 50% egg white sol as above. Ether, to the extent of three times the volume of the coagulum, was poured on top of the cooled coagulum. The system was allowed to stand for a couple of hours in contact with the ether. The ether was poured off and another portion added; this was also allowed to stand for two hours. Immediately upon pouring off this second portion of the ether, part of the coagulum was put into distilled water and heated on a boiling water bath. This treatment drove off the ether and at the same time mechanically disintegrated the albumin particles; the expanding ether probably burst the particles. The albumin then began to imbibe water and further reduce in size. The water sheath is thus, at least in part, restored to the particles, causing them to stay suspended. Potassium thiocyanate was then added to the sol until it was almost saturated. This was accompanied by a distinctly visible decrease in the cloudiness of the sol. At the same time there was no precipitation of the colloid particles. The clearing up was due, therefore, to further peptization of the albumin, by the thiocyanate ion. This sol was dialyzed in the same manner as the one previously described. Again there was a significant amount of albumin in suspension as proved by its precipitation upon the addition of acetic acid. At the end of three days neither the sol nor the dialysate contained the thiocyanate ion as proved by the absence of the red color upon the addition of ferric chloride solution. Both of the sols just described formed an absolutely clear colloid suspension when diluted one to ten with physiological salt solution.

The precipitin reaction was studied by adding the undiluted serum to portions of the two sols which were diluted with physiological salt solution. Approximately 0.2 cc. of the rabbit serum was layered against an equal amount of the antigen in its various dilutions. The following tabulation shows the results that were obtained.

TABLE I

Dilution of Antigen	Reaction of $CO(NH_2)_2$ Repeptized sol	Reaction of KCNS Repeptized sol	Reaction of untreated 15% egg white sol	0.85% NaCl Solution
1;10	+ +	+ + +	+ + +	o
1;100	+	+ +	+ +	
1;1000	o	+	+	

From the data obtained from this reaction it seems quite obvious that urea and potassium thiocyanate both repeptize heat-coagulated egg albumin. Furthermore, it appears certain from these tests that the heat-coagulated and repeptized albumin is chemically no different from the original material.

That the precipitin reaction is extremely specific is also shown by the results of a test performed on egg albumin which was coagulated by alcohol and repeptized by concentrated potassium thiocyanate and six drops of N/20 sodium hydroxide per 40 cc of the sol. Although it was evident that there was repeptization, the dialyzed sol showed no precipitin reaction. This, in addition to what others have found, apparently established beyond a doubt that the test as used here, for this specific purpose, using as antigen and precipitin those things which were used, and only those things, is extremely highly specific. The case of alcohol coagulation will be considered later on.

Although the whole white of an egg was used in this work, there can be no question about whether the globulin was responsible for the precipitation or not. The simple answer to that is that there was no globulin present. Globulins are insoluble[1] or more correctly, form such unstable sols in pure water that they will, as we have seen, precipitate out of an egg white sol upon merely diluting[2] it with distilled water. Ostwald finds that a 10% egg white sol in distilled water contains practically no globulin.

Since native egg white sols that do not contain too large an amount of the disperse phase stay in suspension at the isoelectric point, the claim is made that to prove the identity of the repeptized protein with the native material, it too should not precipitate when brought slowly to the isoelectric point. Quite obviously the native albumin, which stays up at the isoelectric point, is the abnormal case; whereas, the repeptized material which comes down at the isoelectric point acts as it should.

Repeptization of heat-coagulated egg-white sols, using ether to produce mechanical disintegration, gives us a sol which does not precipitate completely when it is brought slowly to the isoelectric point. When the experiment is not carried out correctly, however, the protein precipitates quantitatively upon bringing the sol to the isoelectric point. In other words, the system protein-ether should undergo a sudden and large temperature change when it is immersed in hot water.

Thus, we have advanced further proof that the coagulation of an egg white sol is a reversible physical change, if one is willing to believe that similarity of behavior at the isoelectric point proves anything about chemical constitution.

Many heat-coagulated egg-white sols that are repeptized do not stay up when they are brought slowly to the isoelectric point. The apparent reason for this is that the initial heating destroys the action of some protecting colloid that is present in the original system. This principle is illustrated by the following experiment. When enough Congo Red sol is added to a repeptized

[1] Ostwald: "Practical Colloid Chemistry," 159 (1924); Sumner: "Biological Chemistry," 86 (1929); Lloyd: "Chemistry of the Proteins," 44 (1926).

[2] Ostwald: "Practical Colloid Chemistry," 157 (1924).

albumin sol that would itself precipitate at the isoelectric point, the albumin does not all come down when the system is brought slowly to a pH of 4.8, the isoelectric point of egg albumin.

These experiments prove, therefore, that heat coagulation is strictly a reversible change. How the reversible change can be chemical rather than physical is not obvious. For instance, how potassium thiocyanate, urea, potassium iodide, sodium hydroxide, cane sugar, formaldehyde and ammonium phosphate, in the case of egg albumin, potassium thiocyanate, sodium salicylate, sodium hydroxide, and sodium benzoate, in the case of serum albumin, could each cause the reversal of the same chemical change (were heat denaturation a chemical change) is not at all apparent. These compounds possess no characteristic which is common to all of them; some are alkaline in water solution; while others are neutral; some are electrolytes while others are not; some are reducing agents and others are not. Yet, this divers array of compounds all cause albumin of one kind or another to assume its original form after heat coagulation.

Anson and Mirsky[1] have said that the denaturation of proteins is a truly reversible process, but it is ordinarily masked by the flocculation of the denatured protein. Had the authors inserted the word colloidal, their statement would have completely covered the case as it apparently is.

So-called denaturation has been shown to be a colloidal phenomenon and therefore responsible to the rules of colloid chemistry. The actual mechanism of heat coagulation as well as other types of coagulation of this protein, being somewhat more involved than the mechanism of peptization of the coagulated protein, will be discussed at length in another paper.

If, then, one is willing not to be mystified by the word protein, the word "denaturation" should go by the boards; for we already have in the nomenclature of colloid chemistry terms which describe the process accurately.

The conclusions to be drawn from this paper are:

1.—"Denaturation" has been assumed to be a chemical change.

2.—A satisfactory theory has not been offered for this change.

3.—Other workers have retarded, prevented, and reversed "denaturation."

4.—The problem has not, up to this time, been considered from a strictly colloid-chemical view-point.

5.—Regarding egg albumin as a hydrophilic colloid, the problem to peptize heat-coagulated egg-white sols has been undertaken and solved.

6.—Potassium iodide, potassium thiocyanate, urea, ammonium thiocyanate and sodium bicarbonate, formaldehyde, and cane sugar all peptize heat-coagulated egg-white sols.

7.—Sodium hydroxide was found to peptize heat-coagulated albumin, although there is some possibility that a slight amount of hydrolysis occurred.

8.—Ether does not denature albumin under ordinary conditions.

[1] J. Gen. Physiol., 9, 169 (1925).

9.—Egg-white sols were prevented from coagulating by extracting them with ether.

10.—It is difficult to see how ether could prevent any conceivable chemical reaction that might take place upon heat coagulation.

11.—Therefore, ether prevents "denaturation" by some sort of colloidal mechanism.

12.—The ether probably extracts something from the sol, thus giving it heat stability.

13.—The extracted material was studied as a colloid.

14.—It was shown how it can act as a coagulating agent.

15.—The substance acted like crude lecithin from egg yolk.

16.—"Denaturation" by means of ether, which does occur under some circumstances, is due merely to the removal of adsorbed water from the colloid.

17.—Coagulated egg white repeptizes in boiling water, specially when it contains some ether to disintegrate the particles mechanically.

18.—The presence of electrolytes during heating apparently prevents swelling.

19.—The sodium nitroprusside test for "denatured" egg albumin was found to be wanting.

20.—Dextrose prevents heat coagulation when present in large enough amounts.

21.—Immuno-biological tests for species specificity have shown that coagulated and repeptized egg-white sols are identical with the original, as also have isoelectric point measurements.

22.—A mechanism of peptization has been proposed which initially involves mechanical disintegration of the protein coagulum by hot water, aided in some cases by ether, and followed by further disintegration and peptization by the negative ions of various electrolytes.

23.—The dogma of denaturation has been deleted.

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SWELLING AND HYDRATION OF GELATIN[1]

BY JOHN H. NORTHROP AND M. KUNITZ

The swelling of gelatin when placed in aqueous solutions may be readily separated into three types: 1. Swelling in acid or alkali. 2. Swelling on addition of small amounts of water to dry gelatin. 3. Swelling of dilute gels of isoelectric gelatin in water or in salt solutions.

The swelling in acid or in alkali and the effect of neutral salts on this swelling have been shown by the work of Procter and Wilson,[2] and Loeb[3] to be due to the osmotic pressure of the ions of the electrolyte, in accordance with the Donnan equilibrium. The initial swelling of dry isoelectric gelatin in water—which evidently is not connected with the Donnan equilibrium—has been carefully studied by Katz,[4] who was able to show that the heat effects, volume, pressure, and vapor changes were strictly analogous to those observed in the formation of concentrated solutions of many substances, and that the system as a whole behaved as an ideal concentrated solution. When sufficient water has been added, however, to reduce the gelatin concentration to less than 50 per cent, the heat effects become very small and yet the gelatin may swell, under favorable conditions, until the concentration of gelatin is 5 per cent or less. The third type of swelling has peculiarities which cannot be reconciled with the idea of solution or of hydrate formation and it will be considered here as a distinct type. It is this type of swelling which is discussed in the present paper.

The behavior of gelatin when placed in water has been described by a number of investigators. The more striking peculiarities may be briefly described as follows. In general the swelling increases with the temperature and with the concentration of gelatin. At a concentration of about 10 per cent at 5°C no change in volume occurs, while below 10 per cent the gelatin loses water instead of swelling. A block of gelatin which was brought to a definite concentration by allowing water to evaporate from a dilute gel swells much more than a similar block made by allowing a sol of the same concentration to set. Thin films of gelatin swell to a value which increases only slowly with time while large blocks do not give any indication of a maximum value but continue to swell until dissolved. At higher temperatures there is still less indication of an equilibrium value. If a block of gelatin is allowed to remain in water until it has stopped swelling and then is raised to a higher temperature in air for a short time under such conditions that there is no change in volume, it will swell rapidly when replaced in water at the first temperature.

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[1] The work reported in this paper is a summary of a series of papers on swelling and hydration of gelatin published in J. Gen. Physiol., 1926-1930.

[2] J. Chem. Soc., 109, 307 (1916).

[3] "Proteins and the Theory of Colloidal Behavior," 2nd Ed (1924).

[4] Kolloidchem. Beihefte, 9, 1 (1917-18).

Previous Theories of Swelling

A number of theories have been proposed to account for these peculiarities.[5] Hardy assumed that a gel was a solid in contact with its saturated solution. Katz assumed that the gel is a solid solution of water and gelatin, and that

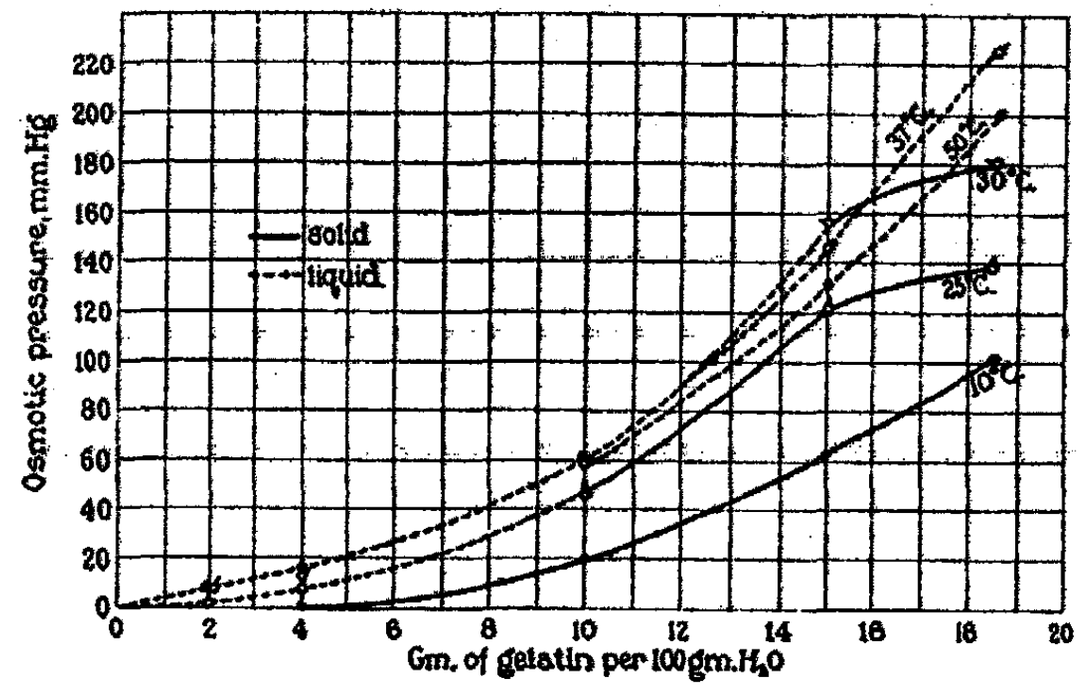

FIG. 1

Concentration and swelling or osmotic pressure of gelatin at different temperatures

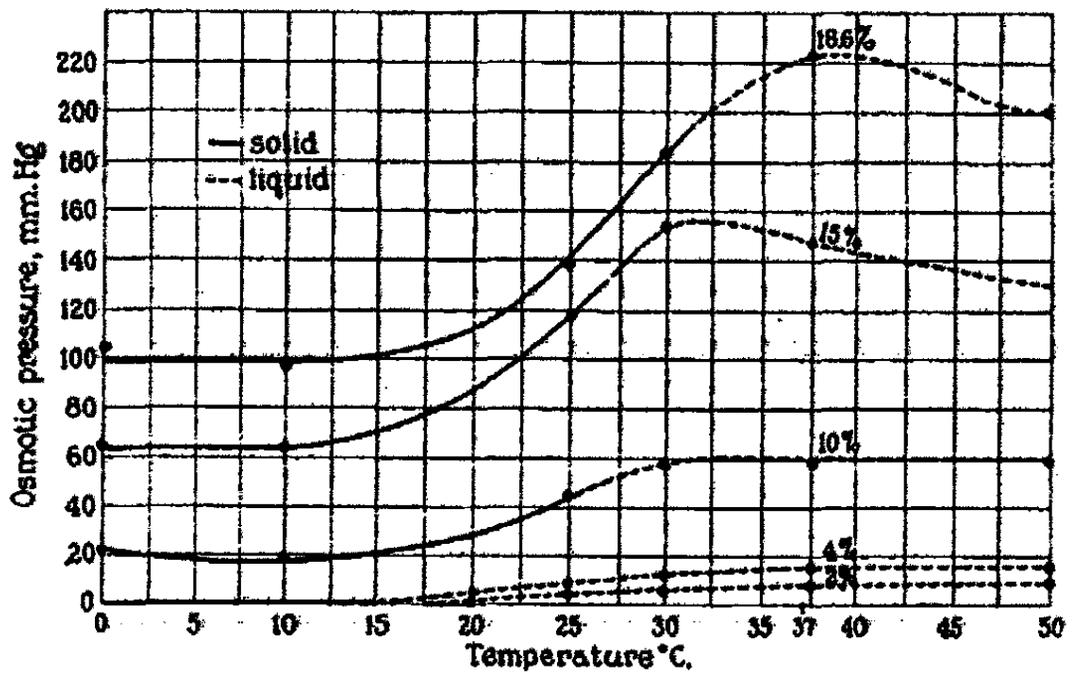

FIG. 2

Osmotic or swelling pressure of various concentrations of gelatin at different temperatures

the gel is therefore one phase. (The writers agree with this idea for very concentrated gelatin-water systems.) Lloyd suggests that gelatin is made of two components, isoelectric gelatin which is insoluble, and gelatin salts which

[5] Cf. Weiser: Bogue's "Theory and Application of Colloidal Behavior," 1, 377 (1924); Bradford: Alexander's "Colloid Chemistry," 1, 751; Lloyd: 767 (1925); Freundlich: "Kapillarchemie" (1923).

are soluble. Swelling is due to the osmotic pressure of the soluble gelatin salts. A number of other workers have outlined more or less similar theories.

It would evidently be a great help in attempting to determine the nature of gels if the number of phases present could be determined. This could be done directly by an analytical phase rule study except for the fact that the (assumed) liquid phase is held in the meshes of the solid and cannot be separated from it, so that the concentration of gelatin in the liquid phase cannot be determined. Since the osmotic pressure is proportional to the concentration, the concentration could be determined indirectly by means of the osmotic pressure; and osmotic pressure-temperature or osmotic pressure-concentration curves could be used in the phase rule diagram. The osmotic or swelling pressure of gels, however, cannot be determined in the same way as the osmotic pressure of liquids owing to the mechanical resistance of the gel. It was found possible to obtain values for the swelling pressure of dilute gels by placing the gel outside a rigid membrane and measuring the pressure required to prevent the entrance of water. The swelling or osmotic pressure curves for different concentrations of gelatin at different temperatures were measured in this way.[6] The results of these measurements are shown in Figs. 1 and 2.[7] The osmotic pressure increases with both temperature and concentration but there are no breaks in the curves at the point where the system becomes solid. If the phase rule be applied to these results it follows that no new phase appears when gelatin-water systems change from liquid to solid either by lowering the temperature or increasing the concentration of gelatin. The number of phases present in the system gelatin-water is therefore the same in either the liquid or solid form. It also follows that there is always present one more component than there are phases, since the system still has one degree of freedom, although the temperature and pressure are fixed. Therefore, if the phase rule is applied in its usual form, it must be assumed either (1) that there are two components, water and gelatin, and that the solid and liquid forms are the same phase, or (2) that there are three (or more) components and two (or more) phases. If n phases are assumed there must be n + 1 components.

The first possibility would agree with the idea that the system is a solution which may be either liquid or solid depending on the composition. It is not possible to assume that it consists of a solid phase of one component in equilibrium with its saturated solution since in the presence of the solid the system would be fixed if the temperature and pressure were fixed.

It is probable that the concentrated gels studied by Katz are solid solutions of water and gelatin, as Katz concluded. It is very difficult, however, to account for the properties of the more dilute gelatin sols or gels on this basis owing to the peculiar hysteresis effects noticed in swelling experiments and the changes in viscosity with time, temperature and pH. The hysteresis

[6] Northrop and Kunitz: J. Gen. Physiol., 10, 161 (1927).

[7] Since gels below 10 per cent lose water the swelling-pressure curve must cross the concentration axis at about 10 per cent gelatin content and then becomes negative. This could not be determined in the form of apparatus used since negative pressures would not be recorded.

effects, on the other hand, are exactly what would be expected of an elastic solid (or of a suspension). The facts that the swelling of gels at low temperatures reaches an equilibrium value and that gels of less than 10 per cent concentration lose water instead of imbibing water, also contradict the assumption of a solution. In general therefore the assumption that dilute gelatin-water systems consist of two phases seems in much better agreement with the facts. It follows then from the pressure measurements summarized above that the system must consist of (at least) three components and since water is certainly one, gelatin must contain the other two. It was assumed therefore as a working hypothesis that the system gelatin-water, whether in the sol or gel state (at a concentration of less than 40 per cent gelatin) consists of (at least) two phases, one solid and one liquid, and (at least) three components, water, "soluble" gelatin, and "insoluble" gelatin.

There are two possible systems which agree with the osmotic pressure measurements: 1. The solid phase is a solid solution of "soluble" and "insoluble" fractions of gelatin and water. The liquid phase is an aqueous solution of the "soluble" and "insoluble" fractions of gelatin. 2. The solid phase is the "insoluble" fraction alone and the liquid phase is a solution of the "soluble" and "insoluble" fractions. In either case the solid phase exists in the sol state as finely divided particles—*i.e.* micellae.

The facts observed in connection with the viscosity of sols and syneresis of gels, however, necessitate the assumption of structure in the particles (micellae) of solid present, since, in order to account for these results it is necessary to assume that the micellae contain liquid phase and that the concentration of gelatin in this "internal" liquid phase is higher than that in the bulk of the liquid phase surrounding the micellae, with the result that the micellae take up water, or swell.

It is difficult to derive this condition from the assumption that the solid phase is a solid solution and it is therefore necessary to conclude that the micellae form a separate system, consisting of an elastic membrane of insoluble gelatin, in equilibrium with the "external" liquid phase and containing an internal liquid phase which is a solution of one or more partly "soluble" components. The walls of the micellae are impermeable to these components. In the sol state therefore gelatin consists of a suspension of micellae in a solution of the "soluble" and "insoluble" components. These micellae are in equilibrium with the surrounding solution, the difference between the osmotic pressure inside and outside of the micellae being balanced by the elastic resistance of the walls. They are therefore capable of swelling or contracting as Loeb assumed. As the total concentration of the sol increases the osmotic pressure of the external liquid-phase increases, while that of the internal liquid remains the same so that the micellae swell less in concentrated sols. This accounts for the effect of concentration on the viscosity and also, as will be shown later, for syneresis of dilute gels.

As the sol is cooled or as more gelatin is added, the amount of the "insoluble" fraction present as solid increases, and the micellae increase in size and possibly in number. When they occupy a large enough proportion of the

total volume the "insoluble" fraction becomes connected to form an elastic network and the sol becomes a gel. The liquid phase surrounding the micellae still contains the "soluble" component in solution and therefore has an osmotic pressure. When a block of gel is placed in water this osmotic pressure causes water to enter and the block swells. As swelling continues the osmotic pressure becomes less owing to dilution, and at the same time an elastic stress appears in the block owing to the stretching of the elastic network. When this elastic stress is equal to the osmotic pressure the system is in equilibrium and swelling stops. Under certain conditions the osmotic pressure of the solution in the micellae is decreased on cooling so that water is forced out of them by the elastic contraction of the walls of the micellae. Under these conditions the block as a whole may lose water.

Any conditions therefore such as higher temperature or strong salt solutions which increase the solubility of gelatin will increase the swelling. The elastic stress of the block shows fatigue as do all elastic bodies and this fatigue accounts for the hysteresis effects and for the difference in the swelling of large and small blocks.

The picture of gel formation and the mechanism of swelling outlined above is similar to that proposed by Duclaux[8] for the swelling of rubber and published during the course of the present work; a somewhat similar mechanism had also been proposed previously by Lloyd.

This mechanism has been found adequate to account qualitatively for all the properties of gelatin of which the writers are aware and quantitatively for a large number. It has predicted several properties which had not been suspected.

Application of the Hypotheses to the Properties of Gelatin

Hydration of Isoelectric Gelatin as determined from Osmotic Pressure and Viscosity Measurements.[9]

Figures 3 and 4 give the curves for osmotic pressure and viscosity of sols of various concentrations of isoelectric gelatin at 35°C. On the same figures are drawn, for comparison, curves for osmotic pressure and viscosity of electrolyte-free isoelectric egg albumin measured at 20°C. The osmotic pressure-curve for egg albumin is a straight line, while in the case of gelatin the curve rises rapidly with increase in concentration of gelatin. The same difference is shown by the viscosity curves. The viscosity of gelatin even in low concentrations is much higher at 35°C than the viscosity of egg albumin at the corresponding concentrations and increases enormously with increase in concentration. This difference in the behavior of egg albumin and gelatin with respect both to osmotic pressure and viscosity is explainable by the difference in their degrees of hydration.[10] Egg albumin is hydrated very little, while gelatin is highly hydrated even at 35°C. The high degree of hydration

[8] Bull., 33, 36 (1923).
[9] Kunitz: J. Gen. Physiol., 10, 811 (1927).
[10] Kunitz: J. Gen. Physiol., 9, 715 (1926).

of gelatin is due to the swelling of the micellae which, in turn, is caused by the difference in the concentrations of gelatin in the internal and external liquid phases.

It is possible to determine approximately the degree of hydration of gelatin independently from both osmotic pressure and viscosity measurements.

Osmotic Pressure and Hydration of Gelatin.—The osmotic pressure of a dilute molal solution of a hydrated substance may be expressed[10] as

$$P = K \frac{C}{1 - \varphi}$$

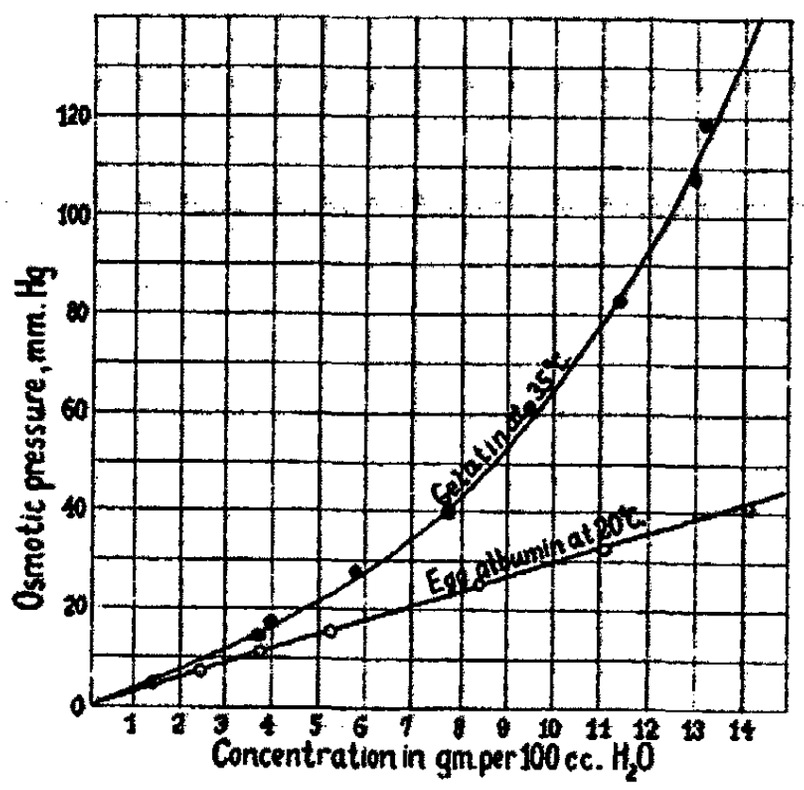

FIG. 3
Osmotic pressure curves of isoelectric gelatin at 35°C and of isoelectric egg albumin at 20°C.

where K = RT/M (M = mole weight of solute)
C = gm. of solute per cc of solution
φ = volume of C gm of the hydrated solute

which means that the osmotic pressure is proportional to the concentration, expressed as moles per cc. of free solvent.

The value of φ can be calculated from the osmotic pressure measurement if K is known.

From the relation

$$K = P/C\ (1 - \varphi)$$

it follows that as C approaches zero, $\varphi \doteq 0$ and $K \doteq P/C$. Thus the value of K may be obtained by plotting P/C against C. The intercept on the P/C ordinate gives the value of K.

Table I gives the values of φ as calculated from the osmotic pressure measurements.

TABLE I

C Gm/cc solution	P Mm Hg	P/C	$\varphi \times 10^5$	q Cc H_2O/Gm gelatin
0.0	—	325		
0.01	3.5	350	7.2	6.45
0.02	7.5	375	13.4	5.95
0.03	12.0	400	19.8	5.85
0.04	17.0	425	23.6	5.15
0.05	23.0	460	29.5	5.15
0.06	29.40	492	34.0	4.91
0.07	37.50	537	39.6	4.91
0.08	47.0	588	44.8	4.85

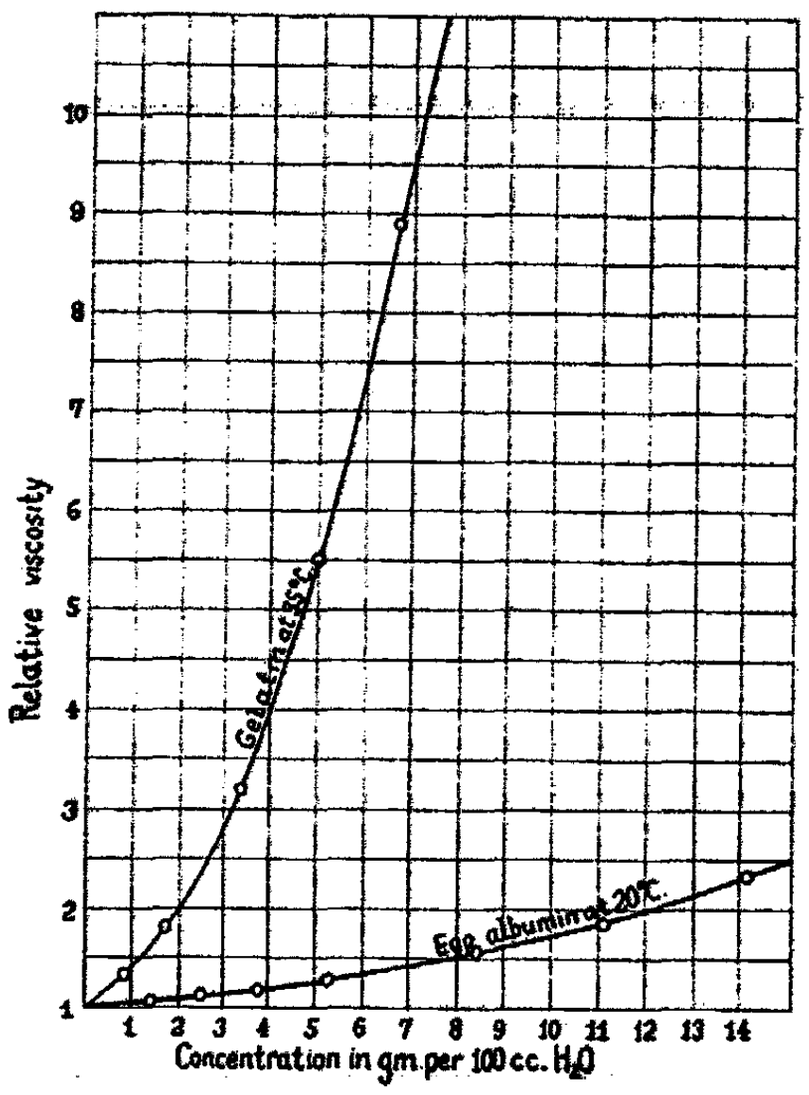

FIG. 4
Viscosity concentration curves of isoelectric gelatin at 35°C and of isoelectric egg albumin at 20°C.

The last column contains the values of the water of hydration per gram of gelatin as obtained from the values of φ, namely

$$q = \varphi / C - 0.75$$

where 0.75 equals the volume of 1 gram of dry gelatin.

Viscosity and Hydration of Gelatin.—The viscosity of a number of colloidal solutions, as well as of various sugar solutions, may be represented approximately by the empirical formula[10]

$$\eta = \frac{1 + 0.5\,\varphi}{(1 - \varphi)^4}$$

where η = relative viscosity of solution

and φ = volume occupied by the solute expressed as a fraction of the total volume of the solution = cc of solute per cc of solution.

In the case of various sugar solutions and also in the case of sulfur suspensions, the volume of the solute as calculated from the viscosity values agrees with the actual volume of the substance in the dry state, as determined from specific gravity measurements. In the case of hydrated or solvated substances φ represents the volume of the solvated solute. This was checked[10] for various colloidal solutions. Thus in the case of solutions of caoutchouc in benzene the values of φ as calculated from the viscosity measurements were found to fit remarkably well in the equation for osmotic pressure of the same solutions.

Table II shows the values for φ and hence also for q as calculated from the viscosity measurements of gelatin by means of the same formula.

TABLE II

C Gm/cc solution	η at 35°C.	$\varphi \times 10^2$	q Cc H_2O/Gm gelatin
0.01	1.43	7.75	7.00
0.02	2.06	15.05	6.78
0.03	2.96	21.80	6.52
0.04	4.24	27.90	6.30
0.05	6.00	33.40	5.93
0.06	8.20	38.10	5.60
0.07	10.85	42.18	5.28
0.08	13.9	45.52	4.94

The values for hydration of gelatin as obtained from the viscosity measurements are quite close to those obtained from the osmotic pressure measurement.

Figure 5 shows that when the various concentration values have been corrected for the values of φ as obtained from viscosity measurements the osmotic pressure values lie on a straight line.

It is to be noted that the value of water of hydration in cc per gm of gelatin becomes smaller as the concentration of gelatin increases. This agrees with the theory that the hydration of gelatin is due to the swelling of the micellae, owing to the difference between the osmotic pressure of the internal liquid phase and the osmotic pressure of the gelatin sol as a whole. The micellae swell until this difference in osmotic pressure becomes equal to the elastic resistance of the walls of the micellae.

The equilibrium state between the micellae and the total sol can be expressed as follows:

$$P_i - P_o = E_i q$$

where P_i and P_o are the osmotic pressures inside and outside of the micellae, E_i is a constant proportional to the bulk modulus of elasticity of the micellae and q is the amount of water held by the micellae (water of hydration) per gram of gelatin. At low concentrations of gelatin the outside osmotic pressure

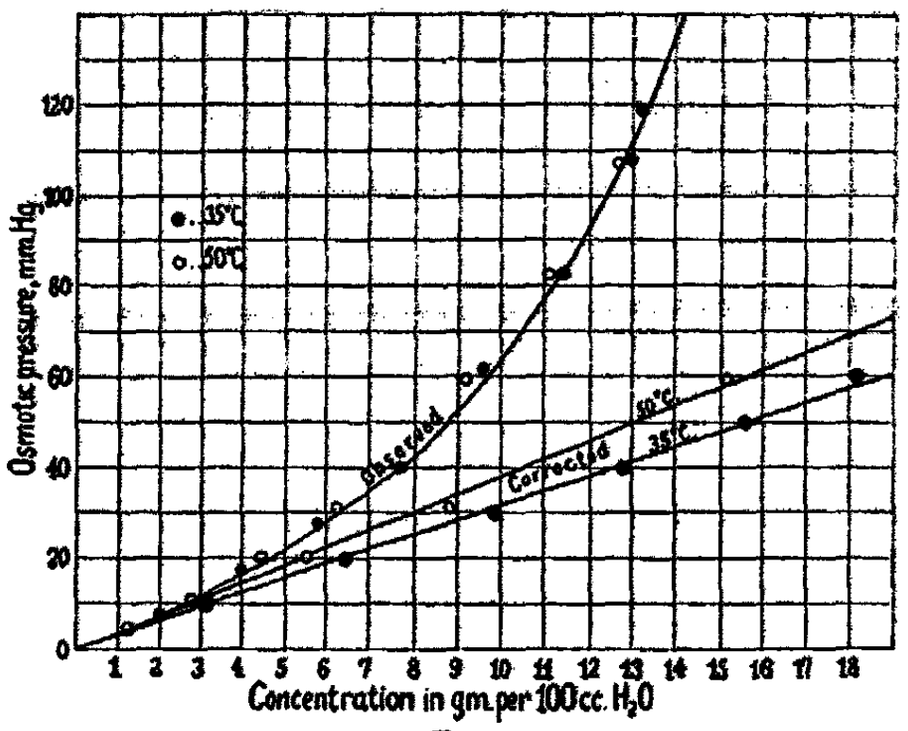

FIG. 5

Effect on the osmotic pressure-concentration curves of isoelectric gelatin of correcting the concentration of the gelatin for the water of hydration as calculated from viscosity measurements

is much smaller than the osmotic pressure inside of the micellae, hence the micellae take up relatively large amounts of water. But as the total concentration of gelatin increases the opposing outside osmotic pressure increases and the micellae swell less with the result that q, *i.e.*, the amount of hydration per gram of gelatin, gradually becomes less and less. Thus, although the micellae are at equilibrium with the outside solution, they are still under an elastic stress exerted by a pressure equal to $E_i q$, the magnitude of which decreases with the increase in the total concentration of gelatin. It is assumed that this elastic stress in the micellae is the cause of syneresis of gels, as will be described later.

Effect of Concentration of Gelatin on the pH—Viscosity Curves.

It is generally known that the addition of either acid or alkali to a freshly prepared gelatin sol raises its viscosity. In the presence of acid the viscosity reaches a maximum at pH 3.0 and then drops again. The pH effect on the viscosity of gelatin has been explained by Loeb as due to the swelling of the micellae in the gelatin sol. It is assumed that the micellae are of higher gelatin concentration than the total concentration of the gelatin in the out-

side solution; hence there is a greater concentration of acid in the micellae than in the solution outside of the micellae. It is this unequal distribution of the acid or alkali which causes the micellae to swell and hence brings about a rise in the viscosity of the gelatin sol. With increase in the total concentration of gelatin the difference in the concentrations of gelatin in the internal and

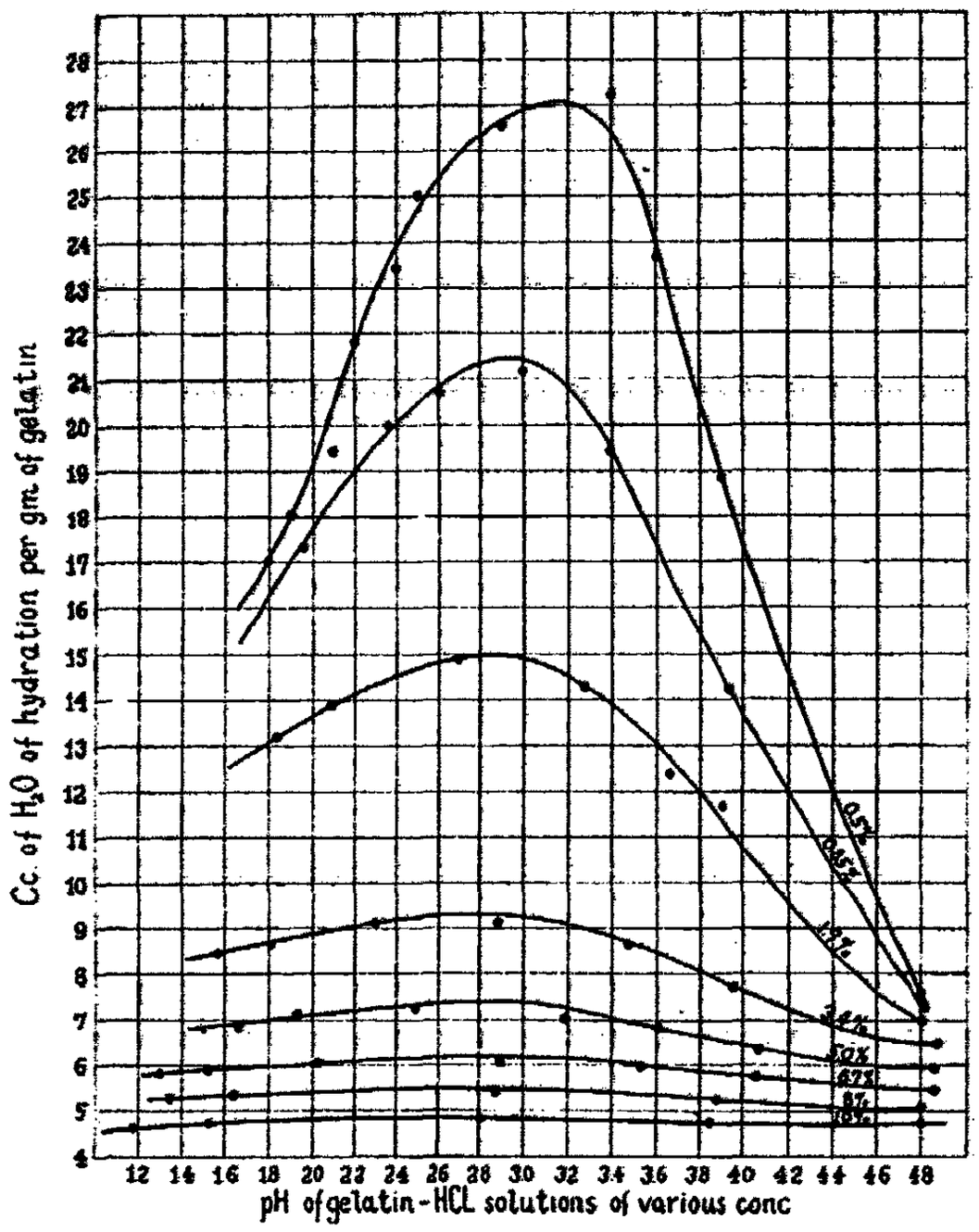

FIG. 6

Effect of concentration on the hydration of gelatin at various pH. The hydration values were calculated from viscosity measurements at 35°C by means of the formula $\eta = \frac{1+0.5\varphi}{(1-\varphi)^4}$

external liquid phases and hence also the difference in the distribution of the ions of the acid or alkali is gradually diminished. At the same time the total osmotic pressure of the gelatin solution which opposes the swelling of the micellae is continually increased. Hence the increase in viscosity at pH 3.0 over that of isoelectric gelatin should become less conspicuous with increase in the total concentration of the gelatin sol. That this is exactly what happens is shown in Table III.

TABLE III

Viscosity Measurement of Various Concentrations of Gelatin pH 4.7 and pH 3.0 at 37°C

Concentration in gm per 100 cc solution	0.5	1.0	2.0	3.0	4.0
Relative viscosity of gelatin pH 4.7	1.16	1.43	1.95	2.75	3.83
Additional viscosity = relative viscosity − 1	0.16	0.43	0.95	1.75	2.83
Relative viscosity of gelatin pH 3.0	1.84	2.39	3.44	4.54	5.78
Additional viscosity	0.84	1.39	2.44	3.54	4.78
Ratio of additional viscosity, pH 3.0/pH 4.7	5.24	3.23	2.57	2.02	1.69

Concentration in gm per 100 cc solution	5.0	6.0	8.0	10.0
Relative viscosity of gelatin pH 4.7	5.28	6.70	12.40	21.3
Additional viscosity = relative viscosity − 1	4.28	5.70	11.40	20.3
Relative viscosity of gelatin pH 3.0	7.12	9.06	14.20	22.0
Additional viscosity	6.12	8.06	13.20	21.0
Ratio of additional viscosity, pH 3.0/pH 4.7	1.43	1.42	1.16	1.03

The effect of the concentration of the gelatin on the hydration of gelatin at various pH is shown in Fig. 6. The hydration values were obtained from viscosity measurements at 35°C of various concentrations of gelatin freshly made up to various pH by means of HCl. The curves show that at a concentration of gelatin of about 10 per cent the pH effect on the viscosity of the sol disappears entirely, which indicates that at this concentration, the concentrations of gelatin inside and outside of the micellae are equal so that the osmotic pressure in the micellae is completely balanced by the osmotic pressure of the total sol.

Swelling and Syneresis of Isoelectric Gelatin[11]

When gels containing various amounts of gelatin are placed in cold water or dilute buffer solution of the same pH as that of the isoelectric point of the gelatin the following results are obtained. Gels of a gelatin content of more than 10 per cent swell while those of less than 10 per cent lose water and shrink. A gel containing about 10 gm of gelatin per 100 cc of solution neither swells nor shrinks. This is shown in Fig. 7.

This striking difference in the behavior of gels of various gelatin content may be explained qualitatively and predicted quantitatively on the basis of the following assumptions:

1. Swelling in gels of concentrations above 10 per cent is caused by osmotic pressure of the "soluble" component of gelatin which exists in solution

[11] Kunitz: J. Gen. Physiol., 12, 289 (1928).

in the liquid phase of the gel at a temperature even as low as 0°C. The amount of the dissolved component gelatin in the liquid phase, and hence the swelling, increases both with the total concentration of gelatin in the gel and with temperature.

2. Shrinking or syneresis in gels of a gelatin content of less than 10 per cent is caused by the elastic stress in the micellae of the gelatin sol before it was cooled and allowed to set. The elastic stress in the micellae is due to the osmotic pressure of the dissolved gelatin in the internal liquid phase in the

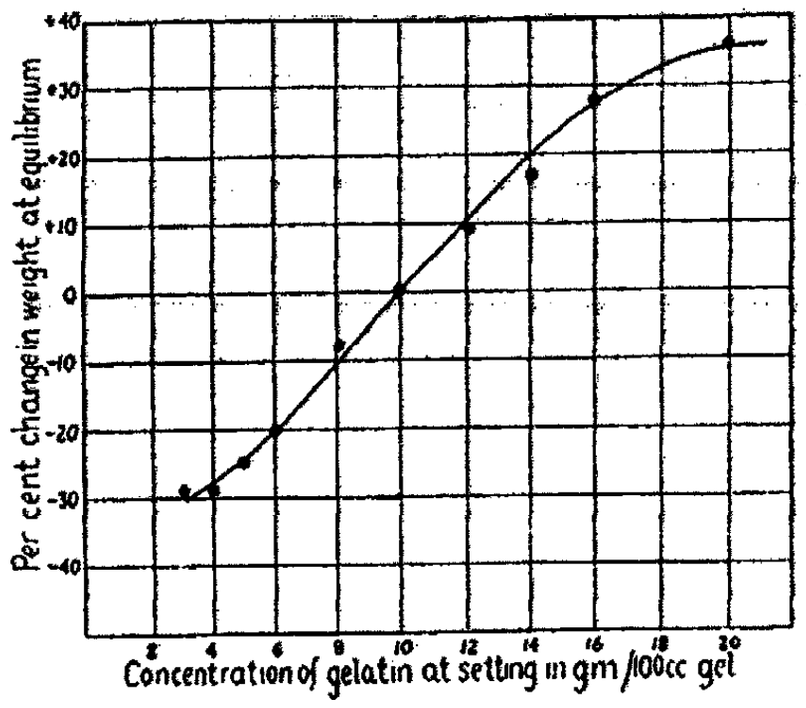

FIG. 7
Percentage change in weight of gels of various concentrations of isoelectric gelatin when placed in M/1000 acetate buffer pH 4.7 at 5°C

micellae. But as the gelatin solution is cooled and allowed to set the dissolved gelatin in the micellae becomes insoluble and precipitates out. The force which kept the micellae stretched is thus diminished. This allows the elastic walls of the micellae to shrink and lose water. The shrinking of each individual micella brings about a contraction of the whole network with the result that water is expelled not only from the micellae but also from the spaces between the micellae and the whole block of gel loses weight. This process is most rapid when the gel is placed in contact with water, since the loss of water from a dry gel is slow owing to the resistance offered by the dry surface film. As stated before, the elastic stress in the micellae of a gelatin sol due to the inner osmotic pressure becomes less as the total concentration of the gelatin increases. Hence when the stress on the micellae is removed by the precipitation of inner liquid on cooling of the sol there is less contraction in the micellar network of concentrated gels than in the dilute ones.

Thus while swelling increases with increase in concentration of gelatin in the gel, syneresis diminishes with the concentration. At a gelatin content of 10 per cent the force that causes swelling apparently balances the opposite force that causes syneresis or shrinking of the gel, and the gel neither swells nor shrinks.

3. A block of freshly set gel is under no elastic stress but becomes subjected to a tensile stress on swelling and to a compressive stress on shrinking, both forms of stresses being proportional to the amount of swelling or shrinking correspondingly. This is confirmed experimentally by double refraction measurements.[12] A block of gelatin at setting has no double refraction. A swollen block shows positive double refraction, corresponding to tension or stretching, while blocks which shrink show negative double refraction, corresponding to compression.

It follows therefore that both forces, namely the osmotic pressure of the liquid phase and the elastic stress in the micellae both of which tend to change the volume of the block, act against the elastic resistance of the block of gel. The amount of either swelling or shrinking of a gel depends then on the three forces, and at equilibrium we have

$$P_o - P_m = K \frac{V_e - V_o}{V_o} \qquad (1)$$

where P_o = osmotic pressure of liquid phase, P_m = pressure due to the stress in the micellae, K = bulk modulus of elasticity of the gel, both for tension and compression, V_o = volume of gel at setting, V_e = volume of gel at equilibrium. It is to be noted that $P_o - P_m$ represents the total swelling pressure of the gel.

The swelling pressures of gels of concentrations of higher than 10 per cent have been measured directly at 10°C and can be expressed approximately as the following function of V_e, where V_e is taken in cc of H_2O per gm of dry gelatin, namely

$$P_o - P_m = \frac{1330}{V_e} - 140 \qquad (2)$$

When
$V_e = 9.5$ then $P_o - P_m = O$
$V_e < 9.5$ " $P_o > P_m$
$V_e > 9.5$ " $P_o < P_m$

that is, at a concentration of 9.5 cc H_2O per gm of gelatin the gel exerts no swelling pressure; while at a lower concentration of gelatin, the swelling pressure becomes negative and the gel loses water, and at higher concentration the swelling pressure is positive and the gel swells.

Combining equations (1) and (2) we get an expression for the relation between V_o and V_e both expressed in cc H_2O per gm of gelatin, namely

$$\frac{1330}{V_e} - 140 = K \frac{V_e - V_o}{V_o}$$

which enables one to compute the amount of either swelling or shrinking of any gel if K is known.

This formula was found to hold quite well for the shrinking and swelling of a series of gels ranging in concentrations from 3 to 20 gm of gelatin in 100 cc

[12] Kunitz: J. Gen. Physiol., 13, 565 (1930).

of total volume. The smooth curve on Fig. 8 represents the equation while the dots are the observed values of the final concentrations of gelatin at equilibrium as plotted against the concentrations of gelatin at setting.

The bulk modulus of elasticity as derived from the equation appears to be independent of the concentration of the gel, but it is difficult to say whether this fact has any theoretical significance. The curve for $P_o - P_m$ has been taken for simplicity as a straight line while the actual values are probably on

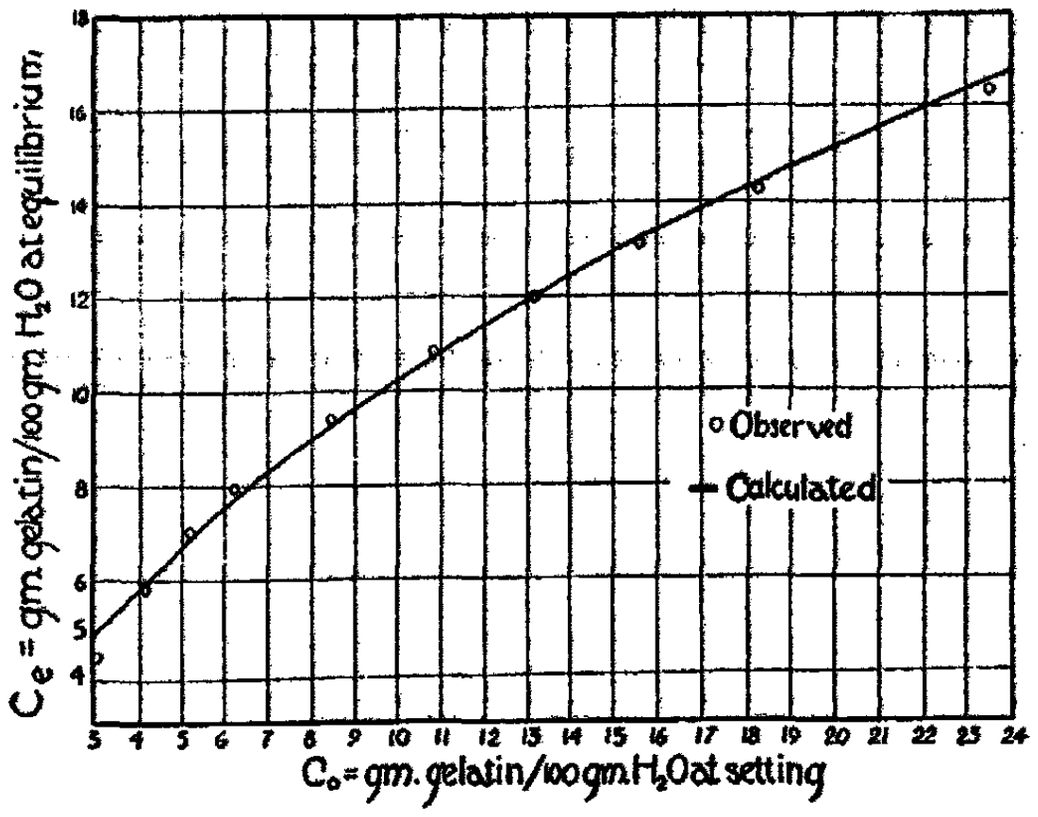

FIG. 8

Relation between the original and the final concentrations of the gelatin in swelling of gels. The continuous curve represents $\frac{1330}{V} - 140 = K\frac{V_e - V_o}{V_o}$ where K = 195 or

$$C_e = \sqrt{4.28 + 14.66\,C_o} - 2.07,\ C_e = 100/V_e,\ C_o = 100/V_o$$

a line which is convex downward. A curve of this form would result in a value of K which varied with the gelatin concentration, as is actually found to be the case when the relation between the swelling and the elastic stresses produced was determined by means of double refraction measurements.

Effect of Previous Treatment on Swelling[13] or Syneresis[11]

It follows from the preceding assumptions that the amount of swelling is determined by the concentration of the gelatin in the gel at the time of setting only and is not affected by subsequent drying or swelling at the same temperature, *i.e.*, a block which has been dried or swollen swells subsequently to the same final concentration as a block of the same original concentration placed directly in water.[14] It also follows that a block which has been dried

[13] Northrop: J. Gen. Physiol., 10, 893; Northrop and Kunitz: 905 (1927).

[14] This behavior may undoubtedly be modified by the "case-hardening" effect described by Sheppard and Sweet.

or swollen is under elastic stress and should therefore show fatigue. If such a block is kept for some time at a low temperature or warmed for a short time, the elastic stress should decrease, owing to fatigue and the block should then behave in the same way as a block which solidifid at the corresponding concentration. This is the result observed.

The effect of temperature, and the size and shape of the block on the equilibrium and also on the rate of swelling may be quantitatively predicted by means of these assumptions.

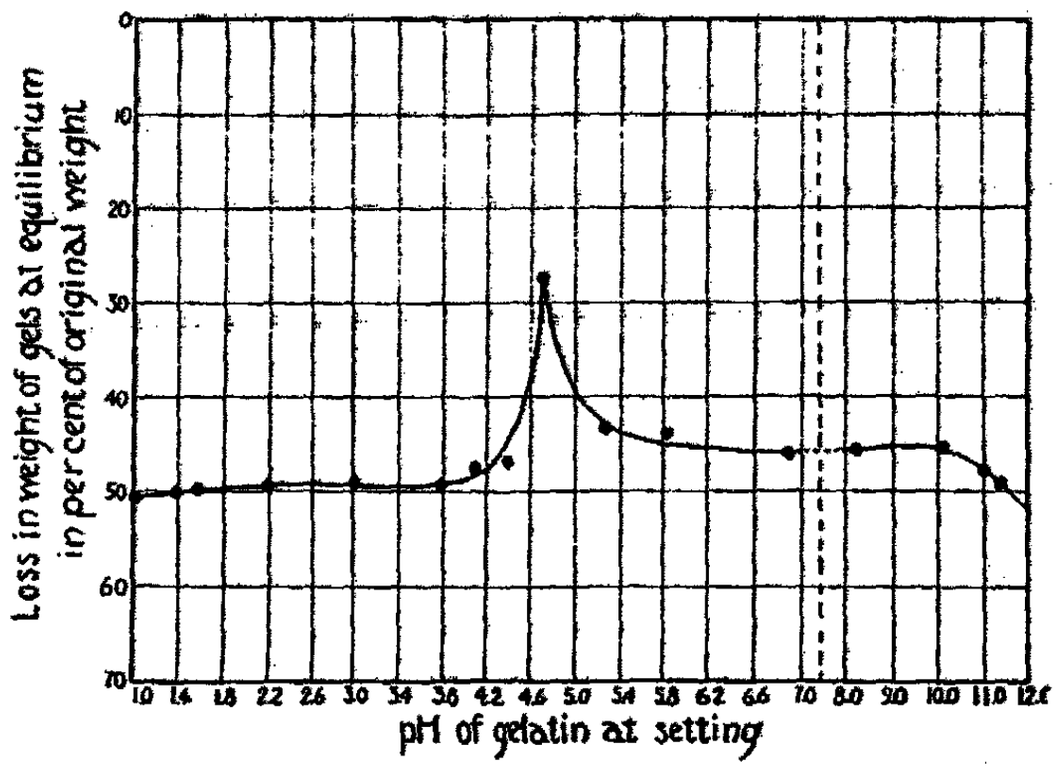

FIG. 9

Effect of pH on syneresis of 3 per cent gel in M/1000 acetate buffer pH 4.7 at 5°C.

Syneresis in Gels containing Acid or Alkali[11]

The amount of shrinking of dilute gels when placed in H_2O or dilute buffer both of pH about 4.7, depends not only on the concentration of gelatin but also on the pH and the electrolyte content of the gel before it was placed in H_2O or buffer solution. The effect of pH is shown in Fig. 9. It is seen that gels which had a pH other than that of the isoelectric point of gelatin lose more weight than gels made of isoelectric gelatin. The shrinking takes place only after the acid or alkali has been removed by neutralization and dialysis. The greater shrinking of gels which contained acid or alkali in solution at setting, over those which were electrolyte-free takes place only in gels of low gelatin content. The difference disappears in case of gels of concentrations above 6 per cent. The peculiar effect of the pH of the original solutions on the loss of water by the gels after the gel was brought back to the isoelectric point becomes clear on the basis of the micellar theory developed here. In dilute sols of gelatin containing moderate amounts of acid or alkali the micellae are much more swollen than at the isoelectric point due to a greater concentration of diffusible ions inside than outside of the micellae, and hence the micellae are

under a greater elastic strain. Cooling and setting does not change this unequal distribution of ions. Hence, until the ions are removed by dialysis the micellae do not lose water and no syneresis takes place. But as soon as the acid or alkali is removed by neutralization and dialysis the micellae shrink much more than in the case of originally isoelectric gels. With increase in the concentration of gelatin the pH effect on the swelling of the micellae in a gelatin sol diminishes rapidly as shown by viscosity measurements, with the result that the pH effect on syneresis in the gels is also diminished with

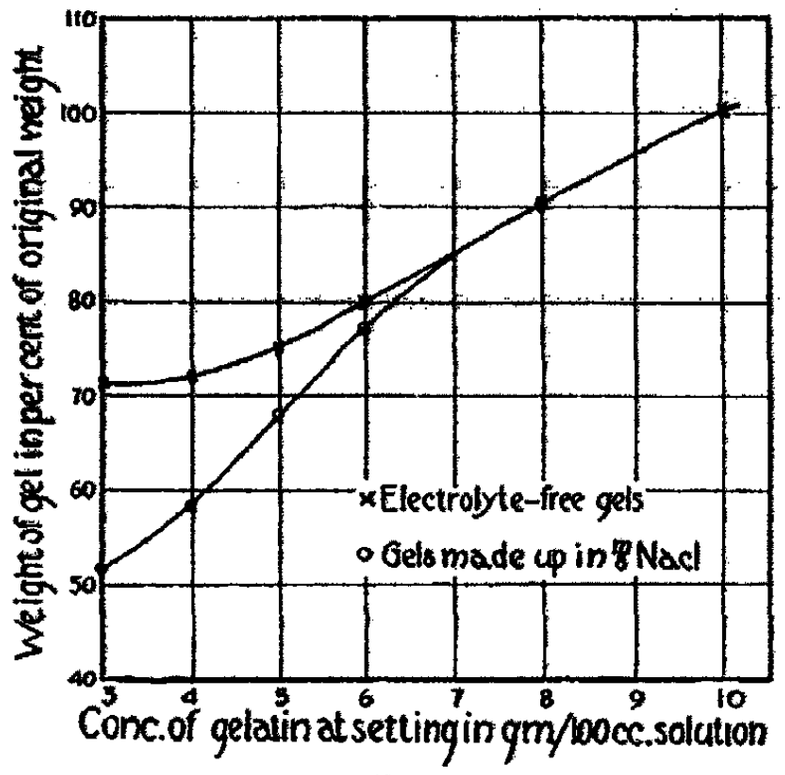

FIG. 10

Effect of NaCl on syneresis of various concentrations of gelatin blocks in M/1000 acetate buffer pH 4.7 at 5°C

increase in concentration of the gelatin. There is also another factor in the effect of acid or alkali on syneresis, namely the solubility effect which is shown also by salts.

The Effect of Salts on Syneresis[11]

The salt-containing gels of a gelatin content of less than 8 per cent are placed in large amounts of M/1000 acetate buffer pH 4.7 at 5°C the salt dialyzes out and the gels begin to lose water. But the amount of water lost in this case is considerably greater than in the case of electrolyte-free gels. This is shown in Fig. 10. Salt increases the solubility of gelatin, hence, in the presence of the salt, the gelatin in the micellae remains in solution instead of precipitating and the micellae do not shrink. But as soon as the salt is removed by dialysis the dissolved gelatin in the micellae precipitates out and the contraction and hence the loss of water results. The net result is therefore a greater loss of water due to syneresis in salt-containing gels than in salt-free gels of pH 4.7.

Acids and alkalies in addition to their pH effect on gelatin have also an enormous effect on the solubility of gelatin. A continuous increase in acid

or alkali concentration has the same effect on the solubility of gelatin as addition of large amounts of salt, and at higher concentration of acid or alkali the solubility effect prevails. This explains why the curve for syneresis effect of pH does not show a maximum point as do the pH viscosity curves.

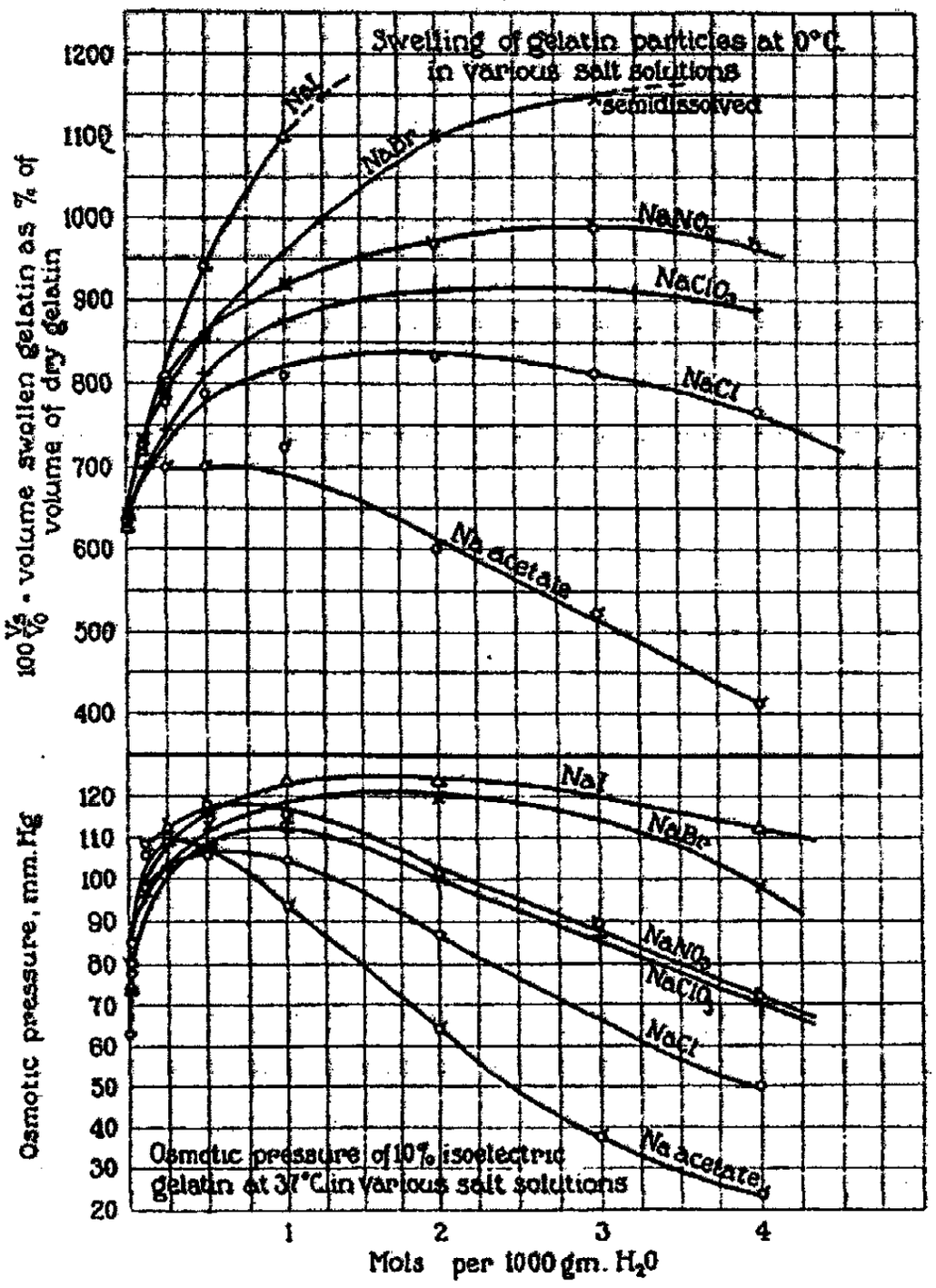

FIG. 11

Comparison of osmotic pressure and swelling of gelatin in various salt solutions

Osmotic Pressure and Swelling of Isoelectric Gelatin in Salt Solutions.[15]

The studies of Loeb have shown that the swelling and osmotic pressure of gelatin, caused by acid or alkali, is depressed by salts; the amount of depression increases with the concentration of the salt and also with the valency of either the anion or the cation, depending on whether the osmotic pressure (or swelling) was caused by acid or by alkali.

[15] Northrop and Kunitz: J. Gen. Physiol., 8, 317 (1926).

The effect of salts on the osmotic pressure and swelling of isoelectric gelatin in the absence of acid or alkali is quite different. This is shown in Figs. 11 and 12. The curves show that salts usually increase both the osmotic pressure and the swelling of isoelectric gelatin, and the effectiveness of the

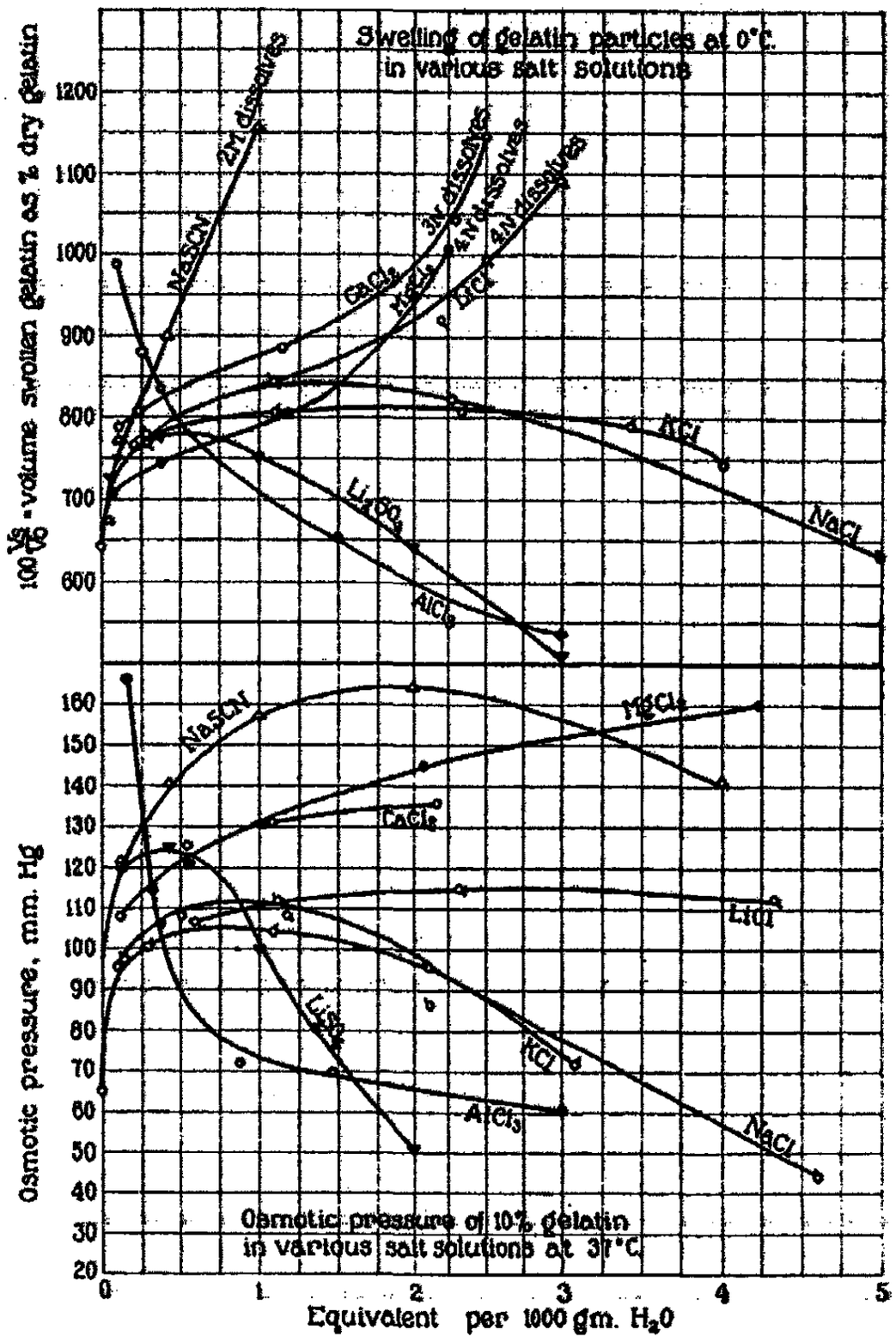

FIG. 12

Comparison of osmotic pressure and swelling of gelatin in various salt solutions

various salts here does not depend on the valency of the salts but on their chemical nature, so that the salts may be arranged in a series quite similar to the Hoffmeister series. The curves both for osmotic pressure and swelling run parallel throughout a wide range of concentrations of salt, which shows

that the increase in the amount of swelling of isoelectric gelatin caused by salt is due primarily to an increase in the osmotic pressure of the gelatin. Some salts such as aluminum chloride raise the osmotic pressure of gelatin through the formation of non-diffusible complex ions between the gelatin and one of the ions of the salt, and thus are able to set up a Donnan equilibrium. But most salts raise the osmotic pressure by splitting the micellae into smaller units. This follows from the experimental fact that salts affect only slightly the osmotic pressure of the soluble component of gelatin, while the osmotic pressure of the insoluble fraction of gelatin is increased enormously

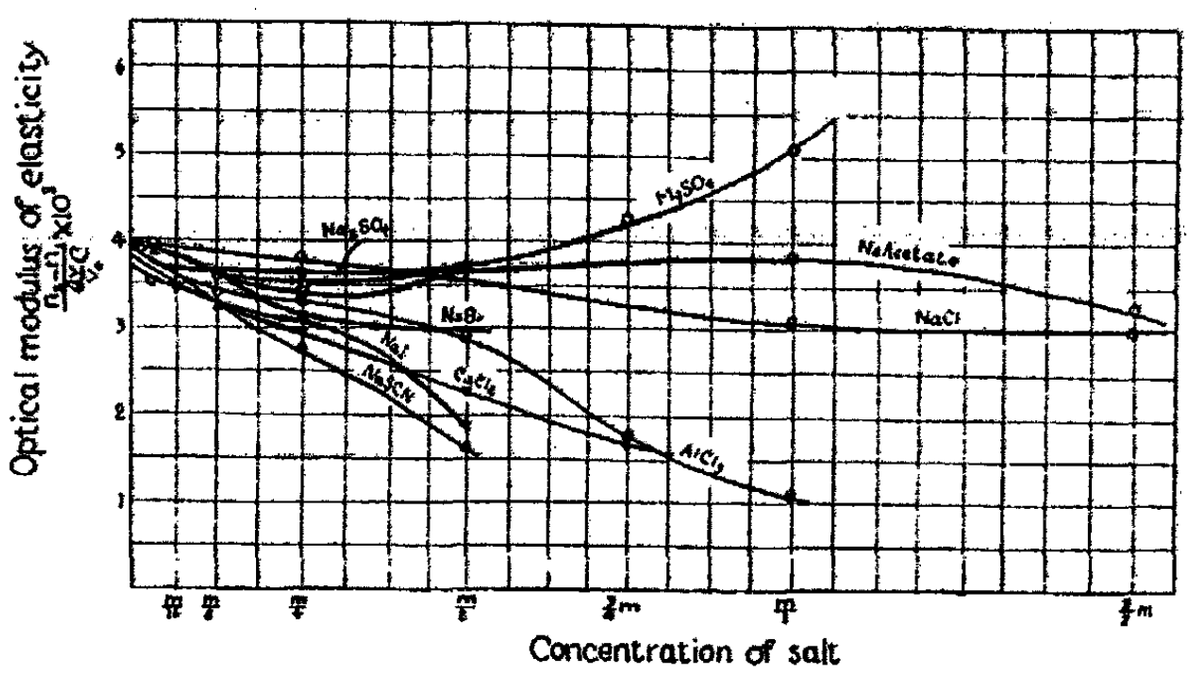

FIG. 13
The effect of salts on the elasticity of 10 per cent gels as calculated from double refraction measurements

by salts. This is shown in Table IV. In the case of gels the swelling pressure is greater in the presence of salt for the reason that salts increase the concentration of dissolved gelatin in the liquid phase.

TABLE IV

Effect of NaSCN on the Osmotic Pressure of 5 Per Cent Soluble and Insoluble Fractions of Gelatin at 37°

Fraction	Soluble		Insoluble	
Concentration of NaSCN inside and outside	0	2M	0	2M
Osmotic pressure, mm Hg	50	61	8	35

In high concentration salts begin to affect the bulk modulus of elasticity of the block of gel. This is especially true of such salts as $CaCl_2$, NaSCN, NaI, and LiCl. In the case of these salts the parallelism between the osmotic pressure and swelling curves holds only for low concentration; at concentra-

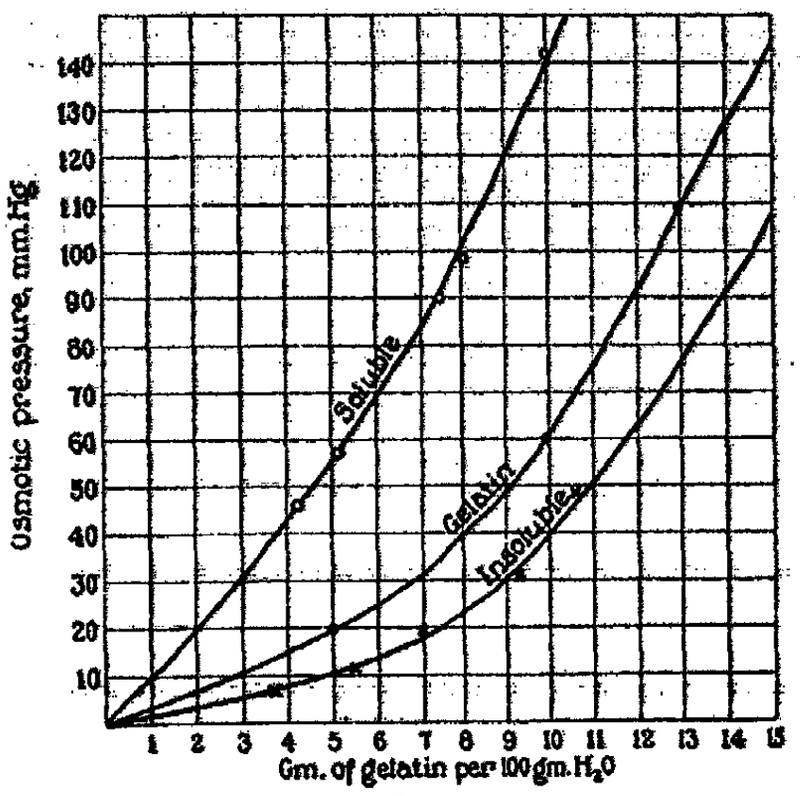

FIG. 14
Osmotic pressure at 37°C of various concentrations of isoelectric gelatin and of the soluble and insoluble fractions

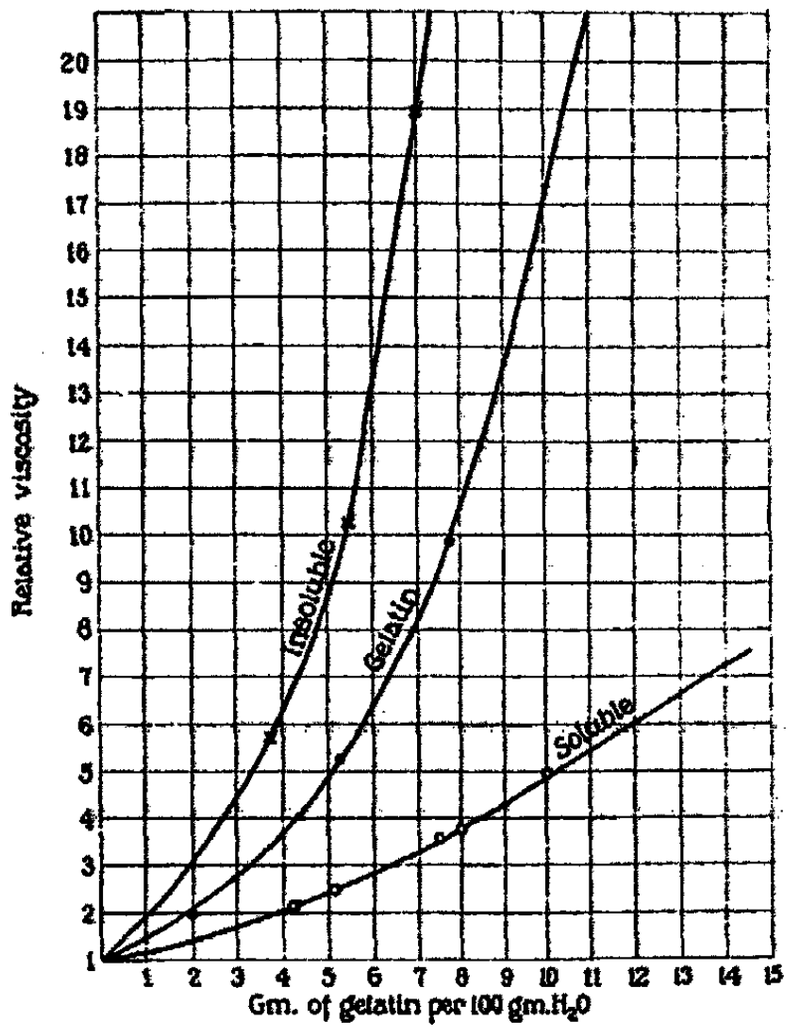

FIG. 15
Viscosity at 37°C of various concentrations of isoelectric gelatin and of the soluble and insoluble fractions

tions above M/2 the osmotic pressure curves begin to drop with increase in concentration of salt, while the swelling curves continue to rise, owing to the rapid drop in the elasticity of the gel, until the gels become too soft to stand any swelling pressure and fall apart (dissolve) completely in very high concentrations of these salts.

A detailed study of the effect of salts on the elastic properties of gelatin during swelling was made[12] by means of double refraction measurements and the results are shown in Fig. 13.

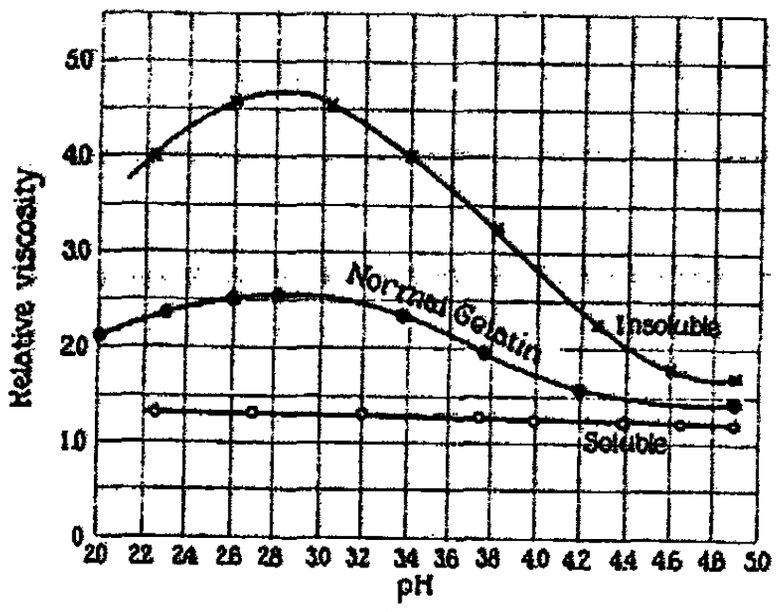

FIG. 16

Effect of addition of HCl on the viscosity at 37°C of 1 per cent solutions of isoelectric gelatin and of the soluble and insoluble fractions

In concentration below M/8 most of the salts investigated have practically no effect on the elasticity of gelatin, while above M/8 salts like NaSCN, NaI, or $CaCl_2$ bring about a rapid decrease in the modulus of elasticity of the gels with increase in the concentration of the salts.

Fractionation of Gelatin[16]

If gelatin really consists of two components it should be possible to separate them at least partly and further the fractions should have very different properties. The "soluble" fraction should have high osmotic pressure, low viscosity and the viscosity should not change much with the addition of acid or alkali since it contains no micellae. The "insoluble" fraction should have very low osmotic pressure, very high viscosity and the viscosity should vary markedly with the pH since it contains a larger percentage of micellae than the original gelatin. The "insoluble" fraction should not swell much in H_2O and mixtures of the two fractions should swell more the larger the percent of soluble fraction. The "insoluble" fraction should swell in acid or alkali.

Schryver[17] and his associates found that gelatin could be fractionated by allowing dilute isoelectric gelatin solutions to set. Syneresis occurs under

[16] Northrop and Kunitz: J. Gen. Physiol., 10, 167 (1927); 12, 379 (1929).
[17] Biochem J., 17, 473 (1923).

these conditions and a soluble compound is found in the filtrate. This observation was repeated and confirmed by the writers and a "soluble" and "insoluble" fraction prepared by a modification of Schryver's method. These fractions had the properties predicted as shown in Figs. 14 to 17.

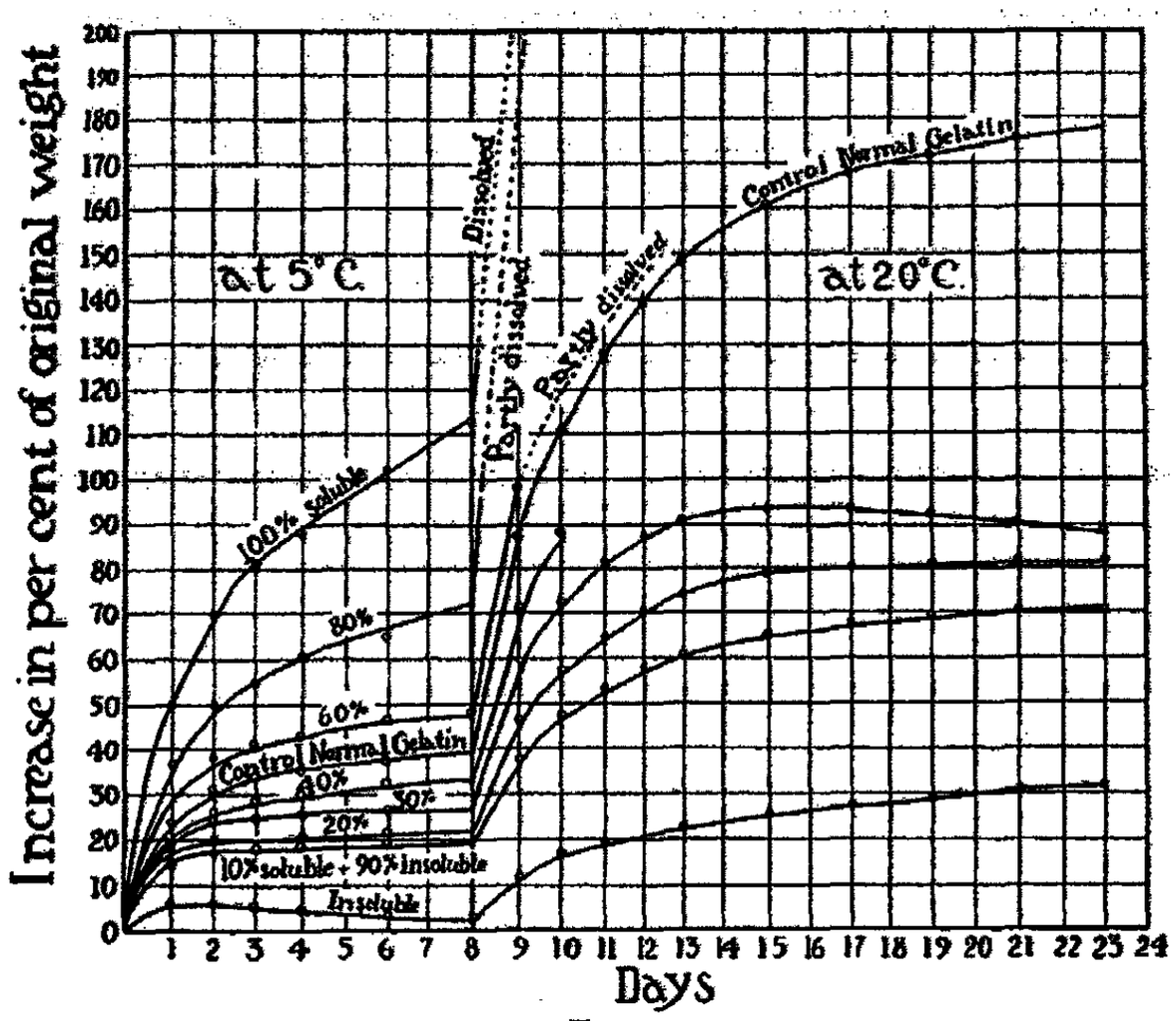

FIG. 17
Swelling of 30 per cent gels consisting of mixtures of insoluble and soluble fractions of gelatin. Blocks of gel weighing about 1.5 gm each were allowed to swell in 200 cc M/30 acetate buffer pH 4.7

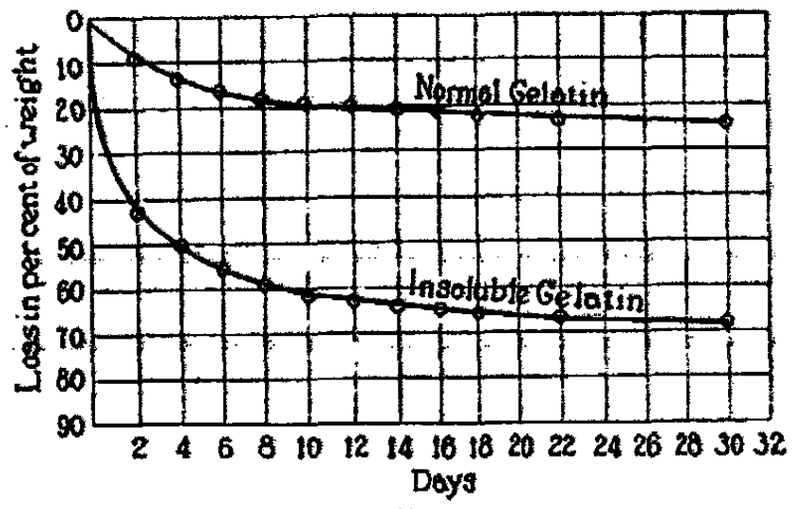

FIG. 18
Syneresis of 5 per cent gels in M/30 acetate buffer pH 4.7 at 5° C

The presence of two components in gelatin gels has been deduced by Trillat[18] from X-ray studies.

[18] Compt. rend., 190, 265 (1930).

Syneresis of Dilute Gels of "Insoluble" Gelatin[19]

In ordinary gelatin the micellae form only a part of the total gelatin, the rest of which is found in solution outside of the micellae. A solution of the "insoluble" fraction of gelatin in dilute NaOH, on the other hand, consists nearly completely of a dispersion of swollen micellae, as shown by the high viscosity of such a solution. Hence it would be expected that a dilute gel made of the "insoluble" gelatin should lose more water when put in dilute buffer pH 4.7 than a corresponding gel made from ordinary gelatin. That this is actually what happens is shown in Fig. 18 where the curves for the rate of shrinking of the 5 per cent gels made of ordinary gelatin and of the "insoluble" fraction of gelatin are given.

Summary

The swelling, osmotic pressure, viscosity and syneresis of gelatin gels or sols may be quantitatively accounted for on the following assumptions.

Gelatin sols or gels are two-phase, three-component systems. The solid phase consists of particles (micellae) of an insoluble ingredient of the gelatin. The liquid phase is an aqueous solution of the "insoluble" fraction and of a "soluble" fraction in water.

Each micella is a separate system consisting of an insoluble, elastic wall or network containing an "internal" liquid phase. This "internal" liquid phase is a solution of the "insoluble" fraction forming the wall of the micella and of one or more other fractions which have a high temperature coefficient of solubility and for which the walls of the micellae are impermeable.

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[19] Kunitz and Northrop: J. Gen. Physiol., 12, 379 (1929).

THE REVERSIBILITY OF PROTEIN COAGULATION

BY M. L. ANSON AND A. E. MIRSKY

Coagulation is the most striking reaction of the proteins. For ages it has been a familiar phenomenon because of the prominent rôle it plays in cookery. The change occurring in egg-white when an egg is immersed in boiling water shows how conspicuous protein coagulation can be. Indeed, with combustion and fermentation, protein coagulation was one of the first chemical processes recognized by man. It was only natural, therefore, that this process should early have attracted those interested in the chemical study of living phenomena. For several hundred years the recognition in plant and animal tissues of what is now called protein depended on its property of coagulating when heated. The result of this was that during the nineteenth century there was widespread among biologists and biochemists an acquaintance with even some of the minor details of protein coagulation. More recently, however, there has been a tendency among biologists to neglect the study of protein coagulation, for it has been supposed that coagulation is a degradation process, that coagulated protein is an early stage in the disintegration of the protein molecule, and finally that coagulation, being irreversible, can be of little physiological interest. Investigation of the acid-base properties of proteins appeared to be of greater physiological significance, so that many physiologists are now familiar with protein properties that can be detected only with refined methods, while they are hardly acquainted with some of the gross, easily-recognizable properties. For the investigator of biological function it is an important difference between the acid-base properties and those associated with coagulation that whereas the former are common to many substances, the latter appear to be unique, peculiar to proteins. If it could be shown that protein coagulation is reversible, its biological significance would be greatly enhanced.

Description of Coagulation. The coagulation of a protein occurs in two distinct steps:[1] first, a chemical change in the protein and second, precipitation of the altered protein. In the first step, the protein is so modified (whether by heat, acid, alkali, alcohol, or a number of other agents) that it is no longer soluble under conditions under which the original protein is soluble. Whereas the original protein is soluble at its isoelectric point, modified protein is insoluble at the isoelectric point. Addition of acid or alkali dissolves modified protein. The process whereby the original, or *native*, protein is changed is called *denaturation* and the changed protein is called a *denatured protein*. The distinctness of the two steps of coagulation is apparent when denaturation occurs at a hydrogen ion concentration removed from the protein's isoelectric point, for under these conditions even after prolonged heating, no visible change may be noticed. Denaturation has, however, taken place, and the

[1] Chick and Martin: J. Physiol., 40, 404 (1910); 43, 1 (1911).

denatured protein has remained in solution, as can be shown by adjusting the hydrogen ion concentration to the isoelectric point, whereupon denatured protein precipitates. Although the second step in coagulation, precipitation of denatured protein, is readily reversible, the first step, denaturation, has been generally supposed to be irreversible.

Flocculation of denatured protein depends primarily upon the change on the protein particles and is therefore probably analogous to the coagulation of colloids in general. Denaturation, on the other hand, is a process peculiar to proteins and should not be confused with the ordinary coagulation of colloids. Investigation of the kinetics of denaturation[1] shows it to be a process following the course of a unimolecular reaction, the velocity of which is increased about 600 times when the temperature is raised 10°C. Denaturation may therefore be slow at one temperature and rapid at a temperature only a few degrees higher. This is the reason why proteins appear to have a definite temperature of coagulation. Perhaps this remarkable temperature coefficient of denaturation will arrest the attention of chemists who may know of some analogous reaction; at present it appears to be unique. It has accordingly been used to detect the rôle of protein in certain processes. When, for instance, bacteria are killed by heat, the process has a temperature coefficient of about 600 for 10°C, indicating that heat causes death in bacteria by denaturing certain bacterial proteins.[2] The inactivation of some enzymes by heat has a temperature coefficient of 600 for 10°C, indicating that denaturing a protein destroys enzymatic activity and that protein is probably part of the enzyme molecule. For crystalline pepsin this has been more directly demonstrated, for its loss of activity is quantitatively paralleled by its denaturation.[3]

A chemist will at once ask what structural changes occur in denaturation. The process has been followed mainly by physico-chemical observations, particularly by the gross change in solubility, and little is known of the underlying structural changes. In addition to the change in solubility it has been observed that denaturation causes a large increase in viscosity, a slight change, if any, in acid-base properties,[4] and, apparently, the loss of ability to crystallize. In the case of hemoglobin the changes are especially conspicuous, for denaturation of globin, indirectly affecting the heme to which it is attached, causes a marked change in color and absorption spectrum and loss of the ability of heme to combine loosely with oxygen. It is not known what modifications in the chemical groups of globin bring about these changes. The only definite structural changes known to accompany denaturation are in the sulfhydryl groups.[5] The presence of sulfhydryl groups can be demonstrated in denatured egg albumin by means of color reactions and oxidation-reduction reactions. When native egg albumin is examined by the same methods these sulfhydryl groups cannot be detected. The same, or a similar

[2] Chick: J. Hygiene, 10, 237 (1910).
[3] Northrop, J. Gen. Physiol. 13, 739(1930).
[4] Booth: Biochem. J., 24, 158 (1930).
[5] Arnold: Z. physiol. Chem., 70, 300 (1910).

difference, can be demonstrated between the native and denatured forms of other proteins. We are now making a quantitative study of protein sulfhydryl groups.

The Supposed Irreversibility of Coagulation. Ever since coagulation has been studied at all, it has been taken as almost axiomatic that coagulation is irreversible. Usually coagulation has been thought to be the first step in the degradation, the breaking down of the protein. As a result, in the study of the chemistry of the normal, native protein coagulation has been considered something to be avoided. And in discussions of the physiological rôle of the proteins, coagulation has hardly been mentioned. It is true that procedures which result in the denaturation of proteins also result in their degradation. Heat, which denatures proteins, also splits off ammonia. Acid which denatures proteins also splits off amino acids. Were such changes an inherent part of denaturation, then obviously reversal of denaturation would be impossible. But, as the Sörensens[6] showed, the splitting off of ammonia by heat has nothing to do with denaturation. It is a secondary change in the protein which takes place slowly when the protein is heated after it has already been denatured. In general, there is no evidence in any case that the decomposition caused by denaturation procedures is anything but a secondary reaction which is entirely separate from denaturation itself. Reversal of denaturation cannot, therefore, be excluded as impossible on the *a priori* ground that denaturation involves decomposition.

The only evidence that denaturation is irreversible has been that denaturation could not be reversed. It has long been familiar, for instance, that if an acid or alkaline solution of denatured egg albumin is brought to the isoelectric point of egg albumin, all the protein precipitates. Indeed, whatever one does to denatured egg albumin apparently one cannot prepare native egg albumin from it again. This negative result might mean that denaturation cannot be reversed. But it might also mean merely that egg albumin is unsuitable material for the experiment, that denaturation can be reversed only with difficulty, or that a special technique is required.

The Reversal of the Coagulation of Hemoglobin. Our experiments[7] on the reversibility of coagulation had their origin in a simple but inconclusive experiment with hemoglobin. An alkaline solution of denatured hemoglobin was neutralized. Practically all the protein precipitated, but (as is not the case with egg albumin) a small fraction of the protein remained in solution. Consequently, the supernatant solution was slightly colored whereas when a precipitate of denatured hemoglobin is shaken with water, the water remains colorless. Furthermore, the spectrum of native hemoglobin is entirely different from that of denatured hemoglobin and the small amount of protein in the supernatant solution had unmistakably the spectrum of native hemoglobin. Either this small amount of hemoglobin had escaped denaturation in the first place or the coagulation of hemoglobin had been partially reversed.

[6] Sörensen and Sörensen: C. r. Trav. Lab. Carlsberg, **15**, No. 9, 1 (1925).

[7] Anson and Mirsky: J. Physiol., **60**, 50 (1925); J. Gen. Physiol., **9**, 169 (1925); **12**, 273 1928; **13**, 121, 133, 469, 477 (1930); Physiol. Rev., **10**, 506 (1930).

The explanation of the result on the basis of incomplete coagulation became unlikely when, with improvement in technique, it became possible to convert not a few per cent but two-thirds and more of the coagulated hemoglobin into a protein with the characteristics of native hemoglobin. Such "reversed" hemoglobin is soluble, coagulable, and crystallizable. It has the spectrum of native hemoglobin and can combine loosely with oxygen.

The technique of the experiments is simple. It consists in reversing the denaturation procedure by neutralizing an acid solution in two steps. Hemoglobin is readily denatured by acid. If an acid solution is rapidly and completely neutralized, that is, brought to the isoelectric point of the protein, then practically all the insoluble, denatured protein is precipitated. In fact, denatured hemoglobin is insoluble not only at its isoelectric point but in a wide region around its isoelectric point. If, however, the acid solution is not completely neutralized in one step, but is brought to the edge of the precipitation zone by adding just insufficient alkali to cause precipitation, then if, after a time, more alkali is added to complete the neutralization, only about a third of the protein is precipitated. The rest seems to be native hemoglobin. Similarly, if just enough alkali is added to make the solution just alkaline enough to prevent precipitation, then if, after a time, the solution is neutralized by the addition of acid, only a fraction of protein is precipitated.

All these reactions can be followed with peculiar ease in the case of hemoglobin because hemoglobin is a pigment. The color of the solution tells immediately about how much protein it contains. The spectrum of the solution tells whether the protein is native or denatured. Hemoglobin consists of a colorless protein, globin, joined to an iron pyrrol pigment, heme. In the blood, hemoglobin transports molecular oxygen from the lungs to the tissues. Heme itself could not act as a carrier of oxygen. It is not soluble enough and it does not combine loosely with oxygen in the way hemoglobin does. It is by combination with globin that heme is modified to give hemoglobin its valuable biological properties. The globin must be native. The compound of heme with denatured globin (called globin hemochromogen and possessing its own type of spectrum) is not soluble in water and does not combine loosely with oxygen.

Changes, then, such as denaturation of globin to which heme is attached in hemoglobin, are reflected in changes of the properties of heme, particularly in the spectroscopic properties which are readily and accurately followed. Heme in hemoglobin may therefore be used as a convenient and sensitive indicator of what is happening to globin. Just as globin influences heme with which it is combined, however, heme also influences globin, for instance by influencing the ease of its denaturation and the reversal of this denaturation. *A priori* it might even be true that the experiments on the coagulation of hemoglobin which have been described are concerned not with the general properties of the coagulable proteins but with the peculiarities of hemoglobin, peculiarities due to the effects of heme on globin. All the available experimental evidence, however, indicates that the results obtained from the study of the coagulation of hemoglobin are entirely general.

In the first place, in all the ways which have been tried hemoglobin behaves like a typical coagulable protein. All the procedures such as heating, exposure to ultra-violet light and to high pressure, shaking, adding acid, alkali, alcohol, acetone, urea or thiocyanate, which convert egg albumin into an insoluble denatured protein have the same effect on hemoglobin. The heat coagulation of hemoglobin like that of egg albumin obeys the equation of a unimolecular reaction and has the extraordinary temperature coefficient of over 600. And denatured hemoglobin has the same general properties as denatured egg albumin.

The Reversal of the Coagulation of other Proteins. The most convincing evidence that the hemoglobin reactions are not due simply to the presence of heme is that precisely the same experiments can be carried out even in the absence of heme. Colorless globin itself behaves just like hemoglobin. If an acid solution of denatured globin is rapidly and completely neutralized in one step, then practically all the protein is precipitated, especially if there is salt in the solution. If the two-step procedure is used, however, then a large yield of soluble, coagulable protein is obtained. With serum albumin the experiments are even easier. Denatured serum albumin is soluble except *exactly* at its isoelectric point or in the presence of concentrated ammonium sulfate. In neutralizing a solution of denatured serum albumin unless one has been very careful to secure the correct hydrogen ion concentration one does not observe any precipitate at all. To obtain from denatured serum albumin a large yield of albumin which is soluble even in concentrated salt solution it is not necessary to neutralize in two steps. Simple, complete neutralization in one step suffices. One need not even let the solution stand before making the test for native protein. In fact, it is hard in neutralization experiments with denatured serum albumin to avoid the reversal of coagulation. So long ago as 1910, Michaelis and Rona[8] probably observed reversal. Unfortunately, there was some confusion at the time about two different kinds of coagulation. And the test for denatured serum albumin was uncertain. As a result, these experiments never received the attention they deserved. Later (at the same time as our hemoglobin experiments) Spiegel-Adolf[9] gave good physico-chemical evidence of the reversibility of the coagulation of serum albumin. More recently (unpublished experiments) we have studied serum albumin in a somewhat different way and have succeeded in obtaining from coagulated serum albumin, crystals of soluble coagulable protein in any desired amount.

With egg albumin, no great amount of reversal has resulted from any procedure so far tried, a result in harmony with previous experience. Just as the great ease of reversal in the case of serum albumin seems to be associated with the great solubility of denatured serum albumin, so in the case of egg albumin the difficulty of reversal seems to be associated with the great insolubility of denatured egg albumin. Denatured egg albumin not only is insoluble over a wide range of hydrogen ion concentration around its isoelectric

[8] Biochem. Z., 29, 494 (1910).
[9] Biochem. Z., 170, 126 (1926).

point, but even beyond the zone of visible precipitation, it has a great tendency to form invisible aggregates (unpublished experiments). This is readily shown by viscosity measurements. In fact, the conditions for reversal in the case of other proteins are, in the case of egg albumin, the conditions for gel formation. It is possible to obtain a clear gel from a solution of denatured egg albumin containing only a half a per cent of protein.

The ease of reversal then, varies from one protein to another; from one hemoglobin derivative to another; from the hemoglobin of one species to that of another; from serum albumin to egg albumin. Such differences in the ease of reversal are not surprising since, as is well known, there are similar differences in the case of denaturation. Where reversal is possible, it is brought about by keeping the protein for a time in a solution that is beyond the precipitation or aggregation zone and yet not too far from the isoelectric point. With denatured egg albumin it does not seem possible to realize such conditions.

It remains to describe the more detailed evidence in favor of the reversibility of coagulation. Clearly it is not sufficient to obtain from a protein which seems to be denatured a protein which seems to be native. There must be adequate tests for the completeness of the coagulation and for the identity of the protein obtained from the coagulated protein with the original native protein. To obtain *completely* conclusive results is at present impossible. Not enough is known either about the changes involved in denaturation or about the means of characterizing completely a native protein.

Evidence of the Completeness of Coagulation. Since the most conspicuous change associated with denaturation is the change in solubility, the most obvious test for complete denaturation is insolubility. This test has been made in all cases. Usually an acid solution was rapidly neutralized with resulting complete precipitation of the protein. In one experiment, it was possible to test for insolubility under exactly the conditions under which reversal took place. To an acid solution of denatured hemoglobin there was added an excess of alkali just sufficient to keep the protein in solution. If this solution was half saturated with ammonium sulfate *immediately*, practically all the protein was precipitated. The later the salt was added, the less protein was precipitated. Finally, two-thirds of the protein remained in solution. In other words, denatured hemoglobin originally brought into slightly alkaline solution was insoluble in half saturated ammonium sulfate. With time it gradually changed into another form which like native hemoglobin was soluble.

It might be objected that precipitation at the isoelectric point is not an adequate test for insolubility or denaturation. *Conceivably*, when a denatured protein is precipitated it *might* carry down any native protein present. To explain reversal on this basis one must assume that only one-third the protein is denatured and that this third, when precipitated carries with it two-thirds which escapes denaturation. Experimentally, however, there is as yet no evidence that this can take place. If one prepares a known mixture of native and denatured hemoglobin or globin and precipitates the denatured protein, the concentration of native protein in the solution is not changed.

About the same yield of soluble protein is obtained from denatured protein if it is left in acid three minutes or eighteen hours; if it is heated, or left in acid, or heated in acid at two different temperatures; if it is denatured by urea, or trichloracetic acid, or 90 per cent acetone containing acid. If obtaining soluble protein were simply an indication of incomplete denaturation the yields ought to vary enormously with the time to which the protein is subjected to the denaturation procedure and with the nature of the denaturation procedure. The only alternative conclusion is that complete denaturation is impossible with the ordinary procedures.

In the case of denaturation by urea, it is possible to follow the course of denaturation by viscosity measurements. Concentrated urea solutions denature proteins slowly and also keep denatured proteins in solution, even at the isoelectric point. As the protein remains in the urea solution, more and more of it is converted into a form which is insoluble in the absence of urea. Associated with this formation of insoluble, denatured protein there is a gradual increase in the viscosity of the urea solution. Finally, all the protein is precipitated if the urea is removed. From this time on there is no further change in the viscosity. The hemoglobin precipitate formed by removing the urea after the viscosity has ceased to change may be largely reconverted by the reversal procedure into soluble, coagulable protein.

Lastly, we have recently been testing the completeness of denaturation by measuring the extent of specific group changes.

Evidence of the Completeness of Reversal. In all, then, the evidence so far obtained indicates that the experiments on the reversibility of coagulation have been started with completely coagulated protein, that at least no significant part of the soluble protein finally obtained is derived from protein which never was denatured. To complete the proof of the reversibility of coagulation it must be shown that the soluble protein finally obtained is the same as the native protein originally coagulated. It might be true that some soluble fraction was extracted from the coagulated protein, or that some parts of coagulation were reversed—enough to give a soluble protein—but that the "reversed" protein was still quite different quantitatively from the original protein.

Normal hemoglobin and "reversed" hemoglobin have accordingly been compared in quite a number of ways, some of them possible only because of the presence of heme in the molecule as an indicator. In the first place "reversed" hemoglobin is not only soluble, but it can by heating be coagulated again. The temperature of coagulation is exactly the same as that of normal hemoglobin. Similarly "reversed" hemoglobin can be crystallized (no denatured protein has yet been crystallized) and the crystals to the unaided eye seem to have the same form as those of normal hemoglobin. Precise crystallographic measurements have not been made. The spectrum of "reversed" hemoglobin has the same pattern as that of normal hemoglobin. The bands are in the same positions within the small experimental error of two Ångström units. Furthermore, "reversed" hemoglobin can be converted into pigments having the same characteristic spectra as the derivatives of normal hemo-

globin. "Reversed" hemoglobin, like normal hemoglobin but unlike denatured hemoglobin, can combine loosely with oxygen. It has less affinity for oxygen than for carbon monoxide and the ratio of the two affinities is the same as in the case of normal hemoglobin.

The tests which have just been described are sensitive enough to distinguish readily between the slightly different hemoglobins of different mammals. Yet they cannot distinguish between "reversed" and normal hemoglobin. It is interesting to notice that although the spectra of the different *native* hemoglobins are measurably different, the spectra of the different *denatured* hemoglobins are not measurably different. This is in harmony with immunological experiments which show a decrease in species specificity on denaturation. When the denaturation of the different hemoglobins is reversed, the original spectra and hence the original spectral specificities reappear.

The comparison of "reversed" globin with normal globin cannot be undertaken at present because there is not yet available any certainly normal globin. The separation of globin and heme by present procedures seems to involve the denaturation of the protein. Hill and Holden[10] believed that they obtained native globin directly from hemoglobin. But no evidence was given in support of this claim. One can, however, synthesize hemoglobin from "reversed" globin and heme and compare the synthetic with normal hemoglobin. We have crystallized synthetic methemoglobin and carbon monoxide hemoglobin but the comparison with normal hemoglobin has not yet been completed.

The native globin of hemoglobin obviously has specific chemical groups with which it combines with heme to form hemoglobin. Denatured globin does not have these groups. At any rate, it cannot combine with heme to form hemoglobin, a substance with the characteristic spectrum and other properties of native hemoglobin. "Reversed" globin can once more form hemoglobin. There is reversal, then, as tested by examination not only of the physical but also of the specific chemical properties of the protein. Recently, we have also been measuring the thiol groups of native and denatured globin and serum albumin to see whether there is reversal of the characteristic changes in these groups.

So far, then, no difference has been found between normal and "reversed" protein. It is, of course, possible that differences might be found were the tests which have been used made more accurate or were other tests used. There is always the difficulty that since it is not known precisely what changes take place in denaturation, it is not known what differences might conceivably exist between normal and "reversed" protein. The most general sort of test which we have been applying recently is the solubility test. If native and "reversed" proteins are different, regardless of the nature of the difference, then their solubilities should be different.

[10] Biochem. J., 21, 625 (1927).

We may summarize the experiments on the reversal of coagulation in the following manner: If an acid solution of denatured egg albumin is neutralized, all the protein is precipitated, the denaturation of egg albumin being *apparently* irreversible just as has always been supposed; but if hemoglobin, globin or serum albumin is denatured by the ordinary procedures, one can, by a suitable technique, obtain from these insoluble denatured proteins, soluble, coagulable proteins which seem to be the same as the original native proteins. Experiments not yet completed or others not yet attempted may change the present conception of denaturation or disclose differences between native and "reversed" proteins. So far as the present evidence permits a conclusion, however, coagulation seems to be reversible. The only reason there ever was for believing coagulation to be irreversible, namely that coagulation could not be reversed, no longer has an adequate experimental basis. If the theory of the irreversibility of coagulation is still to be supported, it must be on the basis of new experiments, experiments which explain the results obtained with hemoglobin, globin and serum albumin.

The Biological Significance of Coagulation. It is a familiar fact that the solid matter of living active tissue consists mainly of coagulable proteins. Denaturation produces gross changes in the properties of proteins. Denaturation seems to be reversible. With these considerations in mind, it is difficult to believe that Nature has not exploited the coagulability of proteins. It is, for the moment, a tempting hypothesis that denaturation and its reversal are biological reactions which are important in ordinary cellular processes. It is this hypothesis at any rate which has led us to the study of the tissue proteins from the standpoint of coagulation. One wants to know whether the coagulation of the tissue proteins can be reversed, what group changes accompany this coagulation, how these changes can be studied under physiological conditions, and what is the nature of their function.

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THE EQUILIBRIUM BETWEEN GLYCOGEN AND LACTIC ACID*

BY WILDER D. BANCROFT AND GEORGE BANCROFT**

Otto Meyerhof, Warburg, A. V. Hill, and others have done considerable work in the last fifteen years on the formation and disappearance of lactic acid in muscles. They find that under anaerobic conditions, that is, in the absence of oxygen, lactic acid is formed from glycogen when the muscle is stimulated. They point out that the amount of lactic acid produced depends on the amount of work done by the muscle so that, in reality, the lactic acid is a measure of the work done. When the muscle is resting after a stimulation, oxygen is absorbed, producing aerobic conditions; part of the lactic acid is burned and part is converted back into glycogen. They assume that this oxidation and synthesis is a coupled reaction; the synthesis cannot take place in the absence of the oxidation which supplies the energy for it. The extent of this coupled reaction is remarkable, for Hill has shown that under suitable conditions the ratio of the amount oxidized to the amount synthesized is one to five or one to six. Such a large ratio is unprecedented, for no coupled reaction of this extent is known in chemistry. In cancer, where there is little accumulation of glycogen in the aerobic phase, this coupled reaction is still assumed to hold; but they believe in this case that the glycogen is broken down nearly as fast as it is formed, so that there is little accumulation. If the resting muscle is stimulated in oxygen and then allowed to rest, there is exactly the same result; part is burned and part of the lactic acid is converted back into glycogen again. There is however the difference that, during the stimulation, less lactic acid is formed in oxygen than in its absence. They assume that this is due to the recovery processes, oxidation and synthesis, going on simultaneously with the stimulation.

It is our purpose in this paper to show that the formation and disappearance of lactic acid in the muscle can be explained equally as well and in many instances better by the assumption that there is an equilibrium between glycogen and lactic acid in the muscle and that this equilibrium is reached by means of enzymes. The equilibrium point of this reaction is well over on the lactic acid side. As we shall see later, the reaction can be forced back from lactic acid to glycogen by the adsorption of glycogen out of solution on the protein, thereby reducing the amount of free glycogen in solution and causing the formation of more to re-establish the equilibrium. When we say that there is an equilibrium between glycogen and lactic acid we do not mean that

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** Holder of Fellowship from the Cancer Research Laboratory of the Graduate School of Medicine of the University of Pennsylvania.

the glycogen necessarily goes directly to lactic acid; on the contrary it probably goes through glucose or some hexose phosphoric ester and may even then go through some other intermediate stage such as methyl glyoxal before it finally reaches lactic acid.

The early work of those interested in the changes in frog's muscles led to a mass of conflicting results, which was not cleared up until the classical work of Fletcher and Hopkins[1] in 1907. They say: "Abundant lactic acid formation is said to accompany the process of natural rigor in a surviving muscle (duBois-Reymond, Ranke, Boehm, Osborne), but this is denied (Blome, Heffter); it is said to accompany contraction, and to mark the advance of fatigue (Heidenheim, Ranke, Werther, Marcuse), but this is also denied (Astachewsky, Warren, Monari, Heffter). Indeed it may be said that since Ranke wrote in 1865, no description of the elementary facts of lactic acid formation, despite the fundamental importance of the subject, has been generally accepted."

Fletcher and Hopkins point out that most of the fallacies are due to faulty methods of extraction of the muscle in order to determine the lactic acid content. Thus, many workers procured values for the lactic acid of the resting muscle as high as that of the fatigued, and so believed that there was no change. Also troubles due to bacterial infection were prevalent.

Fletcher and Hopkins studied the formation of lactic acid under various conditions. Using induced interrupted current from two Daniell cells with a secondary coil (0.5 cm.) they found a maximum production of lactic acid which lay between 0.18 and 0.25% with a high value of 0.28% and an average value of 0.21%. These values also confirm the value of 0.229% found by Marcuse.[2] Meyerhof, as we shall see, got somewhat higher values than this with slightly less cumbersome methods of analysis.

The effect of chemical reagents is to form lactic acid very rapidly. At 20°C four hours exposure to chloroform vapor gives a yield of lactic acid of 0.434% whereas the control showed 0.02%. Similarly a like amount of lactic acid may be produced by heat rigor in the same time. This is accomplished by heating the muscle at 40°C and a maximum of about 0.42% was formed. "We find that an acid maximum is reached on heat rigor effected at or near 40° and this maximum is approximately on the same level with that produced in chloroform rigor, or in the slow death by alcohol." The alcohol in four hours gives values slightly over 0.40%.

Lactic acid may be formed in another way—by anaerobic rest. The rate of formation in this case is very much slower than by fatigue or by chemical means. In the course of 20–25 hours a maximum is reached which amounts to about 0.36% at 20°C. This is slightly higher than found for the frogs stimulated for a much shorter period (2 hours) and it is less than the maximum reached by chemical means in four hours.

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[1] J. Physiol., 35, 247 (1907).

[2] Pflügers Archiv, 39, 425 (1886).

In 1919-1920 Otto Meyerhof published a series of papers[1] on this subject. He fatigues muscles in two ways, namely, by tetanic stimulation and by induction shocks. The results from these two methods were not the same, for he found with single induction shocks values 40-60% higher than by tetanic stimulation. Meyerhof calls attention to the fact that, by using different methods of extraction from Fletcher and thereby shortening the time of manipulation, he obtained analogous maxima but in each case 15 to 20% higher. For tetanic stimulation Meyerhof finds a net increase of 0.205%, occasionally dropping to a value of 0.178% as in December, and with a high value of 0.24%. His values for single induction shocks are about 0.35%, dropping in December to 0.254%. In each case, however, the corresponding values are 40 to 60% higher for the single induction shocks than for tetanic stimulation. Incidentally these values are not affected by the means of inducing the stimulation—namely, whether applied indirectly to the nerves or directly to the muscle.

The rate of formation of lactic acid was studied with respect to single induction shocks and is of interest. Meyerhof carried on a series of experiments with incomplete fatiguing and compared the fatigue maximum reached under similar conditions (frogs from the same source, same time of year, temperature, and method of stimulation). He found in one experiment with indirect stimulation in 20 seconds (spark gap 15-17 cm.) a lactic acid content of 0.139%; in another stimulated for 40 seconds and another for 20 seconds he found 0.13% lactic acid. By using exhaustive tetanic stimulation a fatigue maximum of 0.23% was obtained and in less than one minute over half of the lactic acid was formed.

Metronome stimulation. By exhausting stimulation of fresh fall frogs—0.36%

2	minutes	0.118 %
6	"	0.168%
7	"	0.226%

We can see that 0.118% or a good half of the lactic acid was formed in the first third of the time.

Meyerhof gets results for chemical rigor similar to those Fletcher and Hopkins did, although his are slightly higher. He gets values ranging from 0.42% in the spring to 0.552% in the fall. These values are considerably higher than those found for electrical stimulation at the same times of year. The question naturally comes up as to why these values are higher and also why the chloroform causes the formation of lactic acid anyway. This last question is explained by Meyerhof by assuming that the chloroform in some unknown way causes a stimulation in the muscle which is more vigorous than the electrical stimulation and hence causes the formation of more lactic acid. Heat rigor has a similar action to chloroform and Meyerhof finds practically the same values for this as for chloroform.. This is in confirmation of the similar results found by Fletcher and Hopkins. Lacquer[2] has shown that, if

[1] Meyerhof: Pflugers Archiv, 182, 232, 284; 185, 11 (1920); 188, 115 (1921).
[2] Lacquer: Z. physiol. Chem., 93, 60 (1914).

two percent bicarbonate solution is added to cut-up muscle, a formation of lactic acid takes place which amounts to 0.9% as opposed to 0.4% in the ordinary salt solution. From this he ascribes the increasing acidity as the method which stops the acid formation. This is undoubtedly one of the factors and it is interesting to note, that neutralization of the acid should increase the yield if the reaction were an enzyme as we postulate, for we are taking away one of the final products.

Meyerhof also conducted some experiments on the formation of lactic acid during anaerobic rest; but his values are not easily comparable with those previously given here, because he added $NaHCO_3$ and HCN to his solution. As we have seen, the bicarbonate increases materially the yield of the lactic acid and Meyerhof himself seems doubtful whether the HCN does not also have an effect. However, he did find that the acid accumulation was slow and, even with the bicarbonate neutralizing some of the acid formed, he found an end value of 0.56% whereas Lacquer found a value for heat rigor and bicarbonate of 0.9%. So we see that this value is considerably less than the value procured for heat rigor and this was shown to be the case by Fletcher and Hopkins without the addition of bicarbonate.

In any study of the muscle or analysis of the results there are several factors which must be kept in mind in order to get a true insight into the working on the muscle. The first of these is the effect of the time of year. Fletcher and Hopkins (loc. cit., p. 226) say, "The infliction of heat rigor is a convenient method for determining the potentiality of a muscle for acid production at any time. Selecting observations made in other connections and at different times of year, we find that they fall into two groups according to season, thus giving only one for each six months,

March	.383	October	.54
April	.315	November	.51
May	.420 Av. .36	December	.52 Av. .52

Whilst we have always found a surprising constancy in the value for the acidity of heat rigor, when duplicate determinations have been made on frogs caught under similar conditions, we have constantly found higher acid maximum for the muscles of autumn frogs than for those of frogs caught in the spring."

Meyerhof also finds differences at different times of year for rigor, chloroform, and the two stimulation maximums. The simplest explanation would seem to be that the glycogen content is different in the different months and indeed it has been shown by Mitchell[1] that oysters at different times of year have markedly different glycogen content. This explanation would be perfectly satisfactory from the point of view of our enzyme theory of equilibrium; but it does not seem to satisfy Meyerhof and his beliefs of the metabolic changes in muscles.

He says:[2] "What causes the difference in the lactic acid maxima in the different months? From the experiments of Lacquer on the regulation of the

[1] Mitchell: U. S. Bureau of Fisheries, 35, 151 (1916).
[2] Meyerhof: Pflügers Archiv., 182, 232 (1920).

lactic acid maximum by H ion, we must conclude that there is a changing sensitiveness in the different months rather than a change in the glycogen supply. This is perfectly plausible. One finds that the anaerobic exhaustion through electrical stimulation is restricted by the addition of acid." Moreover he points out that the rigor maximum is smaller in the winter after the frogs have lain dormant for several months than in the fall. This would seem quite natural as the glycogen content should be lower. It is plain that Meyerhof is trying to explain two different factors by one explanation. These two factors are made clear on the basis of the enzyme theory of lactic acid production, for one would expect less lactic acid to be formed in the spring if there was less glycogen present, even as in the fall one would expect more lactic acid to be produced if there was more glycogen present. In any equilibrium if the final product is taken out, more of this product will be formed in order to reestablish the equilibrium. The action of the carbonate is to extract some of the lactic acid by neutralization and hence cause more to be formed. This last has no effect however on the changes of the amount of lactic acid formed due to the time of year.

Another factor which must be taken into consideration is the effect of temperature. Meyerhof found that variations due to temperature affected the maxima formed by all the methods of producing lactic acid. At 0°C the maximum reached by stimulation was singularly small. The difference in the maximum caused by changes from 14° to 22° is much less than from 0° and 20° but the change is still considerable, for Meyerhof found an average value at 14° of 0.17% and at 22° an average value of 0.21%. The muscle apparently becomes fatigued much more rapidly at the lower temperatures, for he found that a muscle fatigued at 5°C was again irritable if heated up to 20°C. This is entirely in keeping with the findings that the muscle will produce more lactic acid at the higher temperature. There is a limit, however, for Fletcher and Hopkins have shown that in boiling water the muscle will not form lactic acid. This is due to the fact that the enzyme has been destroyed.

Cavallo and Weirs[1] showed that a muscle exhausted at 0°C if heated up to 25° and then cooled down again was able to have a new series of contractions. They believed that the process of heating up and cooling down made the muscle irritable again. Meyerhof was unable to verify this result and he points out that, if one waits long enough after the subsequent cooling down in order to insure that the entire muscle is again at the lower temperature, and if one takes precautions to provide anaerobic conditions throughout the manipulation, the muscle after cooling is still unirritable. It is not the change in temperature itself which causes the change in irritability but the fact that at the higher temperature the muscle can produce more lactic acid than at the lower temperature.

We have seen that it is possible to produce lactic acid in the muscle by several different methods. The question immediately arises as to where the

[1] Cavallo and Weirs: J. Physiol. Pathol., 1, 990 (1899).

lactic acid comes from. Meyerhof has demonstrated conclusively that, as the lactic acid increases, the carbohydrate decreases in exactly equivalent amounts. This change moreover, concerns chiefly the glycogen as the amount of change of other carbohydrates is small in comparison. He has shown[1] that during anaerobic rest the carbohydrate decreases as the lactic acid increases.

	Mg. Glucose Before	Mg. Glucose After	Mg. Glucose per gram Before	After	Muscle Difference
Muscle Wt., grams	10.2	10.35			
Glycogen	77.	45.2	7.55	4.35	−3.20
Other Carbohydrates	19.0	15.5	1.85	1.50	−0.35
					−3.55
			Corrected		−3.75
Lactic Acid			0.20	2.82	+2.62

In conjunction with the foregoing experiment Meyerhof also determined the resting respiration and he was then able to calculate the amount of carbohydrate burned by this respiration. This amounted to 1.1 mg. If we subtract this value from the amount of carbohydrate decomposed, we have the amount of lactic acid formed. Taking the value 3.75 mg. from the table and subtracting 1.1 mg, the amount burned, we have 2.65 mg. which should be converted into lactic acid. This checks very well with the value 2.62 mg. of lactic acid determined. So we see that, as the carbohydrate decreases, the lactic acid increases in exactly equivalent amounts.

The foregoing relation was found in whole muscle and in the following we find the same result in minced muscle in phosphate solution.

Time	Lactic acid Increase mg./gr.	Glycogen Decrease mg./gr.
8h. I	+ 0.272	−0.285
2h. II	+ 0.30	−0.34
23h. III	+ 1.056	−1.00
7h IV	+ 0.885	−0.895

The formation of lactic acid from glucose by enzyme action is not a new theory. In attempting to find out what the intermediate products in the decomposition of glucose to lactic acid were, Embden and his co-workers[2] carried out some liver perfusion experiments with glyceric aldehyde and dihydroxy-acetone. They showed that both substances increased the lactic acid in the perfused blood but that the glyceric aldehyde was much more effective. Embden advanced the theory that optically active glyceric aldehyde is the intermediary substance formed in the break-down of glucose into d-lactic acid. Neuberg and Rosenthal[3] found that fresh liver tissue would

[1] Meyerhof: Pflügers Archiv, 185, 11 (1920).
[2] Biochem. Z., 45, 108 (1912).
[3] Neuberg and Rosenthal: Biochem. Z., 49, 502 (1913).

split methyl glyoxal into a mixture of dl and d-lactic acids. Whether methyl glyoxal or glyceric aldehyde or dihydroxy-acetone is the intermediate product between glucose and lactic acid is outside the scope of this work. The important point is that these authors realize the necessity of the presence of an enzyme in order to get optically-active lactic acid. Dakin and Dudley[1] added a solution of phenyl glyoxal to minced tissue and found a 40% to 60% conversion into l-mandelic acid. They found that increasing acidity stopped the conversion completely and that, to get this conversion, it was necessary to add sodium bicarbonate to keep the H ion down. Moreover, the enzyme present here was killed if the tissue was boiled, which is just what would be expected. They also found that an enzyme solution prepared from dog's liver decomposed 4 grams of pure methyl glyoxal into lactic acid completely in 10 minutes. They were unable, however, to get only d-lactic acid but got a mixture. Levene and Meyer[2] showed that leucocytes and kidney tissue formed lactic acid from methyl glyoxal under aseptic conditions and that a mixture of the dl and d-forms were obtained. They also showed[3] that these leucocytes could change glucose into optically active lactic acid. From this they concluded that glucose must break down into lactic acid by way of methyl glyoxal.

Meyerhof refers to these authors in a monograph "Chemical Dynamics of Life Phenomena," 59 (1924) by saying: "They seem to assume that a reversible equilibrium exists between sugar and lactic acid, so that the reaction could go spontaneously either in one or the other direction. This is however, not the case, as will be shown in detail later. The cleavage of sugar into lactic acid is a spontaneous process going to completion. On the other hand the synthesis of sugar from lactic acid requires a supply of energy furnished in the isolated muscle exclusively by oxidation of part of the lactic acid or the corresponding amount of sugar. It can probably be provided also in the other organs only by oxidation."

As we have seen, the methyl glyoxal apparently breaks down completely into lactic acid, yet Dakin has shown conclusively that the equilibrium between methyl glyoxal and lactic acid is reversible.[4] An aqueous solution of lactic acid and the enzyme was digested at 37°C. Upon addition of nitrophenyl hydrazine a precipitate of the insoluble methyl glyoxal dinitro phenyl hydrazone was formed, which could be readily separated and analyzed. The fact that the glycogen breaks down completely into lactic acid under certain conditions does not necessarily mean that there can not be an enzyme equilibrium. The conditions necessary to cause all the glycogen to break down is a considerable excess of phosphate which might have the effect of neutralizing the lactic acid formed, thereby displacing the apparent equilibrium.

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[1] Dakin and Dudley: J. Biol. Chem., 14, 155 (1913).
[2] Levene and Meyer: J. Biol. Chem., 14, 551 (1913).
[3] Levene and Meyer: J. Biol. Chem., 12, 265 (1913).
[4] Dakin: J. Biol. Chem., 14, 555 (1913).

Meyerhof has shown that in phosphate solution all the glycogen is decomposed; but that does not mean that all the carbohydrate has decomposed as one is led to believe. Two of his experiments on this might well be quoted here.

G = Glycogen
K = other carbohydrate

Time from start of mincing		Carbohydrate Content Total mg.	%	Lactic Acid Total mg.	%
	2o	G = 31.4	0.898	2.23	0.064
		K = 9.5	0.27		
August	23h	G = o	o		
		K = 8.6	0.25	39.2	1.12
Total			−1.00		+1.056 corr.
	15	G = 12.4	0.214	4.05	0.010
		K = 13.5	0.231		
	8h 15	G = o	0.0		
		K = 10.5	0.180	20.0	0.342
Total			−0.285		+0.272

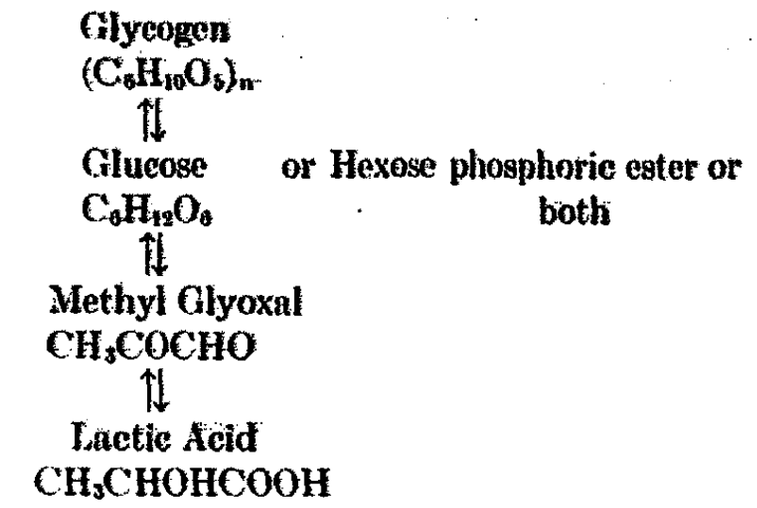
We see from these figures that all the carbohydrate has not disappeared, even though all the glycogen has. The argument that Meyerhof puts forth, that there can be no enzyme reaction because all the glycogen disappears, is not sound. In the first place he may have been neutralizing the final product with the excess of phosphate which would displace the apparent equilibrium. Dakin showed that methyl glyoxal apparently went completely to lactic acid but he was able to show conclusively that the equilibrium was reversible.

Meyerhof has suggested that in all probability glycogen breaks down into lactic acid perhaps through glucose and probably through an intermediate hexose phosphoric ester. Lacquer[1] has found that glycogen is a better source of lactic acid than glucose in the separated muscle. According to him the reason for this seems to be that only α glucose which is a derivative of glycogen yields lactic acid immediately whereas β glucose must first change into the α form.

As we have pointed out before, we assume that the formation of lactic acid is due to an equilibrium between glycogen and lactic acid, whose rate is governed by enzymes. In the decomposition of glycogen there may be an intermediate formation of α glucose and probably a hexose phosphoric ester and

[1] Lacquer: Z. physiol. Chem., 116, 169 (1921).

perhaps some further intermediate compound as methyl glyoxal before the lactic acid is reached. Furthermore the equilibrium point is well over on the lactic acid side.



These might possibly be the steps in the reaction. No attempt is made in this paper to determine the steps; but it is helpful to have a picture of what may happen in a simplified form in order to understand the processes.

Przylecki and Wojcik[1] have shown that protein has an extraordinarily high adsorptive power for glycogen, and that, using appropriate concentrations of the protein, which incidentally correspond to those present in the liver, this adsorption may even for 10% glycogen solutions, amount to as much as 90%. With 30 cc. of a 1% glycogen solution and 30 grams of protein, 99% of the glycogen is adsorbed out of the solution. This adsorption of glycogen is a reversible reaction, for they have shown that by diluting with a sufficient quantity of water the glycogen may be eluted off the protein again. It may be liberated also by the action of various chemicals such as alcohol, and other narcotics. Przylecki worked principally with the enzyme amylase which hydrolyzes glycogen to glucose; he showed that, when the glycogen was adsorbed on the protein, it was so stabilized that the rate of reaction with the enzyme was very slow but in the course of time it was broken down into glucose. If in the muscle the enzyme only reacted with the free glycogen, we should expect during anaerobic rest that the formation of lactic acid would be slow, as the concentration of free glycogen in solution at any time would be small. As the concentration of free glycogen diminished, glycogen adsorbed on the protein would be set free to reestablish that equilibrium, and the free glycogen thus formed would in turn be decomposed to lactic acid until perhaps the increase in hydrogen ions stopped the process.

Fletcher and Hopkins,[2] in order to account for the linear formation of lactic acid, suggested such a possibility as this equilibrium between adsorbed glycogen and free glycogen. They say: "Conceivably the store of precursor in the muscle is partly in insoluble form, partly in solution, the concentration

[1] Biochem. J., 22, 1302 (1908).
[2] Loc. cit., p. 275.

might be kept constant by replacement from the insoluble store, and, for a period, conditions would exist for a linear rate of change. The explanation is probably less simple than this, and it is interesting in any case, to observe how in the quiescent unstimulated muscle the survival processes which lead to lactic acid production are so controlled as to lose the exponential character of an isolated chemical reaction."

In the case of electrical stimulation we have seen that more lactic acid is formed by single induction shocks than by tetanic stimulation. Meyerhof says: "How can one explain that by single induction shocks which are applied sixty times to the minute a much greater amount of lactic acid accumulates in the same time than when twenty-five times the number of irritations were applied tetanically." He points out that by the use of a tension lever it can be shown that the muscle irritated by single induction shocks performs more work than those stimulated by tetanus. Moreover a muscle which has been exhausted by tetanic fatigue is still irritable to single induction shocks. The lactic acid, according to Meyerhof is a measure of the work done; and since more work was done in the stimulation by the single shocks more lactic acid should be formed. This is, of course, arguing in a circle. We have seen that the glycogen is stabilized by adsorption on the protein, and stimulation causes the glycogen to be liberated from its adsorption thereby increasing the concentration in free solution. As the concentration increases in free solution the rate of formation of lactic acid increases. Indeed, we have seen that where 0.22% was formed in seven minutes, over half was formed in the first two minutes when the concentration was the highest. Just how the contraction of the muscle causes the liberation of the glycogen is, at this time, pure conjecture. Bancroft and Richter[1] have shown that a man rendered unconscious by an electric shock is in reality in a state of narcosis. Now in narcosis, as they have demonstrated, the proteins are reversibly coagulated, that is if the cause of the coagulation is removed the proteins will return to their peptized state again. In the case where proteins are irreversibly coagulated the patient dies. Probably the contraction of the muscle coagulates the protein slightly, causing a liberation of some of the adsorbed glycogen. However, this coagulation is not due to the effect of the electrical current itself, for Meyerhof has shown that it makes no difference whether the current is passed directly to the muscle or directly through the nerves. The coagulation due to a single twitch is probably slight with a correspondingly small liberation of glycogen. With a single tetanic stimulation the muscle is tetanized, or fully contracted, so that continuous stimulation would have little further effect on the muscle. If a very short period of rest is allowed between tetanic stimulations, the muscle would tend to relax, thus allowing further stimulation to contract it again. It is for this reason essential to allow short periods of rest in tetanic stimulation in order to procure the maximum yield of lactic acid. These periods of rest are only momentary, as the tetanic stimulations are applied well over sixty times to the minute. We know from

[1] Bancroft and Richter: J. Phys. Chem., 35, 215 (1931).

Meyerhof's work that a muscle is still irritable to single induction shocks even though fatigued to tetanic stimulation, so that there are more contractions with the former method, more glycogen liberated, and hence, just as we should expect, more lactic acid formed. In this particular case, Meyerhof's explanation of lactic acid as due to the work done by the muscle is nearly as satisfactory as our explanation.

In the case of the quiescent unstimulated muscle under anaerobic conditions we should expect to get a slow formation of lactic acid, as the glycogen in free solution would be decomposed to glucose and hence to lactic acid. As the free glycogen diminishes, more glycogen would be liberated from the protein to keep the concentration constant. As the concentration of free glycogen is small at any particular time, we should only expect a slow rate of reaction. Meyerhof's explanation of work done could not hold in this case as no work is done by the muscle in this quiescent state. We can predict what should happen in this case, but do the facts support this prediction? We have seen that a maximum yield of lactic acid in this case is not reached in a few minutes as is the case when the muscle is stimulated electrically but in the course of 23 hours. Moreover, according to Fletcher and Hopkins the rate of formation follows a linear course, which is what we should expect from the fact that the concentration of free glycogen is constant.

We do not need to postulate, as Meyerhof does, that the addition of chloroform in some unknown way causes a stimulation of the muscle and in that way produces lactic acid. We have only to bear in mind the fact that the chloroform coagulates the protein thereby liberating the adsorbed glycogen. The increase of the concentration of the free glycogen would increase the rate of formation of lactic acid. Indeed we find that the addition of chloroform causes a formation of lactic acid which reaches a maximum in four hours or less. The effect of the addition of chemical reagents probably liberates more glycogen than stimulation methods do so that there is more lactic acid formed. Heat rigor may be explained on the same basis, as it is well known that heat will coagulate the proteins. Ether and alcohol apparently have the same effect as chloroform and come under the general head of narcotics. Some other chemicals as arsenate and caffein have slightly different effects. Bancroft and Richter (loc. cit.) have shown that caffein in high enough concentrations acts like a narcotic in coagulating the proteins. According to Przylecki the explanation of the increased formation of lactic acid may not be as simple as this. They say:[1] "The acceleration of the velocity of hydrolysis caused by the addition of narcotics, such as chloroform, ether, or alcohol might on the basis of this research be explained as being due exclusively to elution of polysaccharide. While such an explanation appears to fit very well with experimental findings, it should not be forgotten that in our case we are dealing with a system simpler than that present in our cell, as it contains only one of the components of the latter, namely protein. The possibility remains that, within the cell, enzyme is

[1] Przylecki: Biochem. J., 22, 34 (1928).

adsorbed not only on its protein elements, but also upon lipin or nucleoprotein surfaces, from which elution by narcotics may be much greater than from proteins."

"There can be no doubt that elution of substrate from protein, or change in the state of dispersion of the latter, plays an important part in the acceleration of the velocity of enzyme by hydrolysis of polysaccharides due to the addition of narcotics."

It has been assumed, and qualitatively at any rate the facts seem to bear this out, that the enzyme only affects the free glycogen and not the adsorbed glycogen. However, if there is a combination of enzyme and substrate in the reaction which the enzyme catalyzes, there might also be a combination with some of the adsorbed glycogen. The facts seem to support the belief that the enzyme combines only with the free glycogen, as we have seen in the case of anaerobic rest. Nevertheless this is not the whole story, for the problem might be further complicated by adsorption of part or all of the enzyme under certain conditions. Thus, with the enzyme 100% adsorbed on the lipin surfaces and the glycogen 100% adsorbed on the protein, there would be no reaction. If both are only partly adsorbed the effect of some chemicals might be to liberate only the enzyme, or only the glycogen, or both at once and in each case the resulting effect would be different. There does not seem to be any need in making the problem as complicated as this, for there does not seem to be any evidence as yet that requires us to assume that the enzyme combines with the adsorbed glycogen. On the other hand the enzyme is undoubtedly adsorbed to some extent on the lipin surfaces; but Przylecki has shown that this does not necessarily impair its action on the free glycogen. As Richter and Bancroft have shown, the effect of chemical reagents may be of another class, those which do not coagulate the protein but which are selectively adsorbed on it. These substances, depending on their concentration and the degree of adsorption, would have different influences on the formation of lactic acid. Furthermore substances which would tend to increase the peptization of the protein might increase the degree of adsorption and thereby decrease the tendency towards lactic acid formation.

Another essential, but hitherto unconsidered point, is the question why the lactic acid formed in the muscle is dextrorotatory. Evans[1] has shown that glucose under the influence of strong alkali yields lactic acid, but the product is inactive. This might be due to racemization of the acid by the strong alkali; but this is improbable, as dilute alkali also yields inactive lactic acid. Moreover, if the glucose passed through an intermediate stage of methyl glyoxal or pyruvic acid, both of which are inactive, the final product would be inactive unless an enzyme were present. It has been pointed out earlier in this paper that, methyl glyoxal in the presence of an enzyme known as glyoxalase yields active lactic acid, and leucocytes and kidney tissue can decompose glucose into optically active lactic acid indicating the presence of

[1] Evans: J. Am. Chem. Soc., 47, 3085 (1925).

an enzyme. Indeed Meyerhof[1] has shown that an enzyme can be extracted from muscles which upon purification is many times more active than the muscle itself, and that this enzyme can convert glucose and glycogen into lactic acid. Presumably this is optically active lactic acid although he does not say definitely.

Meyerhof has pointed out that the formation of lactic acid is due to several causes, among which the respiration plays an important part in determining the rate. If however, the formation of lactic acid is due, as we believe to enzyme action, increase of the starting products should increase the rate of formation of lactic acid. Stiven[2] has shown that increasing the concentration of glycogen with the enzyme extracted from cat's muscle, increases the rate of formation of lactic acid. The following diagram shows this increase.

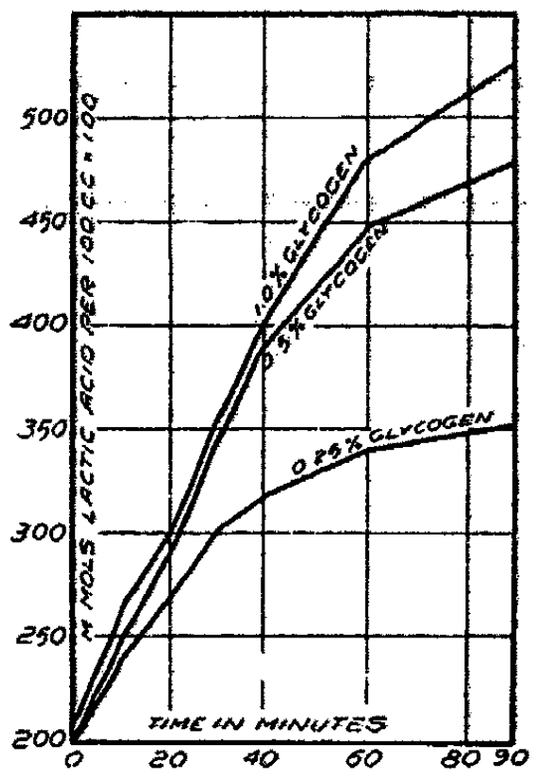


FIG. 1
From Biochem. J., 22, 872 (1928)

We see from this diagram that as the concentration of glycogen increases the rate of formation of lactic acid increases. This is exactly what we should expect from an enzyme reaction. The concentration of the enzyme was constant in the three cases.

What is the fate of the lactic acid during the recovery period in oxygen? So far, we have only considered the anaerobic or working phase. Fletcher and Hopkins found that, with a separated muscle after repeated stimulation and recoveries in oxygen over a period of several days, the yield of lactic acid from heat rigor was practically the same as for fresh muscle. It has been known for some time that a muscle which has been fatigued and then allowed to rest in oxygen recovered its irritability again. In other words the lactic acid, which is a measure of the fatigue, had disappeared. From their experiment Fletcher and Hopkins assume that the lactic acid, all or in part, must be converted back into carbohydrate again in oxygen, for if it was all burned the amount of lactic acid from heat rigor after several days of repeated stimulations and recoveries would be materially reduced.

Hill[3] found that in the oxidative removal of one gram of lactic acid there is a heat production of about 450 calories. Now the oxidation of one gram of lactic acid leads to a heat production of about 3700 calories, which is about eight times as large as the quantity observed. Although the measurements

[1] Meyerhof: Naturwissenschaften, 14, 196, 756, 1175 (1926); Biochem. Z., 178, 395, 462 (1926).
[2] Stiven: Biochem. J., 22, 867 (1928).
[3] Hill: J. Physiol., 48, x (1914).

were not very accurate it is obvious that all the lactic acid is not burned, but that some is returned to its precursor, glycogen, under the influence and with the energy of the oxidation, either (a) of a small part of the lactic acid itself, or (b) some other body.

In 1922[1] a more careful study of the liberation of heat showed that there are three stages in which heat is given off in the working muscle, which Hill characterizes as the initial anaerobic heat, the delayed anaerobic heat, and the oxidative heat. These amount to 285, 85 and 340 calories respectively. If we suppose that of one gram of lactic acid x grams are oxidized in the recovery and $(1 - x)$ grams restored to its previous state as glycogen, the muscle will have returned to normal except for the x grams oxidized. The heat of combustion of glycogen according to Stohmann is 4191 cal./gr. and according to Emery and Benedict 4227 cal/g. If we take the mean of these two quantities, namely cal./g., we see that the heat of combustion of 0.9 g. of glycogen which corresponds to 1 gram of lactic acid is 3788 calories. Hence the total energy available to cover all breakdowns in the complete cycle is $3788 \times$ cal. Equating this to $(285 + 85 + 340 = 710$ cal.,), we find $x = 710/3788$ or 0.188. Thus of one gram of lactic acid passing through the whole cycle of contraction and recovery 0.188 gr. are oxidized and the remainder viz. 0.812 grams are restored to its previous state as glycogen. We can see, therefore, that one-fifth to one-sixth of the lactic acid is burned and the remainder is converted back into glycogen.

These myothermic measurements of Hill's do not show what the lactic acid is converted into, as there was no chemical analysis of the changes. Meyerhof[2] however, in a study of the carbohydrate exchange of frog's muscles demonstrated that, as the lactic acid disappears during the recovery period, so the carbohydrate increases in exactly the extent as calculated from the difference of the lactic acid disappearance and the oxygen consumption (recovery consumption minus resting consumption). Again the change concerns the glycogen chiefly, and there is a synthesis of glycogen from lactic acid. The glycogen content at the end of the recovery period is the same as before the stimulation, minus the carbohydrate disappearance equivalent to the oxygen consumption. To quote one experiment of Meyerhof's where he found the following balance in mg./g. of muscle.

	Before recovery	After recovery	Difference
Glycogen	3.37	4.75	+1.38
Other Carbohydrate	2.01	1.66	−0.35
	5.38	6.41	+1.03
Lactic acid	2.56	0.44	−2.12

In oxygen experiments carried on at the same time, he found 1.20 mg of excess oxygen were used in the recovery period which would burn 1.12 mg. of

[1] Hill: J. Physiol., 56, 367 (1922).
[2] Meyerhof: Pflügers Archiv, 182, 284 (1920).

lactic acid, so we see that 2.12 — 1.12 or 1.00 mg of lactic acid should have been converted back into glycogen. This checks very reasonably with the determination that 1.03 mg of glycogen were formed.

Meyerhof has also shown that, if the muscles are not minced too finely, there is apparently a formation of glycogen in the aerobic phase which indicates that there is no necessary relation between structure of the muscle and the formation of glycogen. When the muscle is minced very finely, the negative results are probably due to a diffusion of phosphate away from the enzyme, thus preventing the esterification of the glucose to the intermediate glucose phosphoric ester. This is in accord with his findings for the necessity of phosphate for the decomposition of glycogen to lactic acid.

Let us now consider Meyerhof's explanation for the recovery period in the muscle. In "Chemical Dynamics of Life Phenomena," 55 (1924), he says: "In the oxidative phase one molecule of sugar or the corresponding amount of lactic acid is burned. The rest of the lactic acid is reconverted with phosphate to the ester (glucose phosphoric ester) and again becomes glycogen. Here we have a coupled reaction similar to the alcoholic fermentation."

In short he assumes that the oxidation and synthesis is a coupled reaction, where the synthesis cannot take place without the oxidation to supply the energy for it. From a purely chemical point this reaction should not require much energy, as glucose stoichiometrically is exactly two molecules of lactic acid, and glycogen is a straight polymer of glucose with a splitting out of water. If this is in reality a coupled reaction, one should be able to take lactic acid, oxidize it in the presence of protein, and form glycogen. It apparently does not require the muscular structure as Meyerhof found a synthesis of glycogen with minced muscle. Lactic acid is oxidized readily in the presence of ferrous salts by hydrogen peroxide but there is no formation of glycogen under these conditions even in the presence of protein which would naturally adsorb any glycogen that was formed. Indeed from our hypothesis of an equilibrium between glycogen and lactic acid, catalyzed by enzymes, we should not expect to form any glycogen under these conditions.

It is our belief that the oxidation of lactic acid is not coupled with the synthesis of glycogen, but occurs simultaneously in the presence of oxygen. We have stated that we assume that glycogen and lactic acid are in equilibrium, the reaction being catalyzed by enzymes. When the muscle is stimulated, considerable quantities of glycogen relatively are liberated from adsorption on the protein, and this free glycogen changes over to lactic acid due to the fact that the equilibrium point between glycogen and lactic acid is well over on the lactic acid side. When the muscle comes to rest, on the other hand, in the presence of oxygen, the concentration of adsorbed glycogen has been considerably reduced from what it was before the stimulation. To re-establish this former state more glycogen must be adsorbed out of solution. We know from the mass law that, when two substances are in equilibrium, extraction of one substance will cause a formation of that substance from the other in order to re-establish the equilibrium. In other words, as the

glycogen is taken out of solution by the protein, more glycogen will be formed from lactic acid in order to keep the equilibrium constant. In this way three quarters of the lactic acid which disappears is reconverted into glycogen. The other one quarter is burned by the oxidation which occurs at the same time. It is not necessary that there should be a great amount of synthesis at any one time for, as glycogen appears, it is extracted from solution by adsorption until the amount of adsorbed glycogen has reached the normal resting value. Bayliss in "The Nature of Enzyme Action," 56 (1925) says: "It might be thought that a synthesis of a small degree could not be of much practical importance. This would be an error, as the following considerations will show. Let us take the case of amylase where the hydrolysis progresses almost to completion, and let us suppose that no more than one percent of starch is formed when the enzyme acts as maltose or dextrin. Since the product is an insoluble body, the equilibrium will exist only for a moment, so that more starch will be formed in order to replace that thrown out of the system by precipitation. As the rate of this reaction is slow, as shown above, the amount of starch per unit time will not be great, although by no means negligible. The process, it will be noted, is analgous to that of the precipitation of chloride as silver salt. It is most likely as Croft Hill[1] points out, that the storage of starch in the plant and that of glycogen in the animal are to be explained on these lines."

In such an enzyme equilibrium where the glycogen is adsorbed out of solution on the protein, thereby displacing the equilibrium and causing the formation of more glycogen, the rate of recovery to the normal state must necessarily be slow, as there is only a small amount of synthesis at any one time. Meyerhof has shown that the recovery period is slow, requiring fifteen to twenty-three hours before the muscle returns to its normal resting state. This could be prophesied from our theory but would not necessarily be so if the synthesis were coupled with the oxidation of lactic acid.

If the glycogen and lactic acid are in an equilibrium whose rate is catalyzed by enzymes, we should expect, all other things being equal, that increase in the amount of glycogen should increase the rate of reaction and the amount of the final product lactic acid. Thus ten milligrams of glycogen with the enzyme should be converted to lactic acid more rapidly than one milligram and with a larger final yield of lactic acid. This was apparently the case in the experiments of Stiven which have been cited. It should be borne in mind, however, what is meant by all other things being equal. The enzyme concentration must be constant throughout the reaction. Moreover the final products must not affect or poison the enzyme. Dakin found that the enzymic conversion of phenyl glyoxal to l-mandelic acid was stopped completely by increasing acidity. In other words, the acid poisoned the enzyme. We know that the addition of bicarbonate increases very materially the lactic acid production in the muscle. This, however, may be a combination of two factors: one, reduction of the acidity; and two, extraction of the final product

[1] J. Chem. Soc., 73, 634 (1898); J. Physiol., 28, Proc. XXVI.

by neutralization. It is possible therefore, that, in any particular case, the increasing acidity might stop the reaction at a definite value of lactic acid.

When the muscle is stimulated and then allowed to recover in the presence of oxygen, part of the lactic acid is burned and part is converted back into glycogen. This means that the store of glycogen is becoming less and less, providing there is no replenishment from outside. This replenishment probably comes in the normal animal from the glucose of the blood. There is no provision in Meyerhof's theory for the formation of glycogen from glucose except by the way of lactic acid which seems improbable. Mitchell[1] has shown that the glycogen content of oysters may be very materially increased by feeding the oysters glucose in the presence of air. It seems distinctly unlikely that this glucose is first broken down into lactic acid before being converted into glycogen. From our enzyme theory it would be perfectly possible for the glucose to go either directly or, after esterification with phosphate, to glycogen, for the two substances must be in equilibrium. The glycogen would be formed as fast as it was adsorbed out of solution by the protein, otherwise the equilibrium would be displaced.

The formation of glycogen from lactic acid, as we have pointed out, depends upon the extraction of glycogen from solution on the protein, thereby disturbing the equilibrium and causing the further formation of glycogen in order to re-establish it. Under these conditions it should be possible to add lactic acid to the enzyme in the presence of a suitable protein adsorbent and perhaps phosphate and form glycogen.

Przylecki (loc. cit.) has shown that glycogen is strongly adsorbed on such proteins as are present in liver, as well as on coagulated egg white. Using 15 cc. of a 0.2% solution of d-lactic acid, 10 cc. of M/2 KH_2PO_4, and 10 cc. of enzyme solution and approximately 30 grams of egg white we attempted to show the formation of glycogen. That we were not able to establish the formation positively may be due to the present methods of analysis of glycogen.

The enzyme solution was prepared according to the direction of Meyerhof[2] in which the rabbit was killed by a blow on the head, the hind legs rapidly skinned, the muscles cut out and placed in a glass evaporating dish surrounded by carbon dioxide snow. The muscles were then cut into thin slices and extracted with 50 cc. of isotonic KCl solution at 0°C. The muscle residue was separated from the solution by centrifuging. The clear solution resulting from this procedure after two hours digestion with 0.8% glycogen solution showed a strong qualitative test for lactic acid. The qualitative test was that recommended by Fletcher and Hopkins on the formation of a cherry red color with thiophene after oxidation with $CuSO_4$ and H_2SO_4. It is interesting to note that in the same period when egg-white was added to the mixture, there was only a faint test for lactic acid. This is entirely in accord with the findings of Przylecki who showed that glycogen was hydrolyzed only very

[1] Loc. cit.

[2] Naturwissenschaften, 14, 196, 756 (1926).

slowly by amylase in the presence of protein. Indeed it could have been prophesied from the theory that this would be the case when the glycogen was stabilized by adsorption on the protein.

Evans[1] pointed out that all the glycogen is not precipitated when using Pflüger's method of analyzing for glycogen which necessitates the use of as much as 90 cc of solution in the precipitation of glycogen by alcohol after treatment with KOH. This will amount to a large percentage error when only small amounts of glycogen are present. In a very recent paper Kerly[2] says that this is probably due to the solubility of glycogen in aqueous alcohol, but there may also be some peptization by the KOH decomposition products of the protein. Holmes and Holmes[3] undertook some experiments to show that glycogen could be recovered from such a large volume of solution and they found that the glycogen could be recovered 100%. They, however, added solid glycogen to water and then precipitated it with alcohol, which according to Kerly does not resemble the true conditions, as she points out that 17 to 18 percent of the glycogen is in solution; but that it dissolves very slowly, taking a week to come to equilibrium. Under these conditions Holmes and Holmes were not precipitating glycogen from solution, and their good results may be attributed to this fact.

Inasmuch as we were working with egg albumin, enzyme, lactic acid, and perhaps glycogen, it seemed that the procedure might be simplified to precipitation of the protein, with a subsequent careful washing in order to remove all the glycogen. The protein was precipitated with mercuric chloride and with thorium nitrate in alkaline solution. Careful washing caused some of the protein to become peptized and pass over into the filtrate. If these last traces are not removed, reducing substances caused by the subsequent HCl hydrolysis affect the results materially, making them too high. The more serious difficulty, however, is that the last traces of glycogen cannot be removed from adsorption on the protein. Where small amounts of glycogen are present this amounts to a large percentage error, and makes the method impracticable for quantitative work.

This question of adsorption has not been considered carefully heretofore in the methods for determining glycogen. It is obvious that the usual means of testing the efficaciousness of a method by adding known amounts of glycogen to tissue already containing glycogen and showing that one can recover 100% of the added glycogen is no criterion for that method. There is the same error of loss due to adsorption both in the portion to which glycogen was added and also in the blank. This error is of course not so serious when one is merely comparing the relative amounts of glycogen in two samples, but it is necessarily of prime importance in our case where we have no glycogen in the blank and wish to show a formation of glycogen. We are now working on a method of analysis with which we hope to surmount these difficulties.

[1] Biochem. J., 19, 1115 (1925).
[2] Biochem. J., 24, 67 (1930).
[3] Biochem. J., 20, 1196 (1926).

It is interesting to note that one of the characteristics of cancer is a disruption of the ordinary metabolic changes in the muscle. The rate of formation of lactic acid is greatly increased and there seems to be little conversion of lactic acid back into glycogen. It is necessary for Meyerhof to postulate that the glycogen is broken down as fast as it is formed, for he claims that the glycogen is formed by the coupled reaction between oxidation and synthesis. This is absurd. Warburg and Negelein[1] have shown that the rate of formation of lactic acid in cancer is very little reduced by the presence of oxygen. On the other hand, in the normal tissue there is very little or no lactic acid formation in the presence of oxygen. This indicates that the formation of glycogen, which reduces the concentration of lactic acid, is reduced to a minimum in cancer tissue.

The increased rate of formation of lactic acid may be due either to an increased amount of available enzyme, or to less adsorption of glycogen on the protein. If some of the enzyme is ordinarily adsorbed on the lipin surfaces, as Przylecki suggests, this might be liberated by the selective adsorption of some foreign substance in cancer which would give an increased concentration of free enzyme. On the other hand, less adsorption of glycogen due either to less protein or to some substance being selectively adsorbed on it might account for the increased rate. With less adsorption of glycogen, according to our theory, there would be no reason for much formation of glycogen from lactic acid, and apparently there isn't. Due to the lack of facilities we have not been able to test whether there is less adsorption of glycogen by cancer tissue than by normal tissue.

Warburg also points out that carcinomas form lactic acid from methyl glyoxal at the same rate as from glucose, which is very surprising if methyl glyoxal is an intermediate compound between glucose and lactic acid. There should be a time factor unless the reaction between glucose and methyl glyoxal is instantaneous. Moreover he points out that liver tissue breaks down glucose at only one-tenth the rate of cancer tissue but breaks down methyl glyoxal at the same rate. He concludes from this that there is no difference between cancer and fresh tissue with respect to methyl glyoxal We conclude from this that either there is some mistake in the determination of the rates of lactic acid formation from glucose and methyl glyoxal, or, in carcinoma, glucose does not break down to lactic acid through the intermediate stage of methyl glyoxal. Warburg also calls attention to the similarity between embryonic and cancer tissue in the rapid growth, increased rate of glycolysis and the small amount of glycogen present.

This fact led Harrison and Mellanby[2] to the belief that the increased rate of glycolysis might be due to a lack of some substance 'the growth regulator' which was absent from the embryo and from the cancer tissue. Inasmuch as cancer seldom attacks the pancreas, they believed that this organ must contain considerable quantities of this hypothetical substance. They found

[1] Warburg and Negelein: Biochem. Z., 152, 309 (1924).
[2] Harrison and Mellanby: Biochem. J., 24, 141 (1920).

that an extract of the pancreas did inhibit glycolysis in cancer tissue from 15 to 100 per cent both in the anaerobic and aerobic phase. They found, moreover, that cancer tissue could not form lactic acid from hexose monophosphate or diphosphate, whereas the normal tissue forms lactic acid from these substances readily. They came to the conclusion that in cancer tissue glucose does not go through the form of a phosphate ester before going to lactic acid, and that in this respect the cancer tissue was different from normal tissue. We know, however, that cancer forms lactic acid from glycogen rapidly. If Harrison and Mellanby are correct, this must mean that in cancer glycogen is not esterified with phosphate during the course of glycogenolysis. There seems to be ample evidence to show the formation of an intermediate phosphoric ester in the normal tissue. Furthermore we have seen from Warburg's work that glucose apparently breaks down into lactic acid without going through the stage of methyl glyoxal. On the basis of these facts we must conclude that glycogen and glucose are converted into lactic acid by different ways in cancer and in normal tissue. This difference in itself might possibly account for the difference in rate of glycolysis.

The problem as outlined here of why and how glycogenolysis takes a different path in cancer than in normal tissue should be of considerable importance in the study of cancer. It is one of the problems which must be solved in the future.

The following general conclusions are made:

1. The theories of Meyerhof, Warburg, and Hill are not the only explanation for the chemical changes during fatigue and recovery in the muscle.

2. The amount and the rate of lactic acid formation may be readily explained on the assumption of an equilibrium between glycogen and lactic acid, whose rate is catalyzed by enzymes.

3. The slow linear formation of lactic acid during anaerobic rest is easily understood and could be predicted on the basis of an enzyme theory where the glycogen is stabilized by adsorption on the protein.

4. The formation of lactic acid as a result of chloroform and heat rigor is obvious when we realize that the effect of these agents is to liberate the glycogen from adsorption on the protein.

5. A suggestion has been made which should account for the effect of various other chemical reagents as caffein, arsenate, oxalate, etc.

6. An adequate explanation is put forward by means of this theory for the formation of dextrorotatory lactic acid in the muscle, a phenomenon which has been more or less ignored in the Meyerhof theory.

7. It has been shown that, despite the fact that the equilibrium point is well over on the lactic acid side, it is quite possible for the lactic acid to be converted back into glycogen again, due to the extraction of glycogen from solution by adsorption on the protein.

8. Some of the errors in the methods of analysis of glycogen have been pointed out which have prevented up to this time the demonstration of the formation of glycogen from lactic acid by means of the enzymes and the adsorption of the glycogen on the protein.

9. Glycogen apparently takes a different path in cancer in the formation of lactic acid from that which it takes in the normal muscle.

10. Several possibilities are suggested, any one or all of which might account for the increased rate of glycolysis in cancer.

We are indebted to Dr. Ellice McDonald of the Cancer Research Laboratories of the Graduate School of Medicine of the University of Pennsylvania who suggested this work and gave us valuable aid in supplying references.

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THE CHEMISTRY OF ANESTHESIA*

BY WILDER D. BANCROFT AND GEORGE H. RICHTER**

The working hypothesis of this paper is Claude Bernard's theory that the reversible coagulation of the colloids of the sensory nerves produces or accompanies anesthesia. This is supplemented by the plausible assumption that the decreasing stability of the colloids during the first addition of the anesthetic is accompanied by an increasing irritability.

Historical and mythological literature abound in fact and fancy concerning narcotics and their uses. Their use was sometimes attended with weird incantations, many strange concoctions, hypnotism, and always with a lack of scientific knowledge of the nature of the phenomena. That narcosis was well known at the beginning of the Christian era is established by the work of Galen and his contemporary, Dioscorides.[1] In spite of its antiquity, there is still considerable mystery surrounding the mechanism of narcosis. Modern textbooks on pharmacology are content to give several theories of narcosis and to point out good and bad features in each without definitely proving or disproving any particular one.

In 1899 Hans Meyer proposed a theory that was immediately followed by E. Overton's theory. Since the two theories were formulated separately and about the same time it is known as the Meyer and Overton theory. This is, perhaps, one of the most popular theories at the present time. It is based upon the fact that narcotics are soluble in lipoids or fats and that the strength of their action is related to the distribution coefficient. Meyer formulated the theory in the following way:

"(a) All chemically indifferent substances, which are solvents for fats and similar bodies, must exert a narcotic action upon living protoplasm, in so far as they can diffuse therein.

(b) The effect must manifest itself first, and most strongly, in those cells in whose chemical structures these fatty or lipoid substances predominate and presumably are the essential carriers of the cell function, namely, in the nerve cells.

(c) The relative efficiency of such narcotic agents must be dependent upon their mechanical affinity for lipoid substances, on the one hand, and for the remaining body constituents, i.e., principally water, on the other hand. It is dependent, therefore, upon the partition coefficient which determines their distribution in a mixture of water and lipoid substance."

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[1] De Med. Mat., Lib. 4, 76; 7, 207.

The work of F. A. Bucholz[1] had shown that many substances could behave like narcotics although, chemically, they were entirely foreign to being classed as narcotics of the alkaloid type. Further, this action ran parallel to the fat-solubility of these substances. This evidence supports the first postulate of the theory. The second postulate is supposed to be accepted upon the grounds of common experience, that narcosis is confined to the lipoid-containing tissues. The third postulate is demonstrated by the work of Baum[2] in showing that there is a pronounced parallelism between the distribution coefficients and the degree of narcosis. This relation is shown in Table I, the threshold values being for tadpoles.

TABLE I

Substance	Distribution Coefficient	Threshold value in Mol/Liter
Trional	4.46	.0018
Tetronal	4.04	.0013
Sulfonal	1.11	.0060
Bromal hydrate	.66	.0020
Chloral hydrate	.22	.020
Ethyl urethane	.14	.040
Methyl urethane	.04	.400

A great deal of research has been done on this part of the theory. One very striking example, that deserves mention, was carried out by Moral.[3] It is known that the distribution coefficients are not independent of the temperature and that the values may either decrease or increase, as the temperature rises. Moral showed that, if this occurred, then the degree of narcosis was altered just as the theory predicted.

TABLE II

Substance	Temp. −3° D. Coef.	Temp. −3° Rel. Strength	Temp. 30°−36° D. Coef.	Temp. 30°−36° Rel. Strength
Salicylamide	22.23	1300	14.00	600
Benzamide	.672	500	.437	200
Chloral hydrate	.053	50	.236	250

However, in spite of such supporting evidence as this, there have developed some very important objections. First, the theory in reality only defines the physical properties which a narcotic must have. Overton's explanation that the cell membrane is altered is not satisfactory, for it is known that during narcosis the permeability is first lowered and then increased. This seems to

[1] Inaug. Diss., Marburg (1895).
[2] Arch. exp. Path. Pharmakol., 42, 119 (1899).
[3] Arch. ges. Physiol. (Pflüger's), 171, 469 (1918).

be an effect rather than a cause. Meyer's later assumption,[1] that solution of the narcotic in the lipoid would disturb the functional activity of this substance, is indefinite and gives no clear picture of what has happened within the cell.

The lipoid solubility does not seem to be the important factor in all cases. The grey substance of the brain contains 8.5% lipoid, and the white matter 16%.[2] Kochmann points out that, in spite of this, narcosis starts much sooner in the gray matter and is stronger than the narcosis in the white matter. Then Winterstein showed that narcotics were capable of exerting their typical effects on organisims that were free from lipoids (e.g., acetone-extracted yeasts). Also, the well-known effects of many narcotics on enzymes could in no way involve lipoid material. So the idea that lipoids are an essential factor in narcosis is wrong.

Attention must also be called to the fact that too great an importance cannot be attached to the distribution coefficients. Superficially, they do run parallel to the strength of the narcotic but there are many exceptions. Monoiodoisovalerylurea has a distribution coefficient of 1.05 but is inactive as a narcotic although one would predict from the distribution coefficient that it would be as active as sulfonal. Then the distribution coefficients of caffeine and theobromine[3] are such that they should be good narcotics but these drugs have an effect just the opposite from a narcotic and behave as stimulants. Furthermore the distribution coefficients are measured for distribution between olive oil and water and not lipoid and lymph.

The experiments of K. H. Meyer and Gottlieb Billroth[4] were very important in spite of the numerous mistakes. They were determining the concentration of inhalation narcotics necessary to produce narcosis in mice. The concentration of the narcotic in the brain lipoids was dependent upon the concentration of the narcotic in the inhaled air. The body fluids were merely passages for the narcotic to reach these structures. The rapidity with which the threshold values were reached depended upon the solubility of the narcotic in the body fluids. The more insoluble narcotics required greater lengths of time to become effective. From this point of view, the theory is rather a theory of *transportation*.

This offers an explanation of the fact that the higher homologs of some narcotics are inactive, although the distribution coefficients are much greater than those of the lower members of the series. It is simply that the water solubility has been so reduced that the substance cannot be transported to the cells faster than these can eliminate them, so a concentration of the narcotic sufficiently great to produce narcosis is never reached.

The foregoing interpretation of the Meyer and Overton theory as a theory of transportations is essentially that outlined by Kochmann.[5] Kochmann's

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[1] *Wiener med. Wochenschr. No. 27 and 28. Sonderdruck (1921).*
[2] Compt. rend. soc. biol., 62, 1153 (1907).
[3] Arch. farmacol. sper., 38, 59 (1924).
[4] Z. physiol. Chem., 112, 55 (1921); Münch. med. Wochenschr., 8 (1921).
[5] "Handbuch. exp. Pharm.," 1, 449.

views seem to make a worthy contribution to the subject but one feels that there is something of greater significance to the distribution coefficients than he has indicated. For the distribution coefficients run parallel to the strength of the narcotic to a much greater degree than the rapidity with which they become effective. If it is considered that the tendency to be concentrated in the oily layer in preference to the aqueous, is a *crude* measure of the extent of adsorption on the colloids of the nerves, it is clear why the strength of the narcotics should be roughly related to the distribution coefficients. In ordinary adsorption there is a partition of the substance between the solvent and the insoluble substrate. It is surprising that the analogy holds as well as it does.

Traube's theory of narcosis,[1] is similar in many respects to the Meyer and Overton theory. Traube has gathered an immense amount of data on the surface tension of solutions of narcotics and has applied this to possible methods of distribution within the cell. His data are useful in showing that the narcotics are not necessarily in solution but are adsorbed and that such colloidal phenomena play an important rôle in narcosis. It was demonstrated by his work that the strength of a narcotic was related to the surface tension of a solution of the narcotic as Table III shows:

TABLE III

Substance	Threshold value in Mols.	Cap. elevation of ¼M. sol.(H_2O 9.15)	Mol. Conc. of iso-cap. sol.
Methyl alcohol	.57	88.6	14.
Ethyl alcohol	.29	84.0	5.
n-Propyl alcohol	.11	74.0	1.6
i-Butyl alcohol	.045	56.5	.46
n-Butyl alcohol	.038	—	.45
Active amyl alcohol	.023	37.4	.14

There is a distinct parallelism between the surface activity of a narcotic and its physiological action, solutions that are iso-capillary are of the same degree of toxicity, etc. Then one can predict, roughly, the effect of isomerism and homology in drugs from a knowledge of the surface activity. What Traube has really shown is that the lowering of the surface tension can be substituted for the Meyer and Overton distribution coefficient. This does not help the theory very much but does get around the fact that lipoid-free organisms can be narcotized, for the surface activity of the narcotic does not depend upon the lipoids.

In accordance with the work of Gibbs it is known that if a substance concentrates at an interface, or is adsorbed, the surface tension at the interface is lowered. Furthermore, the degree of lowering of the surface tension is a function of the extent of adsorption. It must not be forgotten that the interface at which Traube measured these surface activities was the liquid-air interface

[1] Arch. ges. Physiol. (Pflüger's), **153**, 276 (1913); **160**, 51 (1915); **161**, 530 (1915).

while the important interface in the cell is the liquid-colloid interface. His data cannot be expected to be of universal applicability; it is remarkable that the relation holds as well as it does. As mentioned above, the adsorption is only a preliminary phase, and narcosis or toxic effects do not necessarily follow. For it is known that amino acids and sugars are adsorbed but do not behave as narcotics. This adsorption, doubtless, aids the transportation of the narcotic to the cell and facilitates its entrance into structure but does not explain the effective mechanism of narcosis.

Verworn has studied the oxygen metabolism of varied organisms while they were under the influence of narcotics and upon the results of his experiments put forth a theory of narcosis.[1] Verworn's hypothesis is that the loss of response to stimulation is due to the disturbance of the oxygen metabolism. This theory is very often referred to as the "suffocation" or "asphyxiation" theory but it should be pointed out that the asphyxiated state does not occur by excluding oxygen from the cell but arises through the inhibition of the oxidation process by the narcotic. Verworn assumed that the oxygen carriers were in some way related to the lipoids, thus attempting to reconcile the theory of Meyer and Overton with his.

In general, it is true, that during narcosis there is a lowering of the metabolism; but many workers have shown that this is not always the case. Loeb and Wasteneys,[2] in an investigation on sea-urchin eggs, showed that potassium cyanide must decrease the oxidation about two-thirds before the development was hindered, while narcotics such as chloral hydrate, chloroform, ethyl urethane, and alcohol could bring about the same degree of hindrance without materially altering the oxygen consumption. Then Winterstein[3] showed that ethyl urethane when applied to the spinal cord of the frog caused a marked decrease in the oxygen consumption, while ethyl alcohol caused just the reverse under the same conditions. There are a number of organisms that exist without the aid of atmospheric oxygen, the intestinal worm Ascaris is such a one. Winterstein has shown that this worm can be narcotized. Verworn's theory cannot explain this.

However, it must be pointed out that these are just a few of the exceptions which show that any alteration in the oxygen metabolism is not the cause of narcosis but rather an effect.

M. Kochmann[4] presents a rather interesting but inadequate theory of narcosis. It grew out of the observation that many of the common narcotics would inhibit the swelling of various substrates, such as fibrin, in water or dilute salt solutions. This action was found to be reversible and Kochmann felt that it must be the cause of narcosis. The mechanism of this is explained in Kochmann's own words: "Thereby lowering the permeability of the cell membrane which amounts to a diminution and inhibition of the total exchange of material and consequently to a stop of the cell function, or in

[1] "Narkose" (1912).
[2] J. Biol. Chem., 14, 517 (1913).
[3] Biochem. Z., 61, 81 (1914).
[4] Heffters "Handbuch exp. Pharm.," 1, 449.

other words it means the narcosis of the cell." The idea is not new. This is the old alibi of practically all previous workers when they are forced to a definite statement of the cause of narcosis. In fact, this does not explain narcosis but blames the phenomena on something else which in itself is indefinite and has been shown to be an accompanying phenomenon to narcosis and not its cause. What Kochmann has really shown is that narcotics under certain conditions will partially dehydrate some colloidal substances.

Narcosis is not the simple problem that it was once thought to be, for there are many changes taking place in a tissue under the influence of narcotics. Some of these changes are characteristic of only one tissue; the true explanation must point out the phenomenon that is common to all cases. None of the above theories do this; it seems that in each case the observations were confined conclusively to some one of these changes. Consequently, the theories based upon such data are partially right, although they contradict one another in many details. It is the intention of this paper to indicate the basic phenomenon back of all cases of narcosis and to show that the other changes are just some phase of this general phenomenon.

A few of the earlier workers in the field of narcosis foresaw that colloid chemistry undoubtedly would be associated with the phenomena and consequently proposed theories that related to coagulation. Probably the first of these was the theory of Binz.[1] This theory was concerned with the effect of narcotics on the brain. The author showed that brain tissue exposed to dilute morphine hydrochloride solutions would undergo coagulation and that the initial stages of this phenomena were reversible. If the narcotic was allowed to act for too great a time the coagulation was irreversible. The ganglion cell was supposed to be the point of attack of the narcotic agent and if the material was not irreversibly coagulated the cell would return to normality, or if it was in the advanced stage where the protoplasm had become "granulated" then death was inevitable.

Another theory that resembled Binz's theory was proposed by Claude Bernard.[2] This theory was based upon the "semi-coagulation" of the protein constituents of the cell as the cause of narcosis. Although Bernard was not the first to propose such a theory he was the first to investigate its possibilities and to formulate and explain the mechanism on an extensive scale.[3]

The views of Claude Bernard have been expressed by many, but for the sake of clearness the following paragraphs translated from Bernard's "Leçons sur les Anesthésiques" are quoted to cover the important phases of his theory.

"The action of anesthetics is very general. They react not only with animals but also with plants. Thus they stop the movements caused in sensitive plants by external stimuli, the movements of the anthers of some flowers for instance.

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[1] Deutsche Klinik, Nr. 29, 277 (1860).

[2] "L'Anesthésie." Union med., Paris, 8, 109 (1869).

[3] "Leçons sur les anesthésiques et sur l'asphyxie" (1875).

"Ether and chloroform have been used by veterinarians or by physiologists with almost all animals. These were used at first with the large animals, horses, cattle, sheep, etc., but especially with horses. Ether and chloroform are not now used with cattle or sheep if the operation is a serious one. The veterinarians gave up the use of these anesthetics very quickly, because of a fact which had nothing to do with the scientific side. The flesh of animals anesthetized by ether or chloroform has an unbearable taste which prevents selling the flesh as butcher's meat in case the animal dies under the operation.

"It is clear that an animal put under the influence of chloroform cannot be considered normal. It is being treated with a toxic agent, the action of which is usually not carried to the point of killing the animal; but which nevertheless modifies considerably the physiological functions of the organism. That is so true that the most violent poisons may be absolutely without effect on an animal which is anesthetized with chloroform or ether.

"There are two successive and perfectly distinct, or rather opposed phases in the state of cerebral circulation under the influence of anesthetics. The first phase corresponds to the experiments in which we found hyperaemia; the second to the experiments which showed the brain in a state of anaemia. I insist on these contradictory experiments because it is necessary to explain them by different conditions as we have just done in this case.

"The hyperaemia corresponds to the agitation which marks the beginning of the administration of the anesthetic; but it is not a special point, because one can produce it in other ways, for instance merely by making the animal scream. We have already seen that this agitation, observed in the first stages of the administration of chloroform or ether, corresponds to a special irritation quite distinct from the anesthetic effect, and in this first stage there occur phenomena quite foreign to anesthesia.

"On the other hand, during the period of dropping-off and complete insensibility, which is that of true anesthesia, we observe an anaemia more marked than the normal state. We have pointed out in the first lecture that this result agreed perfectly with what we knew in regard to the relative states of the circulation when organs are functioning or resting. During their period of activity, the organs receive much blood; during their period of rest, they receive much less. Anesthesia, being the suppression of sensitiveness, represents certainly a state of absolute rest for the sensory nervous system, and it is therefore perfectly natural that this should be accompanied by anaemia of the brain.

"I do not believe that the cerebral anaemia which we have observed is sufficient to account for anesthesia. It is true that during anesthesia the brain contains a little less blood than under ordinary conditions; but this circulatory decrease does not exceed that of an organ at rest. In the brain there is still quite enough blood to sustain the nervous functions and to permit the sensory system to react to external stimulants as it would do in a state of normal rest. Then, too, the blood of an anesthetized animal contains quite enough oxygen to produce the ordinary effects, since some analyses of

the blood under these conditions have even shown a larger percentage of oxygen than the normal.

"There is, therefore, something besides cerebral anaemia to anesthesia. We have had to raise this point in order to make certain that this is not the proper line of attack on the problem of anesthesia.

"I believe that anesthesia depends immediately and directly on the presence of chloroform in the blood and on its special action on the nerves. The vascular changes are only secondary accompaniments of the phenomenon and not the cause of it. To ascribe anesthesia merely to an anaemia of the brain would be the same thing as considering drunkenness merely as a result of the general change in vascular conditions which are always noticeable. There is certainly something more than that. Drunkenness depends on the alcohol in the blood and on its direct action on the nerves; it is the same for anesthesia which has some things in common with drunkenness.

"I have shown you experimentally that heat will anesthetize frogs perfectly. That, after all, is in harmony with what we know in regard to vital properties in general and to those of the nervous system in particular. At a low temperature, at 0° and even a little above it, a frog benumbed by the cold remains completely insensitive to external influences; at this temperature it is only slightly sensitive, and sometimes completely immune to the actions of the most energetic poisons. As the temperature rises, the sensitivity increases and the frog becomes more and more susceptible to toxins, etc.

"The grand sensory nervous center, the center of centers, is the brain. As such, it reacts on the spinal cord—which plays the part of a nerve with reference to the brain although it is itself a center with reference to the nerves—in the same way that the spinal cord in its turn reacts with the sensory nerves. For anesthesia to occur, it is necessary for ether or chloroform to come in contact with a nervous center. When this condition is fulfilled, anesthesia results in all parts of the nervous system under control of the nervous center affected, except the sensory system of the respiratory and circulatory functions essential to life.

"Without committing ourselves to the nature of the action produced on the nervous center itself, we will prove that there is a special selective action, dealing exclusively with the sensory nerves of the nervous system. Here is a frog which is completely anesthetized. You will note that there are no voluntary movements, that it is quite insensitive to external stimulants, and that it remains absolutely inert even when pinched violently. Nevertheless, the motor nerves in this frog have kept their ordinary excitability.

"To show this, let us bare the sciatic nerve, a mixed nerve which corresponds both to a sensory trunk and to a motor trunk. The sensory fibers are anesthetized; but the motor fibers keep their normal properties. If we excite the nerve with an electrical current, we shall produce movements in the corresponding foot, just as we could have done with a normal frog. Thus the chloroform, which diffuses through the spinal cord produces anesthesia and only destroys the properties of posterior sensory roots without affecting

the anterior motor roots. I will not say that this is a very startling fact, because analogous cases are known; but it is a very remarkable fact and one which deserves the whole attention of the physiologist.

"We have seen that anesthesia can be produced by a great number of ways or reagents: chloroform, ether, hot water, anaemia, asphyxiation, etc. Does this mean that there are many different kinds of anesthesia? No, they are only different methods of producing anesthesia, and the final mechanism must be the same in all cases. We have just shown that they all act in the same portion of the organism, on the sensory cell.

"Let us begin by summing up the effects of anesthetics in approximately the order in which we have studied them:—

(1). An anesthetic is a volatile substance which gets into the blood in the case of the higher animals through the respiratory surfaces. Since the anesthetic is readily adsorbed, it penetrates rapidly. From the beginning of inhalation we find chloroform in the blood, even though a single whiff has been taken. The blood, which takes up the anesthetic, conveys it to the nervous center on which it acts. We have confirmed this previously-stated opinion by direct experimental tests. We have also shown that in the nerve centers anesthesia is not accompanied by congestion, as people had hitherto assumed, but by a relative anaemia.

(2). Are the nerve centers all affected at the same time by the action of the chloroform? No, the brain is affected first—one loses first the consciousness of the ego, the recognition of external phenomena. The spinal cord is not affected until later and one can even distinguish several periods in the action of chloroform in this nerve center. At the beginning of the anesthetic action the reflex movements having their center in the medulla oblongata and in the spinal cord continue to function and are even more energetic and rapid. Then these centers are affected and the reflex movements disappear gradually; but the movements which would be voluntary if the animal had not lost consciousness persist for some time; finally, they also stop and the animal falls into a collapse with complete muscular relaxation. It becomes as motionless as a corpse. The respiratory movements and the movements of the heart alone remain.

"What picture ought we to make of the action of chloroform on the central nerve cell? All the effects produced on an anatomical unit, no matter what they are, can only take place through a physical or chemical modification of of that unit. We can no longer postulate mysterious actions to which we ascribe the word *vital*. When we employ this word it means that we know nothing definite about the phenomenon in question. For a certain number of the toxic actions we are able today to determine definitely the physical or chemical phenomenon which is the cause of the action. Thus carbon monoxide reacts with the red blood corpuscles, combining chemically with the haemoglobin. The demonstration of this chemical action is easy to make and one can produce the compound *in vitro* as well as *in vivo*.

"We are not so advanced as to the action of anesthetics; but we believe that a certain number of arguments based on an exact analysis of the facts will enable us to form a fairly definite idea of the way in which anesthetics act on the nerves. It seems to us that this action consists in a semi-coagulation [Bernard means what we should call a slight, reversible coagulation of the bio-colloids] of the substance itself of the nerve cells, a coagulation which would not be permanent, the anatomical unit being able to return to its normal state after the toxic agent is eliminated.

"To understand this action as postulated, let us remember that chloroform does not act solely on the nerve tissues. Far from that, it has an action on all the tissues and attacks each one at a time which is a function of its susceptibility. Just as chloroform affects birds very rapidly, and frogs and plants slowly, in the same way it will affect one set of tissues in a given animal before another set. The effect shows itself with the other tissues after it has become noticeable with the nerve tissues, the most delicate of all. The plant has no nervous system and yet chloroform and ether act just as fatally on it and stop the activity common to all its anatomical units. With the sensitive plant, for instance, the anesthetic affects at first the irritability of the cells, destroying thus the movements of the leaves. An anesthetic is not a special poison for the nervous system. It anesthetizes all the cells, benumbing all the tissues, and stopping temporarily their irritability.

"We can study elsewhere than in the central nerve cells the phenomenon which causes this stoppage of action and which we consider as a coagulation or as a beginning of coagulation. If we place a muscle in the vapor of chloroform or ether, or if we inject into the muscular tissue some water containing a little chloroform or ether, and if we let this stand for quite a while, the muscle becomes rigid. The content of the fibers has coagulated and we have what is called the chloroform rigor. If we let the chloroform act for a shorter time, we reach a point where the muscle loses its irritability, and is anesthetized. If at this moment we examine the muscular fiber under the microscope we see that it is no longer transparent and that it is in a state of semi-coagulation. . . .

"It is permissible to assume that something similar happens in the nerve cell; but the latter is much more delicate and much more susceptible to the action of chloroform. It is the portion which first undergoes coagulation. As the chloroform is carried away by the blood, it returns to its normal state, coming out of its anesthesia as the muscle comes out of its rigidity."

Since the time of Claude Bernard no one has made any serious attempt to "modernize" these earlier colloidal theories. In fact just the reverse has taken place, for such workers as Winterstein and Kochmann criticize the theory severely and deny any important value to it.[1] The criticism offered by Winterstein, which may be taken as typical, does not seem justified in the light of modern knowledge.

[1] Winterstein: "Die Narkose" (1919).

First let us define the terms "narcosis" and "narcotic." The definition of the German workers is accurate enough: narcosis is the state of a living cell during a reversible paralysis and a narcotic is a substance that will bring about this condition.

There are three basic criticisms directed against the coagulation theory:

(a) The concentrations at which narcotics are active are much less than that required to flocculate the cell colloids.

(b) Coagulation of the cell colloids represents the toxic effect of a narcotic and is irreversible, whereas narcosis is a reversible phenomenon.

(c) The cases in which the dispersion of the colloids is decreased by narcotics are explained as being only apparent.

The objection that the concentration of narcotics during narcosis is too low to produce any decrease of dispersion is not convincing. This conclusion was reached by determining the concentration of narcotics in the blood and different organs during narcosis. The following table from Niclaux[1] is typical of such analysis. The values are given in mgs. per 100 gm. substance and are the quantities found in the organs of a dog. These are upper limits, for they are the amounts found in the organs just after death had occurred, due to the action of the narcotic.

TABLE IV

Organ	Chloroform	Ether
Arterial blood	70–64	161–175
Venous	52–49	160–169
Liver	47–52	102–139
Kidneys	39–46	125–140
Spleen	21–38	107–132
Muscle	15–24	100–120
Brain	46–59	153–163

For these and similar data one is not justified in drawing the conclusions that form the basis of this criticism, for we know that an increase in the distribution coefficient of the narcotic runs parallel to an increase in strength, or what is almost the equivalent, the lower the solution tension in the body fluids, the greater will be the tendency to be adsorbed by the tissues. The mere determinations of concentrations of narcotics in body fluids have no meaning, for the adsorption coefficients are unknown, and the amount of adsorbent is, at the present, indefinite; so that it is impossible to calculate the extent of adsorption. The values obtained for the different organs are just as useless, for they give no information concerning the distribution within the organ. However, the brain is an exception that offers a crude possibility, for the narcotic is adsorbed in the lipoid material. Then from a knowledge

[1] Compt. rend. soc. biol., 60, 206 (1906); Compt. rend., 144, 341 (1907).

of the amount of lipoid material in the brain, one can calculate the amount of narcotic per unit amount of lipoid. The following material in the Table V is a collection of several values from independent workers.

TABLE V

Substance	Amt. in 100 gms brain	Amt. in Millimols per 1000 gms lipoid	Author
Ether	.117	132.	Storm van Leeuwen[1]
Chloral hydrate	.0112	22.	Archangelsky[2]
Adalin	.0112	4.	
Bromural	.0111	4.	Kwan[3]
Neuronal	.0194	8.	
Alcohol	.327	591.	Giebant[4]
Chloroform	.035	24.	

Battelli and Stern[5] have produced important evidence that narcotics are only effective as such when they are in the approximate flocculating concentration. The oxidizing enzyme in the liver that oxidizes succinic acid can be easily narcotized by the common narcotics. The nucleo-proteins of the liver probably serve as the substrate upon which the enzyme is dispersed. Table VI shows the close agreement between physiologically active concentrations and the flocculating concentrations.

TABLE VI

Substance	Molar Concentration which: inhibits oxidation	flocculates nucleo-protein	Substance	Molar Concentration which: inhibits oxidation	flocculates nucleo-protein
Methyl alcohol	5.78	6.31	Methylethyl ketone	.82	.94
Ethyl alcohol	2.97	3.33	Methylpropyl ketone	.34	.39
Propyl alcohol	1.09	1.44	Ethyl urethane	.95	1.06
i-Butyl alcohol	.41	.46	Propyl urethane	.39	.48
i-Amyl alcohol	.18	.24			

The criticism that small amounts of narcotics would not flocculate is based upon observations of protein sols and other bio-colloids when treated with reagents "in vitro." The assumption that is tacitly made is that the material is in the same state as when in the cell. This is not likely.

It is well known that rather large amounts of alcohol are required to flocculate protein sols. Now if such a sol is treated with a small amount of electrolyte the amount of alcohol required to bring about the flocculation is less.[6] If enough electrolyte is added, the flocculation concentration of the

[1] Arch. ges. Physiol. (Pflüger's), 165, 594 (1916).
[2] Arch. exp. Path. Pharmakol., 46, 347 (1901).
[3] Arch. intern. Pharmacodynamie, 22, 331 (1912).
[4] Compt. rend. soc. biol., 127, 746 (1899).
[5] Biochem. Z., 52, 226 (1913).
[6] Cf. Gurchot: J. Phys. Chem., 30, 83 (1926).

alcohol can be made very low. For example a slightly acidified albumin sol was treated with sodium sulphate until it was on the verge of precipitating; one drop of the common alcohols or a small crystal of chloral hydrate was then sufficient to bring about flocculation.

Other proteins were investigated by this method. Edestin, when treated with electrolytes and alcohol, was found not to be sensitized as much as the albumin. The proteins of wheat flour when examined by this method were found to be relatively indifferent towards the common alcohols but show a slight decrease in dispersion when treated with chloroform. This shows that this sensitization is specific both for the different narcotics and substrates and is in line with the fact that all narcotics do not affect the same tissues equally.

The phenomena of sensitization are not characteristic only of the acidified albumin sols and sodium sulphate. For example a slightly alkaline albumin sol required 0.8 cc of alcohol to produce a marked turbidity in a given volume of the sol. The same volume of sol when treated with 3.6% of calcium chloride required only 0.2 cc to produce the same degree of turbidity. Thus in this experiment the addition of a small amount of calcium chloride has made the sol four times as sensitive as the original sol to the effects of the alcohol.

It is quite possible that some of the colloidal systems of the cell may in an analogous manner be so sensitized that the addition of a small amount of a narcotic will flocculate them. The living cell contains such a great variety of organic matter that the possibility of such a condition is very probable. If such a state exists, then low concentrations of narcotics would easily flocculate the colloids.

Any doubt about the existence of such critical states is dispelled when one considers the ionic antagonism in biological systems. Very small amounts of the different electrolytes bring about profound reactions in the protoplasm. There is evidence that other such critical states exist, and the phenomenon may be quite general. Pickering and Hewitt[1] suggested that the initial phases of blood coagulation are a physical process and find that it is reversible. They also demonstrated that this system was made very sensitive by other substances that were present in the blood.

The coagulation temperatures of pure proteins is in general above 50°. Heilbrunn states that "the description of any protein which coagulates at 30°-40° is rather doubtful." Yet there are many cases known where death can be brought about at lower temperatures e.g., Phyllopods at 18°-10°[2] and cuttle-fish sepia at 28°.[3] Heilbrunn[4] found that the protoplasm of sea-urchin eggs was coagulated at 32°-33° and that emulsified fats or lipoids, that were present, were related to this sensitization. Other workers have found that lecithin has a decided influence on the coagulation of proteins.[5] So it is not at all impossible that many colloidal systems of the living cell are in a critical state.

[1] Biochem. J., 15, 710 (1921).
[2] Sitzungsber. Akad. Wiss. Wien., 75, 583 (1877).
[3] "Action de la chaleur et du froid" (1919).
[4] Am. J. Physiol., 69, 190 (1924).
[5] Lloyd: "Chemistry of Proteins."

In making studies on the coagulation of protoplasm, it is well to remember that the coagulation often brings about no visible microscopic change. The protoplasm seems to "set" like a jelly. In experiments on isolated proteins enough reagent is generally added to produce the typical coagulation that can be seen with the eye. The conclusion that such coagulated proteins are similar to coagulated protoplasm is not justified. Many workers seem to overlook this differenee and this may be a reason for much of the conflicting data on the reversibility of coagulated or semi-coagulated biological systems. Where there is no visible change produced, an investigation of the viscosity variation is helpful. The changes in the viscosity of coagulating protoplasm are quite characteristic. The initial stages of coagulation are associated with a phase of lowered viscosity which passes through a minimum and goes above normal as the coagulation progresses.

The second objection, that coagulation is irreversible and represents the toxic action, and the third objection, in which the lowering of the dispersion in known cases is made to appear as being only apparent, must be considered together as they are obviously related. In order that Winterstein's criticisms be coherent and complete, it was necessary to explain the known cases of the lowering of dispersion of the cell colloids as being only apparent because this was found to be reversible. Then since he thought that coagulation was irreversible, he had to consider the two cases separately.

The objections to the decrease in dispersion of the colloids are groundless. Winterstein admits that this phenomena is "probably reversible" but attempts to show that the phenomenon is only apparent and in actuality is not a decrease in dispersion. He attributes the phenomenon to the type of turbidity (decrease in dispersion) that was obtained by Calugareanu[1] in lecithin, chloroform and water emulsions. Calugareanu found that the emulsion in this case was reversible upon the removal of the chloroform phase. This could be effected by warming until the chloroform has volatilized, or upon standing so that the chloroform merely evaporated. The emulsion was obtained by dissolving lecithin in either chloroform or water, then to this solution the other liquid was added until its solubility is exceeded so that there are two layers. Calugareanu observed that at the dineric interface the solutions became turbid and, if allowed to stand long enough, the turbidity extended further into the liquid. The same effect could be brought about more rapidly by shaking. The interpretation of this phenomenon that was offered by Calugareanu and accepted by Winterstein is entirely wrong. They believed that the colloidal lecithin particles adsorbed the chloroform very strongly, thus forming an outer shell around the micellae. This decrease in dispersion is then only apparent.

The type of emulsion that Calugareanu obtained is well known to colloidal chemistry and depends upon the adsorption of the lecithin at the dineric interface. It is known, from the Gibbs equation that if the lecithin

[1] Biochem. Z., 29, 96 (1910).

lowers the surface tension at the chloroform-water interface it will be concentrated at that place. Then according to Bancroft,[1] Gibbs[2] points out that if we call the two liquids A and B, and the film C, we have to consider two surface tensions, the one at the contact A and C, and the one at the contact between B and C. If the surface tension at the water-emulsifying agent interface is less than that at the oil-emulsifying agent interface, the films will tend to curve so as to convex on the water side and we shall have a tendency to emulsify oil in water.[3] If the surface tension at the oil-emulsifying agent interface is lower than the surface tension at the water-emulsifying agent interface, the film will tend to curve so as to be convex on the oil side and we shall have a tendency to emulsify water in oil.

"The simplest general formulation—which we owe to Briggs[4]—is that we get oil-in-water if the emulsifying agent at the interface is chiefly in the water phase and water-in-oil if the emulsifying agent at the interface is chiefly in the oil phase. A couple of illustrations will make this clear. If we start with a water-soluble colloid which is strongly adsorbed at the interface, but is not peptized markedly by the oil, we should expect to emulsify oil in water. If we start with an oil-soluble colloid, which is adsorbed strongly at the interface but is not peptized markedly by the water, we should expect it to emulsify water in oil. As a matter of fact, an overwhleming majority of emulsions come in this class. Since most emulsifying agents will not peptize the second liquid by themselves, it is usually necessary to break up the liquid into fine drops by some form of mechanical agitation."

The observations of Calugareanu were not original; the phenomena had also puzzled Winkelblech[5] at an earlier date.

This type of emulsion is exceedingly improbable in the living tissue, because to produce the dineric interface a concentration of the narcotic sufficient to exceed its solubility in the plasma is necessary. It is known that the concentration of narcotics necessary to produce narcosis is less than enough to saturate the tissues. Even Winterstein himself objects to any theory that requires a high concentration of narcotic to bring about the reaction.[6]

According to Gwathmey[7] in Binz's experiments "fresh sections of the brain cortex of rabbits were placed in a one per cent morphine hydrochloride solution, or exposed to chloroform vapors. The effect of coagulation narcosis was produced, as is seen when protoplasmic poisons of neutral reaction are allowed to act upon large transparent infusoria. The protoplasm at first darkened, and the movements became sluggish; later on the protoplasm becomes granulated, and the movements cease. Recuperation may take place

[1] Bancroft, "Applied Colloid Chemistry," 352 (1926).
[2] Gibbs: "Scientific Papers," 258 (1906).
[3] J. Phys. Chem., 17, 515 (1914); 20, 407 (1916).
[4] Briggs: Unpublished work.
[5] Z. angew. Chem., 18, 1953 (1906).
[6] "Die Narkose," 256 (1919).
[7] "Anesthesia" (1914).

from the first stage, by washing away the poisons, but not from the last stage. The first stage is likened by Binz to the sleep of the cell; the last to death. The first trace of coagulation may redissolve but coagulation itself does not. "Also in regard to Claude Bernard's theory," in his opinion, the mechanism is always the same, in spite of the difference of the narcotic agent; for they all produce one identical modification in the ganglion cell. This modification of the ganglion cell consists in a "semi-coagulation" of the protoplasm of the nerve cell, this semi-coagulation being merely transitory, the protoplasm resuming its previous state after the removal of the narcotic agent from the cell. This view was derived from the rigidity of muscle fibers after exposure to chloroform vapors."

These older experiments were carried out with concentrations of reagents that were not excessive and they confirm the statement that in the stage of decrease of dispersion the phenomena is reversible, but becomes irreversible if coagulation has gone too far. As a matter of fact, Winterstein is wrong in considering that the decrease in dispersion is a phenomenon separate from coagulation. This decrease in dispersion is a preliminary stage of coagulation and is reversible as Binz and others have shown. Whereas if the narcotic is allowed to act in greater amounts or for a longer time a granular coagulation will set in and this is irreversible. This is in agreement with the fact that narcosis cannot be maintained for an indefinitely long time without serious consequences or that narcotics in high concentrations are toxic.

The coagulating action is "freely objected to" because colloidal protein sols are irreversibly coagulated by narcotics.[1] It is quite true that the coagulation of proteins or other bio-colloids often seems irreversible. However the coagulation by narcotics is a different matter because the coagulated proteins are, under certain conditions, reversibly peptized as can be shown.

In the experiments where the protein sols were sensitized by ether to electrolytes it was found that at the beginning of the decrease in dispersion the phenomenon was reversible. That is, if the ether is removed by blowing a stream of air through the solution, the turbidity is decreased. At a later stage when the albumin has been precipitated, the precipitate can be removed by filtration and partially repeptized in a solution of the same composition as the original except that the ether is absent. This peptization becomes increasingly difficult if the ether is allowed to act for longer lengths of time.

As a matter of fact, this type of experiment will also illustrate the invalidity of Winterstein's explanation of the reversible lowering of the dispersion. If the albumin sol is treated with sodium sulphate, as described above, and more of one of the higher alcohols (amyl or butyl) is added than is truly soluble a very voluminous precipitate will be produced. This is an emulsion of the type Calugareanu obtained, and upon shaking appears at once without the preliminary turbid stage. However, if an amount of alcohol is added so that it is in true solution, the formation of the precipitate is much slower and passes through the preliminary turbid stage. In this case an emulsion

[1] "Die Narkose," 257 (1919).

is impossible. The explanation of the precipitate produced by large amounts of alcohol depends upon the fact that the albumin is adsorbed at the water-alcohol interface and forms an emulsion upon shaking.

It is important for the colloid theory of narcosis to make certain that reversible coagulation does take place during narcosis. As noted above, the coagulation of protoplasm is frequently marked by no visible change. Consequently it is highly desirable to attempt to follow such changes by other methods. A method that would indicate such changes is known and has been applied in certain cases. The changes in viscosity of living protoplasm undergoing narcosis have been followed in the cell and afford highly interesting data. Weber[1] has made extensive studies on the viscosity of the protoplasm of Spirogyra by means of the sedimentation velocities of particles within the cell when placed in a centrifuge. Also, Heilbronn[2] made observations on the resistance offered by plant protoplasm to falling starch granules when sections of the tissue were rotated through an angle of 180°, the material being subjected to varying concentrations of ether. Heilbrunn,[3] in a manner similar to that of Weber, followed the viscosity changes of protoplasm during coagulation by heat.

The most trustworthy data agree that there are two distinct phases in change. At low concentrations of the narcotic, or a slight elevation of the temperature in the case of Heilbrunn's study, there is a decrease in the viscosity which passes through a minimum and then increases above normal. The viscosity changes, when properly interpreted, show the varying degree of coagulation. Since the narcosis is produced by the slight, easily reversible coagulation it is found that the narcosis occurs in the stage of decreasing viscosity, as one would expect.

Before going into greater detail on the relation of coagulation to narcosis let us examine some of the theories and state clearly their shortcomings. No theory, except the colloid theory, offers a mechanism of narcosis that is common to all cases and can be adapted to direct experimental proof. It is a recognized fact that narcotics in low concentrations behave as stimulants; other theories are not able to offer any good explanation of this, and in most cases it is ignored. Nevertheless it is a definite part of the problem and an adequate theory must make a working explanation. The problem of recovery, from the effects of the narcotic, has no satisfactory treatment at the hands of other theories. The toxic effect of narcotics, when in high concentrations, must also fit in the theory of narcosis and agree with modern concepts of toxic action. A very outstanding deficiency of other theories is their inability to account for the type of narcosis produced by physical means such as a blow, heat, cold, and electricity. This deficiency becomes more pronounced in explaining the local anesthesia produced by water. The cases of narcosis produced by hydrocyanic acid and magnesium sulphate are also difficult to reconcile on the basis of any of the other theories.

[1] Biochem. Z., 126, 21 (1921).
[2] Jahrb. wiss. Botan., 54, 335 (1914).
[3] Am. J. Physiol., 69, 190 (1924).

These are the outstanding phases of the problem of narcosis. Obviously, they are related to each other for the same narcotic can bring about several effects. An adequate theory must relate these parts coherently and explain them on a common basis. Henderson[1] has given a summary of our knowledge of anesthesia at the end of 1929 which may be of value for people who wish to get the literature references. It cannot be called an adequate critical presentation.

The most obvious thing about the living cell is the colloidal character of its constituents and the extreme sensitivity to changes of this colloidal state i.e., ionic antagonism, etc. Since the criticisms of the colloid theory have been found to be groundless it is desirable to re-examine the evidence and attempt to explain the above phenomena upon this basis.

This flocculation by small amounts of narcotics is stated as a fact and exists independent of any explanation whether it is right or wrong. However, it is beneficial to have some some sort of explanation as it makes us feel that we understand the problem better, because it enables us to draw a mental picture of the phenomena. The cause of the precipitation in the experiments using small amounts of alcohol and other narcotics in the presence of electrolytes has been studied by Freundlich and Rona.[2] The researches of Kruyt and van Duin[3] have shown that a very pronounced influence on the coagulation of a sol can be brought about by capillary-active materials such as: amyl alcohol, phenol, etc., although these substances in the same concentration when alone do not coagulate the sol. Such capillary-active materials behave as sensitizers, that is they make the sols flocculate much easier. The analysis of this phenomenon is taken up in the reverse order relative to its occurrence in the cell. This is due to the fact that the experiments in the laboratory were carried out by treating the electrolyte-free sols with the organic material and examining the effect produced; then adding the electrolyte and studying the flocculation. The explanation that is given by Freundlich and Rona is that the capillary-active material will be adsorbed on the micellae in proportion to their capillary activity as Traube's work showed. The solution of the organic material was treated with the colloid and filtered. Then, by determining the concentration of the capillary material in the filtrate, the authors were able to show that the colloid adsorbed the substance. The concentrations were determined with the stalagmometer. The capillary active materials used in these experiments were: phenyl thiourea, camphor, thymol, tributyrin, methyl urethane, ethyl urethane, propyl urethane, and amyl urethane. The adsorption of this material will lower the charge on the particles, for the dielectric constant is lowered considerably. The dielectric constant of organic material is low relative to that of water; for the materials in the above it ranged from 5 to 20 while that of water is 81. This point is clearer if we assume that the charge on the particle is made up

[1] Physiol. Rev., 10, 171 (1930).
[2] Biochem. Z., 81, 87 (1917).
[3] Kolloidchem. Beihefte, 5, 269 (1914).

of two layers of ions, each layer containing ions of the same sign. In effect the arrangement is similar to that of a small condenser, the charge being a function of the distance between the layers and the dielectric constant of the medium that separates them. That the charge on the particles was actually decreased was proved by measuring the cataphoretic migration velocity. Now, since the charge is lowered, it is much easier to flocculate the colloid by small amounts of electrolytes. So that a sol that was once stable in the presence of low concentrations of electrolytes now becomes so sensitive that it precipitates. In the living cell this mechanism is reversed. The electrolytes are already present and have the colloids in a critical state; the addition of the narcotic brings about the flocculation. Laboratory experiments show that either method of addition will result in the same change and the explanation is the same for both cases. This process is thought to be quite general in relation to the colloids of the living cell and its application to other systems in the body will be pointed out later.

As this phase of the coagulation is progressing, the colloidal systems of the cell or tissue have become so drastically altered that the material may no longer be considered normal. Most of the reactions of the cell probably take place on the surface of the colloids that are present. As the adsorption of the narcotic increases, much of the material will be displaced as in an exchange adsorption. Then as the charge on the colloids becomes less, the particles are not so able to retain polar compounds of the opposite charge. Then if the micellae begin to coalesce, the active surface is decreased. Finally, the stage is reached where the ions can neutralize the charge on the colloids effectively. The adsorption of compounds in the cell will now be very low and consequently the chemical changes of the living cell will be at a very low ebb. This mechanism applies not only to the proteins that constitute the protoplasm but to other bio-colloids such as enzymes, etc.

Indeed Verworn[1] has shown that narcosis is equivalent to the asphyxiation of the tissues. Independent confirmation of such work is so extensive that it is impossible to consider more than a few examples here. Much of the older literature is reviewed by Warburg and Wiesel[2] and Battelli and Stern.[3] Warburg and his co-workers[4] have made extensive studies on the oxygen consumption during narcosis and finds that the variation runs parallel to narcosis. Furthermore, this property of the narcotic did not depend so much on the chemical constitution but rather on the physical properties as one would predict from the work of Meyer and Overton, and Traube. The concentrations of a few of the narcotics required to reduce the oxidation velocity in Vibrio Metschnikoff 30-70% below normal is given in Table VII.

If the organisms were washed, or the narcotic otherwise removed, the oxidation velocity increased to normal, showing that the effect is quite reversible. Warburg has extended this work to other tissues.[4] He has

[1] "Narkose" (1912).
[2] Arch. ges. Physiol. (Pflüger's), 144, 465 (1912).
[3] Biochem. Z., 52, 226, 253 (1913).
[4] Z. physiol. Chem., 66, 305; 69, 452 (1910); 70, 413; 71, 479(1911).

TABLE VII

Substance	Concentration	Substance	Concentration
Methyl urethane	670 Millimols	Phenyl urethane	33 Millimols
Ethyl urethane	400 " "	Diethyl urea	170 " "
Propyl urethane	97 " "	Phenyl urea	18 " "
Butyl urethane	43 " "		

shown that in the case of yeast the same order of concentration of narcotics that were physiologically active in the living cell would also flocculate the colloids of yeast "in vitro." O. Meyerhof[1] showed that the mechanism involved in this coagulation was that outlined by Freundlich and Rona.[2] The yeast colloids were freed from electrolytes by ultrafiltration. When such colloids were treated with narcotics, there was no coagulation. If some of the filtrate was added to the system the material immediately flocculated. Then to show that it was only the electrolytes that caused this he evaporated the filtrate and burnt the residue to an ash. The ash when dissolved and added caused the same effect. In fact other electrolytes would bring about this flocculation also. It will be noticed that here again the mechanism is tested in the reverse order to which it occurs in the cells. In reality the electrolytes have the colloids in the critical state and the narcotic is responsible for the flocculation that is produced.

Battelli and Stern[3] in a very comprehensive extension of the work showed that narcotics inhibit oxidation in the liver and muscles. They isolated the nucleo-protein of the liver and showed that this inhibition ran parallel to the flocculation of the nucleo-protein "in vitro." Winterstein[4] and others showed that this depression of activity in the cells is an effect of narcosis and not the cause.

It is known, however, that there are exceptions to this general reaction. In some cases oxidation is increased and in others it is lowered and in still others narcosis has no pronounced effect on the oxygen metabolism. The reasons for these exceptions become apparent when we consider the nature of the oxygen metabolism.

It is well known that the energy required for the various purposes of the organism is obtained, except in special cases, entirely from oxidation. The high consumption of oxygen by muscle cells doing external work is clear, as also where glands are doing osmotic work. In discussions of this nature it must be kept in mind that the oxidation of one substance is always accompanied by the reduction of another. If an arbitrary zero oxidation potential is not defined, then there is confusion in the interpretation of the results. Assume that the zero is that of the atmospheric oxygen. In compounds whose oxygen potential is higher than that of atmospheric oxygen the region will be

[1] Biochem. Z., 86, 325 (1918).
[2] Biochem. Z., 81, 87 (1917).
[3] Biochem. Z., 52, 226, 253 (1913).
[4] "Die Narkose" (1919).

a place of reduction. But with compounds whose potential is less than that of atmospheric oxygen the same region will behave as a place of oxidation.

Another phase of oxygen metabolism, in certain cases, is to oxidize toxic compounds to other substances that may be readily eliminated. There are many other ways of doing both of these things without oxygen. Now consider the case of a resting cell where the bulk of the oxygen consumption is utilized for the destruction of easily oxidized toxic compounds. Alcohol is a good example. If a small amount more of the substance is added to such a cell there is no reason why the oxygen metabolism should not increase. If the addition of the narcotic is faster then the cell can remove it by oxidation, or otherwise, then narcosis will be brought about and the oxygen consumption lowered. This is the general case. Lauren[1] noticed it in the germs of different plants, Elfving[2] in pea seeds, Markovine[3] in bean leaves, Kosinski[4] in Aspergillus niger, and Zaleski[5] in gladiolus bulbs that an increase in carbon dioxide production occurred when the plant tissues exposed to low concentrations of narcotics and a decrease in higher concentrations. Gerber,[6] Irving[7] and Johannsen[8] were drawn to the same conclusions.

Tashiro and Adams,[9] in their study on the nerves of the crab, *Libinia Caniculata*, found that weak concentration of chloral hydrate and ethyl urethane increased the carbon dioxide output; but, during narcosis by these narcotics, the production was greatly decreased. Baer and Meyerstein[10] studied this effect in the liver and Lussana and Roli[11] examined the effect in other tissues.

If oxygen is not used in some stage of the detoxication process then the narcotic will progressively decrease the oxygen consumption during the time the cell is undergoing narcosis. In this case it means that the cell is detoxicating the compound by some other means such as conjugation with substances in the cell as glycine, cystein, glutamine, ornithine, or glycuronic acid; sulphonation, methylation, hydrolysis, deaminization, etc. In many cases more than one of these methods is used on the same compound in successive steps such as hydrolysis followed by oxidation, etc. Another possibility is that the narcotic is diffusing into the blood stream and is being removed by some other organ such as the liver. Detoxication by means other than oxidation is of necessity employed by anerobic forms of life. It is well known that all compounds are not eliminated in the same way; one mechanism may be employed for a certain compound, while an entirely different method may be used on another substance in the same cell. The

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[1] Reference in Bot. Jahrb., 20, 92 (1892).
[2] Ofversigt of Finska Vetensk. Societet, Forhandl., 28, 36 (1885-86).
[3] Rev. gén. botan., 13, (1901).
[4] Jahr. wiss. Botan., 37, 137 (1902).
[5] Botan. Centr., 95, 251(1904).
[6] Compt. rend. soc. biol., 54, 1497 (1902).
[7] Ann. Botany, 25, (2) 1077 (1911).
[8] Naturwiss. Wochenschr., 18, 97, 109 (1902).
[9] Intern. Z. physik. Chem. Biol., 1, 405 (1914).
[10] Arch. exp. Path. Pharmakol., 63, 441 (1909).
[11] Boll. Sci. Bologna (8), 9 (1909).

experiment of Winterstein[1] in which ethyl alcohol increased the oxygen consumption and ethyl urethane brought about a decrease illustrates the point.

Another phase must be considered, the enzyme systems may not be incorporated on the colloids of the protoplasm. If they exist as separate systems in the cell, then we have no assurance that a concentration of narcotic sufficient to flocculate the protoplasmic colloids will also flocculate the enzyme colloids to the same degree. The enzyme systems may be more or less sensitive to the narcotic than the other systems so that in such cells the decrease in oxygen consumption will not be necessarily parallel to the extent of narcosis.

All of the above data can be explained just as well from this point of view. As a matter of fact, it is believed that this is the more general of the two cases for it also explains the increased activities of other systems. It is a recognized fact among careful workers that many systems, other than the oxidizing one referred to above, show exactly the same phenomenon. This, in effect, amounts to the stimulating action of narcotics, when they are in low concentrations. For the purpose of discussion it is desirable to divide the stimulating effect into two divisions, one deals with the stimulation of growth, chemical reactions, etc., and the other with the increased irritability of protoplasm.

There is a great mass of data on the first division of the subject, but unfortunately no one has offered an adequate explanation. Nevertheless, the facts in the case are so numerous that they have been stated as a law, sometimes referred to as the Arndt-Schulz law.

The explanation offered above for the increased oxygen metabolism is believed not to be very general. This is due to the fact that it does not explain a case where the oxygen consumption is greater than enough to oxidize the toxic compound. If such data can be produced in future research to show this point it will settle the question. Up to the present time no such data have been found, so it was desirable to include this point in the discussion. At any rate such a mechanism would unquestionably play a minor rôle in a few cases.

As examples of this stimulating action on growth, chemical reactions, etc., Fokker[2] found that chloroform in low concentrations would stimulate the growth and activities of bacteria. Kochmann[3] mentions that ether in low concentrations stimulates the enzymatic processes of yeast. O. Nasse[4] found that curare stimulated many enzymes. If the normal action be given the arbitrary value of 100 then for invertase 100:249, ptyalin 100:124, and for pancreas ferment 100:119. The same author found that strychnine would inhibit the hydrolysis of proteins by pepsin but stimulated ptyalin 100:109. This effect of stimulation is completely abolished if the narcotic is allowed to act in higher concentrations; but, as the concentration is increased, the enzymes, as a general rule, are not affected as rapidly as the other substrates.

[1] Biochem. Z., 61, 81 (1914).
[2] Ned. Tijdschr. v. Geneesk., 1, 168 (1891).
[3] "Handbuch exp. Pharm.," 1, 221.
[4] Arch. ges. Physiol. (Pflüger's), 11, 138 (1879).

It is this fact that allows us to add toluene, chloroform, etc., to enzymatic digestion experiments to prevent the growth of micro-organisms while not materially affecting the activities of the enzyme.

Now consider the theoretical case of a cell the enzymes of which behave in this manner, that is they are slightly less sensitive than the other colloids. The speed of the chemical reactions will be dependent upon the concentration of the reaction substances for the enzyme is only a catalyst. The amount of enzyme present will also govern the speed of the reaction; but, since the amount is constant, this effect may be neglected. The materials that are undergoing the reaction are adsorbed upon the many different colloidal substrates and are in equilibrium with a small amount of the substance that is in true solution. This amount in solution is the "effective concentration" as far as the speed of the reaction is concerned. Now as the narcotic is added to such a system, and the enzymes are less affected than the other bio-colloids, the narcotic will be first adsorbed upon these colloids in preference to the enzymes and will displace some of the reacting material from the surface of these inactive substrates. This amounts to an increase in their effective concentrations; hence the speed of the reaction will be greater. As more narcotic is added, the surfaces that were first affected become saturated and eventually narcotic reaches the concentration where it is adsorbed upon the enzyme, thus inhibiting its reactivity. As a general case this concentration is about the concentration at which the sensitive colloids have flocculated and the cell is already in a state of narcosis.

In this argument the concentration of the enzyme was taken to be constant. Assume a theoretical case in which the concentration of the narcotic that is stimulating is held constant and the amount of enzyme varied. We should predict from the above hypothesis that as the amount of enzyme was decreased the amount of adsorption per unit weight of enzyme would be greater, thus the inhibition of its activity would be greater. If the concentration of enzyme was increased, then the adsorption per unit weight of enzyme would be less and consequently the inhibition less. This case has been studied by Kaufmann.[1] He found in a digestion experiment with trypsin that a given concentration of chloroform had no effect, or was not harmful, when the concentration of chloroform had no effect, or was not harmful, when the concentration was 0.2% trypsin (Grübler). If only 0.1% was present the digestion was somewhat slowed; at a concentration of 0.08% enzyme the reaction was partially inhibited and at 0.02% completely inhibited.

R. Boehm[2] has also observed a very interesting phenomenon. Nasse[3] found that curare stimulated invertase in the ratio of 100:249. R. Boehm discovered that if the invertase was highly purified, that is if the bulk of the excess colloids were removed, the effect of the curare was practically nil. This is in line with the hypothesis and is what we would predict.

[1] Z. physiol. Chem., 39, 444 (1903).
[2] Boehm: Unpublished work.
[3] Arch. ges. Physiol. (Pflüger's), 11, 138 (1879).

This suggestion of the possible mechanism is not stated as a strict law nor is further proof offered for its validity. It does explain the facts, it is simple, and since no one has offered a rational explanation of the phenomenon, it serves as a useful working hypothesis. The difficulty of the situation is that at the present time there are not enough of the necessary data at hand to unravel the problem completely and give a rigid proof.

The second division of the phenomena of stimulation, that is the increase in irritability, has been known for some time. Since it does not fit in with the scheme of other theories, it is often neglected and regarded as something that is "vital" and not to be explained in the usual manner. Nevertheless, protoplasm in the general case can be stimulated by narcotics, that is the movements of the organism are increased, certain nerves may be made more sensitive to stimuli, different organs and glands show a greater than normal amount of activity, etc.

As an instance of this, Nagai[1] found that the movements of amoeba were increased; also the ciliated epithelial cells of both higher and lower animals are found to be more active in the presence of a small amount of ether.[2] Balser[3] found that dilute alcohol favored the growth of certain bacteria. There are a great number of examples of this increase in irritability. Schurmayer[4] found that the movements of infusoria were easily made violent by dilute cocaine solutions and Alms[5] noticed the analogous increase in irritability of nerve endings when treated with cocaine solutions. Joachimoglu[6] discusses many other cases.

The explanation of this is that, when the protoplasm is completely coagulated or peptized, the organism is in a low state of activity; it is only when the protoplasm is on the border line of flocculation and peptization that the phenomena of irritability become pronounced. In the flocculation of the biocolloids by the narcotic the approach to this border line can be made very gradual. So that at the critical state the phenomena of irritability can be made more pronounced, because one is able to approach nearer to the critical state. Since this is also the approximate concentration at which the enzymes are stimulated the phenomena are quite marked in some cases.

The question then arises as to the status of a stimulant. Can stimulants in higher concentrations behave as narcotics? There is some evidence that this is the case. If stimulants affect the nervous substrates, then there is no reason why they should not behave as narcotics in higher concentrations. Whereas, if they affect some less obvious substrate, in higher concentrations, they will narcotize only this system; so in some circumstances it will not appear to be acting as a general narcotic, because by narcosis one generally thinks of the narcosis of the nervous system.

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[1] Z. allgem. Physiol., 6, 195 (1907).
[2] Engelmann-Hermann: "Handbuch der Physiologie," 1, (1879); Lillie: Am. J. Physiol., 24, 14 (1909); 29, 372 (1912); Nerlich: Inaug.-Diss., Halle (1920).
[3] Inaug-Diss., Giessen (1914).
[4] Jena. Z. Naturw., 24, 438 (1890).
[5] Arch. Anat. Physiol. Abt., 1888, 416.
[6] Biochem. Z., 156, 224 (1925).

Caffein is classed as a stimulant and is not usually considered as a narcotic but when applied directly in higher concentrations to nerves it behaves exactly like a narcotic.[1]

Also strychnine, which will be discussed in detail later, has been found to be a very potent narcotic despite its classification as a stimulant. Strychnine frequently interferes with the oxygen metabolism and the toxic effect appears before the narcosis, so this result is not well known. Nevertheless, when proper provisions are made to correct for this it leads to a very pronounced narcosis. Theoretically, it might be possible to find compounds that would be so weakly adsorbed that in higher concentrations they were not quite able to flocculate the colloids and thus be a pure stimulant but such compounds have not yet been found.

The converse of the above question, whether all narcotics will behave as stimulants can also be answered. They should all show this phenomenon, although the stage of excitability may be passed over so rapidly that it will not be pronounced and consequently be overlooked.

Indeed this must be a very perplexing state of affairs to that large group of research workers who attempt to relate physiological action to chemical constitution. The chemical constitution of drugs is independent of concentrations, so this change in physiological action can only be interpreted from the point of view of the physical or colloidal state. The constitution of a compound will determine its physical properties such as solubility, etc., and indicate certain substrates in the body upon which it will be adsorbed but it does not indicate the mechanism by which it becomes effective. This effect of concentration is not confined to that group of compounds classed as narcotics or stimulants. Saccharine, for example, is very sweet only when dilute, higher concentrations seem to paralyze the sense of taste for it. Then again the well-known effect of dilution on perfumes. A perfume may have a very pleasant odor when dilute but in higher concentrations the odor is drastically altered and often weaker. The blending of perfumes is as much a problem of concentrations as the actual combination of several essences.

The experiments of Binz, Claude Bernard, and others have offered good evidence that reversible coagulation actually does take place within the living cell. However, one would like to make the experiments more convincing, first proving that coagulation does occur in the normal cell and secondly, that this coagulation is reversible. The most convincing manner in which this could be proved would be to examine the colloids of a cell under the ultramicroscope and observe what takes place. Then, in order that the cell be perfectly normal we can take some unicellular organism in its normal environment. This has the added advantage of being not only simple but that we are able to examine all the organism at the same time, thus seeing a complete picture of the mechanism of narcosis.

Also, if the narcotic is removed we shall be able to see whether the coagulated material is peptized or not. This important point then will not depend

[1] "Handbuch exp. Pharm.," 2, 527.

upon indirect evidence. Such an experiment would be independent of theories and hypotheses and it would show directly whether coagulation occurred and whether it was reversible.

This interesting experiment was carried out, using ordinary baker's yeast as the living cells. Young, vigorous cultures were prepared by inoculating yeast into Laurent's medium made up with 1.5% dextrose. Subcultures were made every twenty four hours, the third subculture being used in the experiments. A portion of the culture was then placed under the ultra-

FIG. 1
Normal yeast cells

FIG. 2
Narcotized yeast cells

microscope and the normal state of the colloids observed. The colloidal material is easily visible and the Brownian movement is pronounced. In some cells small vacuoles can be seen. Sometimes one is able to see a few dead cells, these are easy to identify for all the material within then is completely coagulated. A photograph was then taken to make a permanent record and is reproduced in Fig. 1.

The culture was then treated with the narcotizing concentration of amyl alcohol, about 2% and again placed under the ultramicroscope. At first nothing happens, after about ten minutes the Brownian movement is noticed to be decreased and a few minutes later small aggregates of colloids are seen. The coagulation now goes much faster and in a few minutes a light but very pronounced flocculation occurs. The complete change usually requires about twenty-five minutes, although, the time naturally depends upon the concentration of the narcotic, the temperature, and the individual culture. This same experiment was then tried with such other narcotics as chloroform, paraldehyde, ether, and chloral hydrate. The result in all cases was the same —coagulation. Thus the first postulate of the theory is shown to be an actual fact. A photograph of this change was then made and is reproduced in Fig. 2.

The narcotized culture was then placed in a centrifuge and the cells thrown down. The supernatant liquid was poured off and fresh sterile medium added. The cells were washed in this way twice and again examined under the ultramicroscope. The material in the cells is still coagulated but in a few minutes a very slight Brownian movement within the cells can be seen. The aggregates break up into smaller particles and the motion becomes more pronounced.

At the end of twenty-five or thirty minutes the material is completely peptized and the cell is normal in every respect. The yeast will ferment the media and reproduce just like the normal cells. Thus it is shown that the second postulate is a fact. However, this recovery does not always follow. If the narcotic has acted in high concentrations or for a too great a length of time the material cannot be peptized again. This merely shows the toxic effect of an excess of the narcotic.

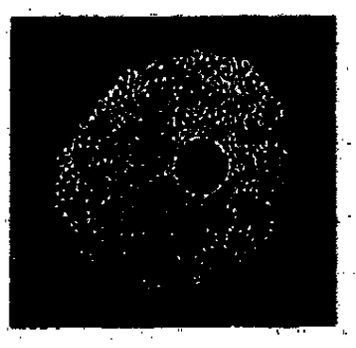

Fig. 3
Spinal ganglion cell of dog, not narcotized (Marinesco).

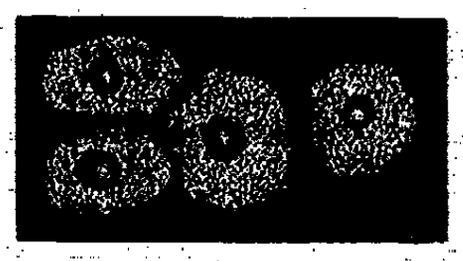

Fig. 4
Spinal ganglion cell of dog, narcotized (Marinesco).

It was desired to try an electrolyte of higher valence and it was found that cerium chloride in a dilution of 1-3000 was not injurious to yeast cells.[1] The experiment was carried out exactly as described above and it was observed that the flocculation occurs much faster but is otherwise the same. When such cells are washed with media free from cerium chloride and narcotizing agent the peptization is also much faster being almost complete in ten or fifteen minutes.

The researches by Professor F. Marinesco[2] on the colloidal structure of living nerve cells has dispelled such erroneous conceptions as neurofibrils and Nissl bodies; that can be seen only in fixed and properly stained preparations. His experiments involved the direct observation of the colloids of the nerve cells under the ultramicroscope. These careful experiments also give positive evidence that this same sort of coagulation occurs in the living nerve cell. Fig. 3 is a reproduction of one of his photographs of the colloids in a spinal ganglion cell of a young dog. This may be considered as the normal appearance it would present if it could be observed in the body. The only aliphatic narcotic that he studied was ethyl alcohol. Fig. 4 is a reproduction of a photograph of the nerve cells after treatment with dilute alcohol.

The coagulation is seen to occur not throughout the whole cell but only in a small portion of the nucleus. The extranuclear material is unchanged, showing the specificity of the adsorption of alcohol upon the different substrates of the same cell. Marinesco made no experiments to determine the reversibility of the coagulation; but, since we know that reversibility is possible, this point is not now important.

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[1] Arch. exp. Path. Pharmakol., 100, 226 (1924).

[2] Kolloid-Z., 11, 207 (1912); IIIe Congrès internationale de Neurologie et de Psychiatrie, Gand, 20-26 (1913).

As pointed out in the first postulate, this reversibility exists as an independent fact, and whether our speculations as to the cause are right or wrong it will not change the status of the theory. The recovery depends upon the peptization of the flocculated material in the cell. Peptization may be regarded as the reverse of coagulation and can usually be accomplished in the laboratory by one of three ways. In some cases it can be effected by adding an ion that is adsorbed and thus raising the potential difference between the particle and the solution. In other cases the removal of the coagulating ion by washing is sufficient; an example of this is the peptization of arsenious sulfide by washing. Another method depends upon the adsorption of a different colloid. The peptization in the cell is in all probability brought about by the removal of the narcotic and peptization by the electrolytes.

The removal of the narcotic can be accomplished in two ways; by diffusing into the surrounding blood or lymph and being later destroyed in some other part of the body, and removal by chemical destruction within the cell. Both of these factors contribute to the elimination. It is recalled, that in attempting to remove an adsorbed substance from a substrate by washing it is extremely difficult to remove the last traces. Within the cell this elimination is facilitated by the fact that chemical reactions are occurring on the surface of the colloids and consequently the removal is much faster than if it were being accomplished by physical means alone.

Since the peptization of the agglomerates depends upon the adsorption of the ions within the cell another factor is introduced. The coagulation may be of two types. If the particles have just had their charge lowered to the point of instability they flocculate without much change in surface. On the other hand, if the narcotic is concentrated enough so that after flocculation the lowering of the surface tension will permit the aggregates to coalesce, then the active surface is much less. The material is in larger aggregates and appears granular. Since this is responsible for the slow peptization it is also responsible for the toxic action. It is easy to distinguish between the two types of coagulation when the material is examined under the ultramicroscope. Figs. 5 and 6 are reproductions of two photographs of Marinesco showing the toxic effect of zinc sulphate and of hydrochloric acid on the nerve cell. Compare these with Fig. 4.

Winterstein and others are quite right in insisting that coagulation is responsible for the toxic action; they are wrong in assuming that all coagulations are irreversible.

In this connection it is interesting to note that disinfectants such as mercuric chloride produce this type of coagulation. If the disinfectant is in low concentrations then it behaves similar to the narcotics. First it stimulates the growth and activities of the organism upon which it is acting, then in slightly higher concentrations it inhibits their growth but does not kill them. Under certain conditions mercuric chloride will produce a reversible coagulation[1] and thus behaves as a narcotic.

[1] Arch. Hyg., 89, No. 8, (1920); 93, 252 (1923); Münch. med. Wochenschr., 67, 1166 (1920).

However the manner of elimination, the film of narcotic is replaced by water and the peptizing agents originally displaced by the narcotic. Provided that the coagulation is not extensive and granular, on complete removal of the narcotic the cell again returns to normal. Since there are several independent colloidal systems within the cell with specific functions, these may not recover at the same rate. However, if these systems recover at the same relative rate and in the same order in which they were narcotized *the cell should pass back over in the reverse order the phenomena it exhibited when undergoing narcosis.* It is recalled that narcosis is preceded by a stage of excitability; on recovery the normal state should be preceded by this stage of increased irritability.

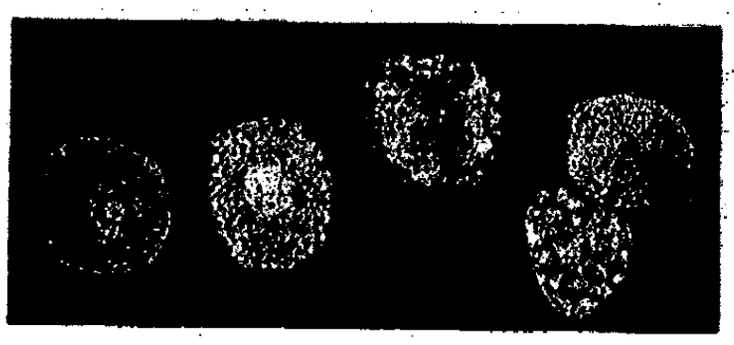

FIG. 5
Coagulation by zinc sulphate (Marinesco).

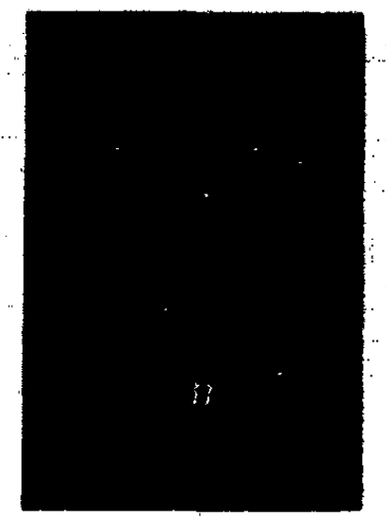

FIG. 6
Coagulation by hydrochloric acid (Marinesco)

This is usually described as the "after effect" of the narcotic; that is, the subject is more reactive to smaller stimuli than usual. Gwathmey's "Anesthesia" gives an excellent description of the after effect of ether narcosis: "It has been stated that if ether is administered according to modern methods, with the utilization of preliminary and accompanying factors, the subject emerges, as a rule, from the anesthetic state as if from normal sleep, feeling no ill effects so far as the anesthetic is concerned. Under circumstances, however, even with the most careful technique, the recovery period may be marked by retching, nausea, and vomiting. . . . Transient mental disturbances, amounting in some cases to mania and dementia, have been reported. Muscular excitement may be noted for a brief period, and in rare instances coreiform movements have been known to last for two or three weeks." Hiccoughs, vomiting, retching, chorcoid movements, general uneasiness, etc., are symptoms of this increased irritability. Often these are not very pronounced and are overlooked. If they are marked, the tendency seems to be to describe the patient as "abnormal" or "neurotic and hysterical."

To obtain a more exact view of this prediction a case should be taken where "hysterical symptoms" are excluded and use a drug that is both a powerful stimulant and a potent narcotic. Strychnine shows both of these properties and one could not interpret the tetanic spasms produced in frogs as being due to hysteria or abnormality. One would predict in this case that, if the recovery of the colloidal systems is in the same order, the animal will go back

through the tetanic stage after narcosis before returning to normal. This very thing has been known for a long time; but its explanation and relation to narcosis has not been clear. It has been noted that small doses of strychnine will produce violent tetanic spasms in human beings, and larger doses will produce death. In frogs the same thing occurs except that the death is only apparent when the concentrations are not too great. First after the injection the tetanic spasms occur, the time of appearance depending upon the animal used, then these slowly decrease in intensity and finally the animal loses all response to stimulation and is in a deep narcosis. The narcosis is very pronounced and may last for several days, nearly the only sign of life being a very weak heart action. If the frog is placed in fresh water frequently, to aid the elimination, the animal recovers and goes back through the violent tetanic spasms again. This may be for a much longer time than the original spasms, for the elimination is not rapid. Vulpian[1] noted that this second period of tetanus often extended over a period of time up to thirty days.

E. Poulsson[2] describes the phenomena in relation to Esculenta. The first day of the experiment 5 mgs. of strychnine nitrate were injected subcutaneously; the animal was paralyzed ten minutes later. From the second to the sixth day complete paralysis. On the seventh day there appeared weak breathing movements and barely noticeable fibrillar contractions. During the eighth and ninth days the attacks of convulsions became more frequent. From the tenth through the sixteenth day the animal was in complete tetanus. The animal died on the seventeenth day in convulsions. This is an exaggerated picture of narcosis and the recovery, but, nevertheless, the simplicity of the experiment and the overemphasis of the phenomena illustrate the point in question.

The next question one is interested in is: if strychnine is such a good narcotic why does death occur in human beings before narcosis is produced? It is known that in cases of death due to strychnine poisoning the person is conscious up to the time of death. Pharmacologists have already investigated this problem and found that death is due to other causes than the direct toxicity of the strychnine. For instance, strychnine brings about profound disturbances in the transmission of oxygen by the blood. Harley[3] analyzed samples of blood treated with strychnine and found in one case, with calf's blood, that the ability to yield up oxygen was greatly decreased. The hypothesis at that time was that the poisoning was due to asphyxiation. Richter[4] and W. Lerab[5] showed that artificial respiration with oxygen would decrease the toxic effects tremendously. Although this fact is well known there are many other interpretations. Rosenthal,[6] Brown-Sequard,[7] Filehne,[8] Ananoff,[9]

[1] "Leçons sur l'action physiol. des substances toxiques," (1882).
[2] "Handbuch exp. Pharm.," 2 (1), 341.
[3] Lancet, 1, 619, 647 (1855).
[4] Z. rat. Med., 76 (1863); Göttinger. Anz., 1862, 165.
[5] Arch. Anat. Physiol., 29 (1867).
[6] Compt. rend., 64, 1142 (1867).
[7] Arch. Physiol., 4, 204 (1870).
[8] Arch. Anat. Physiol., 1873, 361.
[9] Centr. med. Wiss., 1874, 417.

Gies and Meltzer,[1] have all made important contributions to the explanation of this effect. This phase is more of a physiological than a colloidal problem so no attempt will be made to cover it here.

It was mentioned above in connection with the work of Alms,[2] that cocaine increased the irritability of nerve endings. This effect is also pronounced in the recovery. In fact it is so marked that cocaine is not used on areas which are to be cauterized for as the effects of the cocaine wear off the pain becomes greater than normal.

This effect will be noticed with most narcotics though the stage may be passed over so rapidly that little or no inconvenience will be experienced. On the other hand if the drug is eliminated slowly, as in the case of strychnine, the effect is very marked. Thus, there are two ways to keep this effect at a minimum; avoid an overdose so that there will be less to eliminate and secondly hasten the elimination.

We can see that this increased irritability is not desirable as far as the medical practice is concerned. There is one interesting way in which recovery from this phase can be made very rapid. As mentioned above the adsorption of narcotics is specific; but the common inhalation narcotics, in general, are extensively adsorbed by all tissues. Now if a large field of such tissue could be removed from the circulation and thus could not adsorb the narcotic the recovery could be made very rapid. For in the first place less anesthetic would be required. Then when the tissue is thrown back into circulation again it would literally "blot up" the narcotic until the concentration was at a lower level than the excitatory concentration.

Corning[3] did this experiment by cording the thighs of an individual, so as to interrupt both the arterial and venous circulation. The tissue below this area was then entirely free from the narcotic. He cites an example of a case in which it required six-seven minutes to anesthetize a patient but by cording the thigh and cutting off "one third of the man" the patient was anesthetized in three minutes. After the operation the ligatures were removed and the patient recovered from the effect of the anesthetic instantly.

This rapid recovery depends upon the general adsorption of the narcotic and will not be noticeable in cases where the narcotic is specifically adsorbed by small amounts of tissues, for example the nerves, for the extra tissue used as an adsorbent is not great enough to make a decided difference in the concentration when thrown back in circulation.

This can be at the most only a superficial survey of the mechanism of narcosis but since we are interested in the theory as much as in the mechanism perhaps it would be well to look for confirmation of the theory on other grounds. It may have already been noticed that in this theory there is no mention of the manner in which the coagulation is brought about. That is,

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[1] Am. J. Physiol., 9, 1 (1903); Berl. klin. Wochenschr., 1776 (1910).
[2] Arch. Anat. Physiol., 1888, 416.
[3] N. Y. Med. J., Oct. 1887, 22.

if this change could be brought about by physical means the result should be the same. There is evidence that this is the case.

Theoretically there is another manner in which agglomeration is possible. Consider a case in which the stabilizing ions are not strongly adsorbed. If such a system is treated with water the concentration of the ions will be decreased and their adsorption lowered. If this is extended the charge on the colloids can be cut down to a value such that the particles are no longer stable and flocculate. Anyone who has purified sols by dialysis is familiar with the

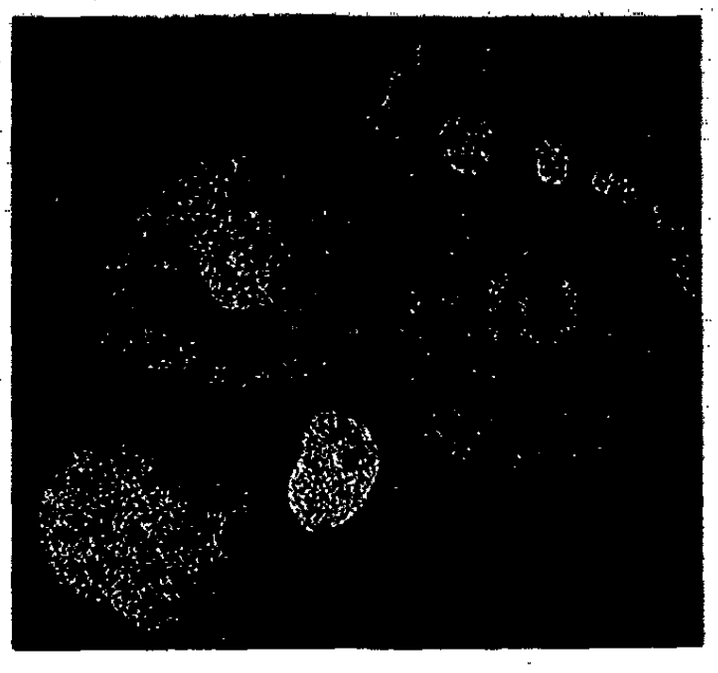

FIG. 7
Action of water on the nerve cell (Marinesco).

fact. So here is a case where water can act as a narcotic and any explanation based upon distribution coefficients, membrane permeability, or loss of water is doubtful. Such states as this may not be well known but they are not uncommon. Wyeth[1] has studied the use of water as a local anesthetic. At one time water was used in dentistry and certain minor surgical cases. Heilbrunn[2] found that in the case of sea-urchin eggs the protoplasm could be coagulated by distilled water, or diluted sea water, and that this effect was reversible if not carried too far. This method of local anesthesia has not found favor due to the fact that the injections of large amounts of water causes mechanical damage to the tissues and is painful. This type of local anesthesia has been called "anesthesia dolorosa" by Liebreich.

Fortunately, Marinesco has investigated the effects of water upon the nerve cell and the data support the theory that coagulation is produced. Fig. 7 is a reproduction of his photograph showing this effect. No other theory of narcosis is able to account for this peculiar effect of water.

Heat is a physical phenomenon and has a very marked effect on protoplasm. The first effect of heat is to induce narcosis, that is the organism loses

[1] N. Y. Med. J., Jan. 6 (1906).
[2] Biol. Bull., 39, 307 (1920); Exp. Zool., 30, 211 (1920).

all response to stimulation. If the organism is removed to a lower temperature it recovers. Continued exposure or a higher elevation of the temperature will result in death. Heilbrunn[1] has shown that in the initial stages of heat treatment of the eggs of the sea-urchin and the clam *Cumingia* there is a reversible coagulation of the protoplasm. This is exactly what the theory would predict. This coagulation is not reversible if the eggs are kept at the coagulation temperature, 32°-33°, for too great a time. Furthermore, this

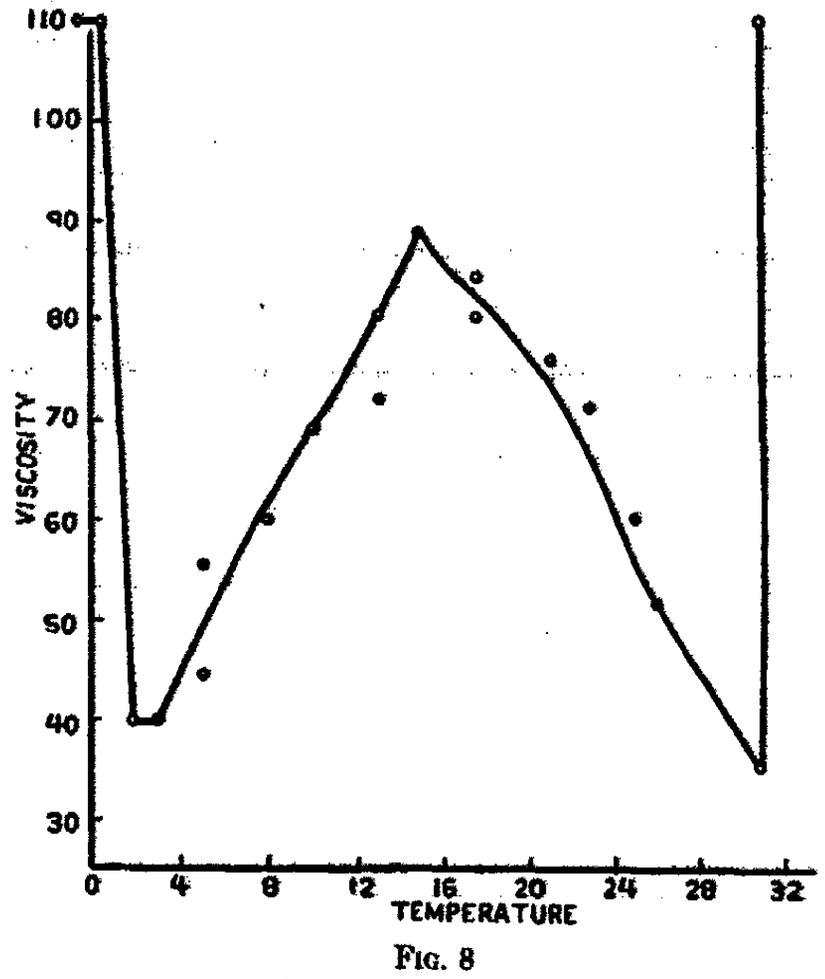

FIG. 8

Heat coagulation of protoplasm (Heilbrunn).

coagulation procedes the death of the cells. There are other workers that have noticed the reversible coagulation of protoplasm by heat. Sachs[2] studied the phenomenon in relation to plants and Gotschlich[3] in the case of heat rigor in frog muscle. Heilbrunn finds that the effect of ether is similar to that produced by heat, in fact the effects are *additive*. If the eggs are first treated with ether they become more sensitive to heat; the reverse was not tried. Heat prostration in human beings may also be related to this type of phenomenon.

The effect of cold upon sensibility is probably more familiar. At the present time the production of local anesthesia by freezing with ethyl chloride is quite common. This is quire an old practice; an Italian surgeon, Severino and his pupil, Thomas Bartholinus, called attention to this effect of cold in the sixteenth century. Napoleon's surgeon, Larrey, in 1807 again called

[1] Am. J. Physiol., 69, 190 (1924).
[2] Flora, 22, 5 (1864).
[3] Arch. ges. Physiol. (Pflüger's), 54, 109 (1893).

attention to the fact that amputations carried out on the battle fields at very low temperatures (1°-19°) were not painful. At the present time there is no direct evidence that coagulation does take place as one would predict on the basis of the colloidal theory; provided this phenomenon is a true narcosis. However, the extensive researches of Heilbrunn on the viscosity of protoplasm[1] give every indication that coagulation does occur. It is known that heat coagulates protoplasm and the viscosity changes during this coagulation are exactly like those produced by cooling. Fig. 8, which is the same as that on p. 109 by Heilbrunn, illustrates this point.

Heilbrunn is quite definite on this point[2]: "It was shown previously that in the *Cumingia* egg a marked increase in viscosity occurred at one degree above freezing. It is quite possible that such a coagulative effect would be an important factor in causing the death of cells at temperatures just above the freezing point of water. Mammalian muscle contracts on cooling to 5°.[3] There is thus a cold rigor as well as a heat rigor of muscle. In the *Cumingia* egg, the coagulation due to cold is reversible, just as is the heat coagulation. But it is not at all improbable that after a lengthy exposure to 1°C., the protoplasm may be permanently injured. Concerning the reasons for the sudden increase in viscosity at temperatures just above the freezing point, we have at present no real information. A few scattered observations show that in this case too there may be a change in the physical properties of the lipoids of the cell. In the *Cumingia* eggs centrifuged at 1°C., the lipoids present a very characteristic appearance, quite different from that found in similar cells at normal temperatures.

"Most animals and plants are killed by cold only when their temperatures drops below the freezing point of water. Owing to various economic phases of the subject, there have been many more studies of the cold death of plants than of animals. In temperate or cold climates, the death of plants as a result of exposure to cold is an important agricultural problem.

"The older literature on the effect of freezing temperatures on plants has been well summarized by Pfeffer.[4] For later summaries see Chandler,[5] Rosa,[6] Newton,[7] Doyle and Clinch,[8] and Akerman.[9] Generally speaking, death in plant cells depends on the formation of ice crystals. At one and the same temperature, death occurs if crystals of ice are formed, whereas if no crystals appear, the cells live on. The crystals may be formed either within the cells or outside of them. Concerning the cause of death, the leading theory is that of Müller-Thurgau.[10] This author holds that as ice forms, the salt

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[1] Protoplasma—Monographien, Vol. I.
[2] "Colloid Chemistry of Protoplasm," 123.
[3] XIth Intern. Physiol. Congress, Quart. J. Exp. Physiol., Supplement, 69 (1923).
[4] "Pflanzenphysiologie," (1904).
[5] Missouri Agr. Exp. Station Research Bull., No. 8 (1913).
[6] Missouri Agr. Exp. Station Research Bull., No. 48 (1921).
[7] J. Agr. Sci., 12, 1 (1922).
[8] Sci. Proc. Roy. Dublin Soc., 18, 219 (1926).
[9] "Veröffentlichungen der Knut und Alice Wallenberg Stiftung," No. 10 (1927).
[10] Landwirt. Jahrb., 9, 133 (1880); 15, 453 (1886).

concentration of the rest of the protoplasm increases until the death point is reached. Müller-Thurgau's theory is supported by Molisch[1] and by Maximow.[2] However, the latter author believes that in addition to the salt effect following ice formation, there is also a mechanical effect of the ice crystals on the colloids of the protoplasm. If the Müller-Thurgau theory is correct, then cold death at freezing temperatures is really a special case of the toxic action of high concentration of salt in the cell.

There is still another kind of anesthesia that must be considered, that is electrical anesthesia. About the beginning of the twentieth century a number of workers discovered independently that electrical currents under certain conditions would produce narcosis. The subject has received quite a bit of publicity and is quite novel. Both general and local anesthesia can be produced by this method. The bulk of the work seems to be confined to the determination of the optimum conditions under which the effect can be best produced. When used under these conditions it could be employed in minor surgical operations to some advantage.

The method consists in placing two electrodes in such a position that the chosen part of the body or limb is included in the circuit. L. G. Robinovitch gives an excellent summary of the method and literature in "Anesthesia" by Gwathmey.

The most interesting thing of the whole situation is how can this effect be explained upon the older theories of narcosis. There is no relation between an electrical current and distribution coefficients nor could the effect be included in Kochmann's dehydration theory. On the colloidal theory one suggests that the current caused a slight flocculation of certain colloidal systems. It is known that the inorganic salts are, in part, responsible for the peptization or stability of the colloids in biological systems. Now if two electrodes are placed such that the cell is between them and a current passed, we know that the ions will migrate either to the anode or cathode depending upon their charge. Since the stabilizing concentration of these ions in the cell is very critical any small deviation will cause a flocculation. The case is similar to an electrical dialysis. When the current is disconnected the blood will enable a uniform distribution to take place and equilibrium is again established; this is responsible for the recovery.

The experimental researches of Heilbrunn[3] support this view: "Electric currents have a marked effect on various types of living material. In muscle and nerve physiology, the electric current is the most common means of stimulation. Lower forms of animal life and various plant tissues also show a characteristic response to the passage of electricity. It is to be expected, therefore, that the protoplasmic colloids should undergo changes following exposure to electric currents. There is an abundance of evidence to prove that this is the case

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[1] "Untersuchungen über das Erfrieren des Pflanzen" (1897).
[2] Jahrb. wiss. Botanik, 53, 327 (1914).
[3] "Colloid Chemistry of Protoplasm."

"In 1862 Brücke showed that electric currents produced a cessation of Brownian movement in the salivary corpuscles or leucocytes of human saliva.

"Kuhne[1] found that the passage of an electric current from an induction coil caused a cessation of Brownian movement in the protoplasm of the stamen hairs of *Tradescantia*. Chifflot and Gautier[2] also found that the passage of an electric current stopped the Brownian movement in the cells of the alga *Cosmarium*. Bayliss[3] studied the effect of currents from an induction coil on Brownian movement in the protoplasm of ameba. The amebae were placed on a slide in a drop of water, and the electrical current was led to the drop through strips of platnium foil. With this technique, there is of course the possibility that various chemical substances formed at the electrodes may have an effect on the protoplasm. But Bayliss' observations were usually made very rapidly, so that this was probably not a factor. In studying the Brownian movement, Bayliss used a Zeiss paraboloid condenser, and he focussed his attention on the ectoplasm of the pseudopodia. Here one can observe a very vigorous movement of granules invisible with bright field. On the passage of an electrical current, this movement "ceases almost instantly, as if the protoplasm had been frozen." Then when the current is stopped, the Brownian movement begins again. In order to obtain these results it is necessary to use currents that are neither too weak or too strong. The latter produce an irreversible coagulation of the protoplasm.

"From these studies on Brownian movements; it is apparent that electric currents can produce a reversible gelatination or coagulation of the protoplasm. A much more exact study of the effect of the electric current on the colloidal properties of protoplasm was made by Bersa and Weber.[4] These workers were careful to exclude any possible error due to the formation of chemical decomposition products at the electrodes. The current passed from carbon electrodes through troughs containing tap water, and then to the tissue by way of long strips of moist filter paper. Water and filter paper were changed from time to time, so that there was no possibility of the diffusion of chemicals from the electrodes to the cells. The material used was the stalk (epicotyl) of the bean plant *Phaseolus multiflorus*, and the current was passed through pieces of stalk about 1-2 cm. long. The viscosity of the protoplasm was determined by the centrifuge method. The results of the experiments are very clearly summarized by Bersa and Weber, and the account that follows is practically a translation of their words.

"In order to produce a viscosity increase in the protoplasm, an exposure of only ¼ to ½ minute is necessary, if the current is relatively strong (5-10 milliamperes). With weaker currents (0.15-5 milliamperes), an exposure of 1 to 4 minutes is necessary to produce the same effect. The increase in viscosity produced by these currents is considerable, for it is at least a three-fold increase. The effect is reversible, and after a recovery period of 20 to 40 minutes,

[1] "Untersuchungen uber das Protoplasma und die Contractilitat" (1864).
[2] J. de Bot., 19, 40 (1905).
[3] Proc. Roy. Soc., 91B, 196 (1920).
[4] Ber. deutsch. botan. Ges., 40, 254 (1922).

the viscosity becomes as low or nearly as low as it was before exposure to the electric current. The results of Bersa and Weber find confirmation in some experiments of Zeidler.[1]

While these physical methods may never enjoy the popularity of chemical narcosis, still they are important from a theoretical standpoint and must be taken into consideration. An important phase of the colloidal theory is that it is able to account for this data. It is impossible to explain these cases on the other theories.

A peculiar case of narcosis that finds no good explanation in other theories is that produced by magnesium salts. S. J. Meltzer[2] found that subcutaneous, intravenous or intraspinal injections of magnesium sulphate would produce narcosis. Meltzer pointed out, as secondary actions, undue prolongation of the paralysis and retention of the urine. However, these effects could be minimized by washing out the spinal canal with normal saline solution. Tucker[3] showed that solutions of magnesium sulphate could be used as a local anesthetic. Wiki[4] has extended the study and investigated the relation of concentration of the salt to strength of narcosis. Meltzer found that in certain cases the combination of magnesium salts and ether could be used to advantage. The injection of one cc of sterile 25% solution of magnesium sulphate per kgm. of animal into the femoral muscle brought about greater relaxation with smaller amounts of ether. The well known antagonism between calcium and magnesium salts suggested that calcium salts would greatly facilitate the recovery from the effects of the magnesium.

H. B. Weiser[5] has formulated clearly the colloidal mechanism of the antagonism of ions in biological systems, so it is not necessary to discuss the reason further in this place. Meltzer found that the injections of calcium salts would quickly remove the influence of the magnesium ion.

No attempt is made to review the literature on the subject but the brief outline just given showing the use of magnesium salts for spinal anesthesia justifies the opinion that this type of narcosis is no passing fancy. It does not depend upon some peculiar property of certain cells, for it is quite general; and the explanation must not be based upon any usual assumptions. Clearly, the theory of Meyer and Overton offers no explanation nor would this theory even predict that magnesium salts would behave in this manner, for the solubility of such salts in lipoids or fats is very low relative to the solubility in water. Neither does Traube's theory offer an explanation, the surface tension of a 23% solution of magnesium sulphate at 18° is 78. While that of water at the same temperature is 73. There is no lowering of the surface tension here, quite the contrary. To explain this phenomenon on the basis of the colloidal theory however, is quite simple. We only have to postulate that

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[1] Botan. Archiv. 9, 157 (1925).

[2] Berlin klin. Wochenschr., Nr. 3, 73 (1906).

[3] Therap. Gaz., Nr. 5 (1907); Revista espec. medicas, Nr. 199. 475 (1907); Merk's Archives, Nr. 6, 178 (1907).

[4] Arch. Intern. Pharmacodynamie, 21, 415.

[5] J. Phys. Chem., 30, 20 (1926).

the magnesium ions will partially flocculate some one of the colloids in the part that is affected i.e. the nerve cell. This postulate is no idle assumption. Marinesco has studied the effect of magnesium sulphate on the spinal nerve cell and found that indeed the predicted flocculation occurred. Fig. 9 is a reproduction of his photograph showing this coagulation.

In the zone of flocculation in the extranuclear material one can still distinguish between the individual agglomerates of the coagulated material, thus, showing that this partial or "semicoagulation" is different from the normal coagulation or denaturation of proteins in that the material is not coagulated to such a point where the repeptization would be excessively slow, due to a marked decrease in the surface of the agglomerates. As was pointed out, such a state as this would be unfavorable to the recovery of the cell. Should such an extensive flocculation occur, then the cell could not be expected to recover and the agent that would bring about this condition would be classed as a toxic drug. It has been known for a long time that zinc sulphate could not be used in intraspinal injections due to its high toxicity. Fig. 5 shows the same type of ganglion cell after treatment with zinc sulphate. It is easy to see why one behaves as a narcotic and the other as a toxic agent. The flocculation of the colloids is quite marked and can be seen to be quite different from that produced by magnesium sulphate. The large close-packed agglomerates show definitely that repeptization of the colloids in these cells would be difficult.

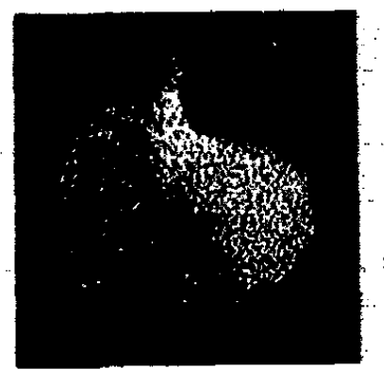

FIG. 9
Coagulation by magnesium sulphate (Marinesco).

The ease in which narcosis is produced by HCN or certain metallic cyanides is interesting, in that the amount required to bring about narcosis is so small that flocculation of the colloids seems excluded.

Dontas[1] found that concentrations of sodium cyanide of 0.005%. or less were narcotic for tadpoles, higher concentrations were so toxic that there was no recovery from the effect. At first sight this seems to exclude flocculation, for HCN, which is formed by the hydrolysis of the dilute solution, will not flocculate proteins in concentrations below 40%.[2]

The cyanide ion has a very marked effect on certain enzymes while other enzymes such as lipase, ptyalin, pepsin, and trypsin are not disturbed. However, such enzymes as catalase, platinum black and enzymes whose action depends upon the presence of metallic elements such as iron and copper are easily poisoned. Warburg's explanation[3] that the inhibition is due to the formation of complex ions may be wrong. For in some well-studied cases the phenomena are reversible, e.g., if the HCN is removed by blowing a stream of air through the solution; the enzyme is active again.[4] This seems to indicate

[1] Arch. exp. Path. Pharmakol., 59, 430 (1908).
[2] Gaz. med. de Paris (35), 4, 675 (1849).
[3] "Handb. d. experim. Pharm.," 1, 703.
[4] Meyerhof: "Chemical Dynamics of Life Phenomena."

that adsorption is more important, for the complex cyanide ions are relatively stable. This is also in line with the work of Dixon[1] in that there is no definite stoichiometrical relation between the concentration of the cyanide ion and the inhibition.

When a tissue is exposed to the cyanide ion there is an inhibition of the oxidation process, in higher animals this is shown by the fact that the amount of available oxygen is practically the same in both the venous and arterial blood, that is, the tissue has been unable to utilize the available oxygen. On lower animals the effect is similar to an atmosphere of hydrogen.[2]

As an explanation of the narcotic effect we may assume that the products that are normally oxidized will accumulate within the cells until their concentration is sufficient to flocculate the colloidal systems. Experiments on protoplasm bear out this point of view.[3] Protozoa were found to react in all physical appearances just as if they had been treated with quinine or morphine alkaloids. It was found that in many cases the protoplasm became swollen, this is probably due to the accumulation of the acidic products which cause the proteins to increase the degree of imbibition.

The conditions for recovery are not different from those of an ordinary narcotic, that are outlined in another part of this paper. The oxidation within the cell is not completely destroyed[4] but is lowered and the cell can regain its activity upon the removal of the CN ion if the dose has not been so great that irreparable damage has been done.

This paper suggests that the action of narcotics is due to a reversible coagulation of the bio-colloids. This effect, as already indicated, can be accomplished in two general ways: by direct coagulation due primarily to the narcotic, and secondly by indirect action, by interference with some normal function of the cell such that products are allowed to accumulate which will cause the coagulation.

The question was raised by A. P. Mathews[5] concerning the ability of nitrous oxide to flocculate bio-colloids. This question may be generalized by extending it to other physiologically active gases. There is no reason why gases should behave differently from solid and liquid narcotics, i.e., there exists the possibility of direct action, indirect action, or inertness depending upon the physical and chemical properties of the substance in question.

The recent introduction of ethylene oxide as a strong gaseous disinfectant[6] and its rapid action at low concentrations would suggest that this gas might coagulate bio-colloids directly. This was confirmed in the case of yeast by direct observation under the ultramicroscope. The gas was slowly bubbled through a young culture of yeast in Laurent's medium for a few minutes and then examined in the manner mentioned above. Concurrent with this

[1] Ber., 30, 2668 (1898).
[2] Am. J. Physiol., 1, 210 (1898).
[3] Am. J. Physiol., 1, 210 (1898).
[4] Biol. Reviews, 4, Nr. 4 (1929).
[5] Private conversation with W. D. Bancroft.
[6] Ind. Eng. Chem., 20, 805 (1928).

flocculation there was an inhibition of growth in the yeast culture as was to be expected. Ethylene oxide then, is a direct narcotic. As a matter of fact, chloroform and ether are always administered in the gaseous state so properly speaking they also belong to this class.

The action of nitrous oxide on living organisms is very interesting. If the partial pressure is kept very near one atmosphere the gas will narcotize the higher forms of life in a short time. The singular thing about nitrous oxide is that it has no effect on the lower forms of life unless the pressure is raised very high, i.e., about 45 atmospheres. Furthermore, it has little or no effect on the anaerobic forms of life.[1]

This is indeed exceptional, for in the series of direct narcotics of low molecular weight the specificity is very low. That is, ether and chloroform, etc., act on both the higher and lower forms of life and in addition will also affect plant protoplasm; whereas, nitrous oxide will only act on the higher forms of animal life. The fact that it shows so little effect on anaerobic organisms seems to indicate that its effect is linked up with the oxygen assimulation. This suspicion is strengthened by the fact that, in general, nitrous oxide affects only animals that carry on respiration through haemoglobin.

Thus one would be led to believe that nitrous oxide is an indirect narcotic. That is, it will not flocculate colloids within itself. This is in keeping with its physical properties. A. Findlay[2] found that there was no marked change in solubility of nitrous oxide in solutions of various colloids, i.e., no great adsorption. In this laboratory yeast cultures were exposed to the gas for several days and then examined under the ultramicroscope, there was not the slighest indication of flocculation. Naturally, the gas did not inhibit the growth of the cultures, since the cell colloids were not altered.

If nitrous oxide interferes with the oxygen metabolism it is reasonable to assume that acidic products, that normally would be oxidized to carbon dioxide and water, would accumulate and that these products are responsible for the flocculation. Also, since these products are the normal intermediates it is easy to see why the organism recovers so rapidly when the gas is removed.

In this connection the findings of T. D. Casto[3] that when animals are exposed to nitrous oxide there was a progressive decrease in the haemoglobin of the blood are very interesting. Also, G. W. Crile[4] showed that nitrous oxide caused an increase in the hydrogen ion concentration of the blood, spinal fluid, and bile. This is to be expected.

H. Wieland[5] whose critical study on nitrous oxide led to the discovery of the use of acetylene as an anesthetic, was the first to emphasize the necessity of separating nitrous oxide and acetylene from the narcotics of the alcohol-chloroform type. He points out that these gases have an effect similar to

[1] H. Wieland: Arch. exp. Path. Pharmakol., 92, 96 (1922).
[2] J. Chem. Soc., 105, 292 (1914).
[3] Dental Cosmos, 57, 881 (1915).
[4] J. Am. Med. Assoc., 67, 1830 (1916).
[5] Arch. exp. Path. Pharmakol., 92, 96 (1922).

"mountain sickness." According to his researches he is led to the view that there is an inhibition of oxidation especially in the brain.

Casto's researches[1] are very interesting in explaining the cause of the decrease in oxidation. However, an outstanding physical property of this group of gases, nitrous oxide and acetylene, is their relative greater solubility than other inert gases as Wieland has already pointed out. It may well be that this property would decrease the solubility of the oxygen in the blood serum to such an extent that the haemoglobin can no longer transport the required amount to the cells, although the haemoglobin is not chemically altered.

The theory of Verworn is, this author believes, intimately related to this class of narcotics. The interference with the oxygen transportation will in general lead to narcosis; the cause of this is not the interference, but the flocculation of the bio-colloids by the accumulated waste products. One can readily see that this is just one general method of causing the flocculation. The other is the direct flocculation of the bio-colloids by the narcotic itself. In either case the actual cause of narcosis is the colloidal change that occurs in the cell protoplasm, namely,—a reversible coagulation.

In nature many forms of animals are equipped with such structures and chemicals that they can bring about a narcosis in their prey or enemies. One can readily appreciate the value of such an arrangement as this. Consequently, it is not surprising that man, who was not so favored by nature, at an early period made quite an effort to provide himself with such desirable advantages. We are just now beginning to appreciate the scientific importance of the solution of this problem by our prehistoric ancestors. They found that anesthetics grew on every tree, even the rocks on the ground could bring about this change. In short by simply pounding on their prey with a stick or rock, or better still by a hammer made from both of these, they could cause it to undergo narcosis or even death.

From the point of view of the prehistoric men this was a very great discovery. Since the "narcotics" abounded on every hand and there were no shipping problems or fire hazards and the process of administration so simple that a child could handle the situation it is no wonder that the method met with such widespread favor. In fact it is such a good method that it is still in use today, policemen and thugs often put their patients to sleep by means of the black-jack. Other examples of this phenomenon are the knock-out in boxing or striking our "funny bone" which paralyzes our arm for a few moments.

This is a particularly important phase in the development of the theory of narcosis for it shows two things definitely: that there is no relation between chemical structure and physiological action, and secondly it shows the weakness of other theories of narcosis. Indeed it would be a difficult proposition to show the relation between the chemical composition of black-jacks filled with lead or cotton and the degree of narcosis produced. One can readily see that

[1] Dental Cosmos, 57, 881 (1915).

the chemical composition is secondary, it is only the physical properties that are important. Also there is no relation between boxing gloves and distribution coefficients or surface tensions, nevertheless, boxing gloves can under certain conditions produce narcosis. The theories of Traube, Winterstein, Meyer and Overton, Höber, and Verworn would not predict this.

However, in all fairness to the problem of narcosis, will the theory developed in this paper account for this phenomenon? The theory of coagulation would demand that reversible coagulation take place. There are examples of mechanical agitation causing coagulation; the stirring of fresh blood will coagulate the fibrin. But would mechanical action cause a reversible coagulation of the protoplasm? Heilbrunn[1] answers the question: "In 1910, Lepeschkin described what he called a mechanical coagulation of the protoplasm of Spirogyra. Filaments of Spirogyra were placed under a cover slip and distorted several times by pressure from above. Following this treatment, according to Lepeschkin, the outer protoplasmic layer coagulated and the inner protoplasm broke up into a number of balls. Sometimes the cells burst and the balls passed out into the surrounding medium. After half an hour, all the balls were coagulated too. Lepeschkin's criterion of coagulation is wholly a morphological one, and depends in the main on the appearance of new granules.

"Many authors describe the appearance of vacuoles following mechanical injury. Thus Heilbronn[2] states that mechanical injury produces vacuolization in slime mold plasmodia. Buenning[3] states that countless vacuoles appear in onion cells following mechanical coagulation.

"There are two different ways in which mechanical forces act on protoplasm. Cells may be subjected to pressure insufficient to cause any rupture of the cell membrane, or they may be compressed so as to force out the interior protoplasm until it comes in contact with the outer medium. Cutting and tearing of cells also exposes the interior protoplasm to the surrounding medium. When a cell is cut, torn or compressed so that its protoplasm comes in contact with the outer medium, the naked protoplasm often reacts by forming a film about itself.

"The physical changes occur in protoplasm following an injury to cells in the neighborhood have also been studied by botanists. Heilbronn[4] found that when sections were cut through bean seedlings (*Phaseolus* and *Vicia*), the viscosity was abnormally high for 10–15 minutes after the sections were made. During this time, the starch grains in the starch sheath cells did not move at all under the influence of gravity, although they moved rapidly enough later. Similar observations have been made by various other workers who have used the gravity method of measuring protoplasm viscosity.

[1] "Colloid Chemistry of Protoplasm."
[2] Jahrb. wiss. Botanik, 61, 284 (1922).
[3] Botanisches Archiv, 15, 4 (1926).
[4] Ber. botan. Ges., 30, 142 (1912).

"The coagulation or increase in viscosity is reversible. Thus in *Tradescantia*, centrifuge tests showed that 6-7 minutes after cutting the viscosity had returned to normal. When, however, thin sections were made, a longer time was necessary for recovery. Under these conditions, in *Tradescantia*, the viscosity only returns to normal within ten minutes at the earliest. In a similar experiment with *Raphanus*, the return to normal required thirty minutes. Buenning points out that a longer time is necessary for recovery than for the development of maximum viscosity.

"The increase in viscosity following a cut through the stalk is quite considerable. In the cells of *Secale*, one minute after the cut, the viscosity rose to four times its original value. In *Tradescantia*, after half a minute, it rose

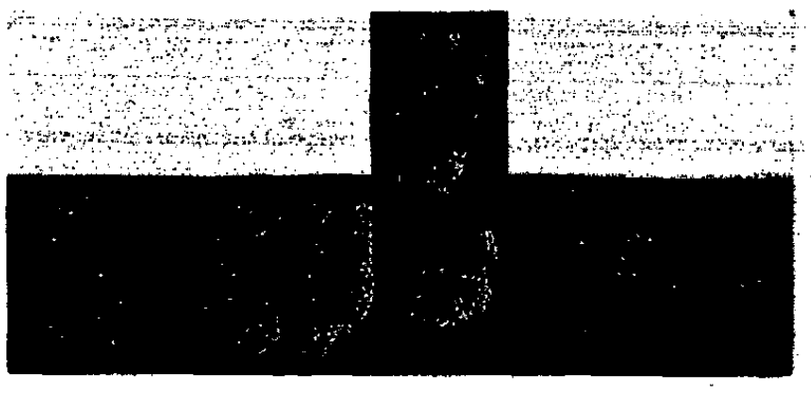

FIG. 10
Mechanical coagulation (Marinesco).

to three and a half times the original value; and in *Raphanus*, after two and a half minutes, the viscosity was at least five or six times as great, as before cutting."

Fig. 10 is a reproduction of Marinesco's photograph showing mechanical coagulation in the nerve cell.

Practically all the theories of narcosis in the ultimate analysis are theories of coagulation. The "membrane theories" postulate that the cell membrane will become permeable or impermeable, to fit the data, and the process by which this is accomplished is usually coagulation. Other theories postulate a lipoid structure to such necessary membranes and then show that the effect will be a function of the distribution between the body fluids and the lipoids, still other theories postulate that the drugs will concentrate just at the proper membrane by surface tension forces. They differ among themselves in the manner in which the narcotic is conveyed to the critical membrane. The photographs in this discussion, showing the effects of narcotics upon nerve cells, were produced by G. Marinesco, a man of unquestionable ability and technique, and *they do not give the slightest indication of coagulation at any boundary in the cell that could possibly be considered as a membrane.* Also the work of Heilbrunn and others shows directly that the coagulative effects are in the *interior* of the cells.

It is pointed out that the other theories of narcosis do not give a complete picture of the cell during narcosis. Therefore, as theories of narcosis they are inadequate.

In the first part of this paper it was pointed out that numerous workers had observed characteristic changes in the viscosity of the cell during narcosis. It is desirable that a working hypothesis of this phenomenon be suggested and to determine whether any conclusions can be drawn from it. The narcotic decreases the viscosity of the cell during the narcosis, higher concentrations of the drug will cause the viscosity to pass through a minimum and return above normal.

Einstein[1] has deduced an equation for the viscosity of sols which holds only under certain conditions: the particles should be spherical, elastic, and large in comparison with the molecules of the dispersing medium. The equation relates the viscosity of the disperse system to that of the dispersion medium and the volume of the dispersed particles. In applying this equation to many biocolloids there is a wide deviation from the actual values, the calculated values being too small. Kruyt[2] suggests that this discrepancy can be best explained through the assumption that the particles are hydrated and have a larger volume than that calculated for the dry particles.

It is well known that most bio-colloids are highly hydrated and consequently they are classed as lyophile colloids. Such colloids have a layer of water around the micellae that is commonly called the water sheath. The water that makes up this sheath is not free but is bound to the surface of the particles. In the first phase of coagulation the narcotic is adsorbed upon the colloidal substrates of the cell and displaces the material that was previously adsorbed there. This amounts to an increase in the effective concentration of these substances. Hence as the narcotic is adsorbed the water sheath and other substances will be progressively displaced. This increase is the amount of the free water will have the same effect on the viscosity of the sol as dilution, i.e., a decrease. The decreasing volume of the particles, due to the loss of the water sheath, will also decrease the viscosity. So it is not difficult to understand why, with increasing small amounts of the narcotic there will be a continuous decrease in the viscosity.

Another factor that might contribute to the decreasing of the viscosity would be the dissolving of fat globules or of films of fat by the anesthetic. However, this is not very general, for simple physical effects such as heat and cold will cause the same type of change.

Smoluchowski[3] has pointed out another correction to the viscosity equation, that of the charge on the particles. In case the particles are charged, they are surrounded by a repelling sphere whereby their active volume is virtually increased. In the initial phase of the coagulation the discharging of the particles will also contribute to the lowering of the viscosity. However, this electro-viscous effect will not be very large unless the particles are small and the specific conductivity of the medium is low.

As soon as the charge on the particles is lowered to such a value that flocculation occurs the particles come together to form the agglomerates.

[1] Ann. Physik, 19, 289 (1906); 34, 591 (1911).
[2] "Colloids" (1927).
[3] Kolloid-Z., 18, 190 (1916).

Considerable water is trapped in the voids and interstices of these structures, and this water can no longer be counted as free water. Hence as the coagulation progresses the amount of free water is lowered which causes the increase in viscosity. Also the chain structure of the material, as in jellies, would tend to increase the viscosity. So both phases of viscosity are changing aspects of the phenomena of coagulation.

The viscosity variations of the protoplasm of marine eggs, when exposed to various narcotizing agents, have been extensively investigated. In this connection the following quotations from Heilbrunn are of interest.

"Heilbrunn studied the effect of ether and other fat solvents on the protoplasm of sea-urchin eggs. Using the centrifuge method, he was able to show that various fat solvents caused a decrease in viscosity when present in certain dilute concentrations. In somewhat higher concentrations, they produced a coagulation with a great increase in viscosity. The decrease in viscosity produced by dilute solutions of fat solvents was always reversible. On the other hand the coagulation caused by the more concentrated solutions was always irreversible and involved the death of the cell. In a later chapter it will be shown that the decrease in viscosity produced by the fat solvents is related to the anesthetic action these reagents have in preventing cell division in the sea-urchin egg. For the present we are concerned only with the physical action of the fat solvents, and not with any physiological correlations.

"The action of fat solvents has been carefully studied in the starch sheath cells of bean plants, in sea-urchin eggs, in slime mold plasmodia, in the leaf cells of Elodea, and in the stalk cells of Callisia repens. The results on all these different types of protoplasm are fully concordant, and it can now be regarded as scientific fact that, in general, dilute solutions of fat solvents cause a decrease in protoplasmic viscosity, whereas more concentrated solutions cause increase in viscosity or coagulation.

"In 25% distilled water, the viscosity of the Arbacia protoplasm is about 60% of its normal value. In 2½% ether, it will be remembered, the viscosity drops to 53% of what it is in the controls. Moreover, just as in higher concentrations of ether coagulation occurs, so too as the concentration of the distilled water increases beyond a certain limit, there is a sudden coagulation of the protoplasm. It is certain, therefore, that when the protoplasm of the sea-urchin egg becomes diluted with distilled water, there is actually a pronounced decrease in viscosity. This is quite comparable to the effect of ether.

"Concerning the coagulative action of more concentrated solutions of fat solvents, we now have some real information. This coagulative action can be seen morphologically to be accompanied by certain distinctive visible changes. In Arbacia eggs, for example, there is a very noticeable loss of pigment from the pigment granules of the cell, and this is soon followed by the appearance of numerous vacuoles throughout the protoplasm. All these changes are associated with a very definite and characteristic series of reactions which are found not only in sea-urchin eggs, but in other cells as well.

The fat solvent, when present in sufficient concentration, can initiate this series of reactions, and the ultimate result is a coagulation of the protoplasm."

In order to better correlate the viscosity changes with reference to coagulation the following experiments on inorganic sols are of interest. It is now known that the rays from radio-active substances can coagulate many sols.[1] The β rays are quite effective in coagulating positive sols such as hydrated ferric oxide, ceric oxide sols, and alumina sol. Fernau and Pauli[2] have carefully investigated the effects of radium salts on ceric oxide sols. The radio-active material was placed in a tube; the tube was then dipped into the sol. Twenty percent of the β radiation was able to penetrate about 2.5 cm of the sol. In 24 hours exposure the material coagulated to a stiff jelly. The unexposed sol, when left to itself, showed no tendency to coagulate for over a year.

The reason this study is so important is due to the fact that the viscosity variations, due to the coagulation, can be observed without introducing any other substances which in themselves would influence the viscosity.

The variations in viscosity of the above sol during the coagulation period are quite interesting. The same type of changes are observed as in coagulating protoplasm; at first there is a distinct decrease in viscosity. This was followed by a strong rise in viscosity. The decrease in viscosity is explained by the discharging of the particles, as is to be expected in accordance with the theory of Smoluchowski discussed above. The increase in viscosity occurs upon the association of the flocculi. This same type of coagulation can be produced by adding an electrolyte such as sodium chloride.

The most interesting thing about the viscosity changes and coagulation is that the radium radiation causes only the *decrease* in viscosity. If the tube of radium is withdrawn at the moment when the viscosity is at a minimum, the rise in viscosity occurs just the same. This is conclusive proof that the decrease in viscosity is the preliminary stage of coagulation and is just as characteristic of the coagulation as the increase in viscosity. The variations of viscosity merely show the *successive* phases of coagulation.

These cases of coagulation are quite clear, and there can be little doubt but that the process is a simple discharge and coagulation of the sol.

Since this action of radium is so clear-cut, let us investigate its effects on protoplasm. Heilbrunn has already summarized the literature: "Similar effects have been found to follow radium treatment. Thus Forbes and Thacher found a decrease in viscosity of the protoplasm of the eggs of Nereis (an annelid), following treatment with radium. In their own words, "Nereis eggs radiated with β rays, fertilized, and then centrifuged from 7 to 65 minutes after fertilization, show slightly sharper separation of resulting zones than is found in unradiated controls." The difference is most easily explained as due to decreased viscosity of the protoplasm in consequence of radiation.

"Williams studied the effect of beta and gamma rays of radium on the protoplasm of Saxifraga umbrosa. Short exposure caused an increase in the

[1] Compt. rend., 138, 521 (1904).
[2] Kolloid-Z., 20, 20 (1917).

amplitude of the Brownian movement of the small particles of the protoplasm, together with an increase in the rate of protoplasmic streaming. Evidently a decrease in viscosity is produced. Longer exposure to radium caused visible coagulation, and vacuolization of the protoplasm. Comparable results were also obtained by Zuelzer and Philipp on ameba. These authors found that short exposures to radium caused an increase in the speed of ameboid movement, longer exposures resulted in a coagulation of the protoplasm."

In the face of such evidence as this, we can feel certain that the variations in viscosity are trustworthy indicators of the series of changes that occur in coagulation. As is to be expected, the preliminary phase of coagulation, i.e. the stage of decreased viscosity, is easily reversible, while the later stage of increased viscosity is more difficult to reverse. Since the colloid theory is concerned with the reversible type of coagulation it is not surprising that narcosis occurs, as a general rule, in the phase of decreased viscosity.

It should be noted that in the first phase water is liberated, and in the second it may be bound again, though not in the same way. This interchange may not exactly balance, and there is considerable evidence that in certain cases it does not. Kochmann[1] has shown that in many tissues which are under the influence of narcotics, there is an actual loss of water. Knaffl-Lenz[2] showed that in 1/1.5N ethyl alcohol, 1/7.5N diethyl ether 1/50N urethane, 1/100N salicylamide and 1/100N benzamide the volume of red blood cells would decrease without causing haemolysis. Kochmann extended this work to other tissues. A typical experiment is as follows: the gastrocnemius muscle of R. temporaria was placed in an isotonic salt solution, this was used as the control. A similar arrangement was made with another muscle except that various narcotics were added to the salt solution. From time to time the muscles were stimulated by electrical means until it was certain that narcosis had occurred in the muscle which was treated with the drug. The weight of the muscle before and after narcosis when compared to that of the control showed that the narcotized muscle underwent a loss in weight. This change ran parallel to the phenomena of narcosis for if the muscle was placed in a narcotic free solution again it recovered and increased in weight. Table VIII contains some of Kochmann's results.

TABLE VIII

Narcotic	Conc. in Millimols	Loss in weight
Chloroform	4.1	1.9%
Chloral hydrate	6.1	10.7%
Amyl alcohol	20.0	4.3%
Butyl alcohol	66.6	5.4%
Diethyl ether	190.0	2.6%
Ethyl urethane	250.0	3.0%
Propyl alcohol	250.0	3.5%

[1] "Handbuch exp. Pharmak.," 1, 499.

[2] Arch. ges. Physiol. (Pflüger's), 171, 51 (1918); Arch. exp. Path. Pharmakol., 84, 66 (1918).

However, it must be added that Kochmann preferred to regard this effect as the cause of narcosis.

The antagonism shown by various groups of drugs towards one another is well known. Perhaps, with this brief survey of the state of the colloids under the influence of drugs, we may approach the question from a different point of view. The older theories on this subject are closely related to the theories of narcosis, for it was frequently found that small amounts of two narcotics given were much more effective than one would predict from the algebraical sum of the concentrations. On the other hand cases were found where the effect of the two drugs was less than either alone. The explanation that was frequently advanced was that one of the substances increased or decreased the distribution coefficient of the other, hence the combined effect was greater or less, or that the permeability of the various cell membranes were altered in the necessary way to allow more or less narcotic to enter as the case demanded.

It can be readily seen that these theories are just as sterile as the corresponding theories of narcosis. Another theory is based upon the supposed chemical reaction between the antagonists, thus neutralizing the effect. This belief has been disproved by the fact that if chemical neutralization is taking place there will be some definite molar ratio at which the effect will be abolished and if increasing concentrations, of this definite ratio of drugs, the tissue will be normal; such is not the case however, as Dixon points out that in the atropine-pilocarpine antagonism "a solution of pilocarpine and atropine cannot be prepared in which the effects of both drugs are lost, and what is more surprising is that a mixture can be made which in small doses has a pilocarpine effect and in larger doses an atropine effect."

There is a very close relation between the synergism and the antagonism of drugs, and one reason why this field has been so unfruitful is that the early workers did not fully understand this relationship. It has already been shown that there is no relation between chemical constitution and physiological action and that the effect of drugs, in the general case, is not a chemical but a physical process. Furthermore, since the substances that are exerting this effect act upon the colloids of the cell and must be transported from the body fluids to these substrates, the number of the different substrates and the extent of adsorption upon each are important factors. Furthermore, in considering the effect of mixtures of two drugs it is important to know what is the effect on the adsorption of either of the substances by the presence of the other.

We have already discussed the mechanism by which narcotics can behave as stimulants. Now it is often observed that after a narcotic has produced its effect, another substance, that can behave as a stimulant, if given, will stimulate narcotized area again until it recovers, i.e., the substance behaves as an antagonist. Many theories have been advanced to explain this; but it is clear that this stimulation is exactly like the stimulation produced by narcotics and is clearly a case of displacement. It is evident that there can be no displacement if both drugs are not adsorbed upon the substrate which is effected.

Cases are known where this condition is not fulfilled and other adequate explanations have already been offered by others. Antagonism is concerned

with elimination; may be accomplished by increasing the flow of blood, dilation of the capillaries in the affected area, increased ventilation of the lungs if the compounds are volatile, or by purgatives if the substances are eliminated by the intestines, etc. We are not dealing with such cases here, it is only when the elimination from a substrate is brought about by displacement adsorption that it is considered in this presentation.

Consider the simplest possible theoretical case, in which the drug is affecting only one substrate. The possible methods of elimination of the drug have already been discussed in the paragraph on recovery, suppose that these methods of elimination are slow and we desire to hasten it. Another substance is given which will be adsorbed upon the same substrate and displace some or all of the original material, thus increasing its effective concentration so that it may undergo the reactions of detoxication faster or diffuse out more rapidly. This method is very effective provided that the antagonist does not complicate the situation by its own action. It can be seen that the drug has been displaced by another whose physiological action is less but whose adsorption is greater. The extent of adsorption is determined by the concentration, so there will be antagonizing concentrations below which this effect will be very small. If the concentration of the antagonist is increased very much above this value the antagonist will begin to exert its own physiological action. In such displacements there is a mutual hinderance in the adsorption of both substances so for a given concentration both substances will be less active. When the two substances have identical physiological actions in the same concentration then antagonism will not be evident. Also if the elimination of the drug is not hastened by the displacement the effect of the antagonist will only be transient.

Claude Bernard studied a case that illustrates the last point. He narcotized rabbits with ether, then injected hydrocyanic acid and found that the hydrocyanic acid was inactive so long as the ether was present, but upon recovery from the ether the animal became poisoned from the effects of the hydrocyanic acid. Here the ether is more strongly adsorbed than the hydrocyanic acid, so the latter can not exert its toxic effect due to its extensive displacement. On the other hand, the hydrocyanic acid was not rapidly eliminated, so on recovery from the ether its effect was produced, i.e. a case of temporary antagonism. Claude Bernard[1] describes the experiment as follows: "I have in connection with M. Paul Thénard made experiments consisting in injecting into etherized rabbits quantities of anhydrous hydrocyanic acid much greater than the doses which would kill the animals rapidly in the normal state. The rabbits showed no toxic effect so long as they remained unconscious. Poisoning took place when the animals waked up and the anesthetic no longer modified the normal properties of the nervous system." It could hardly be expected that Bernard would know of displacement adsorption at that early date.

However, within the body there are a great number of substrates; if a drug is administered and is preferentially adsorbed, for example, by the motor

[1] "Leçons sur les Anesthésiques," p. 99 (1875).

nerves then narcotizing concentrations will paralyze the motor nerves. If the drug is adsorbed by other nerves or glands, then with increasing concentration all the phenomena of narcosis will be exibited in that tissue. It frequently happens that while most drugs show a preferential adsorption for one tissue they are also adsorbed to a less extent on other tissues. The physiological effect does not become pronounced until relatively high concentrations are reached and it is the symptoms exhibited by the action on these secondary substrates that usually inform us that toxic concentrations have been attained. As an example of this, narcotics will generally narcotize the sensory impulses before the wink reflex of the eye is effected, in higher concentrations the wink reflex is abolished; this fact is often used to ascertain the depth of narcosis.

This is the more general case. Normally, if the drug is in low concentrations its relative adsorption will be greater and the amount adsorbed upon the secondary substrates will be too small to exert a physiological action, so its effect is relatively specific. However, if a drug is given that is strongly adsorbed upon the principal substrate, and relative to the first substance has a lower degree of adsorption on the secondary substrates, the original material is displaced, thus raising its effective concentration. This will cause the displaced material to be adsorbed upon the secondary substrates just as if the actual concentration were as great as the effective concentration produced by the displacement. The drug can now exert its physiological action on these secondary substrates and the total effect on the organism appears to be produced by a high concentration of the first drug minus the effect it normally produces on the principal substrate plus the effect of the displacing drug on the principal substrate, if it is in physiological concentrations.

Morphine is adsorbed and exerts its physiological effect on the cerebral nervous system; in higher concentrations it will affect the sensory nervous system, i.e. this is the secondary substrate. Chloroform is adsorbed by both the cerebral and sensory centers and exerts its effect on both substrates, it differs from morphine in that the difference between the action on the cerebral and sensory systems is less marked. The state of affairs is this: morphine is strongly adsorbed in the cerebral region and to a less extent in the sensory region, chloroform is adsorbed in the cerebral system and to a greater extent than morphine in the sensory area.

Now suppose that an animal is under the influence of a small amount of chloroform; the sensory region will not now be affected and the first manifestations of the action will occur in the cerebral center. If a given amount of morphine is administered to the animal, it will be adsorbed within the cerebral center and exert its physiological effect, it will also displace some of the chloroform and increase the effective concentration of the latter. Now since this cannot exert its own effect in the cerebral region it will be adsorbed and act upon the secondary substrates i.e., the sensory centers. The animal will then be in the same state as if a large dose of chloroform had been given, both the cerebral and sensory centers will be narcotized, provided the original concentrations were great enough. It can be readily seen how small amounts of two similar drugs can have a combined effect greater than either alone.

The above experiment was one that was performed by Claude Bernard,[1] he describes it as follows: "Five years ago, in 1864, I made some experiments on the properties of opium. A dog had been given a dose of chloroform and was just coming out of it, the cornea having already recovered its sensitivity, when we injected under the skin five centigrams of morphine hydrochloride. The animal was soon narcotized, as was to be expected, since we had given him the dose of morphine sufficient to produce this effect; but the extraordinary thing is that the insensibility due to chloroform came back at the same time. It was not surprising that the two effects co-existed because both substances had been administered; but it was very singular that the insensibility due to chloroform should reappear after it had disappeared, since no new dose of chloroform had been given which would account for the return of the anesthesia.

"Here is a dog which was given morphine some time ago. It is in the usual state that morphine produces at first. Its sensitivity or rather excitability is very exaggerated. We make it inhale chloroform in a much weaker dose than would be necessary to anaesthetize it in the normal state and the excitability disappears very rapidly even though it was well above normal at first.

"If a pigeon is given a considerable dose of morphine, there is almost no effect. A slight dose of chloroform will then anesthetize the bird; but, curiously enough, the symptoms are due much more to morphine than to chloroform."

The antagonistic action of many drugs is not different from the simple ionic antagonism observed in colloid chemistry. A large number of drugs are electrolytes and the fundamental work of H. B. Weiser[2] will explain the colloidal aspect of this action. A careful study of (1) the effect of each precipitating ion on the adsorption of the other, (2) the stabilizing action of ions having the same charge as the sol, (3) relative greater adsorbability of ions at low concentrations has led Weiser to conclude that the effect of the first two of these factors will be to raise the precipitating concentrations of mixtures above the additive value while the effect of the third will be to lower the precipitating concentrations below the additive value. It was found that when there is a marked difference in the adsorbability the two substances may show antagonism, that is, there will be a mutual hindrance to both. When the precipitating concentration is practically the same then the combined effect is additive. In displacements that occur in the body the drug can act upon secondary substrates, if it is not rapidly removed, so in this respect it differs from the antagonism shown in the test tube.

If the colloids of a cell are reversibly coagulated and the agent that caused the flocculation is displaced by a substance of weaker flocculation capacity for the given concentration, naturally the bio-colloids are peptized again by the electrolytes. Concurrent with this peptization there will be the return of irritability and consciousness. Now the agents that are responsible for the

[1] "Leçons sur les Anesthésiques."

[2] J. Phys. Chem., **30**, 20, 1527 (1926).

peptization are the electrolytes within the cells. However, it might be possible that organic electrolytes could bring about this peptization under suitable conditions. In this connection it is interesting that many primary and secondary amines of the aliphatic series will behave as antagonists to acid amides and chloral hydrate.[1] The same phenomenon was observed in connection with cocaine, caffeine, ephedrine, and β-tetrahydronaphthyl amine where it was found that they behave antagonistically to chloral hydrate.[2]

It is easy enough to understand the how and why of most phases of flocculation and peptization; but it must not be overlooked that other effects always accompany these phenomena in living tissue. When there is a flocculation of the colloids there is also a loss of irritability. What happens when

FIG. 11
Sodium iodide (Marinesco).

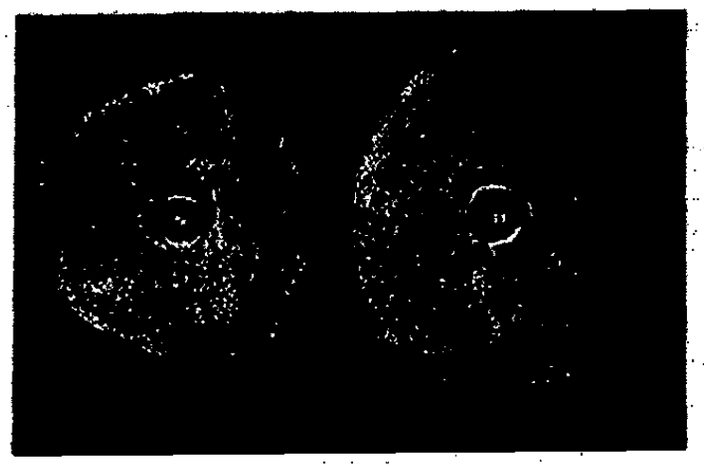

FIG. 12
Antipyrine (Marinesco).

there is a peptization of the cell colloids? This is indeed an important question for the understanding of the action of drugs. Without delving into details it is pointed out that the phenomena of irritability are associated with equilibria phenomena, i.e., as long as the material is in a state of flux tending away from equilibrium it shows various degrees of response towards external stimuli, the nearer the approach to coagulation the more pronounced this effect is. In the equilibrium of the cell that concerns the flocculation-peptization system we know that flocculation is accompanied by a loss of response to external stimuli. Furthermore, the gradual approach to this point is associated with increased irritability; on the same basis then a peptization might be expected to lead to a decrease in irritability.

This is no groundless speculation; at the present time there are two things that would indicate whether there was any probability of such a phenomenon. It has been established that sodium bromide has a quieting effect on the nerves, which means that the irritability is lowered. It is also known to colloid chemistry that the bromine and iodine ions can peptize many biocolloids. Fortunately, Marinesco has examined this effect. He found that the colloids of the nerve when exposed to sodium iodide were actually in a

[1] Arch. exp. Path. Pharmakol., 36, 451 (1895).

[2] Arch. internat. Pharmacodynamie, 23, 453 (1913); Arch. exp. Path. Pharmakol., 78, 218 (1915).

state of higher dispersion than normal. Also, antipyrine, which behaves as an analgesic, does identically the same thing. Figs. 11 and 12 are reproductions of Marinesco's photographs showing this peptization. It is impossible at the present time to determine whether this is a general phenomenon but it is very interesting and is an excellent starting point for future research.

Warburg's adsorption theory of narcosis has recently aroused the interest and some favorable criticism from several biological workers.[1] The authors of this paper wish to point out however that this adsorption theory is only a special case of the coagulation theory and, as it is stated by Warburg, is both indefinite and incomplete. Obviously the adsorption of a narcotic by the sols of the affected tissue will tend to do either one of two things: peptize or coagulate the colloids. Warburg forgets to tell us which takes place. The theory of Binz and Claude Bernard is quite definite, it is coagulation. The coagulation theory also recognizes that narcosis can occur without adsorption of narcotics i.e., by heat, cold, electricity, mechanical force, and water. In fact, the last case depends upon a *desorption* of the stabilizing ions. The phenomena of narcosis can be explained only upon the basis of the theory of Binz and Claude Bernard.

In conclusion we can say that the chemistry of anesthesia is the chemistry of sols, gels, displacement adsorption, coagulation, viscosity changes, peptization, adsorption, swelling, and catalysis; briefly, colloid chemistry applied to the muscles, nerves, glands, and cells of the affected tissues. The ultimate effect of a narcotic is the reversible coagulation of the cell colloids. This is preceded by a state of stimulation which depends upon the decreasing stability of the colloids before coagulation.

Summary

(1). The criticisms directed against the theory of Binz and Claude Bernard, that low concentrations of narcotics will not coagulate the cell colloids and further that any coagulation produced is irreversible, have been shown to be wrong; due to the fact that the effect of the electrolytes of the cell were neglected.

(2). It was demonstrated both in vitro and in vivo, by the ultramicroscope, that low concentrations of narcotics flocculate the cell colloids. The coagulation is reversible upon the removal of the narcotic.

(3). The converse of this (2) also follows: a reversible coagulation of the cell colloids, produced by whatever means, will cause narcosis. The cases of narcosis due to heat, cold, electricity, water, and mechanical effects are due to this fact.

(4). The decreasing stability of the colloids at low concentrations of the narcotic is accompanied by an increasing irritability. Thus narcotics in low concentrations should behave as stimulants and stimulants in high concentrations should behave as narcotics. Thus the common aliphatic narcotics are stimulants to growth, motion, chemical reactions, enzyme action, etc. when

[1] Physiol. Rev., 10, 171 (1930).

they are in low concentrations. On the other hand, stimulants such as caffeine and strychnine behave as typical narcotics in high concentrations.

(5). Narcotizing agents are divided into two groups: direct narcotics, which coagulate the cell colloids by direct action, and indirect agents which interfere with some normal function of the cell such as oxidation, and the coagulation is produced by the accumulated waste products. Ether, chloroform, and alcohol are examples of the direct class and nitrous oxide, acetylene, and hydrocyanic acid behave as indirect narcotics.

(6). The distribution coefficients of the Meyer and Overton theory are to be regarded as a rough measure of the rate of transport of the various narcotics. The relative degree of adsorption determines the extent of coagulation, in other words, the narcosis.

(7). The depression of the surface tension of water by various narcotics (Traube's theory) is to be regarded in the same light as the distribution coefficients.

(8). Verworn's theory is interpreted as a special case of the coagulation theory in that it deals with only the indirect narcotics. The depression of the oxidation alone does not cause the narcosis, the accumulated waste products coagulate the colloids of the cell and are responsible for the effect.

(9). The work of Heilbrunn on the viscosity of protoplasm offers a substantial confirmation to the coagulation theory.

(10). Marinesco's researches on the colloidal structure of nerves also presents a striking confirmation to the salient points of the coagulation theory.

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THE CHYLOMICRON EMULSION

BY S. DeW. LUDLUM, A. E. TAFT AND R. L. NUGENT

Introduction

The blood distributes the products of the digestion of protein and carbohydrate in true solution. From the colloidal point of view, it is a matter of great interest that the third important foodstuff, fat, is distributed as an emulsion of minute droplets. Those of measurable size are estimated to be mostly from 0.5 to 1 μ in diameter.[1] Many are smaller than this and are visible only by means of dark-field illumination. These droplets are best known as chylomicrons because they enter the blood with the chyle, a milky fluid containing absorbed food from the intestine which pours directly into the blood stream. Blood containing chylomicrons thus has, in addition to its better known characteristics, that of a lipoid emulsion,[2] which may be called the chylomicron emulsion. Although it is obviously an emulsion system of extraordinary importance, it has received little attention from colloid chemists.

It is the purpose of the present paper to describe such results as have been obtained to date in an investigation of the chylomicrons considered as emulsion particles. It is offered as a contribution to the colloid chemistry of the chylomicrons.

The study of these tiny fat droplets in blood has a truly fascinating history as related by Gage and Fish[3] in their classical paper on the digestion, absorption, and assimilation of fat in the animal body. A brief account of this well precedes the presentation of the particular results of this paper.

Outline of the History of Chylomicron Study

It has been known for about three hundred years that the presence of food in the small intestine brought about the appearance of a milky chyle which poured directly into the blood stream, in turn causing the blood serum to assume a milky appearance. A century and a half later, we find the description of experiments to show that this milky fluid contains an exceptional amount of fat, for, if dried upon a piece of paper, it leaves an obvious grease spot. Hewson,[3] who made this observation, also discovered that the microscopic study of such milky chyle and serum disclosed many exceedingly small particles not present in the clear liquids.

Seventy years preceded the next advance in chylomicron knowledge. Gulliver,[3] in 1840, took up the study of the small particles which had been discovered by Hewson, and described their Brownian motion, and compared them with the fat globules of milk. For some reason best known to himself, he called them "the molecular base of the chyle."

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[1] Gage and Fish: Am. J. Anatomy, 34, 1 (1924); Bloor: Physiol. Rev., 2, 92 (1922).

[2] Ludlum, Taft, and Nugent: Colloid Symposium Annual, 7, 233 (1929).

[3] Gage and Fish: Am. J. Anatomy, 34, 1 (1924).

Modern chylomicron study begins some thirty years after Gulliver with Edwards[4] who in 1877 observed blood with the dark-field microscope and remarked that it appeared as a wholly new substance with multitudes of dancing particles which looked like motes in a sunbeam. Hewson and Gulliver could only have observed comparatively few, exceptionally large chylomicrons in their light-field studies. A proper idea of the number of the chylomicrons and the beauty of their observation was revealed by the work of Edwards. Their similarity in appearance to motes in a sunbeam led to calling them the "haemoconia" or "blood dust."[5] These terms are frequently used to-day.[6] At various stages in their history, the chylomicrons have also been called "elementary granules",[3] "a fine granular dust"[3] and, more correctly, "fat dust."[7]

Even during the past thirty-five years many ingenious and far-fetched explanations have been advanced for the presence of the chylomicrons in the blood, and it was not until the very modern work of Gage and his associates[8] that their true nature became generally known. Gage devised the name "chylomicron" and first applied it to the particles in 1920.[9]

The Question of the Relation of Chylomicron Counts to the Fat Contents of Blood Plasma and Serum

After a meal containing fats, the number of chylomicrons in the blood gradually increases to a maximum and then decreases to the fasting level, practically zero. Fig. 1 is reproduced from the paper of Gage and Fish. The left half represents the dark-field microscopic appearance of a blood drop taken just preceding a meal containing fats and the right half the appearance several hours after fat ingestion. One sees the various elements characteristic of the clotted blood-smear, and notes particularly the rise in number of chylomicrons after the meal. The bright points in the dark field give a very good idea of the appearance of the chylomicrons, but no static picture compares with the actual observation which discloses their rapid and brilliant Brownian motion.

Fig. 2 likewise taken from the paper of Gage and Fish illustrates their method of counting chylomicrons. It shows also a typical curve obtained when chylomicron counts on a series of blood drops are plotted against the lengths of time after a meal containing fats at which the respective drops were taken. It is impossible to count the number of rapidly moving particles in a whole microscopic field, but the number in a small division of a field may be

[4] Monthly Micr. J., 18, 78 (1877).

[5] Mueller: Centr. allgem. Path. und Path. Anat., 7, 529 (1896).

[6] Bayliss: "Principles of General Physiology," Longmans, Green and Company, New York, 375 (1927).

[7] Munk and Rosenstein: Arch. path. Anat. Physiol., 123, 239 (1891).

[8] Gage: The Cornell Veterinarian, 10, 154 (1920); Gage and Fish: J. Am. Vet. Med. Assoc., 53, 384 (1921); The Cornell Veterinarian, April (1921) p. 230; Am. J. Anatomy, 34, 1 (1924); Gage-Day: Am. J. Surg., 36, (4) 53 (1922).

[9] The Cornell Veterinarian, 10, 154 (1920).

readily observed. Small field divisions are obtained with a net-micrometer ocular. The observation of the number of chylomicrons in a sufficient number of small divisions in a sufficient number of fields with the establishment of an average number, gives a good relative measure of the number of chylomicrons in a given blood specimen.

The fluid in which the blood cells are contained is called the blood plasma. When blood clots, a jelly-like mass is formed which contains all the cellular elements and a minor portion of the salts and protein from the plasma. This mass contracts and expresses a fluid which is plasma minus the plasma constituents contained in the clot, and is called the blood serum. It has been

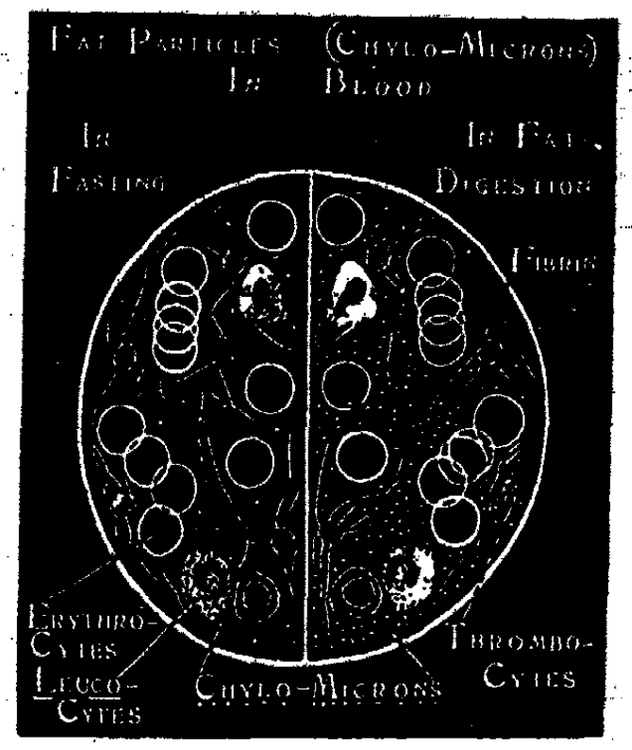

FIG. 1

Fresh blood under the high-power dark-field microscope. The left half after sixteen to twenty-four hours' fast. The right half three to four hours after a meal with plenty of fat. *Chylo-microns* or fat particles. They are numerous in the right half, and few in the left half. *Erythrocytes*, red blood corpuscles. *Fibrin*, the fine, cobweb like filaments present in coagulated blood. *Leucocytes*, or white blood corpuscles. *Thrombocytes*, or blood plates. (Fig. 1 and the accompanying legend are reproduced by permission, from the paper of Gage and Fish: Am. J. Anatomy, 34, 1 (1924).

the subject of a very large number of investigations because it is readily obtained, and because it bears a definite relation to the plasma of the living animal although differing somewhat from the latter in composition.

If a drop of serum from a blood containing a goodly number of chylomicrons is examined with the dark field microscope, it appears somewhat as shown in Fig. 3. As far as one can observe, the chylomicrons remain in full force in the serum. From the colloid chemical as well as from the biochemical point of view, it is of interest to inquire to what extent chylomicron counts parallel serum and plasma fat determinations. If all the fat in serum or plasma is in the form of chylomicrons of uniform size and, if accurate counts are possible, a chylomicron count could be used as an accurate determination of serum or plasma fat. If, on the other hand, all the serum or plasma fat is

in the form of chylomicrons which can be accurately counted and the results of chylomicron counts and fat determinations do not parallel each other, important evidence is furnished as to the variation in size of chylomicrons under different conditions.

Since the paper of Gage and Fish, several people have compared chylomicron counts and the corresponding serum or plasma fat determinations. The general conclusion is that, although a relation between the two is quite apparent, the counting of chylomicrons does not offer a means of determining serum and plasma fat contents with any accuracy. Although further work on this

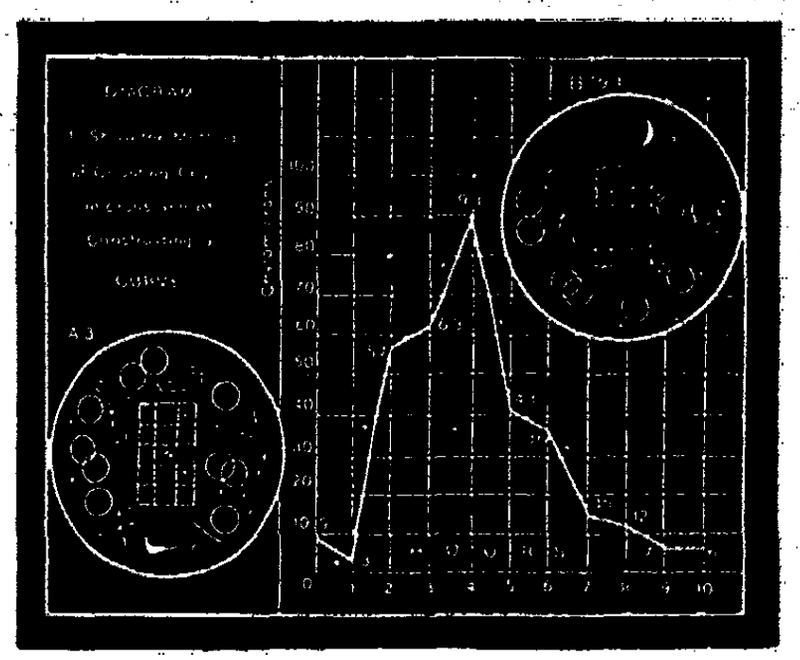

FIG. 2

Chylomicron curve and two microscopic fields to show how the data for the curve were obtained. At the lowest point of the curve there were but three chylomicrons in the net-micrometer, and at the peak of the curve, 91. The numerals along the curve show in the same way how many chylomicrons were in the net-micrometer at the different hours of the experiment. It will be noted that the number at the beginning was 9 and at the end of the first hour three. This means that the previous meal had not been completely assimilated when this experiment began. (Fig. 2 and the accompanying legend are reproduced by permission, from the paper of Gage and Fish: Am. J. Anatomy, 34, 1 (1924)).

point seems highly desirable, particularly on the basis of results obtained by the authors,[2] the foregoing general conclusion is entirely to be expected simply on the basis of observed variations in the size of the particles. Gage and Fish note that chylomicrons may vary at least three-fold in diameter which represents a twenty-seven fold variation in volume.

Gage and Fish further note a tendency toward increase in particle size at that time after a meal containing fat when the absorption is at its height. This latter observation may well explain the result of Knudson and Grigg[10] that, after a meal containing fat, the maximum chylomicron count precedes the maximum fat content by several hours. If we postulate that the chylomicrons gradually increase in size with the time of absorption to twice their original size, a count of half as many at the absorption maximum as at the

[10] Proc. Soc. Exptl. Biol. Med., 20, (8) 462 (1923).

chylomicron count maximum might well represent several times as much fat. The conclusion of Knudson and Grigg is confirmed by a comparison of the free-fat contents and chylomicron counts of the plasma of the normal dogs studied by Bloor, Gillette, and James.[11] It affords confirmatory evidence for the observation of Gage and Fish, that the size of the chylomicrons tends to increase with the time of fat absorption.

Regardless of its absolute accuracy as a method for serum and plasma fat determinations, there is no question but that the chylomicron count is sufficiently accurate to be a valuable adjunct to such determinations,[11] and affords an extremely useful method for the investigation of the absorption and assimilation of fat both in physiological and clinical studies.[3,12]

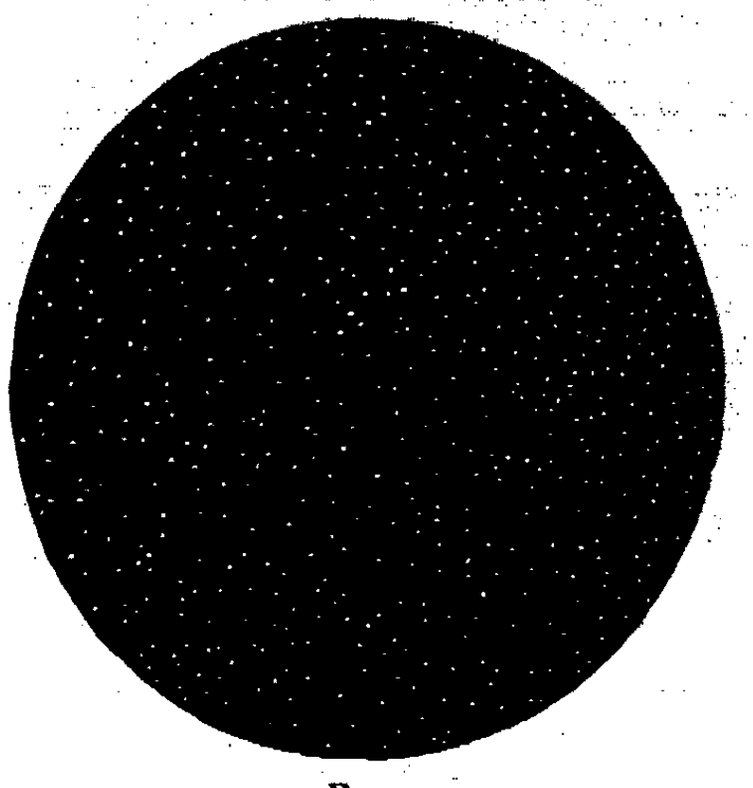

FIG. 3

A drawing to illustrate the dark-field microscopic appearance of blood serum containing chylomicrons. (Oil immersion objective.).

The Question of the Existence and Potential Importance of Surface Films on Chylomicrons

In a recent paper, the authors[12] discussed the dual colloidal aspect presented by human blood serum containing chylomicrons. It is not only a protein solution as ordinarily considered but also a lipoid emulsion and hence of exceptional interest from the two points of view.

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[11] J. Biol. Chem., 75, 61 (1927).

[12] Schilling: "The Blood Picture" (Translation by Gradwohl) The C. V. Mosby Co., St. Louis, 38 (1929); Hubbard: J. Biol. Chem., 55, 357 (1923); Schroeder and Holt: Am. J. Dis. Children, Feb., 1926, p. 201; MacArthur: J. Biol. Chem., 87, 299 (1930).

[13] Ludlum, Taft, and Nugent: Colloid Symposium Annual, 7, 233 (1929); See also Ludlum and Taft: Alexander's "Colloid Chemistry," The Chemical Catalog Co., Inc., New York, 2, 695 (1928).

So far as could be determined at that time, there was no record of any investigation directed toward the determination of the stability factors involved in the chylomicron emulsion and even no discussion of their possible nature and importance.

Oil-in-water emulsions which may be as concentrated as the chylomicron emulsion, always involve a third substance, the emulsifying agent which concentrates in the oil-water interface, forming a film around the dispersed oil droplets and preventing their coalescence.[14] Knowing the composition and size of the chylomicrons and the reason for their existence, the remaining all-important question from the emulsion point of view is that of the nature of their surface films.

On the physiological side these films determine the stability of the chylomicrons in the plasma and thus the very act of transportation by the blood. The physiology of the assimilation of food fat from the blood and its storage and final utilization is by no means an open book.[1] It is highly probable that the discovery of the nature of the surface films on the chylomicrons would be of importance in the future study of these problems. It seems quite likely that the chylomicrons may be taken up as such by cells. In this case their surface properties, that is the properties of the substance which forms their surface films, are all important.

It has been shown[15] that acid-fast bacteria, which have lipoid-like surfaces, are not readily taken up by phagocytic cells. However, when they are treated with the proper serum, a protein film forms around them, and they are then readily phagocytized. In other words, the cell material must wet the bacterium in order to enclose it; it is able to wet a protein surface but not a lipoid surface. By analogy, the whole process of the removal of food fat from the blood may depend upon the presence of protein films around the chylomicrons which may be wet by the material of the assimilating cells.

In storage tissues, fat is often found in droplets much larger than chylomicrons. Apparently the tissue cells bring about the coalescence of chylomicrons. To do this, they must act upon whatever films may be present around them. The final utilization of food fat must apparently also often involve the destruction of protective films around the chylomicrons, since such films must be removed before the chylomicron fat can be saponified or otherwise acted upon chemically. If the films consist of protein, there is a ready mechanism for their destruction in the action of proteolytic enzymes within the cell.

Furthermore as previously mentioned by the authors,[2] a knowledge of surface films on chylomicrons may be useful in the study of the serum diagnosis of syphilis. The precipitation tests appear to involve the addition of a suspension of lipoid droplets to blood serum.[16] If the serum is syphilitic, the

[14] Bancroft: "Applied Colloid Chemistry," McGraw-Hill Book Co. Inc., New York, 351 (1926).

[15] Mudd, Lucké, McCutcheon and Strumia: Colloid Symposium Monograph, 6, 131 (1928); J. Exptl. Med., 52, 313 (1930); Strumia, Mudd, S., Mudd, E. B. H., Lucké and McCutcheon: J. Exptl. Med., 52, 299 (1930).

[16] Kahn: Alexander's "Colloid Chemistry," 2, 757 (1928).

drops aggregate and if non-syphilitic, they remain dispersed. The aggregation or non-aggregation of the droplets presumably depends upon differences in the nature of the surface films which form around them in the two cases. The naturally occurring surface films on native lipoid droplets in the serum may well bear some relation to those which form around the droplets of so-called antigen suspension.

Thus it appeared that the study of the surface films on chylomicrons was by all means the next important step in the study of chylomicrons as abstract emulsion particles, and further might well be of value in special physiological and pathological studies. Because of these facts it seemed important to follow up preliminary results reported last year,[2] in order better to establish the existence of protective films around the chylomicrons and to learn more of their nature.

All the experiments have been done with chylomicrons in human blood serum. In view of the results obtained, it is believed that the extension to human plasma and to the serum and plasma of animals should be a relatively simpler matter. Blood was taken in Keidel tubes, allowed to clot, and then centrifuged to separate the clot and the serum. The serum was either removed with a syringe for immediate use or with a second Keidel tube for storage in the ice chest.

The Isoelectric Point of the Chylomicrons determined by a Maximum Flocculation Method

When an emulsion particle is coated with a film of protective agent its surface properties should presumably be those of the film-forming substance. An interesting case demonstrating this to be a fact is that of lecithin sols.[17] The pure sols show a maximum flocculation tendency at pH 2.3. If a little albumin is added to the solution, this value changes to pH 4.7, the isoelectric point of albumin; and, if globulin is added instead of albumin, it changes to pH 5.3, close to the isoelectric point of globulin. The protein in each case forms a film over the lecithin surface of the particles.

This case not only illustrates the point but is peculiarly applicable to the chylomicron problem. An examination of the composition of human serum[18] indicates that the two major constituents well known as protective agents in oil-in-water emulsions[19] are lecithin and protein. It would appear from the foregoing paragraph that, even though lecithin tended to concentrate in the chylomicron-plasma interface, protein would in turn concentrate in the resulting lecithin-plasma interface and the surface properties of the chylomicrons would be those of protein.

The obvious thing to do was to attempt to determine the isoelectric point of the chylomicrons to see whether it occurred in the region pH 4.7 – 5.4,

[17] Höber: "Physikalische Chemie der Zelle und der Gewebe," Wilhelm Engelmann, Leipzig, 752 (1926).

[18] Gram: Am. J. Med. Sci., 168, 511 (1924).

[19] Seifriz: Am. J. Physiol., 66, 124 (1923).

characteristic of the serum proteins or, for example, in the region pH 2.0 — 3.0, characteristic of lecithin. The first attempt was by means of a maximum flocculation method.

The pH of serum is about 7.4. As a preliminary experiment equal volumes of different strengths of hydrochloric acid from N/16000 to 4 N were mixed with sera containing chylomicrons on a microscope slide. It is important that not more than an equal volume of acid be added, because greater dilution than this may lead to the precipitation of globulin in the isoelectric region. Each preparation was then covered with a cover glass which was sealed with vaseline or paraffin. After a definite time interval, examination was made for signs of flocculation of the chylomicrons using the dark-field microscope with an oil immersion objective. In this way it was determined that there was indeed a definite maximum flocculation zone corresponding to mixtures of sera with acid strengths of the order of thirtieth normal. As implied, in mixtures with somewhat stronger hydrochloric acids the chylomicrons remained dispersed. This qualitative observation of a maximum flocculation zone was made on a large number of sera.

The next question was as to the pH of the maximum flocculation mixtures. Equal volumes of sera and the acids which gave a maximum flocculation mixture were mixed in small test tubes and the pH of each resulting mixture determined electrometrically. Fifteen such determinations gave values ranging from about pH 4.0 to 6.0 with an average pH of 5.1. The pH of the maximum flocculation of the chylomicrons was thus in the range of those of particles coated with protein films rather than of particles with lecithin surfaces.

Serum protein consists very largely of serum albumin whose isoelectric point is at pH 4.7[20] and serum globulin whose isoelectric point is at pH 5.4.[21] The average isoelectric point as determined above lies between these two values, but the fact could not be considered significant because of the wide variation of the values from this mean. Obviously a more accurate method was needed to definitely establish the isoelectric point to be in the protein range.

If this could be found, the possibility existed that a sufficiently definite value might give information as to the particular protein or proteins forming the protective films. Thus an isoelectric point very close to pH 4.7 would afford strong indication that the chylomicrons were coated with films of serum albumin. Likewise an isoelectric point very close to pH 5.4 would point to serum globulin as the important constituent. Any intermediate value would be open to interpretation as due to films of mixed albumin and globulin and, finally, values higher than pH 5.4 or lower than pH 4.7 would quite definitely indicate the presence of a third constituent.

It was decided to add N/10 hydrochloric acid gradually to about 2 cc. of serum into which dipped a Hildebrand hydrogen electrode and the salt bridge

[20] Michaelis and Davidsohn: Biochem. Z., 33, 456 (1911); See Mudd: J. Gen. Physiol., 7, 389 (1924-25) for a valuable table of isoelectric points.
[21] Rona and Michaelis: Biochem Z., 28, 193 (1910).

connection from a saturated calomel electrode for the electrometric determination of the pH at each state of the titration. A Leeds and Northrup type K potentiometer was employed and the electrodes were platinized according to the method of Popoff, Kunz, and Snow.[29] To test the technique of electrode preparation and the entire potential measurement system, three electrodes were prepared and used to measure the pH of N/10 hydrochloric acid; 1.037 being taken as the correct value. The three electrodes checked each other to within a fifth of a millivolt and the accepted value for the pH of the solution to within 0.01 pH.

After each addition of the acid the system was allowed to come to equilibrium and the pH read. A drop of the mixture was then examined with the dark-field microscope for signs of flocculation of the chylomicrons.

Ordinarily in making determinations of the pH of maximum flocculation, the disperse material is suspended in a series of buffer solutions. After a definite time, the degree of flocculation in each solution is determined by macroscopic observation. A separate portion of the suspension to be examined is required for each pH value. The method described above has the advantage,

TABLE I

The Flocculation of Lecithin Sols on Gradual Acidification with N/10 Hydrochloric Acid

Sol	pH	Flocculation
One per cent lecithin in distilled water.	5.60	—
	5.35	—
	4.80	—
	3.90	—
	2.70	++
	2.30	+++++
One per cent lecithin in Ringer's solution.	8.20	—
	6.90	—
	6.30	—
	5.40	—
	4.75	—
	3.50	+
	2.60	+++++
One per cent lecithin in five per cent egg albumin solution.	8.70	—
	7.06	—
	6.52	—
	6.02	+
	5.50	+
	5.17	+
	4.80	+++
	4.50	+++++

[29] J. Phys. Chem., 32, 1056 (1928).

when working with a limited supply of material, that one sample is used successively at different pH values. It further rules out any possible effects of foreign buffer salts, and the microscopic feature allows the observation of flocculation conditions which would not be macroscopically visible. It has the disadvantage that there is danger of "lag" in going from one pH value to another, which becomes a certainty in case irreversible transformations occur.

It was decided to try some preliminary experiments with lecithin sols. One per cent sols were prepared, according to the method of Porges and Neubauer,[23] in distilled water, Ringer's solution, and five per cent egg albumin solution. If a flocculation were obtained only at pH 2.0–3.0 in the case of the protein-free sols and close to pH 4.7 in the case of the sol containing albumin, the experiments would not only be an interesting example of the applicability of the titration method, but also confirm the results reported in the literature as to the formation of protein films on lecithin surfaces.[17] Furthermore it was of interest to know what effect the salts of Ringer's solution might have upon the pH of maximum flocculation of lecithin sols, since the value pH 2.3 was reported for a fairly pure sol. The results are shown in the foregoing table.

The results in Table I indicate the usefulness of the method and confirm the shift of the flocculation zone from pH 2.0 – 3.0 to the isoelectric region of albumin when the protein is added to the solution, indicating that a protein film has formed around each lecithin particle. They further show that, so far as the purposes of the present investigation are concerned, the salts of Ringer's solution have a negligible effect upon the pH flocculation of lecithin sols.

Two runs were next made with sera containing chylomicrons with results, as in the case of the lecithin experiments based simply upon a general observation of the relative number of aggregates and of single particles in each preparation. To eliminate the possibility of error due to "lag" in redispersion the first serum was gradually acidified and the second immediately taken to, pH 4.05 with a drop of stronger acid, and then titrated back with tenth normal sodium hydroxide solution. The results are shown in Table II.

TABLE II

The Flocculation of Chylomicrons at Different pH Values

Serum Number 1		Serum Number 2	
pH	Flocculation	pH	Flocculation
7.25	–	7.25	–
6.70	–	4.05	–
5.90	+	4.50	–
5.40	+++	4.60	+
5.22	+++	4.70	+
4.90	+++++	4.85	+++
4.65	++++	5.04	+++++
4.40	+++	5.24	++++
3.62	+	5.66	+++
		6.20	+

[23] Biochem. Z., 7, 152 (1907-08).

The first run indicates a maximum flocculation between pH 5.22 and 4.65, and the second between pH 5.24 and 4.85, both lying very definitely between the isoelectric points of the two serum proteins.

It was highly desirable to check the results of Table II by some quantitative method. It seemed best to use particle counts as a measure of the degree of flocculation in any preparation. The chylomicrons and their aggregates were the only visible particles. Obviously the greater the aggregation of the chylomicrons in any case, the smaller the relative particle count. The counts were made in a similar manner to the chylomicron counts of Gage and Fish[3] which have been previously described. Two further sera were run on this basis using a slightly different procedure with regard to the time factor in the two cases. In the first, after each regulated addition of acid and attainment of a constant pH value, the serum was allowed to stand for one half hour before the drop was removed for immediate examination. In the second, the drops were removed immediately after attainment of a constant pH value, but were then allowed to stand over night under sealed coverslips before counting. The results are shown in Table III.

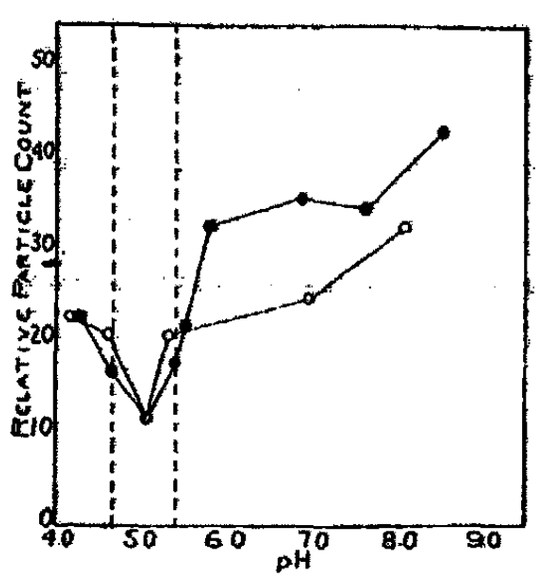

FIG. 4
Particle counts plotted against pH values in the determination of the maximum flocculation of chylomicrons.

TABLE III

Quantitative Data on the Flocculation of Chylomicrons at Different pH Values

Serum Number 3		Serum Number 4	
pH	Relative Particle Count	pH	Relative Particle Count
8.50	43	8.05	33
7.60	35	6.93	25
6.85	36	5.30	21
5.80	33	5.07	12
5.51	22	4.62	21
5.40	18	4.16	23
5.08	12		
4.66	17		
4.28	23		

The results of Table III are plotted in Fig. 4, where the ordinates are relative particle counts and the abcissas are pH values. The points for serum number three are shown as dots and those for serum number four as circles. Both runs clearly indicate a maximum flocculation zone at pH values between those of the isoelectric points of serum albumin and serum globulin, which fact in turn indicates that the isoelectric point of the chylomicrons lies within this range.

The Isoelectric Point of the Chylomicrons determined by a Cataphoretic Method

There is every reason to believe that the pH of maximum flocculation of chylomicrons is also that of their isoelectric point. It seemed necessary however to check this fact by demonstrating that the sign of their surface charge reversed approximately in this pH range. If their isoelectric point in serum lies between those of serum albumin and serum globulin, they should be positively charged at pH 4.7 and negatively charged at pH 5.4. It is apparent that checking this point amounts to a second determination of their isoelectric point. Fortunately a well-known method and standard apparatus are available which may be applied to the determination of the isoelectric point of chylomicrons by a cataphoretic method.

Portions of serum containing chylomicrons were diluted fifty times with a series of fifth molal sodium acetate-acetic acid buffer solutions covering the range from pH 4.4 to 5.6 at 0.2 pH intervals. The direction of migration of the chylomicrons in each buffer mixture was observed in a Northrop-Kunitz[24] microcataphoresis cell with arrangement of accessory apparatus according to Mudd.[25] Observations were made at the levels where electrical endosmotic effects are theoretically negligible.[26] The object in each determination was to find two successive buffer mixtures between which reversal of the sign of charge of the chylomicrons took place.

Preliminary experiments were run using the lecithin emulsions in Ringer's solution and five per cent egg albumin solution in place of serum. The results of these are shown in Table IV.

TABLE IV

The Direction of Migration of Lecithin Emulsion Particles in Buffer Solutions

Buffer pH	Particles from 1 per cent lecithin emulsion in Ringer's solution	Particles from 1 per cent lecithin emulsion in 5 per cent egg albumin solution
5.0	To anode	To anode
4.8	To anode	To anode
4.6	To anode	Practically motionless
4.4	To anode	To cathode

At pH 4.4 the emulsion particles from Ringer's solution were still strongly negatively charged, while those from the five per cent albumin solution had reversed sign at approximately pH 4.6, and were definitely positively charged at pH 4.4. These results are obviously in agreement with the flocculation results obtained with lecithin sols.

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[24] Colloid Symposium Monograph, 6, 134 (Footnote) (1928).

[25] The cell with accessory apparatus may be obtained from the Arthur H. Thomas Company, Philadelphia.

[26] Von Schmoluchowski in Graetz: "Handbuch der Elektrizität und des Magnetismus," 2, 366 (1921).

Four determinations were next made on three sera with the results as shown in Table V.*

TABLE V

The Direction of Cataphoretic Migration of Chylomicrons in Buffer Solutions

Buffer pH	Serum A	Serum A'	Serum B	Serum C
6.0	To anode	To anode	To anode	To anode
5.0	To anode	To anode	To anode	To anode
5.6	To anode	To anode	To anode	To anode
5.4	To anode	To anode	To anode	To anode
5.2	To anode	To anode	To anode	To anode
5.0	To anode	To anode	To cathode	To anode
4.8	To cathode	To cathode	To cathode	To cathode
4.6	To cathode	To cathode	To cathode	To cathode
4.4	To cathode	To cathode	To cathode	To cathode

In three cases the isoelectric point of the chylomicrons was shown to lie between pH 4.8 and 5.0 and in the fourth between pH 5.0 and 5.2. They are all in striking agreement with those obtained by the maximum flocculation method, and establish the conclusion that the isoelectric point of the chylomicrons in human serum lies between the accepted isoelectric points of serum albumin and serum globulin in the seven cases studied.

There is thus no question but that the isoelectric point of the chylomicrons in human serum lies in the range of those of the serum proteins. Isoelectric-point evidence is probably the strongest which can be brought to prove the presence of protein films on chylomicrons. A possibly correct, and at least an interesting interpretation of the position of the isoelectric point between those of the serum proteins, is that the protein films consist of a mixture of serum albumin and serum globulin.

According to Mudd,[27] acetate buffers have little effect in shifting the pH of the isoelectric point of protein surfaces. The agreement of the values obtained for the isoelectric point of the chylomicrons determined by the maximum flocculation method involving no addition of buffer salts and by the cataphoretic method involving the suspension of the chylomicrons in acetate buffer solutions is interesting as in agreement with this point of view.

The Destruction of the Surface Films on Chylomicrons

Since the chylomicrons are emulsified droplets of fat it should be possible to cause them to coalesce to form larger drops. It will be remembered that this is apparently what may happen in tissues which store fat. Analogous experiments with chylomicrons in serum would be interesting from this point of view.

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* Determinations have since been made with chylomicrons from three more sera. The reversal point was between pH 4.8 and pH 5.0 in each of these cases.

[27] J. Gen. Physiol., 9, 73 (1925-26).

Furthermore, if the chylomicrons are surrounded by protein films, we should expect that reagents which precipitate protein or otherwise alter its properties would be effective in causing such coalescence. If they are, we have independent evidence of the existence of protein films.

It is apparently quite generally agreed that the fat drops in milk are surrounded by protein films which recent work indicates may consist of casein.[28] It has been known for a long time that it is quite difficult to extract milk fat with ether until acid, alkali, or rennet has been added, presumably to destroy these films.[28] According to Bancroft,[14] protective films of a substance may not form under conditions which cause the salting out of that substance. Presumably if present they would become dehydrated and brittle, and proceed to crack with coalescence of the emulsion droplets.

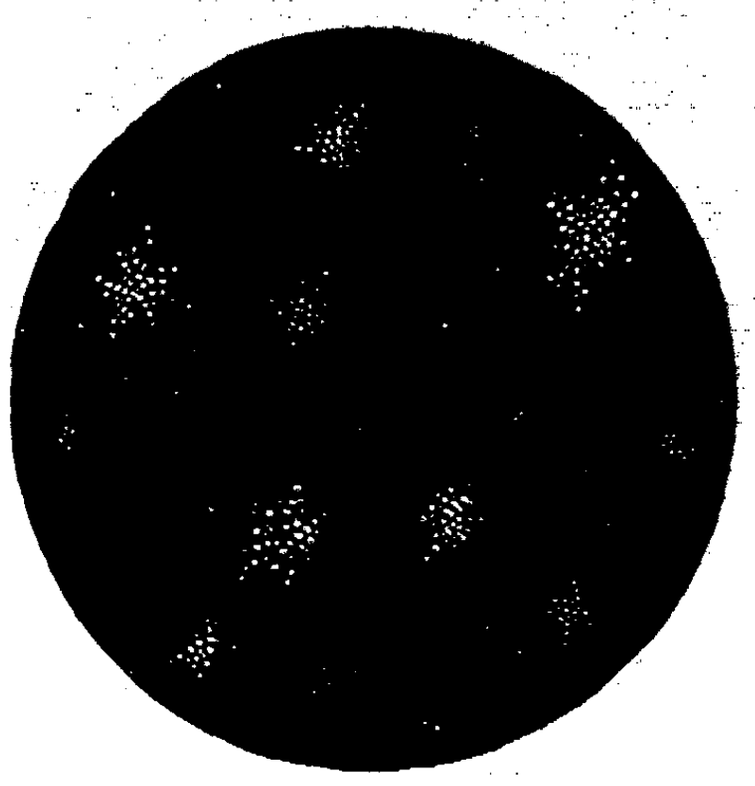

FIG. 5
A drawing to illustrate the mode of aggregation of chylomicrons at their isoelectric point.

The first experiments in connection with the isoelectric flocculation of the chylomicrons lead to evidence on this point. The isoelectric flocculation occurred when equal volumes of serum were added to about N/30 hydrochloric acid. With strengths from N/30 to about N/8 acid, the chylomicrons were dispersed as positively charged particles. In all cases with 2 N acid, copious precipitation of protein occurred presumably due to a "salting-out" action of the concentrated acid.

With strengths between N/8 and 2 N acids, an interesting phenomenon was noted, best observed after the sealed preparations had stood for at least an hour. A combined coalescence and aggregation of the chylomicrons apparently occurred. A good impressionistic idea of the difference in appearance between the isoelectric aggregates and these coalesced aggregates is given by

[28] Titus, Sommer and Hart: J. Biol. Chem., 76, 237 (1928).

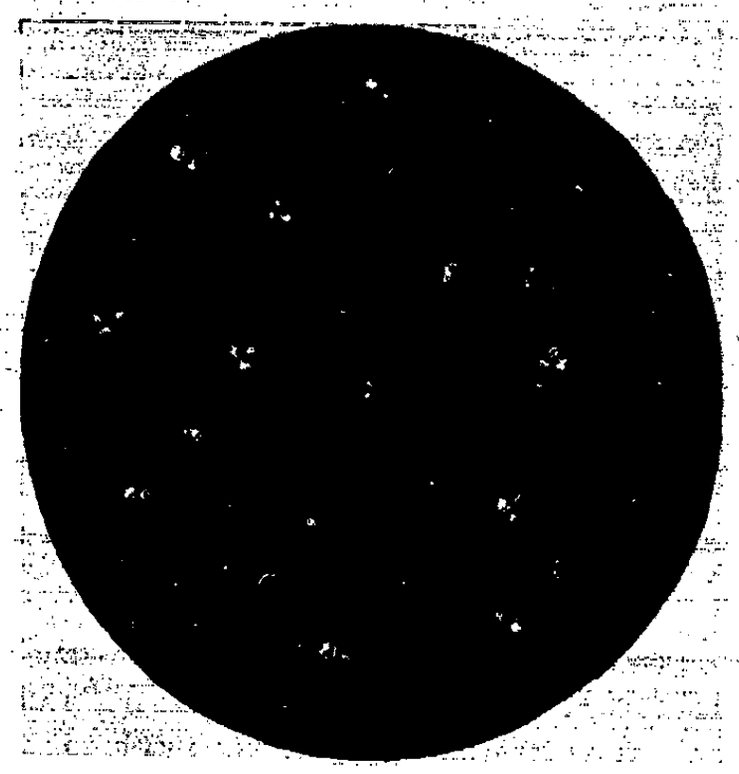

FIG. 6

A drawing to illustrate the aggregation and coalescence of chylomicrons on partial destruction of their protein films.

FIG. 7

A photomicrograph showing fat drops which resulted from the coalescence of chylomicrons on treatment of blood serum with an equal volume of normal hydrochloric acid. (Dark-field microscope with oil immersion objective.).

the accompanying drawings. Figure 5 represents isoelectric aggregation and Fig. 6 aggregation with coalescence. They are by no means accurate pictures of the two, but convey the idea of the difference between them better than photomicrographs which have been secured up to the present time.

Large lipoid-looking drops frequently accompanied the coalesced aggregates and there was a decided tendency for them to appear when the preparations stood overnight. The combined coalescence and aggregation always occurred with acids just insufficiently strong to cause protein precipitation. The appearance of large lipoid droplets frequently occurred, but did not always do so.

The interpretation given to the phenomenon was the one just suggested, that the protein films around the chylomicrons had been dehydrated with resulting aggregation of the chylomicrons accompanied by more or less coalescence due to the cracking of the brittle dehydrated films.

If this were the correct interpretation of the phenomenon, it was thought that other substances which precipitate protein should bring about the same result. It was decided to test the hypothesis along these lines. Accordingly equal volumes of serum containing chylomicrons were mixed on microscope slides with different dilutions of 95 per cent alcohol and saturated ammonium sulfate. The mixtures were then covered with cover glasses which were sealed with paraffin. An exceptional procedure was necessary in the case of pure 95 per cent alcohol where two to three volumes to one of serum were required to cause the precipitation of protein. In the case of ammonium sulfate one drop of saturated solution to one of serum brought this about. The preparations were examined in the usual manner using a dark-field microscope with an oil immersion objective.

With strengths of each just insufficient to cause protein precipitation, the same type of aggregation with coalescence was observed as with the corresponding strengths of acid. The coalescence to large lipoid drops did not always occur with ammonium sulfate, although it was definitely observed several times. A beautiful regularly occurring coalescence was, however, observed with alcohol, as described in the following paragraph.

When actual protein precipitation occurred with alcohol, definite small lipoid drops begin to appear floating about among the protein masses very shortly after mixing the serum and alcohol. They gradually increase in size with disappearance of any visible coalesced aggregates. The total volume of droplets was roughly of the order of volume of the free-fat content of a drop of serum. In common with the drops in the other preparations, they were shown to have a higher refractive index than the surrounding medium[29] and thus to be lipoidal by process of elimination.

It has been remarked that the addition of alkali to milk is said to aid the extraction of milk fat with ether, presumably because alkali in proper concentration, destroys the protein films around the fat droplets. Serum containing

[29] Chamot: "Elementary Chemical Microscopy," John Wiley and Sons, Inc., New York, 230 (1921).

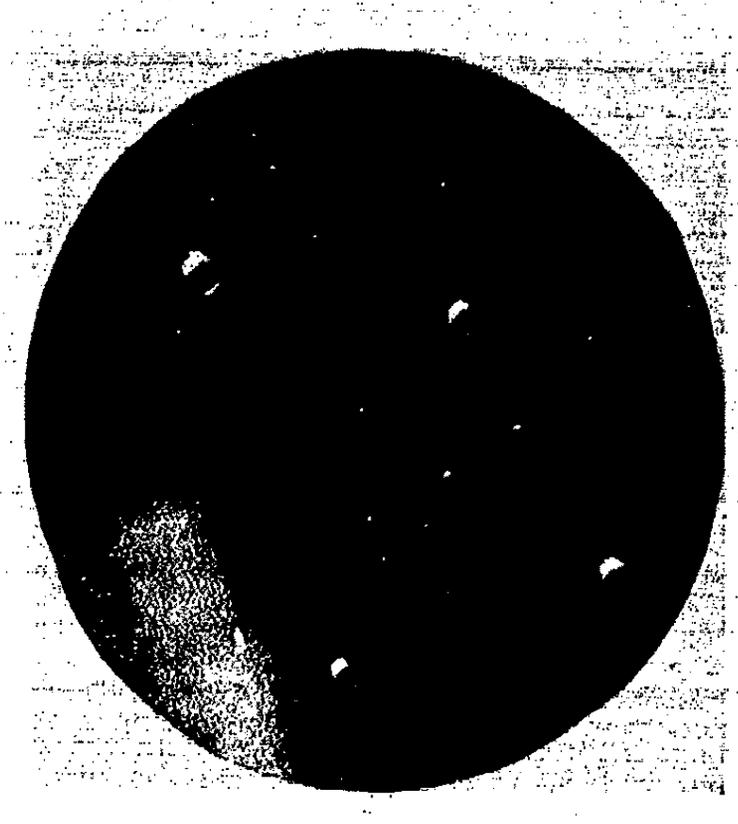

FIG. 8

A photomicrograph showing fat drops which resulted from the coalescence of chylomicrons on treatment of blood serum with an equal volume of sodium hydroxide solution of strength > one per cent. (Dark-field microscope with oil immersion objective.).

FIG. 9

A photomicrograph showing precipitated protein and fat drops (one in center of picture) which resulted from the coalescence of chylomicrons on treatment of blood serum with two to three volumes of 95 per cent alcohol. (Dark-field microscope with 8 mm objective.)

chylomicrons was accordingly mixed with equal volumes of different strengths of sodium hydroxide solution. With one per cent and more concentrated solution, the formation of coalesced aggregations occurred as regularly as clockwork. Large lipoid drops frequently formed on standing.

Figures 7, 8, and 9 are photomicrographs of fat drops caused by the coalescence of chylomicrons due to the action respectively of normal hydrochloric acid, strong sodium hydroxide solution, and 95 per cent alcohol. In the latter, two small drops are seen in the midst of large masses of precipitated protein. The average diameter of all drops shown was about 4μ.

The behavior of chylomicrons when a protein precipitant or alkali is added to serum is thus in accord with the view that they are normally surrounded by protein films. The experiments afford a picture of the probable coalescence of chylomicrons when large fat globules are formed in storage tissues. In this case the protein films would presumably be destroyed by a proteolytic enzyme.

The Application of the Mudd Interface Technique in Chylomicron Study

The interface technique of Mudd and Mudd[30] has given to workers in pure and applied colloid chemistry a most useful research method and to teachers of the subject a splendid method of demonstration. With such a technique available for the investigation of surface properties the authors could not feel satisfied until an attempt had been made to apply it in the present problem.

As ordinarily employed, a drop of solution containing the particles to be investigated is placed on a microscope slide with a drop of a suitable oil. A coverglass is placed over the two in such a manner that the oil spreads under the glass driving the water phase before it. The slowly advancing oil-water interface, appearing as a bright line, is followed by observation with the dark-field microscope.

The behavior of particles or groups of particles when struck by the interface yields most interesting and important information as to the nature of their surfaces and often as to their consistency, structure, and mode of aggregation.[31] Non-acid-fast bacteria are not readily wet by oil and resist passage into the advancing oil phase. Acid-fast bacteria, on the other hand, have lipoid-like surfaces. They are readily wet by the oil, and consequently readily pass into it. Clumps of bacteria may be entirely dispersed by the interfacial forces.

To the time of writing it has only been possible to examine the behavior of isoelectric aggregations of chylomicrons when struck by an advancing film of triolein. These clumps were formed in the usual manner and the serum containing them then diluted from one to fifty times with a pH 5.0 acetate buffer solution. Generally the whole aggregate seemed to "explode" into the oil, that is, the advancing phase simply dissolved the constituent chylomicrons. Occasionally the clumps were dispersed into constituent smaller

[30] J. Exptl. Med., 40, 633, 647 (1924).

[31] Seifriz: Alexander's "Colloid Chemistry," 2, 437 (1928).

clumps or single chylomicrons and spread along the interface, either traveling along it until out of the field of view or "exploding" individually into the oil.

In the first place the "explosion" of the chylomicrons into the oil affords a beautiful visual demonstration of their fatty constitution. The dispersion of aggregates is a most interesting structural phenomenon. The temporary stability of single particles in the interface, observed in some cases, indicates the presence of protective films which are, or course, here also indicated by the fact that the original clumped particles do not coalesce to form one large drop.

The "explosion" of the majority of the isoelectric aggregates immediately upon being touched by the oil might appear to be evidence against the existence of protein films in those cases. However, milk-fat drops which are known to be surrounded by protein films, are also known to show somewhat similar behavior.[32] The authors diluted cream with 200 volumes of pH 4.6 acetate buffer solution to bring the fat droplets to the isoelectric point[33] of their "casein" films. Drops of the mixture were then examined with the interface reaction. In all observed cases the fat drops "exploded" immediately upon being struck by the interface. It would appear that the interfacial forces are sufficient to destroy films of isoelectric protein on fat drops. It may therefore be said that results obtained to date in the application of the Mudd interface technique to the study of chylomircons are entirely in accord with the view that the chylomicrons are surrounded by protein films.

The foregoing results together with certain observations of Mudd and Mudd[34] on the action of the interface on single particles in blood and serum indicate that the application of the interface technique in chylomicron study should be continued.

Summary

The blood transports food fat as an emulsion of minute droplets called chylomicrons.

As emulsion particles the chylomicrons should presumably be surrounded by protective surface films. Preliminary considerations show the examinaton of these films to be the next logical step in the study of the chylomicron emulsion, and of probable importance in special physiological and pathological problems.

Consideration of the nature of the chylomicrons and the composition of blood serum strongly suggests that the films around the chylomicrons consist of protein.

The pH of the isoelectric point of the chylomicrons in human serum has been determined both by a maximum flocculation and a cataphoretic method. In all cases the value lay between pH 4.6 and 5.4, and definitely between the

[32] A personal communication from Dr. Stuart Mudd. The authors take this opportunity to express their appreciation of Dr. Mudd's interest in this problem and for advice which he has given in connection with the cataphoresis and the interface-technique experiments.

[33] Michaelis and Pechstein: Biochem Z., 47, 260 (1912).

[34] J. Exptl. Med., 43, 127 (1926).

accepted values for the isoelectric points of serum albumin and serum globulin. The more exact cataphoretic method indicates that the isoelectric point lies between pH 4.8 and pH 5.0. In this connection it is most interesting and significant that Abramson[35] has recently shown that quartz particles and paraffin oil droplets both have isoelectric points between pH 4.7 and pH 4.8 in 1150 serum dilutions, very close to the above values for the chylomicrons, as would be expected.

The fact that the isoelectric point of the chylomicrons is thus definitely within the range of the isoelectric points of the proteins, is probably the best evidence that can be brought to prove the hypothesis that they are surrounded by protein films.[17,36]

The position of the isoelectric point between those of the principal serum proteins leads to the interesting hypothesis that the surface films may be composed of mixed serum albumin and serum globulin.

In checking the values reported here and in extending the results to human plasma and to the plasma and serum of animals, the cataphoretic method is strongly recommended. The results are more exact and clearcut, than is the case with the maximum flocculation method, and the technique is less complicated and requires much less time and effort. The isoelectric precipitation of globulin sometimes interferes with the maximum flocculation method, presumably when the serum is too much diluted with acid.

The isoelectric point results lead to the hypothesis that protein precipitants and alkali, which would be expected to dehydrate or otherwise destroy protein films, should cause aggregation and coalescence of chylomicrons. Experiments with strong acid, alkali, 95 per cent alcohol and ammonium sulfate have confirmed this hypothesis and thus afford important independent evidence of the existence of protein films on chylomicrons.

Results obtained to date in the application of the Mudd interface technique to the study of chylomicrons are in accord with the view that the chylomicrons are lipoid droplets surrounded by protein films.

The general conclusion is that the chylomicrons are surrounded by protein films. This fact is of the utmost importance in the act of transport of food fat by the blood. It is further of possibly great importance in the assimilation of fat from the blood and its storage and final utilization. Finally, any knowledge of the surface films on these naturally occurring lipoid droplets in blood serum may be of value in clinical procedures such as precipitation tests for syphilis, in which suspensions of foreign lipoid droplets are added to it.

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Gladwyne, Pennsylvania, and
The Department of Industrial Research,
University of Pennsylvania,
Philadelphia, Pennsylvania.

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[35] Abramson: J. Gen. Physiol., 13, 177 (1929).

[36] In this connection see Abramson: Colloid Symposium Monograph, 6, 115 (1928); J. Gen. Physiol., 13, 169 (1929); Clayton, "Theory of Emulsions," P. Blakiston's Son and Co., Philadelphia, 88 (1928).

THE INFLUENCE OF SIZE, SHAPE, AND CONDUCTIVITY ON CATAPHORETIC MOBILITY, AND ITS BIOLOGICAL SIGNIFICANCE. A REVIEW

BY HAROLD A. ABRAMSON

I. The Cataphoresis of Sub-microscopic and Microscopic Particles

Introduction. The characterization of the surfaces of microscopically visible particles by means of electrical mobility measurements is achieving more importance with the development of methods designed to measure accurately cataphoretic mobilities and streaming potentials. Thus the

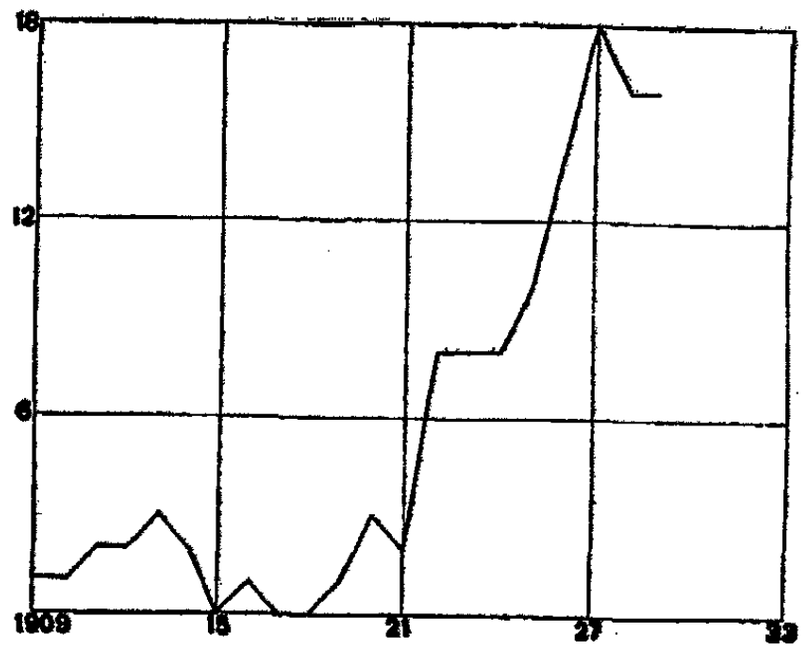


FIG. 1

The abscissa is marked off in years from 1909 to 1930. The ordinate values are the number of the references given under the heading *cataphoresis* in the yearly index of Chemical Abstracts during this period. This chart indicates the general increase in the number of investigations dealing with electrokinetic phenomena.

electrokinetic properties of cellulose particles, latex particles, oil droplets, blood cells, bacteria, inert surfaces covered more or less completely with proteins, protein particles, particles of clay and of fine metal wires have been of particular interest to the physicist, the chemist, and the biologist (Fig. 1). Indeed, the general chemical composition of the surfaces of particles suspended in liquids can be approached most satisfactorily by the study of electrokinetic phenomena.

Before satisfactory conclusions can be drawn, however, regarding the chemical composition of the surfaces of microscopic particles suspended in liquids, the influence of the size, shape, and conductivity of the particle on electrical mobility must be ascertained. It is the purpose of this communica-

tion to review data relative to these questions which the author has obtained or considered since the Symposium of 1928. Certain problems then presented are here brought to a more satisfactory solution.[1]

Theoretical. According to the theory developed first by von Helmholtz and subsequently extended by Lamb, Perrin, Pellat, and von Smoluchowski,

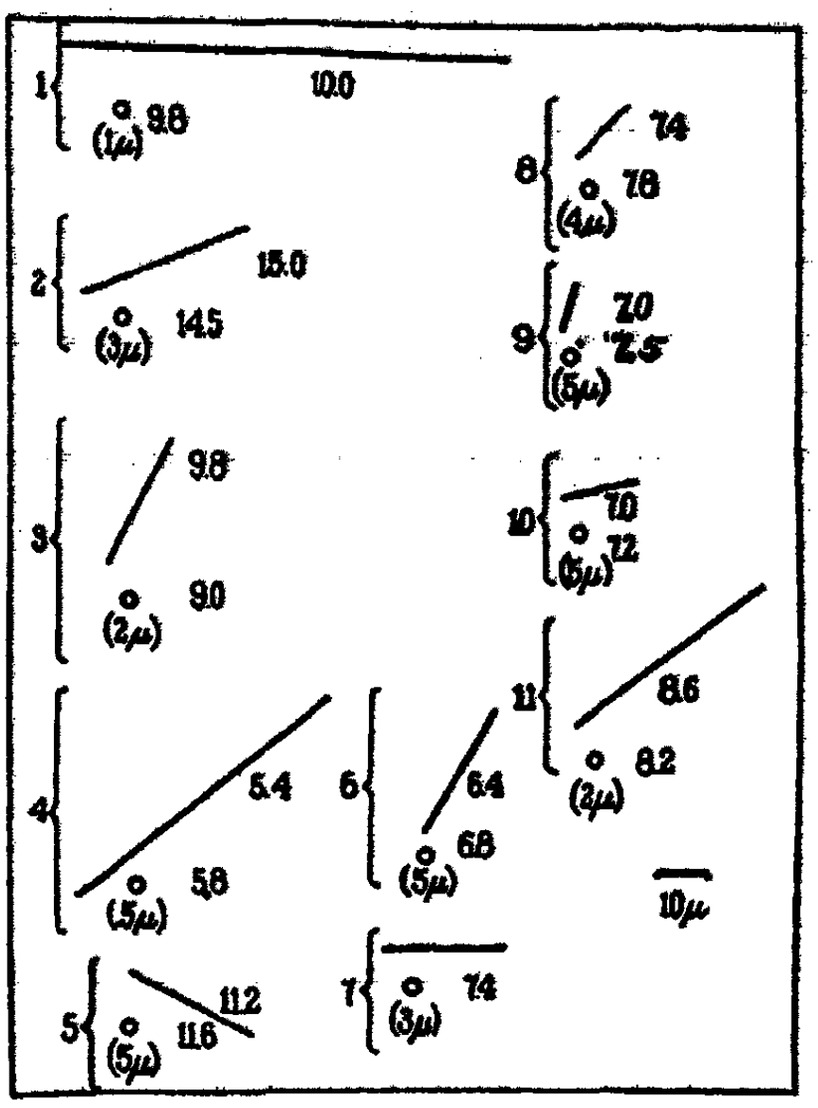


FIG. 2

The brackets indicate needles and globules studied in pairs. Nos. 1-3 are m-aminobenzoic acid crystals and mastic globules covered with gelatin. Nos. 4-10 are asbestos needles and paraffin oil globules covered with egg albumin. No. 11 is a m-aminobenzoic acid crystal and a paraffin oil globule covered with gelatin. The oil globule and mastic particles are all drawn the same size but their diameters are given in parentheses near the particle. The needles were drawn to the scale in the lower right hand corner. Each pair was studied at the same level in the cell. The numbers following each particle are the relative speeds. It is evident that when particles which vary as widely as these in size and shape have similar protein surfaces, there is no difference in cataphoretic velocity. (From the Journal of General Physiology).

the equation for V_p, the cataphoretic velocity of a particle relative to a given medium is

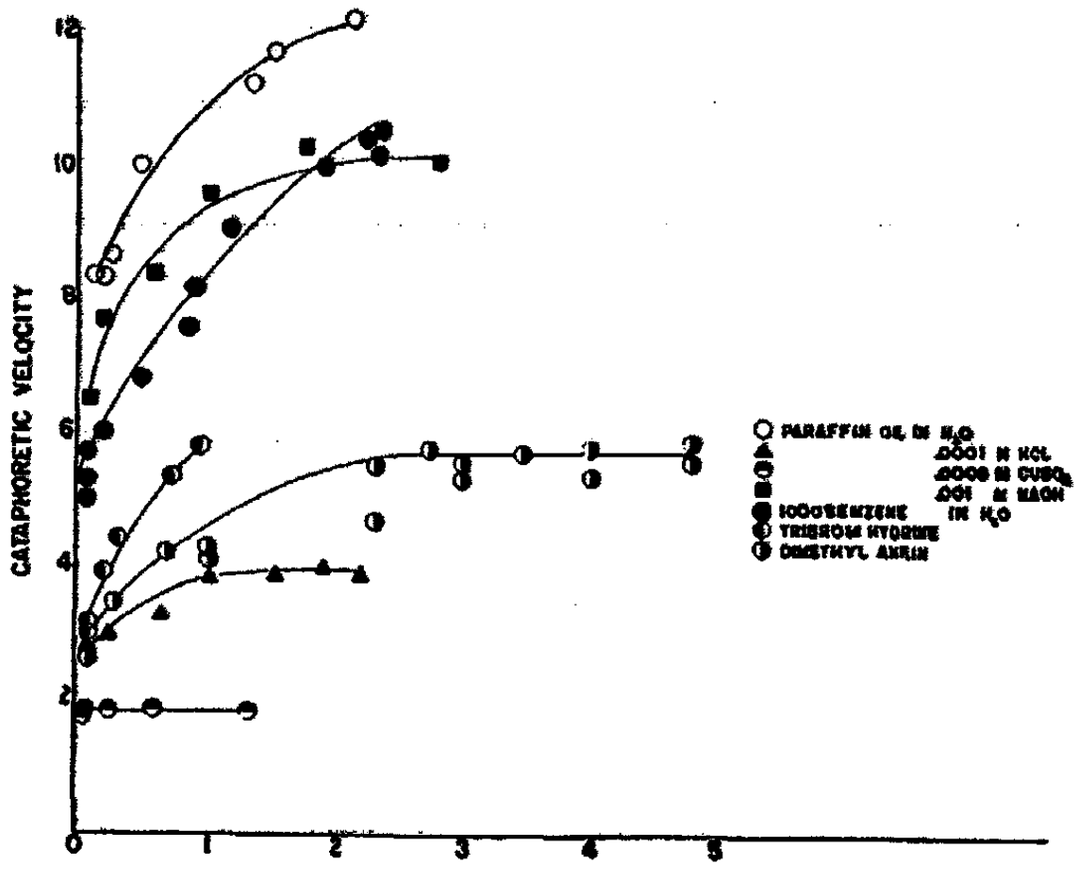
$$V_p = 1/4\pi \frac{XD\zeta}{\eta} = C\frac{XD\zeta}{\eta} \qquad (1)$$

(X = field strength; D = dielectric constant of the medium; ζ = electrokinetic potential; η = viscosity of the medium; all units c.g.s. electrostatic.)

[1] Abramson: Colloid Symposium Monograph, 6, 115 (1928).

Equation (1) predicts that: (a) cataphoretic mobility should be independent of the size and shape of the particle, and (b) for similar surfaces (ion atmospheres), V_E, the electroendosmotic velocity of a liquid past the flat surface, should be equal to V_p, the velocity of the particle relative to the liquid.

Debye and Hückel,[2] on the other hand, have maintained on theoretical grounds that the constant, $1/4\pi$, in equation (1) was valid only for the cataphoresis of cylindrical particles. For spherical particles the factor $1/6\pi$ was substituted. In other words, according to this theory, the constant, C, in equation (1) is dependent upon the shape of the particle.



DIAMETER OF DROPLET x $\frac{1}{605}$ AL

FIG. 3

Data of Mooney. Relative cataphoretic mobilities of the droplets of various emulsions in water and dilute electrolytes.

The Influence of Size and Shape of Particle on Cataphoretic Mobility. Table I summarizes the types of particles and the experiments in which the electrical mobility of the particle has been found to be independent of size and shape. The data there assembled are particularly striking if one recalls that the velocity of a spherical particle moving in a liquid in a gravitational field is proportional to the *square of the radius* and that the frictional resistance encountered by an uncharged spherical particle moving in a liquid is proportional *to the radius*. Fig. 2 illustrates a striking experiment comparing the mobilities of small spheres and very long cylinders.

Of particular importance in the conduct of experiments designed to study the influence of size and shape on electrical mobility is the technic that has

[2] Physik. Z., 25, 49 (1924).

TABLE I

A Summary of Particles that have Cataphoretic Mobilities independent of Size and Shape as determined by Experiment

Kind of Particle	Size Range (approximate)	Migration Velocity Independent of	Medium	Authority
Protein Sols	Differed sub-microscopically	Size	Acetic Acid	Hardy[3]
Silver Sols	Differed sub-microscopically	Size	Water	Burton[4]
Gas Bubbles	60μ to 160μ	Size	Water: Electrolytes	McTaggart[5]
Paraffin Oil Droplets	18μ to 28μ	Size	0.001 M NaOH	Mooney[6]
	33μ to 44μ	Size	0.0001 M NaOH	
	1μ to 16μ	Size	0.0008 M $CuSO_4$	
	16μ to 24μ		0.0001 M HCl	
Dimethyl Aniline Droplets	33μ to 50μ	Size	Water	Mooney[6]
Polymorphonuclear Leucocytes and their Aggregates	5μ to 10μ	Size and Shape	Serum; Plasma	Freundlich and Abramson[7]
Blood Platelets and their Aggregates	2μ to 15μ	Size and Shape	Plasma	Abramson[8]
Single Red Cells and their Aggregates	4μ to 30μ	Size and Shape	Serum	Freundlich and Abramson[7]
Air Bubbles in Gelatin Gels	2μ to 50μ	Size	Dilute Electrolytes	
Quartz, Glass, Clay	3μ to 15μ	Size and Shape	Dilute Electrolytes Distilled Water Sugar Solutions	Abramson[9] Freundlich and Abramson[7]
Nujol	0.5μ to 30μ	Size	Water-Ethyl Alcohol and Phosphate Buffer	Abramson and Michaelis[10]
Castor Oil	1μ to 10μ	Size		
Benzyl Alcohol	1μ to 45μ	Size	HCl Solution and Gelatin	
Cocoa Butter	1μ to 8μ	Size		
Nujol	1μ to 25μ	Size	HCl Solution and Gelatin	Abramson[10,11]

TABLE I (Continued)

A Summary of Particles that have Cataphoretic Mobilities independent of Size and Shape as determined by Experiment

Kind of Particle	Size Range (approximate)	Migration Velocity Independent of	Medium	Authority
Asbestos Needles	5μ to 50μ	Length	Distilled Water	Abramson and Michaelis[10]
Tyrosine Needles	2μ to 100μ	Length	Dilute HCl	Abramson[11]
Dissolved Crystallized Egg Albumin	5×10^{-7} cm (approx.)	This protein has been studied by these investigators in N/50 acetate buffer from pH 3.6 to 5.4. The mobilities of all three kinds of particles of egg albumin are very nearly alike.		Svedberg and Tiselius[12]
Gold Particles covered with Crystalline Egg Albumin	5×10^{-6} cm (approx.)			Prideaux and Howitt[13]
Quartz Particles covered with Crystalline Egg Albumin	0.5μ to 10μ			Abramson[11]
Paraffin Oil	1μ to 5μ (droplets)	When these particles which vary widely in size and shape are covered with gelatin, electrical mobility is independent of size and shape. See Fig. 2.		Abramson and Michaelis[10]
Asbestos Needles				
m-Amino-Benzoic Acid Needles	12μ to 150μ (needles)			

[3] J. Physiol., 29, xxvi (1903).
[4] "Physical Properties of Colloidal Systems," 2nd ed., 144 (1921).
[5] Phil. Mag., 27, 297 (1914).
[6] Phys. Rev., 23, 396 (1924).
[7] Z. physik. Chem., 128, 25 (1927); 133, 51 (1928).
[8] J. Exptl. Med., 41, 445 (1925); 48, 677 (1928).
[9] J. Am. Chem. Soc., 50, 390 (1928).
[10] J. Gen. Physiol., 12, 587 (1929).
[11] Unpublished data.
[12] J. Am. Chem. Soc., 48, 2272 (1926).
[13] Proc. Roy. Soc., 126, A, 126 (1929).

been developed to insure chemical uniformity of surface. In the case of solid particles like quartz, glass particles, asbestos needles, and tyrosine needles electrical mobility is independent of size and shape in the size range indicated[14] regardless of the medium. Emulsions behave differently. Mooney[6] found that the migration of paraffin oil droplets increased with increasing radius. The addition of a trace of gelatin or other protein which is adsorbed by the droplets to these systems gives all the droplets, regardless of size, the same migration velocity. The gelatin, in all probability, gives the oil droplets similar surfaces. That in these instances the protein surfaces behave during cataphoresis very much like the dissolved protein has been pointed out previously. This point will be amplified further on.

Electrolytes have the same effect as the proteins, for in their presence the differences between large and small oil droplets become less or disappear.

The Cataphoretic Mobility of Oil Droplets. Figure 3 summarizes the data Mooney has obtained for the cataphoretic velocities of the droplets of various emulsions. The electrical mobility, as Fig. 3 demonstrates, increases with increase in radius. It seems likely that this variation in mobility with size must be related to changes in surface rather than to a purely frictional phenomenon. Even though it has been shown in the previous section that mobility is independent of size and shape for certain microscopically visible particles, and even though there does not seem to be an easily measureable difference between dissolved protein of radius about 10^{-6} cm and adsorbed protein of particle radius to about 10^{-2} cm this can by no means be extended to all particles below the size range investigated in particular.

The meaning of the differences in behavior between the particles listed in Table I and the oil droplets investigated by Mooney has been discussed with Professor H. Müller of the Massachusetts Institute of Technology. Before our discussion with Professor Müller we had believed that the differences were primarily due to a variation in charge density, σ, with curvature of the surface of the droplets. This viewpoint is discussed in section 2 below. Professor Müller has contributed the viewpoint presented in section A following. It is with much pleasure that we are able to incorporate his treatment here.

A.[15] According to Debye and Hückel[16] the cataphoretic velocity of a colloidal particle of spherical form is

$$V_p = \frac{1}{6\pi} \frac{XD\zeta}{\eta} \qquad (2)$$

[14] Tyrosine particles less than 2μ in length may move more slowly than the larger needles, according to the results of a preliminary investigation. If one could obtain tyrosine needles smaller than 2μ, but still perfectly formed crystals, it seems likely that the mobility of these small needles would be like that of the larger ones. Pulverization of a crystal changes the surface energy and consequently, also, the ions adsorbed. It would be of interest to study the solubility of finely pulverized tyrosine. The amphoteric nature of this substance may lead to an unusual increase in solubility.

[15] Section A is a personal communication from Müller, Massachusetts Institute of Technology, May 28, 1930.

[16] Physik. Z., 25, 49 (1924); Hückel: 25, 205 (1924).

To explain the observed variation of the mobility with the radius we note that in this formula only the electrokinetic potential, ζ, may depend on the radius. This potential is due to the electric double-layer around the particle. It therefore depends on the charge density, σ, *i.e.*, the electric charge per cm.^{2}, and on λ, the thickness of the double layer. If we consider the double layer as a rigid system in the sense of a Helmholtz double layer, we would have

$$\zeta = \frac{4\pi\sigma}{D}\lambda. \tag{3}$$

There are consequently two possibilities to explain the observed variation in cataphoretic velocity according to this formulation. It may be due to a dependence of σ or of λ on the curvature of the surface.

In fact we can show that either quantity may be responsible for the observed variation.

1. *Dependence of the thickness of the double layer on the radius of the particles.*

According to Gouy,[17] Debye and Hückel, etc. we must assume that the electrical double layer is not rigid, but that the outer layer is "diffuse," *i.e.*, it is formed by those ions in the solvent which are electrostatically attracted to the surface. Debye shows that within this ionic atmosphere the potential, φ, decreases with the distance, r, from the center of the ion as

$$\varphi = K\frac{e^{-\kappa r}}{r} \tag{4}$$

where

$$\kappa^2 = \frac{4\pi N\epsilon^2}{1000\,D\,k\,T}\Sigma\,\gamma_i\,z_i^2$$

N = Avogadro's number; ϵ = electronic charge; k = Boltzmann constant: γ = concentration of ions of the "ith" type in mol/liter having valence of the "zth" type.

For water at 0°C

$$\kappa = 0.229\sqrt{\Gamma}\cdot 10^8\ \text{cm}^{-1} \tag{5}$$

$\Gamma = \Sigma\,\gamma_i\,z_i^2$ = ionic strength of the electrolyte.

The constant K depends on the density of the adsorbed charges and is determined by the condition that on the surface r = R. (R = radius of particles)

$$\left(\frac{d\varphi}{dr}\right)_{r=R} = -\frac{4\pi\sigma}{D}. \tag{6}$$

The electrokinetic potential is the value of φ on the surface, hence

$$\zeta = K\frac{e^{-\kappa R}}{R}. \tag{7}$$

Differentiating φ and introducing in (6) gives

[17] J. Phys., (4) 9, 457 (1910); Ann. Phys., 53, 239 (1917).

$$\zeta = \frac{4\pi\sigma}{D}\frac{1}{\kappa}\cdot\frac{\kappa R}{1+\kappa R}. \tag{8}$$

Comparison with (3) shows that this diffuse double layer is equivalent to a rigid double layer of the thickness

$$\lambda = \frac{1}{\kappa}\cdot\frac{\kappa R}{1+\kappa R}. \tag{9}$$

This formula shows that, in general, the thickness of the double layer depends on the radius R of the particle. This dependence can, however, be neglected if $\kappa R >> 1$ for then $\lambda = 1/\kappa$, approximately. The dependence of λ on R will only manifest itself if κR is small. In order to find how small R has to be in order to produce any effect we plot in Fig. 3a the function $f(\kappa R) = \kappa R/1 + \kappa R$.

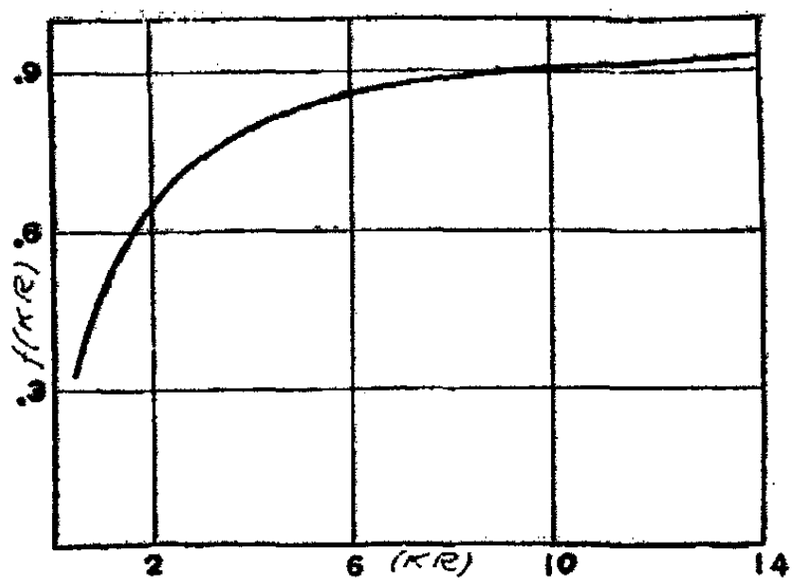


FIG. 3a
See text for explanation of this figure.

This diagram shows that the thickness of the double layer shows an observable variation with size of the particle only if

$$\kappa R \leq 5$$

or if

$$R \leq \frac{5}{\kappa} = \frac{2.2}{\sqrt{\Gamma}}\,10^{-7}\ \text{cm} \tag{10}$$

(for particle in water at 0°C).

Qualitatively, this theory gives, indeed a decrease of the thickness of the double layer, and hence also a decrease of the potential, ζ, and of the mobility, V_p, with decreasing radius of the particle. This is in good agreement with the observed facts. The theory also accounts for the fact that with an addition of any electrolyte the size-effect is shifted to smaller radii or disappears in the range investigated. An addition of electrolyte increases the ionic strength, Γ, hence according to equation (10) the radius, R, has to be correspondingly smaller to produce any variation.

Quantitatively however, the theory does not check very well. According to equation (10) the concentration of the electrolyte would have to be smaller than one micromol/liter in order to produce a measurable effect for particles of microscopic size ($1\mu - 10\mu$) while the effect is observed on even larger particles in solutions with probably stronger concentrations.

If the effect were due to the variation of the thickness of the double layer, it would only depend on the concentration of the electrolyte and not on the character of substance on the surface of the particle. Since the experiments indicate that the surface material is an important factor for the existence of the effect, it is more probable to find the reason for its existence in the dependence of the surface density, σ, on the curvature of the surface. (This is the end of Professor Müllers communication).

2. Dependence of the adsorbed charge density on the radius of the particle.

It is well known that the vapor pressure of very small liquid droplets is greater than the vapor pressure of large ones. The thermodynamic relationship between the vapor pressure of droplets and their radii has been given by Thomson[18]

$$\frac{RT}{M}\ln\frac{p_2}{p_1} = \frac{2S}{\rho}\left(\frac{1}{r_2} - \frac{1}{r_1}\right) \qquad (11)$$

(R = gas constant; T = absolute temperature; M = molecular weight of the liquid; S = the surface energy (interfacial energy); ρ = density of the liquid; p = vapor pressure of the droplet; r = radius of the droplet.)

In equation (11) S is unknown and may be influenced by the differences in adsorption by droplets of different sizes and by the change in charge incidental to this adsorption. Similarly the vapor pressure of the liquid drops of different radii is also unknown. It is apparent, however, that the smaller droplets and solid particles can have higher vapor pressures (solubility) than the larger ones. If the adsorption of ions decreases with increasing vapor pressure, the decrease in velocity of the smaller droplets can be explained at least qualitatively as follows. If we assume S to remain constant for droplets of different radii in solutions of the same ionic strength, and the velocity of the droplet to vary inversely proportional to its vapor pressure, then, we may state,

$$\frac{RT}{M}\ln\frac{V_1}{V_2} = \frac{2S}{\rho}\left(\frac{1}{r_2} - \frac{1}{r_1}\right)$$

approximately.

It seems likely from Mooney's data that large droplets approach a limiting value, V. In that case $r_1 \to \infty$ and $V_1 \to V$. We would then have

$$\frac{RT}{M}\ln\frac{V}{V_2} = \frac{2S}{\rho r_2}. \qquad (12)$$

Since Mooney's data are qualitative the validity of equations (12) can not as yet be exactly tested. From (12) it follows that

$$-\ln V_2 \propto 1/r_2.$$

[18] Cited by H. Freundlich: Colloid Chemistry, p. 45 (1926).

Table II

The Bulk Conductivity of Microscopic Particles covered with Protein Films does not influence their Cataphoretic Mobility

Particle	Time to migrate given distance sec.	Medium
B*	9.4	N/100 HCl plus a trace of gelatin
Q	9.0	
Q	9.4	
B	9.0	
Q	8.8	
Q	9.6	
B	9.2	
Q	9.4	
B	9.1	
P	6.4	In equilibrium with N/50 Acetate Buffer and trace of gelatin
A	6.4	
A	6.4	
A	6.6	
P	6.7	
A	7.0	
A	6.8	
A	6.5	HCl plus trace of hemocyanine
A	6.4	
A	6.8	
P	7.2	
A	7.0	
A	7.0	
P	7.8	N/100 HCl plus trace of gelatin
A	7.0	
A	7.0	
P	6.0	
C	6.0	
P	5.8	
C	5.8	
P	4.5	
C	4.8	

* B = benzyl alcohol, Q = quartz, A = agar particles in equilibrium with medium, P = paraffin oil, C = carbon.

That is, the negative logarithm of the droplet velocity should be inversely proportional to the radius of the droplet.

The proteins studied, as mentioned previously, hardly change their mobilities when the radii of the particle range[19] from approximately 10^{-6} cm to 10^{-3} cm. These substances acquire their charge in the systems studied not primarily by adsorption of ions but most probably by a stoichimetrical reaction. They possibly represent a special case. And it may be anticipated that when solid particles of pulverized quartz or tyrosine needles are investigated in the ultramicroscopic region, differences in mobility incidental to diminution in radii may be encountered. It is doubtful if the analogy with oil droplets is altogether strict. The pulverization of crystals produces changes in interfacial energy because of changes in the type of crystal surface made available to the solvent. What difference in mobility would exist between perfectly formed tyrosine needles 100μ and 0.01μ in length is unknown.

The influence of the bulk conductivity on cataphoretic mobility. Equation (1) is only strictly applicable to particles that are insulators. Particles homogeneous as a whole cannot be compared in order to study the effect of the conductivity of the particle on electrical mobility for the specific conductivity of the particle cannot be changed with varying the chemical composition of the phase boundary. Particles having identical surface films but varying in the specific conductivity of the enclosed bulk can be obtained by suspending various particles in dilute protein solutions. Table II summarizes experiments performed with Michaelis.[10] Particles of about the same size of quartz, paraffin oil, benzyl alcohol, carbon, and swollen agar covered with protein films, as indicated in the table, migrate independent of the bulk conductivity of the particle. In Table I the electrical mobilities of dissolved egg albumin, of submicroscopic gold particles, and of microscopic quartz particles covered with the same protein are similarly seen to be apparently unaffected by the bulk conductivity of the particle. Zakrzewski[20] has observed in a somewhat different type of experiment, however, that the streaming potentials set up in silvered glass capillaries are a function of increasing thickness of the silver film. The conditions of Zakrzewski's experiments are somewhat different from ours. But they emphasize that a good deal of similar experimentation is necessary before the problems dealing with bulk conductivity and electrokinetic phenomena are solved.

The Factor of Proportionality for Cataphoretic and Electroendosmotic Mobilities[21]

Theoretical. The data presented in the foregoing sections make it likely that microscopic particles having identical surfaces migrate independent of size and shape. This is, as previously stated, contradictory to the theory

[19] It will be shown in the next section that the range of radii of curvature over which a given protein does not change its mobility is from about 10^{-4} cm to 10^{3} cm where $a \rightarrow \infty$.

[20] Physik. Z., 2, 146 (1900).

[21] This section has since appeared in J. Gen. Physiol., 13, 657 (1930).

postulating that the factor C in equation (1) is a function of the shape of the particle. While these experiments deal with rather extreme variations of size and shape they are not definitely a test of that boundary condition of Debye and Hückel's theory which assumes that the radius of curvature of the cylinder is very large in comparison with the thickness of the ion atmosphere.

An experimental investigation including a test of the boundary condition involves the measurement of cataphoretic mobility of particles in a given medium simultaneously with the electroendosmotic mobility of the medium relative to a flat surface[22] having an ion atmosphere identical with that of the particle. Substituting the values of Debye and Hückel[2] for C in equation (1) and solving for R, the ratio of E_E and V_p, we obtain

$$R = V_E/V_p = 1.5$$

In other words, according to this theory electroendosmotic mobility must be 50 per cent greater than cataphoretic mobility.

Historical. Mooney[6] appears to be the first investigator to attempt to evaluate R. He found that the mobility of oil droplets was independent of size in $CuSO_4$ solutions (Fig. 3). Taking advantage of this fact, Mooney wet the inside of a round capillary tube with a paraffin oil and studied in this system the cataphoretic velocity of the oil droplets and the electroendosmotic velocity of the liquid against a surface presumably covered with oil. In one system V_p was very nearly equal to V_E.

The data of van der Grinten,[23] obtained in a flat cataphoresis cell, are in contrast to the finding of Mooney that R = 1.0 (approximately) for a round capillary. Van der Grinten studied the cataphoresis of small glass particles in distilled water, the particles composed of the same glass coverslips from which his flat cataphoresis cell had been assembled. He thus assumed that the surfaces of the particles of glass powder obtained by breaking up his coverslips were the same as that of the flat uninjured coverslips. Van der Grinten interpreted his data to give a mean value of R = 1.59, thus apparently confirming fairly well the theory of Debye and Hückel. Abramson[1] powdered pyrex glass and repeated the experiments of van der Grinten with a cell made of the same pyrex glass. This author found that for a given cataphoretic cell, R varied from 1.27 to 3.2 as a function of the nature of the medium. This cell of pyrex glass was not of uniform rectangular cross-section. The values obtained for R were consequently not considered absolute but rather pointing to the fact that a complete reinvestigation of the value of R was necessary under known hydrodynamic conditions and where the flat surface and surface of the particle were chemically identical.

The Movement of Liquids produced by Electroendosmosis in Flat Cataphoresis Cells. The movement of liquids in flat cataphoresis cells has been previously considered adequately for cells of various types by numerous investigators.

[22] An absolutely flat surface is, of course, not realizable experimentally.

[23] J. Chim. phys., 23, 14 (1916).

Since the recalculations to be made here of certain data depend upon the movement of liquids in cataphoresis cells we shall briefly review the facts pertinent to our subsequent recalculations and investigations.

The theories of Ellis and von Smoluchowski (based upon an old observation of Quincke) have made possible the quantitative measurements of cataphoretic mobility. Ellis assumed that for a closed flat cataphoresis cell of depth x, the observed cataphoretic velocity of a particle was, at any level in the cell, (for a system with no turbulence)

$$V_{obs.} = V_p + V_w \tag{13}$$

(V_p = absolute mobility relative to the liquid due to the charge, constant at all levels; V_w = the velocity of the liquid). The velocity of the liquid, as is well known, may vary from level to level so that if the electroendosmosis be in one direction, the return flow in the midregions of the closed cell must be in the opposite direction in closed systems like those considered. $V_{obs.}$ is, therefore, a function of the liquid streaming. The absolute velocity of a particle is, then, the mean velocity, M, of the particle within the cell,

$$M = 1/x_1 \int_0 V_{obs.}\, dx. \tag{14}$$

Substituting (13) in (14)

$$M = 1/x_1 \int_0^{x_1} (V_p + V_w)\, dx = V_p + 1/x_1 \int^{x_1} V_w\, dx. \tag{15}$$

For a closed cell $1/x_1 \int_0^{x_1} V_w dx = 0$ and since V_p is a constant for a given field strength,

$$M = 1/x_1 \int_0^{x_1} V_{obs.}\, dx = V_p \tag{16}$$

TABLE III

Recalculation of van der Crinten's Data

Curve No.	$V_{1/5}$ μ/sec.	V_E* μ/sec.	$V_{(3/4\ V_{1/6}+\ 1/4\ V_{1/2})}$	V_R μ/sec.	$V_{\text{Graphical Integration}}$ μ/sec.	V_R μ/sec.	Mean. R
1 (Fig. III)	2.7	6.6	2.8	6.6	2.8	6.4	2.4
2 (Fig. III)	2.7	6.2	2.8	6.0	2.9	5.8	2.15
3 (Fig. III)	2.7	7.2	3.0	6.6	2.9	6.8	2.4
Fig. 4 Van der Crinten p. 228	2.5	7.2		2.5	7.4	6.8	2.8

* V_E is calculated by means of equation (4).

By measuring V at various levels, V_p may be calculated from the analytic expression relating $V_{obs.}$ to x or V_p is readily obtained by graphical integration.

Von Smoluchowski simplified the method adopted by Ellis by proposing that

$$V_p = \tfrac{3}{4} V_{1/6} + \tfrac{1}{4} V_{1/2} = V_{1/5} = V_{4/5}, \text{ very nearly,} \qquad (17)$$

where the small sub-numerals represent level $\left(\text{level} = \frac{\text{depth}}{\text{total depth}}\right)$ in the cataphoresis cell. From the foregoing it can also be readily shown that

$$V_E = 2(V_{1/2} - V_p). \qquad (18)$$

(V_E = mobility of the liquid relative to the wall of the cataphoresis cell.) The data of Ellis and of Svedberg and Anderssen have amply confirmed von

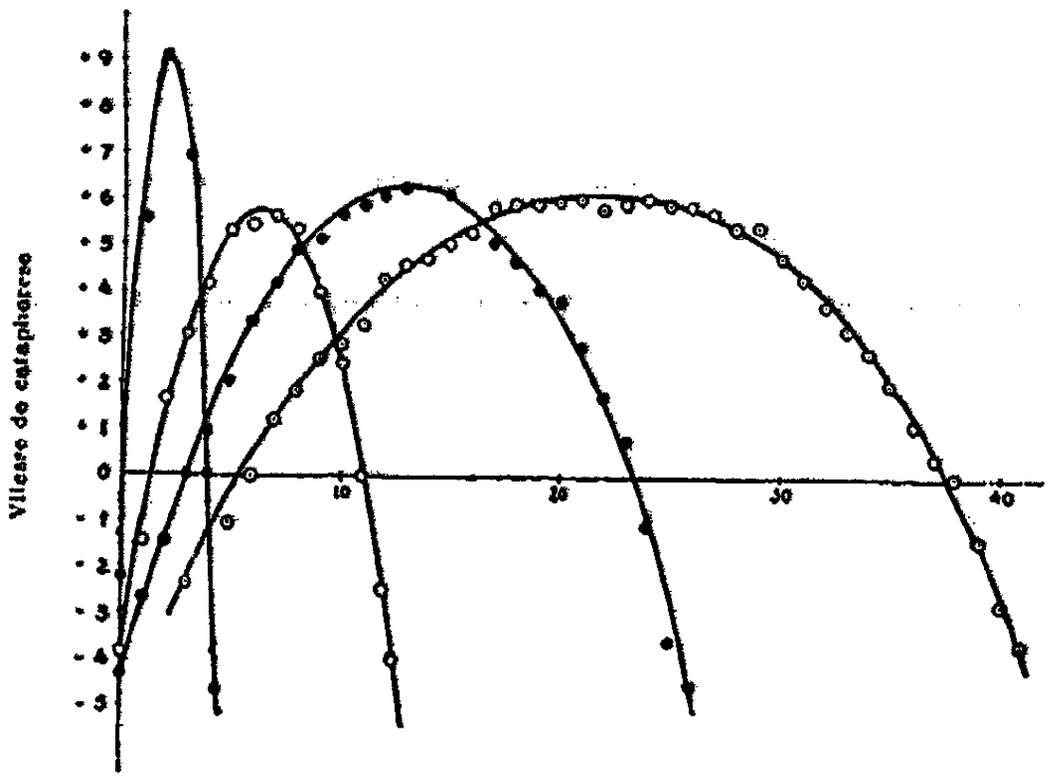


FIG. 4

Data of van der Grinten. (From J. Chim. phys.)

Smoluchowski's theory for the simple type of systems used by Ellis and by Svedberg and Anderssen. Their experiments are in accord with equation (17) in that

$$V_{1/5} = V_{4/5} = V_p = 1/x_1 \int_0^{x_1} V_{obs}\, dx \qquad (19)$$

for flat cells from 50μ to about 1.0 mm thick. This means that *in cataphoresis cells of this type and depth the mobility is constant at a given level. And conversely if flat cells of different depths have mobilities in agreement with equations (18) and (19), then the absolute mobilities of the particles measured are governed by equations (18) and (19).* This is of the utmost importance in the recalculation of van der Grinten's data.

Recalculation of van der Grinten's data. It has been mentioned that van der Grinten found R = 1.5, approximately. The data submitted by van der Grinten are of the type given in Fig. 4 which is reproduced from the paper of this author. Curves 1, 2, 3, and 4 in Fig. 4 demonstrate that when van der Grinten's cataphoresis cells were more than 0.52 mm thick, the cataphoretic

velocity of the particle (as well as the endosmotic velocity) remained practically constant for the same level in cells of different thicknesses. This does not mean, as van der Grinten interpreted it, that V_p, the speed of the particle relative to the liquid is that found in the midregions of the cells. It is rather, as Table III demonstrates, a further confirmation of the theory of von Smoluchowski. The table gives the values of V_p and V_E calculated by equations (17), (18), and (19) from the curves of Fig. 1 and another curve of van der Grinten's not reproduced here. It is evident that R is much greater than 1.5 in these systems and varies between 2.15 and 2.8. These data so calculated are in agreement with the author's previous experiments where similar high values of R for glass particle-glass surface systems similar to those of van der Grinten's were obtained. If one considers the data submitted by Lachs and Kronman[24] one could postulate *a priori* that to determine R by means of a flat glass surface and glass particles would be impossible. Lachs and Kronman, after a series of careful streaming potential measurements on glass and quartz surfaces, concluded that no true electrokinetic equilibrium was reached. Furthermore, consideration of the well known sensitiveness to stresses of metal surfaces as determined by measurements of thermodynamic potentials makes it not unlikely that localized changes in surface energy due to pulverization of the glass leads to the high value of R. To determine R, a stable system was here sought where R would be independent of the electrolyte content of the medium, and where, with a reasonable degree of certainty, the particle surface and the flat surface were the same.

The Determination of V_E/V_p *for Flat Surfaces.* It has been shown by Davis,[25] Abramson,[26] and Freundlich and Abramson[27] that surfaces of quartz and glass are practically completely coated with certain proteins when in contact with dilute solutions of these proteins on either side of the isoelectric point,—the particles then acting very much like the native protein in cataphoresis experiments. The most varied substances in addition to quartz and glass coat themselves with gelatin and egg albumin. Thus cystine crystals,[11] menthol,[11] camphor,[11] oil droplets, agar, charcoal, zinc oxide powder and air bubbles behave in this fashion. Briggs[27] has also found that glass capillaries coat themslves with proteins. By suspending glass, quartz and other particles in a protein solution both particles and flat surface of the cataphoresis cell therefore can be coated with the same substance fulfilling the condition of chemical similarity of glass and particle surface.

In the experiments to be reported, R was determined in two different flat cataphoresis cells of uniform cross-section. One of the cells was a cemented cell, similar in arrangement to that described by Northrop[28] and constructed

[24] Ext. Bull. l'acad. Pol. Sci. Lettres (A), 1925, 289.

[25] J. Physiol., 58, xvi (1923).

[26] J. Am. Chem. Soc., 50, 390 (1928); J. Gen. Physiol., 13, 169 (1929).

[27] Briggs has obtained streaming potentials with protein-coated glass capillaries remarkably similar to those obtained by Abramson by the method of cataphoresis. The concentration and kind of electrolyte however differed in these experiments. Until the experiments are repeated under similar conditions of ionic strength and ionic species, *R* cannot be evaluated from these data; J. Am. Chem. Soc., 50, 2358 (1928).

[28] J. Gen. Physiol., 4, 629 (1923).

in the fashion previously described.[28] The approximate dimensions of this cell were length 7.0 cm.; thickness 0.1 cm; width 1.0 cm. The second cell, of fused glass, was the modification of the Northrup-Kunitz cell described by Abramson.[29] The approximate dimensions of this cell were: length 3.5 cm; thickness 0.08 cm; width 0.9 cm.[30]

It has been demonstrated for this type of flat cataphoresis cell that "the movements of the water and particle within the cell follow the theory of von Smoluchowski. . . . When the curve of particle velocity at different levels is parabolic, the curve of velocity as plotted against level is the same near the fused ends of the cell itself as in the middle. The stream lines of the liquid throughout the cell are therefore uniform."[29] The value of R may, therefore, be readily calculated by means of equations (17), (18), and (19).

Table IV gives the value of R for 16 experiments performed with various protein covered particles and the flat glass surfaces of the cataphoresis cells covered with the same proteins. These experiments were performed with two kinds of proteins on both sides of the isoelectric points of the proteins and in

TABLE IV

Experiments to determine R. G. = Fused Glass Cell; C = Cemented Cell

Exp. No.	Cell	Nature of System	V_p μ/sec.	V_E μ/sec.	$R=\frac{V_E}{V_p}$
1	G	Glass of cell, powdered. pH 3.6 N/50 Acetate Buffer + 0.1% Gelatin	11.1	11.8	1.08
2	C	0.004 N HCl Quartz Powder + 0.1% Gelatin	6.4	6.2	0.97
3	G	0.004 N HCl Quartz Powder + 0.1% Gelatin	8.7	8.3	0.95
4	G	Benzyl Alcohol + 0.2% Gelatin	6.0	5.4	0.90
5	G	As above	Data misplaced		0.97
6	G	Powdered Glass in Distilled Water	7.3	20.4	3.3
7	G	Quartz in M/150 pH 7.4 Phosphate Buffer + 1.3% Gelatin	1.23	1.28	1.12
8	C	As above	8.6	7.8	0.91
9	C	As above	9.6	9.1	1.06
10	C	As above but in Acetic Acid	10.0	7.8	0.78
11	C	As above	1.00	9.6	0.96
12	C	As above	10.5	11.4	1.08
13	G	0.1% Egg Albumin Quartz in M/50 Acetic Acid	3.2	3.3	1.06
14	G	As above	10.3	11.8	1.14
15	G	As above but in Phosphate Buffer	8.75	11.1	1.14
16	G	1/3% Gelatin + N/200 H_2SO_4	6.15	5.9	0.96
17	G	As above	12.0	13.9	1.16

For protein coated surfaces (except No. 10) Mn. R = 1.01 ± 0.088. Probable error ± 0.02.

[29] J. Gen. Physiol., 2, 469 (1928).

[30] The diameter of the side tubes connecting cataphoresis cells and stopcocks were large in comparison with the thickness of the cells themselves.

the presence of different cations and anions. The field strengths were also varied. The values of R for 15 of these experiments varied between 0.90 and 1.16. The sixteenth value was 0.78. The mean (excluding value 0.78) was equal to 1.01 ± 0.088 with the probable error of the mean equal to ±0.02. These data point clearly to the conclusion that, under the given conditions, the ratio of cataphoretic to electroendosmotic velocity is very close to 1.00; and that the factor, C, in equation (1) is the same for V_p and V_E.[31]

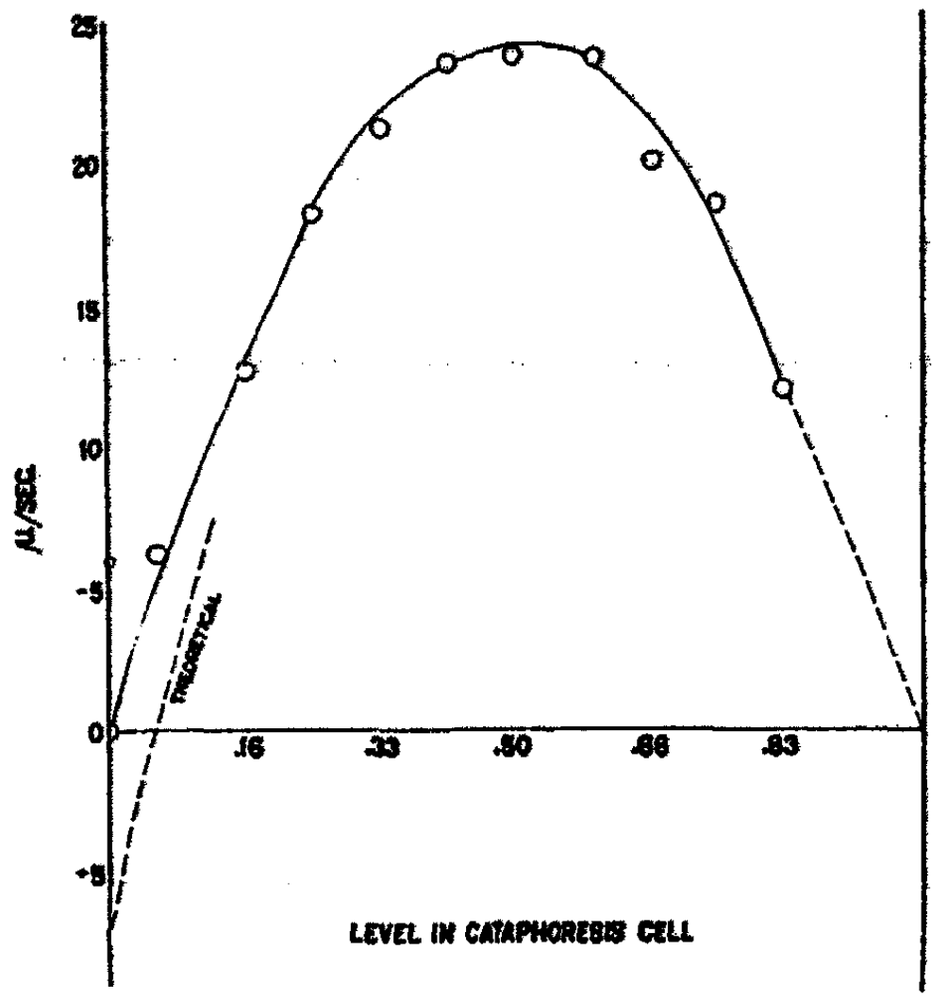


FIG. 5

The smooth curve extrapolated to $x = 1.0$ has been drawn through points of cataphoretic mobility of protein covered oil droplets. The curve passes through the origin. Since the origin ($x = 0$ or 1.0) is the wall of the cell it follows that $V_E = V_p$, or $\frac{V_E}{V_p} = 1.00$ approximately. The dotted line gives an idea of how the curve would look if $\frac{V_E}{V_p}$ were equal to 1.50. (From the Journal of General Physiology).

The Determination of V_E/V_p for a Round Surface. By proceeding as in the preceding section, V_E/V_p was determined in a round microcataphoresis cell by coating particle and glass surface with a protein, here gelatin. The curve drawn through the points in Fig. 5 is typical of the data of four similar experiments. The absolute mobility of the protein covered particle, V_p, is here at the level 0.15, approximately. The curve passes through the origin. This is only possible when

$$V_E = V_p \text{ or } V_E / V_p = 1.00$$

[31] This constant has not been determined experimentally.

The dotted line in Fig. 5 follows the approximate course of the curve calculated on the assumption that $V_E/V_P = 1.5$. That this ratio does not obtain under these conditions is obvious, confirming, therefore, the data for flat cells.

Significance of Data for Biological Objects

The Cataphoretic Mobility of Mammalian Red Blood Cells. Until more is known of the laws governing the cataphoresis of substances such as those ordinarily isolated from living cells, it is difficult to draw far-reaching conclusions concerning the data at present available dealing with the electrical mobilities of cells. There are, in fact, very few investigations which describe systematically, as *quantitatively* as the methods of cataphoresis permit, the comparative electrical mobilities of microscopic unicellular organisms. However, certain values given for the cataphoresis of mammalian red blood cells are of interest in view of the preceding discussion of the influence of size and shape on electric mobility. The data given in Table V show that very wide differences in the cataphoretic velocity of the red cells of different mammals exist.[32] Further, these values are independent of accidental impurities such as serum, etc. They are actually representative of the physicochemical make-up of the cell surfaces. But how much justification does there exist for the comparison of these values with one another?

If the surfaces of the cells were composed of protein exclusively, or of substances whose surfaces behaved like tyrosine needles, asbestos, etc., the problem would be simple; for it seems most probable that under such conditions curvature of the surface is not of much significance in determining cataphoretic mobility. Since it is most likely that fatty substances and other more complicated materials are chief components of certain red-cell surfaces, it is evident that curvature of the surface could affect the electric mobility of the red cells in exactly the same way that curvature affects the mobility of the oil droplets.

The following considerations are in favor of the tenability of the viewpoint that the electrical mobilities of the red cells studied are representative of chemical make-up of the surface rather than of variations in curvature of the surface:

a) There is too little known about the cataphoresis of organic substances in different states to accept curvature of the surface as a factor in determining red cell mobilities. The investigation of super-cooled emulsions and solid crystalline compounds of the type investigated by Mooney as well as the constituents of the red cell stroma must first be accomplished.

b) The "ghosts" (stromata) of red blood cells formed by hemolysis with dilute electrolytes can simultaneously be studied with single intact red cells. These hemoglobin-free lipoid portions of red cells undergo during hemolysis important changes in shape and stress incidental to swelling, besides losing

[32] J. Gen. Physiol., 12, 711 (1929).

their hemoglobin. They have, in consequence, a new shape after hemolysis. The "ghosts" migrate with practically the same speed as normal intact red cells, in phosphate buffer.[31] The same has been found to be true for stroma debris.[32] Changes in curvature do not, therefore, seem to be of primary importance here.

c) Salts diminish the differences between droplets of the size of blood cells, particularly in the salt concentrations used.

d) There is no correlation between size and mobility. The diameter of rabbit cells are 7.16μ. Those of the dog are 7.20μ.[33] Yet these two types of cells have the lowest and highest values of mobility, respectively, among the mammals investigated. Similar examples can be cited for other cells of the group.

e) Red blood cells obtained from cases of primary and secondary anemias show very marked changes in size and curvature of the surface.[30] These differences in equivalent radius may be greater than 100 percent in suspensions from one patient. In suspensions from the same patient very little if any

TABLE V

The Cataphoretic Mobility of Mammalian Red Cells at pH 7.35 in M/15 Phosphate Buffer

Order	Animal	mn. μ/sec./volt/cm	Average Deviation
Primate	Man (White)	1.31	±0.02
	Man (Negro)	1.30	±0.05
	Monkey (*Macacus Rhesus*)	1.33	±0.02
Carnivor	Dog	1.65	±0.03
	Cat	1.39	±0.01
Ungulate	Pig	0.98	±0.03
Rodent	Rabbit	0.55	±0.05
	Guinea Pig	1.11	±0.02
	Mouse	1.40	±0.06
	Rat	1.45	±0.02
Edentate	Sloth (Two-toed)	0.97	One series of measurements
Marsupial	Opossum	1.07	±0.02

[32] One experiment.

[31] Tabulae Biological, Berlin, 2, 459 (1925).

difference is found amongst the cells themselves. The values of mobility obtained for a series of anemia cases did not differ from the normal or differed very slightly, the difference being near the limits of experimental error. The cells, incidentally, also varied in hemoglobin content. This is excellent evidence that size and shape do not primarily invoke changes in red cell mobility.[35,36]

In conclusion we wish to re-emphasize that when data are available for other types of cells, a critique similar to that employed in the foregoing must be applied. The biologist in the meantime must wait upon the further acquisition of values of electrical mobilities of organic compounds in various states and in different suspending media before hoping to understand the chemical make-up of the surface and the many curious phenomena occurring at the phase boundaries of living and non-living microscopic particles and surfaces.

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Harvard Medical School,
Boston.

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[35] It is not insinuated that no change in physico-chemical make-up occurs in the red cells in anemia. The changes that do occur cannot profoundly change the constitution of the surface.

[36] Since this paper was written Dr. G. Payling Wright and I have observed that foul red cells which vary in size, shape and cytoplasmic structure may have very much the same electrical mobilities.

STUDIES ON ELECTROKINETIC POTENTIALS. VI

Electrical Phenomena at Interfaces[1]

BY HENRY B. BULL AND ROSS AIKEN GORTNER

Historical and Theoretical

The existence of electrical conductance at a solid-liquid interface which increases the conductance of a system above that normally expected can hardly be doubted since it has been demonstrated by several workers. Thus Stock[2] showed that quartz powder in such liquids as nitrobenzene and aniline greatly increased the apparent conductivities of these liquids. Briggs[3] found that surface conductance must be taken into consideration in determining the specific conductance of a liquid for the purpose of calculating the ζ-potential from streaming-potential data. McBain, Peaker, and King[4] have made accurate quantitative determinations of the surface conductance of KCl solutions at glass and silica interfaces and find it to be appreciable.

Stock[2] at the suggestion of Smoluchowski undertook to investigate the question of surface conductance. He employed in this research certain of Smoluchowski's equations.

Smoluchowski considered a system of capillary tubes and proceeded to calculate the ratio of the current carried by the surface potential, *i.e.*, that due to surface conductance, to that carried by the bulk of the liquid.

The infinitesimal amount of current, dI_s, carried by an infinitesimal element of the double layer moving with a velocity, u, is given by the following relation.

$$dI_s = q\,u\,dS\,dr \qquad (1)$$

where q is the charge per unit area on the double layer, dS is an infinitesimal section of the circumference, and dr is an infinitesimal normal to the wall.

Then

$$I_s = \int q\,u\,dS\,dr \qquad (2)$$

But the velocity at any point is given by

$$u = \frac{\partial u}{\partial r}r \qquad (3)$$

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[1] From the Division of Agricultural Biochemistry, University of Minnesota. Published with the approval of the Director, as Paper No. 951, Journal Series, Minnesota Agricultural Experiment Station. This paper is taken from Part III of a thesis presented by Mr. H. B. Bull to the Graduate School of the University of Minnesota in partial fulfillment of the requirements for the degree of Doctor of Philosophy, June 1930.

[2] Anz. Akad. Wiss. Krakau, (A) 1912, 635.

[3] J. Phys. Chem., 32, 641 (1928).

[4] J. Am. Chem. Soc., 51, 3294 (1929).

Then substituting (3) in (2)

$$I_s = \int q \frac{\partial u}{\partial r} r \, dS \, dr \quad \ldots\ldots (4)$$

Integrating part of this expression

$$\int q' r \, dr = -\frac{1}{4\pi} \int_0^\infty \frac{\partial^2 \phi}{\partial r^2} = \frac{D}{4\pi} (\phi_2 - \phi_1) = \frac{D\zeta}{4\pi} \quad \ldots\ldots (5)$$

where $\phi_2 - \phi_1$ is the potential difference across the double layer and is equal to the ζ-potential. D is the dielectric constant.

Substituting (5) in (4)

$$I_s = \frac{D\zeta}{4\pi} \int \frac{\partial u}{\partial r} dS \quad \ldots\ldots (6)$$

Integrating through the entire circumference and assuming a linear relation between u and r, we have

$$I_s = \frac{D\zeta}{4\pi} S \frac{u}{d} \quad \ldots\ldots (7)$$

where d is the thickness of the double layer.

The movement of the layer of ions with a charge, q, per unit area is produced by an externally applied electrical potential. The resulting force acting on the double layer is

$$F = q \frac{\partial V}{\partial x} \quad \ldots\ldots (8)$$

where $\frac{\partial V}{\partial x}$ is the potential gradient of the externally applied electrical potential.

Now at equilibrium the electrical forces tending to produce motion of the liquid must exactly equal the forces tending to retard the flow of the liquid. This resisting force is

$$R = \frac{\partial u}{\partial r} \eta \quad \ldots\ldots (9)$$

where η is the coefficient of viscosity. When equilibrium has been reached (9) must equal (8)

$$q \frac{\partial V}{\partial x} = \frac{\partial u}{\partial r} \eta \quad \ldots\ldots (10)$$

Assuming a linear relation between u and r, we have

$$\frac{u}{d} \eta = q \frac{\partial V}{\partial x} \quad \ldots\ldots (11)$$

where d is the thickness of the double layer.

Substituting the value of u/d in (7), we have

$$I_s = \frac{D\zeta S}{4\pi\eta} q \frac{\partial V}{\partial x} \quad \ldots\ldots(12)$$

Now the current carried by a cross-section of the liquid is

$$I_A = A\kappa \frac{\partial V}{\partial x} \quad \ldots\ldots(13)$$

where A is the area of the cross-section occupied by the liquid and κ is the specific conductance of the liquid.

Dividing (12) by (13)

$$\frac{I_s}{I_A} = \frac{D\zeta Sq}{4\pi\eta\kappa A} \quad \ldots\ldots(14)$$

$$\text{Now } q = \frac{\zeta D}{4\pi d} \quad \ldots\ldots(15)$$

Substituting (15) in (14)

$$\frac{I_s}{I_A} = \left(\frac{D\zeta}{4\pi}\right)^2 \frac{S}{\eta\kappa A d} \quad \ldots\ldots(16)$$

which is the final equation of Smoluchowski.

It is to be noted that in the derivation of this equation the same assumptions are involved which are used in the derivation of the equation for electroosmosis, cataphoresis, and streaming potential. No additional assumptions have been made.

It is possible to modify equation (16) by the appropriate substitution so that two new equations are obtained, one expressing the thickness of the double layer and the other the charge per unit area.

Briggs[5] pointed out that

$$\frac{\kappa_s - \kappa}{\kappa} = \frac{I_x}{I_A} \quad \ldots\ldots(17)$$

where κ_s is the specific conductivity of the liquid in the capillary pores and κ is the specific conductivity of the liquid in bulk. $\kappa_s - \kappa$ is taken to be the so-called surface conductance. Then substituting in (16)

$$\frac{\kappa_s - \kappa}{\kappa} = \frac{S}{\kappa A\eta d}\left(\frac{D\zeta}{4\pi}\right)^2 \quad \ldots\ldots(18)$$

$$\kappa_s - \kappa = \frac{S}{A\eta d}\left(\frac{D\zeta}{4\pi}\right)^2 \quad \ldots\ldots(19)$$

From the streaming potential equation

$$\frac{D\zeta}{4\pi} = \frac{H\eta\kappa_s}{P} \quad \ldots\ldots(20)$$

[5] Colloid Symposium Monograph, 6, 41 (1928).

Substituting (20) in (19) we have

$$\kappa_s - \kappa = \frac{S}{A\eta d}\left(\frac{H\eta\kappa_s}{P}\right)^2 \quad \ldots\ldots(21)$$

and

$$d = \frac{S\eta}{(\kappa_s-\kappa)A}\left(\frac{H\kappa_s}{P}\right)^2 \quad \ldots\ldots(22)$$

which is a convenient equation expressing the thickness of the double layer.

Now substituting the expression $\frac{\zeta D}{4\pi} = d\,q$ in (16) we have

$$\kappa_s - \kappa = \frac{S}{A\eta d}(dq)^2 \quad \ldots\ldots(23)$$

$$= \frac{S}{A\eta} q^2 d \quad \ldots\ldots(24)$$

Substituting the value of d as given by (22), we have

$$\kappa_s - \kappa = \frac{S}{A\eta} q^2 \frac{S\eta}{(\kappa_s-\kappa)A}\left(\frac{H\kappa_s}{P}\right)^2 \quad \ldots\ldots(25)$$

$$= \frac{S^2 q^2}{A^2(\kappa_s-\kappa)}\left(\frac{H\kappa_s}{P}\right)^2 \quad \ldots\ldots(26)$$

or

$$q = (\kappa_s - \kappa)\frac{A}{S}\frac{P}{H\kappa_s} \quad \ldots\ldots(27)$$

which is an equation expressing the charge per unit area at the interface.

The dielectric constant does not appear in either equation for the thickness of the double layer (22) or for the charge (27) which relieves us of making any assumptions concerning the magnitude of this constant.

Now it is not possible in our work with a cellulose diaphragm to determine the actual numerical ratio of A/S in equations (22) and (27), but we can at least assume that *it is a constant for any given diaphragm throughout a series of determinations.* It should be possible therefore to determine the behavior of the charge on and the thickness of the double layer upon the addition of electrolytes by use of the above equations. This is the object of the present research.

The streaming potential apparatus used in this investigation was a modification of that developed by Briggs[5] and later again modified by Martin and Gortner.[6]

The technic is described and the apparatus is figured in diagrams 1 and 2 of the paper by Martin and Gortner.[6]

All volumetric apparatus used in this research was calibrated and the corrections used when necessary.

The quadrant electrometer and potentiometer were adjusted in the usual manner.

[6] J. Phys. Chem., **34**, 1509 (1930).

The diaphragms used in this research were in all cases made from cellulose. At the beginning of the research, four packages of Schleicher and Schüll filter paper, No. 589, were ground in a ball mill with 95 per cent ethyl alcohol to a pulp. The cellulose was then filtered and dried *in vacuo* at 95° for 8 hours and stored in sealed glass containers. The cellulose was suspended in the liquid to be studied at least 48 hours before it was used.

The cellulose was packed quite tightly in the cell. After the diaphragm was in place in the apparatus, at least 700 cc of the solution to be studied was streamed through it before any determinations were attempted. The washings were discarded.

The two halves of the streaming potential cell were cleaned carefully before each determination with sulfuric acid dichromate solution and rinsed out with distilled water and finally with some of the solution to be used in the experiment.

Determination of the Specific Electrical Conductance of the Liquid in the Diaphragm

Immediately following the determination of the streaming potential, the streaming potential cell was connected to the conductivity apparatus and the resistance of the diaphragm determined.

Later, when the series of experiments on a particular diaphragm was completed, the cell constant of the diaphragm was determined by replacing the liquid in the diaphragm by N/10 KCl. Knowing the cell constant and the resistance, the specific conductivity is calculated in the usual manner.

Calculation of the ζ-Potential

From the observed values of the pressure, the electromotive force, and the specific conductance, the ζ-potential may be calculated. The pressure must be expressed in dynes per square centimeter and the specific conductivity observed in ohms^{-1} must be multiplied by 9×10^{11} to convert it to C.G.S. electrostatic units.

Substituting these conversion factors in the following equations

$$\zeta = \frac{4\pi H \eta \kappa_s}{DP}$$

and collecting constants we have

$$\zeta = 847{,}649{,}000 \frac{\eta}{D} \frac{H\kappa_s}{P}$$

where H = observed electromotive force in millivolts, η = coefficient of viscosity of the liquid, κ_s = specific conductivity of liquid in diaphragm in ohms^{-1}, D = dielectric constant of liquid, P = pressure in centimeters of mercury, ζ is expressed in millivolts.

In order to determine the surface conductance a conductivity measurement of the liquid in bulk was necessary. This was done at the same temperature as the streaming potential determination and on the liquid which

had actually been used in the streaming potential measurements. A Washburn conductivity cell designed for high precision work was used.

The surface conductance was obtained by subtracting the specific conductance of the liquid in bulk from that in the diaphragm.

Chemicals

The water used throughout this investigation was doubly distilled and had a specific conductance of 4.8×10^{-6} ohms^{-1}. It was used fresh.

The salts were the purest obtainable on the market. No additional purification was attempted.

Criteria of Validity Results

It is essential, if we are to attach any meaning to our results, that they must be reproducible. It is to be emphasized, however, that in order to compare results they must have been obtained from material treated in an identical manner. This is particularly true in respect to the time that the cellulose has been allowed to remain in contact with the liquid, since it is generally agreed that the ζ-potential decreases with time when the material is allowed to remain in contact with the liquid. That this is true is clearly shown by the work done by Martin and Gortner[6] and by Lachs and Kronman.[7] The data on three diaphragms with water-cellulose are shown in Table I.

TABLE I

Showing Variability in Streaming Potential Measurements

Diaphragm	Pressure cm Hg	$H\kappa_s/P \times 10^5$	Pressure cm Hg	$H\kappa_s/P \times 10^5$
1	71.9	−10.23	75.9	− 9.85
	75.1	− 9.90	79.1	− 9.70
	78.9	−10.02	72.0	− 9.70
	Average $H\kappa_s/P = -9.90 \times 10^{-5}$			
2	69.0	− 9.48	72.1	− 9.53
	75.5	− 9.48	78.1	− 9.68
	79.8	− 9.45	82.7	− 9.82
	Average $H\kappa_s/P = -9.58 \times 10^{-5}$			
3	65.7	−12.04	73.9	−11.34
	74.5	−11.72	78.1	−11.26
	81.4	−11.67	83.4	−10.97
	Average $H\kappa_s/P = -11.50 \times 10^{-5}$			

[7] Bull. acad. Polonaise sci. lettres, (A) 1925, 286.

These results were selected purely at random and may be said to represent the usual variations encountered. They perhaps leave something to be desired from the point of view of reproducibility, but when it is remembered that with pure water the observed potential is extremely sensitive to traces of electrolytes and is more erratic than with salt solutions, the disagreement is not serious.

Due to the fact that the gold electrodes are not reversible in the usual sense of the word, it was feared that marked polarization might develop. To satisfy ourselves on this point, we determined the streaming potential as a function of the pressure. The results are shown in Fig. 1.

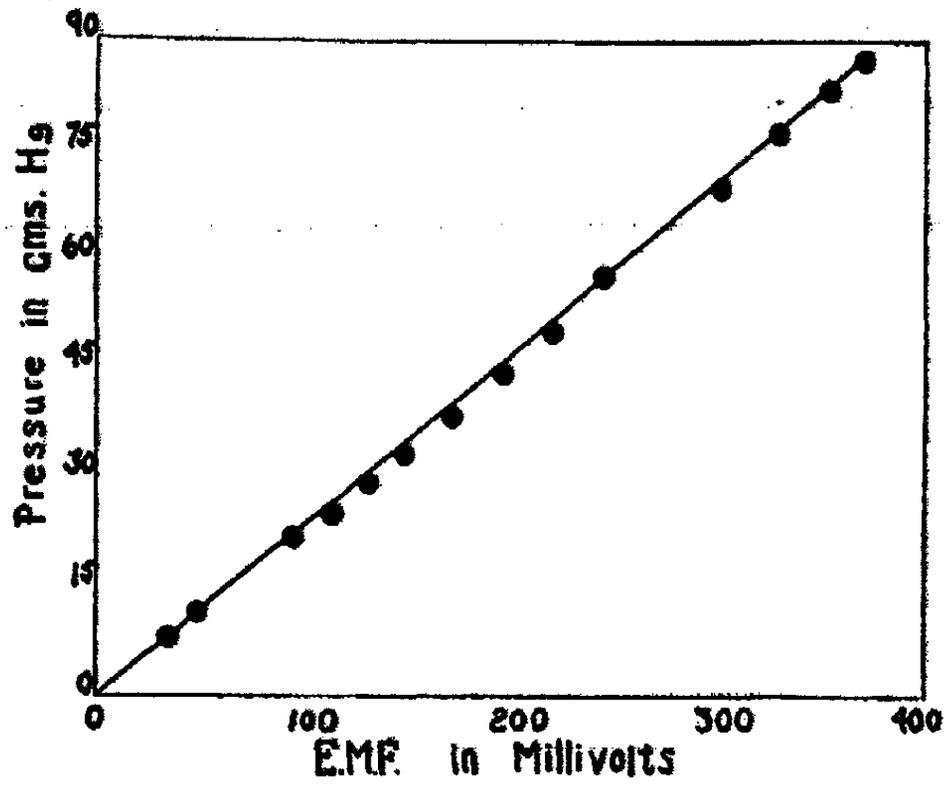

FIG. 1

Showing the relation between the streaming potential and the pressure, as experimentally determined in our apparatus using a cellulose diaphragm and 0.1×10^{-4} NaCl as the liquid being streamed through the diaphragm.

It will be noted that the result is a straight line passing through the origin. Had there been polarization of the electrodes, this would not have been the case.

That the diaphragm had attained equilibrium with the liquid was tested for in every determination by obtaining at least three values while streaming the liquid in one direction and three more values in the reverse direction.

Results

The data for the function, $H\kappa_s/P$, are given in Tables II through IX and summarized along with data for $\frac{\eta}{\kappa_s - \kappa}\left(\frac{H\kappa_s}{P}\right)^2$, $(\kappa_s - \kappa)\frac{P}{\kappa_s H}$, and the ζ-potential in Tables X through XVII and the results graphed in Figs. 2 through 9 for various concentrations of aqueous solutions of KCl, NaCl, $MgCl_2$, $CaCl_2$,

K_2CO_3, K_2SO_4, K_3PO_4, and $ThCl_4$ at a cellulose interface. As a convenience the function, $\frac{\eta}{\kappa_0 - \kappa}\left(\frac{(H\kappa_0)}{P}\right)^2$ which is proportional, though not equal, to the thickness of the double layer is designated by d′, and the function, $(\kappa_0-\kappa)\frac{P}{\kappa_0 H'}$, which is proportional to the electrostatic charge per unit area is designated by q′.

TABLE II

Data for $MgCl_2$

Concentration $MgCl_2$	Pressure	$H\kappa_0/P \times 10^5$	Pressure	$H\kappa_0/P \times 10^5$
	cm Hg		cm Hg	
0.00	61.3	−15.5	57.2	−15.5
	78.1	−15.5	79.6	−15.5
	75.5	−15.5	78.3	−15.3
	Average $H\kappa_0/P = -15.48 \times 10^{-5}$			
0.10×10^{-3}	66.3	−10.5	74.5	−11.4
	80.9	−11.1	81.7	−11.1
	73.9	−11.5	75.7	−10.7
	Average $H\kappa/P_0 = -11.05 \times 10^{-5}$			
0.20×10^{-3}	51.2	− 8.52	58.9	− 8.84
	80.6	− 9.95	80.6	− 9.42
	78.5	− 9.76	78.9	− 9.45
	Average $H\kappa_0/P = -9.32 \times 10^{-5}$			
0.4×10^{-3}	60.5	− 8.83	63.0	− 8.05
	80.9	− 8.72	81.4	− 8.50
	79.5	− 8.60	79.3	− 8.24
	Average $H\kappa_0/P = -8.50 \times 10^{-5}$			
0.8×10^{-3}	50.1	− 6.90	61.8	− 5.10
	80.6	− 6.94	81.3	− 6.75
	76.5	− 6.68	78.1	− 6.52
	Average $H\kappa_0/P = -6.75 \times 10^{-5}$			
1.6×10^{-3}	81.9	− 2.69	66.9	− 3.10
	80.7	− 2.00	81.1	− 2.71
	Average $H\kappa_0/P = -2.62 \times 10^{-5}$			

TABLE III

Data for $CaCl_2$

Concentration $CaCl_2$	Pressure	$H\kappa_s/P \times 10^5$	Pressure	$H\kappa_s/P \times 10^5$
	cm Hg		cm Hg	
0.00	77.2	−13.7	68.3	−13.4
	72.0	−13.8	72.9	−13.6
	69.5	−14.0		
	Average $H\kappa_s/P = -13.7 \times 10^{-5}$			
0.1×10^{-3}	63.5	−10.5	51.8	−11.6
	74.9	−10.4	73.7	−10.5
			78.4	−10.5
	Average $H\kappa_s/P = -10.7 \times 10^{-5}$			
0.2×10^{-3}	53.8	−9.80	57.9	−10.1
	76.9	−9.45	76.9	−9.4
	82.3	−9.20	82.9	−9.3
	Average $H\kappa_s/P = 9.55 \times 10^{-5}$			
0.4×10^{-3}	80.3	−9.2	52.2	−10.8
	82.8	−9.3	73.1	−9.5
	75.5	−9.2	80.4	−9.2
	Average $H\kappa_s/P = -9.55 \times 10^{-5}$			
0.8×10^{-3}	59.0	−10.0	66.0	−9.5
	78.2	−8.9	80.2	−8.5
	83.5	−8.0	82.9	−8.4
	Average $H\kappa_s/P = -8.90 \times 10^{-5}$			
1.6×10^{-3}	70.5	−9.0	67.8	−9.5
	79.0	−8.8	80.3	−8.6
	82.3	−8.7	76.4	−8.6
	Average $H\kappa_s/P = -8.87 \times 10^{-5}$			

TABLE IV

Data for NaCl

Concentration NaCl	Pressure	$H\kappa_s/P \times 10^5$	Pressure	$H\kappa_s/P \times 10^5$
	cm Hg		cm Hg	
0.00	71.9	−10.23	75.9	−9.85
	75.1	−9.90	79.1	−9.70
	78.9	−10.02	72.0	−9.70
	Average $H\kappa_s/P = -9.90 \times 10^{-5}$			
0.05×10^{-3}	70.3	−12.80	69.7	−12.84
	78.5	−12.34	74.7	−12.50
	73.9	−12.45	78.6	−12.58
	Average $H\kappa_s/P = -12.6 \times 10^{-5}$			
0.10×10^{-3}	72.9	−13.90	74.1	−14.30
	75.7	−13.85	76.5	−14.40
	79.7	−13.70	73.5	−15.50
	Average $H\kappa_s/P = -14.1 \times 10^{-5}$			
0.2×10^{-3}	71.3	−14.0	72.9	−13.8
	75.1	−13.8	75.9	−13.6
	79.0	−13.7	79.2	−13.6
	Average $H\kappa_s/P = -13.75 \times 10^{-5}$			
0.4×10^{-3}	69.5	−13.4	73.2	−13.3
	74.7	−13.4	76.9	−13.0
	78.3	−13.5	80.2	−13.1
	Average $H\kappa_s/P = -13.30 \times 10^{-6}$			
0.8×10^{-3}	61.5	−12.40	71.7	−11.6
	70.1	−12.45	75.7	−11.6
	77.7	−12.35	82.1	−11.2
	Average $H\kappa_s/P = -11.95 \times 10^{-5}$			
1.6×10^{-3}	67.8	−10.02	75.2	−11.6
	74.8	−10.20	79.4	−11.6
	80.5	−10.25	82.3	−11.8
	Average $H\kappa_s/P = -10.90 \times 10^{-5}$			

TABLE V

Data for KCl

Concentration KCl	Pressure cm Hg	$H_{K_s}/P \times 10^5$	Pressure cm Hg	$H_{K_s}/P \times 10^5$
0.00	51.9	−13.0	51.6	−11.5
	78.4	−12.6	83.0	−12.4
			78.2	−12.6
	Average $H_{K_s}/P = -12.4 \times 10^{-5}$			
0.05×10^{-3}	77.4	−13.8	80.6	−13.8
	82.4	−13.8	77.2	−13.8
	76.0	−13.6		
	Average $H_{K_s}/P = -13.8 \times 10^{-5}$			
0.10×10^{-3}	48.7	−15.1	59.1	−12.4
	82.2	−14.3	77.4	−14.1
	76.1	−14.3	84.4	−14.2
	Average $H_{K_s}/P = -14.01 \times 10^{-5}$			
0.20×10^{-3}	36.7	−13.7	63.3	−13.1
	79.0	−14.3	82.4	−14.2
	85.5	−13.9	78.2	−14.4
	Average $H_{K_s}/P = -13.9 \times 10^{-5}$			
0.4×10^{-3}	81.2	−12.7	50.3	−12.50
	66.8	−12.4	82.9	−12.95
	71.4	−13.5	72.2	−13.40
	Average $H_{K_s}/P = -12.9 \times 10^{-5}$			
0.8×10^{-3}	41.6	−11.75	53.2	−13.7
	76.7	−12.3	76.8	−12.6
	83.3	−12.2	68.7	−13.4
	Average $H_{K_s}/P = -12.8 \times 10^{-5}$			

TABLE VI

Showing Values of H/P for Various Concentrations of K_2CO_3 at a Cellulose Interface

Concentration × 10^3 Normality	Pressure cm Hg	H/P mv/cm	Pressure cm Hg	H/P mv/cm
0.00	65.7	−4.611	73.9	−4.343
	74.5	−4.489	78.1	−4.314
	81.4	−4.471	83.4	−4.202
	Average H/P = −4.405			
0.10	72.2	−3.518	70.6	−3.392
	79.5	−3.515	78.4	−3.475
	84.7	−3.536	83.3	−3.397
	Average H/P = −3.472			
0.20	67.6	−1.819	65.9	−1.904
	81.9	−1.807	81.7	−1.903
	85.1	−1.815	85.4	−1.896
	Average H/P = −1.8573			
0.40	66.6	−1.216	82.1	−1.230
	74.6	−1.206	84.5	−1.207
	83.6	−1.202	87.6	−1.176
	Average H/P = −1.2061			
0.80	75.5	− .7019	76.6	− .6984
	80.9	− .7169	81.3	− .6703
	84.6	− .6973		
	Average H/P = −0.6969			

TABLE VII

Showing Values of H/P for Various Concentrations of K_2SO_4 at a Cellulose Interface

Concentration × 10^3 Normality	Pressure cm Hg	H/P mv/cm	Pressure cm Hg	H/P mv/cm
0.00	69.0	−3.536	72.1	−3.557
	75.5	−3.536	78.5	−3.611
	79.8	−3.527	82.7	−3.663
	Average H/P = −3.5716			
0.10	68.9	−2.721	82.6	−2.451
	82.5	−2.406	85.1	−2.391
	85.3	−2.432	70.7	−2.595
	Average H/P = −2.499			
0.20	80.5	−1.623	80.7	−1.629
	83.1	−1.632	83.5	−1.622
	85.5	−1.674	85.7	−1.621
	Average H/P = −1.633			
0.40	82.7	−0.9068	83.0	−0.9638
	84.2	−0.9086	85.0	−0.9764
	85.9	−0.8789	86.6	−0.9815
	Average H/P = −0.9360			
0.80	76.1	−0.5519	81.5	−0.4969
	81.1	−0.5610	83.9	−0.4946
	85.1	−0.5699	86.3	−0.4866
	Average H/P = −0.5268			

TABLE VIII

Showing Values of H/P for Various Concentrations of K_3PO_4 at a Cellulose Interface

Concentration × 10^3 Normailty	Pressure cm Hg	H/P mv/cm	Pressure cm Hg	H/P mv/cm
0.0	78.0	−2.756	76.5	−2.771
	81.4	−2.751	77.9	−2.766
	84.7	−2.727	80.4	−2.754
	Average H/P = −2.754			
0.1	68.3	−2.554	77.9	−2.734
	76.5	−2.555	71.9	−2.566
	83.7	−2.526	86.1	−2.601
	Average H/P = −2.591			
0.2	84.1	−1.688	75.7	−1.803
	74.6	−1.702	79.2	−1.799
	79.3	−1.683	82.8	−1.793
	Average H/P = −1.744			
0.4	83.4	−1.270	74.4	−1.384
	70.6	−1.288	77.3	−1.384
	77.2	−1.275	79.3	−1.374
	Average H/P = −1.3291			
0.8	71.1	−.6962		
	76.7	−.6844		
	83.1	−.7099		
	Average H/P = −0.6968			

TABLE IX

Data for $ThCl_4$

Concentration × 10^3 Normality	Pressure cm Hg	H/P mv/cm	Pressure cm Hg	H/P mv/cm
0.00	63.1	−5.594	73.6	−5.407
	73.4	−5.585	79.2	−5.290
	80.0	−5.606	83.5	−5.227
	Average H/P = −5.4515			
0.05	72.8	−3.372	75.0	−3.560
	77.8	−3.348	79.2	−3.491
	81.3	−3.327	83.7	−3.453
	Average H/P = −3.4251			
0.10	54.3	−0.9484	65.7	−1.278
	72.0	−0.9097	76.3	−1.238
	79.8	−0.9273	82.2	−1.180
	Average H/P = −1.0803			
0.20	72.3	+1.916	68.3	+2.057
	78.3	+1.948	77.2	+2.014
	81.5	+1.926	82.3	+2.023
	Average H/P = +1.981			
0.40	65.1	+1.590	74.4	+1.660
	71.8	+1.643	79.6	+1.608
	80.2	+1.658	83.6	+1.585
	Average H/P = +1.624			
0.80	56.2	+0.9252	75.2	+0.9973
	74.5	+0.9127	80.0	+1.043
	81.6	+0.9068	84.2	+1.021
	Average H/P = +0.9677			
1.60	68.6	+0.5612	73.3	+0.4570
	78.8	+0.5964	80.0	+0.5250
	82.7	+0.5985	84.2	+0.5403
	Average H/P = +5.464			

TABLE X

Summary of Data for KCl

$1 = \text{Concentration} \times 10^3$; $2 = \zeta$; $3 = \frac{H\kappa_s}{P} \times 10^5$; $4 = (\kappa_s - \kappa) \times 10^6$;

$5 = \eta \times 10^2$; $6 = \frac{\eta}{\kappa_s - \kappa}\left(\frac{H\kappa_s}{P}\right)^2 \times 10^7$; $7 = (\kappa_s - \kappa)\frac{P}{H\kappa_s} \times 10^{12}$

1	2 mv	3	4 mhos	5 poise	6	7
0.00	−10.91	−12.4	26.5	0.8	46.37	−21.36
0.05	−12.14	−13.8	34.8	0.8	43.72	−25.23
0.10	−12.37	−14.01	42.4	0.8	37.06	−30.23
0.20	−12.23	−13.9	56.2	0.8	27.51	−40.41
0.40	−11.35	−12.9	67.0	0.8	19.84	−51.92
0.80	−11.26	−12.8	96.0	0.8	13.63	−74.98
1.60	−11.96	−13.6	125.0	0.8	11.84	−91.87

TABLE XI

Summary of Data for NaCl

$1 = \text{Concentration} \times 10^3$; $2 = \zeta$; $3 = \frac{H\kappa_s}{P} \times 10^5$; $4 = (\kappa_s - \kappa) \times 10^6$;

$5 = \eta \times 10^2$; $6 = \frac{\eta}{\kappa_s - \kappa}\left(\frac{H\kappa_s}{P}\right)^2 \times 10^7$; $7 = (\kappa_s - \kappa)\frac{P}{H\kappa_s} \times 10^{12}$

1	2 mv.	3	4 mhos	5 poise	6	7
0.00	−10.00	− 9.90	20.5	0.950	45.44	−20.71
0.05	−12.83	−12.60	27.7	0.960	55.02	−21.99
0.10	−14.10	−14.10	32.2	0.938	57.99	−22.83
0.20	−13.75	−13.75	35.5	0.938	50.01	−25.81
0.40	−13.14	−13.30	41.7	0.925	39.27	−31.36
0.80	−12.07	−11.95	55.3	0.950	24.55	−46.29
1.60	−10.90	−10.90	67.0	0.938	16.61	−61.44

TABLE XII

Summary of Data for $MgCl_2$

$1 = \text{Concentration} \times 10^3$; $2 = \zeta$; $3 = \frac{H\kappa_s}{P} \times 10^5$; $4 = (\kappa_s - \kappa) \times 10^6$;

$5 = \eta \times 10^2$; $6 = \frac{\eta}{\kappa_s - \kappa}\left(\frac{H\kappa_s}{P}\right)^2 \times 10^7$; $7 = (\kappa_s - \kappa)\frac{P}{H\kappa_s} \times 10^{12}$

1	2 mv	3	4 mhos	5 poise	6	7
0.0	−14.36	−15.48	24.0	0.855	85.23	−15.5
0.1	−10.00	−11.05	30.2	0.83	33.5	−27.2
0.2	− 8.43	− 9.32	31.2	0.83	23.1	−33.4
0.4	− 8.02	− 8.50	35.9	0.874	20.2	−42.2
0.8	− 6.37	− 6.75	52.5	0.874	7.56	−77.7
1.6	− 2.39	− 2.69	40.0	0.84	15.20	−148.7

TABLE XIII

Summary of Data for $CaCl_2$

1 = Concentration $\times 10^3$; 2 = ζ; 3 = $\frac{H\kappa_s}{P} \times 10^5$; $(\kappa_s-\kappa) \times 10^6$;

5 = $\eta \times 10^2$; 6 = $\frac{\eta}{\kappa_s-\kappa}\left(\frac{H\kappa_s}{P}\right)^2 \times 10^7$; 7 = $(\kappa_s-\kappa)\frac{P}{H\kappa_s} \times 10^{12}$

1	2	3	4	5	6	7
	mv		mhos	poise		
0.0	−12.93	−13.70	27.8	0.874	58.89	−20.26
0.1	−10.10	−10.70	33.9	0.874	29.52	−31.66
0.2	−9.36	−9.55	36.2	0.916	23.06	−37.00
0.4	−9.36	−9.55	44.5	0.916	18.79	−46.59
0.8	−8.72	−8.90	51.0	0.916	14.22	−57.27
1.6	−8.69	−8.87	61.0	0.916	11.82	−68.75

TABLE XIV

Summary of Data for K_2CO_3

1 = Concentration $\times 10^3$; 2 = ζ; 3 = $\frac{H\kappa_s}{P} \times 10^5$; 4 = $(\kappa_s-\kappa) \times 10^6$;

5 = $\eta \times 10^2$; 6 = $\frac{\eta}{\kappa_s-\kappa}\left(\frac{H\kappa_s}{P}\right)^2 \times 10^7$; $(\kappa_s-\kappa)\frac{P}{H\kappa_s} \times 10^{12}$

1	2	3	4	5	6	7
	mv		mhos	poise		
0.0	−11.57	−11.50	14.23	0.945	87.86	−12.36
0.1	−16.44	−17.09	32.43	0.894	80.42	−18.97
0.2	−17.58	−17.40	66.50	0.950	43.14	−38.24
0.4	−17.19	−16.95	91.10	0.955	30.18	−53.75
0.8	−15.87	−15.78	133.6	0.945	17.65	−84.57

TABLE XV

Summary of Data for K_2SO_4

1 = Concentration $\times 10^3$; 2 = ζ; 3 = $\frac{H\kappa_s}{P} \times 10^5$; 4 = $(\kappa_s-\kappa) \times 10^{12}$;

5 = $\eta \times 10^2$; 6 = $\frac{\eta}{\kappa_s-\kappa}\left(\frac{H\kappa_s}{P}\right)^2 \times 10^7$; 7 = $(\kappa_s-\kappa)\frac{P}{H\kappa_s} \times 10^2$;

1	2	3	4	5	6	7
	mv		mhos	poise		
0.0	− 9.63	− 9.58	16.63	0.945	52.12	−17.35
0.1	−12.16	−12.64	26.45	0.894	53.99	−20.92
0.2	−12.80	−12.62	38.73	0.955	39.24	−30.67
0.4	−11.39	−11.23	56.43	0.955	21.32	−50.22
0.8	−11.10	−11.04	90.4	0.945	12.78	−81.90

TABLE XVI

Summary of Data of K_3PO_4

1 = Concentration $\times 10^3$; 2 = ζ; 3 = $\frac{H\kappa_s}{P} \times 10^5$; 4 = $(\kappa_s - \kappa) \times 10^6$;

5 = $\eta \times 10^2$; 6 = $\frac{\eta}{\kappa_s - \kappa} \cdot \left(\frac{H\kappa_s}{P}\right)^2 \times 10^7$; 7 = $(\kappa_s - \kappa)\frac{P}{H\kappa_s} \times 10^{12}$

1	2 mv	3	4 mhos	5 poise	6	7
0.0	− 9.06	− 9.01	25.10	0.945	30.53	−27.83
0.1	−12.20	−12.69	38.38	0.894	37.58	−30.24
0.2	−16.41	−16.18	71.30	0.955	35.00	−44.06
0.4	−16.87	−16.89	95.72	0.937	27.79	−56.67
0.8	−13.61	−13.36	113.4	0.960	15.08	−84.94

TABLE XVII

Summary of Data for $ThCl_4$

1 = Concentration $\times 10^3$; 2 = ζ; 3 = $\frac{H\kappa_s}{P} \times 10^5$; 4 = $(\kappa_s - \kappa) \times 10^6$;

5 = $\eta \times 10^2$; 6 = $\frac{\eta}{\kappa_s - \kappa} \cdot \left(\frac{H\kappa_s}{P}\right)^2 \times 10^7$; 7 = $(\kappa_s - \kappa)\ \frac{P}{H\kappa_s} \times 10^{12}$

1	2 mv	3	4 mhos	5 poise	6	7
0.00	− 9.92	−10.97	17.3	0.83	57.73	−15.76
0.05	− 7.44	− 8.23	14.23	0.83	39.52	−17.29
0.10	− 2.96	− 3.27	8.70	0.83	10.19	−26.60
0.20	+ 8.27	+ 9.14	1.51	0.83	45.92	+16.52
0.40	+11.96	+13.22	1.77	0.83	81.94	+13.38
0.80	+13.05	+14.43	14.81	0.83	116.7	+10.26
1.60	+13.14	+14.53	19.60	0.83	89.37	+13.48

Discussion

The curves in Figs. 2 through 9 present a clear and definite picture of what is happening at a water-cellulose interface as we increase the salt concentration of the electrolyte. In all cases, the charge on the double layer which is proportional to $(\kappa_s - \kappa\ P/H\kappa_s$ increases. This finding is not in agreement with the common idea which supposes an electrolyte to discharge the electrostatic charge on a surface. In general the thickness of the double layer which is proportional to $\left(\frac{H\kappa_s}{P}\right)^2 \frac{\eta}{\kappa_s - \kappa}$ decreases. That the thickness of the double layer decreases with increasing salt concentration has been demonstrated experimentally in the case of KCl solution in contact with gold electrodes by McClendon[8] and predicted from theoretical considerations by Gouy[9].

[8] Science, 66, 200 (1927).

[9] J. Phys., (4) 9, 457 (1910).

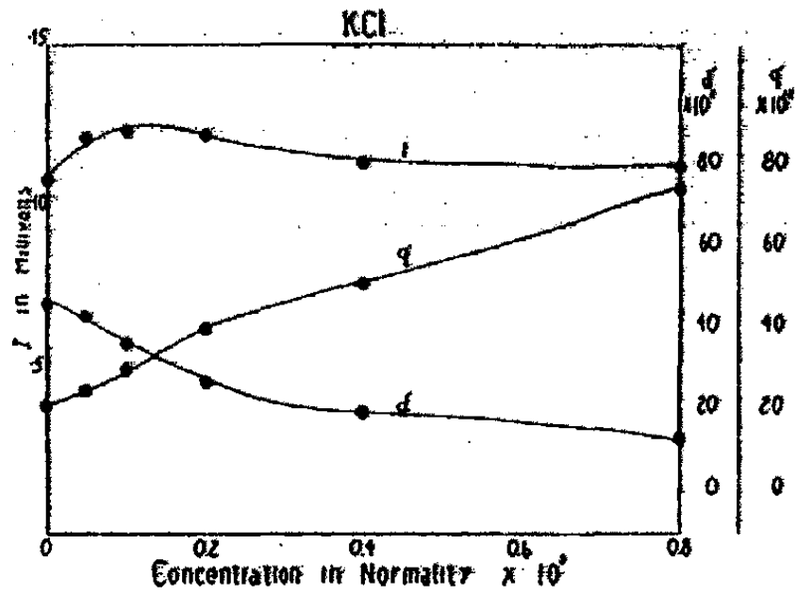

FIG. 2
Showing the effect of KCl on the electrokinetic conditions at a water-cellulose interface.

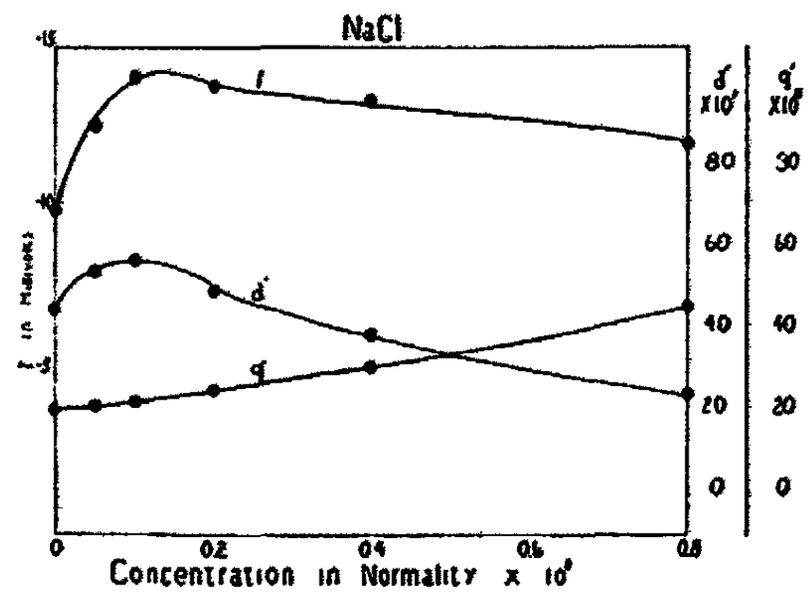

FIG. 3
Showing the effect of NaCl on the electrokinetic condition at a water-cellulose interface.

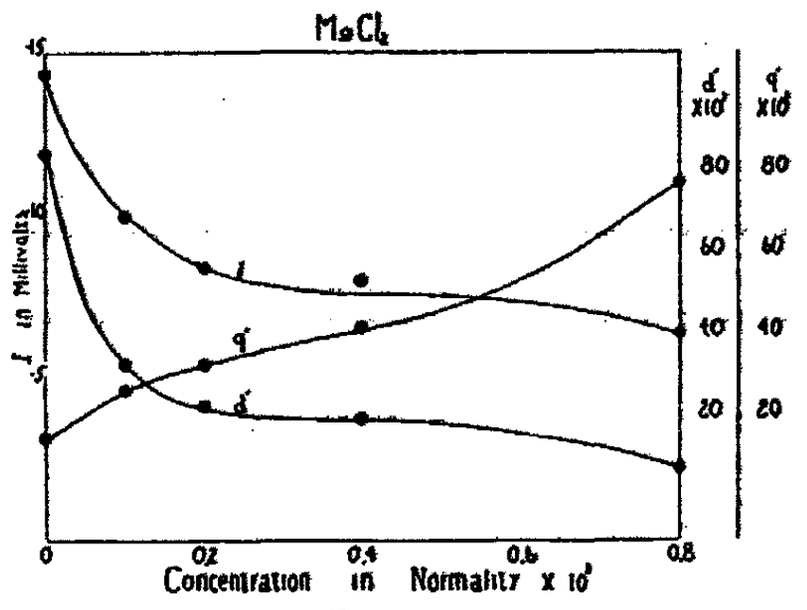

FIG. 4
Showing the effect of $MgCl_2$ on the electrokinetic conditions at a water-cellulose interface.

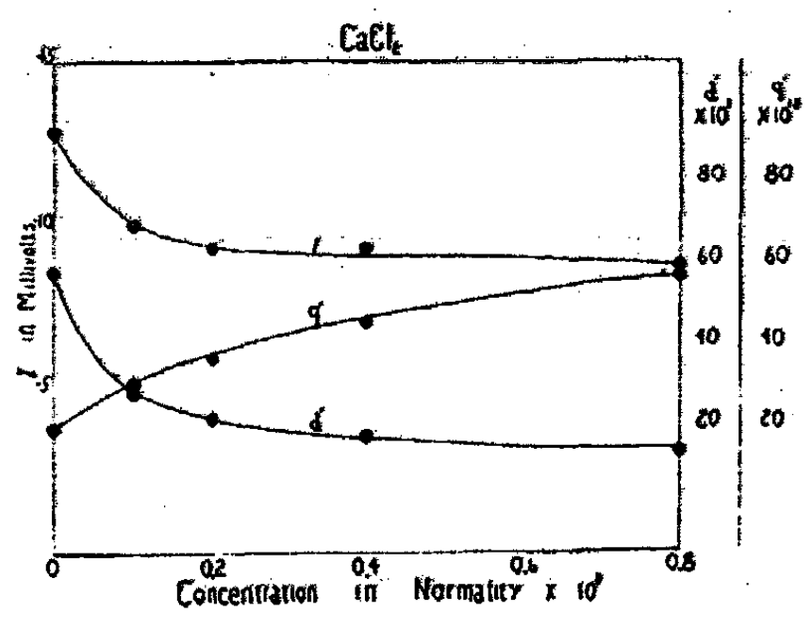

FIG. 5

Showing the effect of $CaCl_2$ on the electrokinetic condition at a water-cellulose interface.

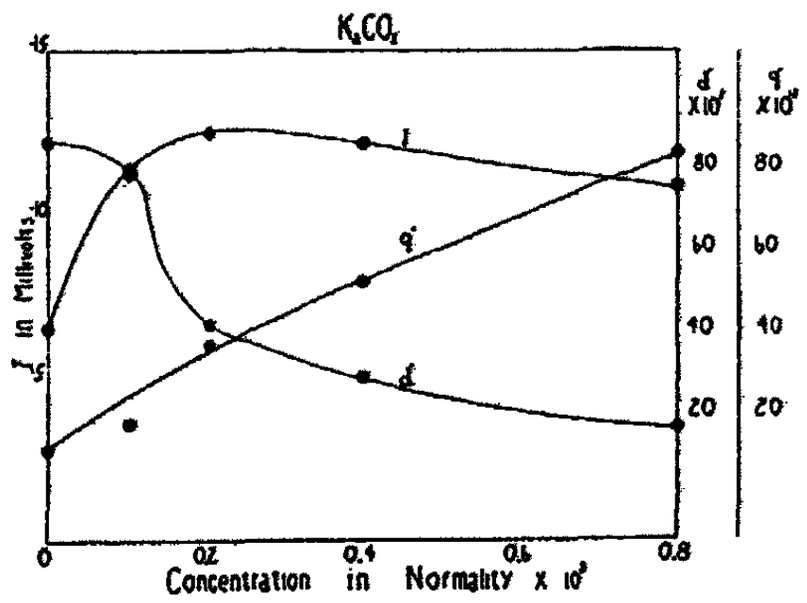

FIG. 6

Showing the effect of K_2CO_3 on the electrokinetic conditions at a water-cellulose interface.

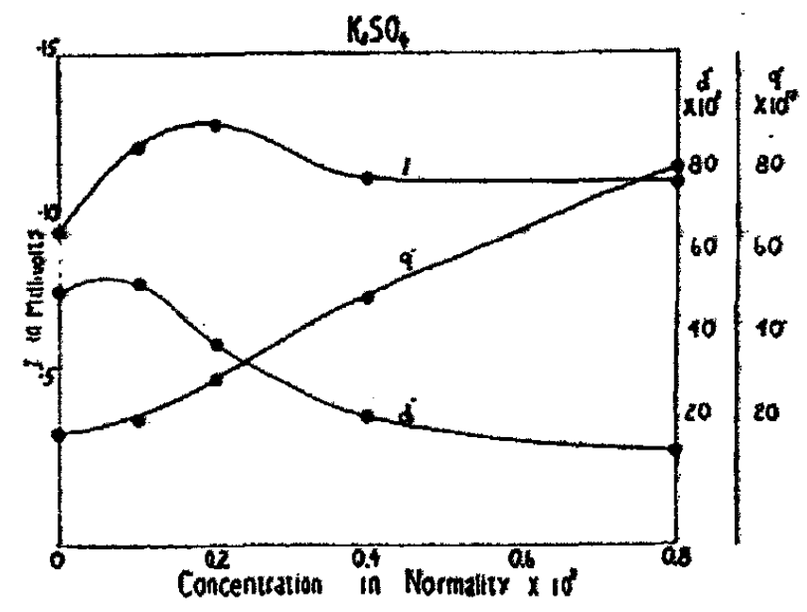

FIG. 7

Showing the effect of K_2SO_4 on the electrokinetic conditions at a water-cellulose interface.

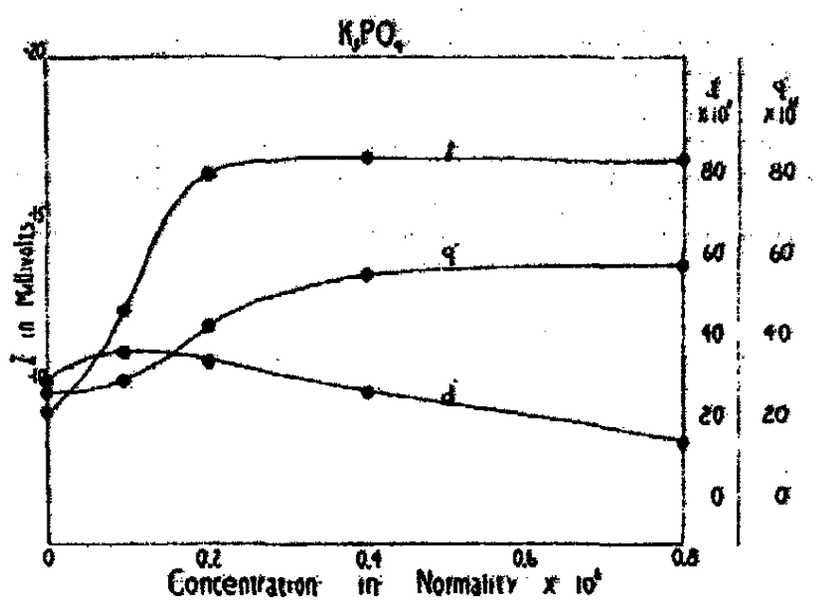

FIG. 8
Showing the effect of K_3PO_4 on the electrokinetic conditions at a water-cellulose interface.

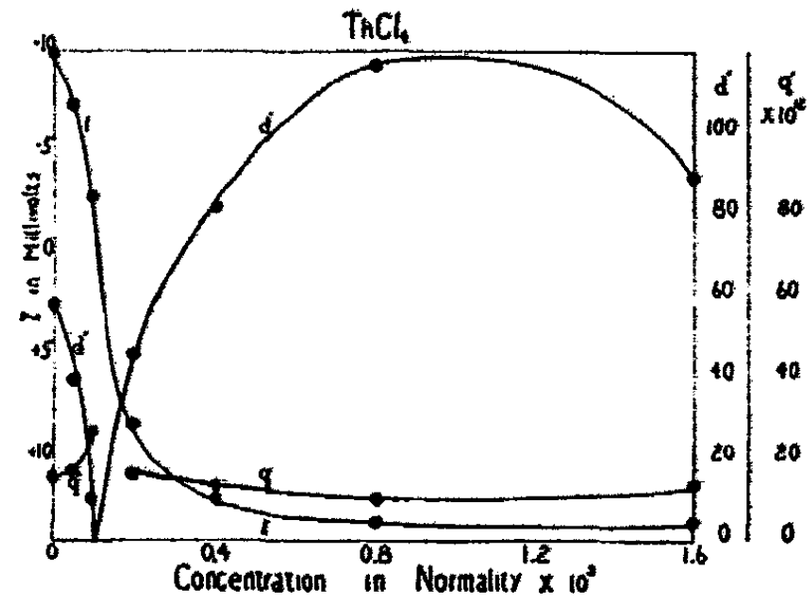

FIG. 9
Showing the effect of $ThCl_4$ on the electrokinetic conditions at a water-cellulose interface.

The curves for NaCl, K_2SO_4, and K_3PO_4 present some complications. The thickness of the double layer apparently at first suffers a slight increase followed by the usual decrease. We cannot at present say why this should be. It is, however, in sharp contrast to the usual view that the slight increase in the ζ-potential which is shown in these curves be due to an adsorption of anions, since this would have been evident in the curves showing the behavior of the charge with increasing salt concentration.

$ThCl_4$ is the only salt investigated which reversed the sign of the electric charge on the cellulose. It is very difficult to see exactly what is happening in this case, and to attempt an explanation at this time would be premature.

Perhaps the most important feature of this investigation is its bearing on our ideas of precipitation of colloidal particles by electrolytes. By definition the electrical work done in bringing two charged particles together is exactly equal to the ζ-potential, and it might be thought that the value of the ζ-

potential would determine rather definitely the behavior of colloidal particles in the presence of electrolytes in respect to their effect on coagulation. This point has been brought out by Powis[10] who proposed a so-called critical potential to which the ζ-potential must be reduced before the colloidal particle can precipitate. We, however, while recognizing the importance of the electrical work term as expressed by the ζ-potential, feel that there are additional factors which must be considered.

It is not our purpose to propose a theory of precipitation but simply to point out that in the case of those monovalent cations where the ζ-potential of a colloidal particle is usually considerably higher than the critical potential when precipitation occurs, the action is simply to decrease the thickness of the double layer as is shown in the figures, allowing the particles to approach more closely before electrical repulsion is experienced and thus allowing a greater chance for molecular attraction between the colloidal particles to play a rôle. For example, with KCl the ζ-potential over the range of concentration investigated is almost constant but the thickness of the double layer has been decreased over 300 percent.

Summary

1. Smoluchowski's equation for surface conductance has been modified by the appropriate substitutions so that two equations were obtained, one expressing the charge per unit area on the surface and the other having to do with the thickness of the double layer.

2. The ζ-potential and surface conductance at a cellulose interface have been measured for aqueous solutions of KCl, NaCl, $MgCl_2$, $CaCl_2$, K_2CO_3, K_2SO_4, K_3PO_4, and $ThCl_4$.

3. The physical significance of the results are discussed. These studies indicate that the ζ-potential in general *decreases* with increasing concentration of electrolytes in the aqueous phase, but that this decrease in the ζ-potential may be accompanied by an actual *increase* in the charge on the particle, the decrease in the ζ-potential being more nearly related to a decrease in the thickness of the double layer.

4. The theoretical considerations of Gouy and the experimental findings of McClendon for KCl are confirmed for a series of electrolytes, *i.e.*, the thickness of the double layer is decreased with increasing salt concentrations.

5. A new conception of the action of electrolytes on affecting the stability of a colloid is suggested, *i.e.*, that the salts do not reduce the electric charge on the particle to zero or even to a "critical threshold," but rather that there is a *decrease in the thickness of the double layer* which allows the particles to approach each other closely enough so that they adhere to each other. With polyvalent ions, the charge itself may actually be decreased so as to approach zero.

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[10] Z. physik. Chem., 89, 186 (1915).

ELECTROPHORESIS AND THE DIFFUSE IONIC LAYER

BY MELVIN MOONEY*

Introduction

In a previous publication[1] the author has reported some electrophoresis measurements according to which the electrophoretic mobility of an oil drop suspended in distilled water increases with the diameter of the drop. A few measurements with dilute solutions of electrolytes indicated that electrolytes decrease this variation in mobility with diameter.

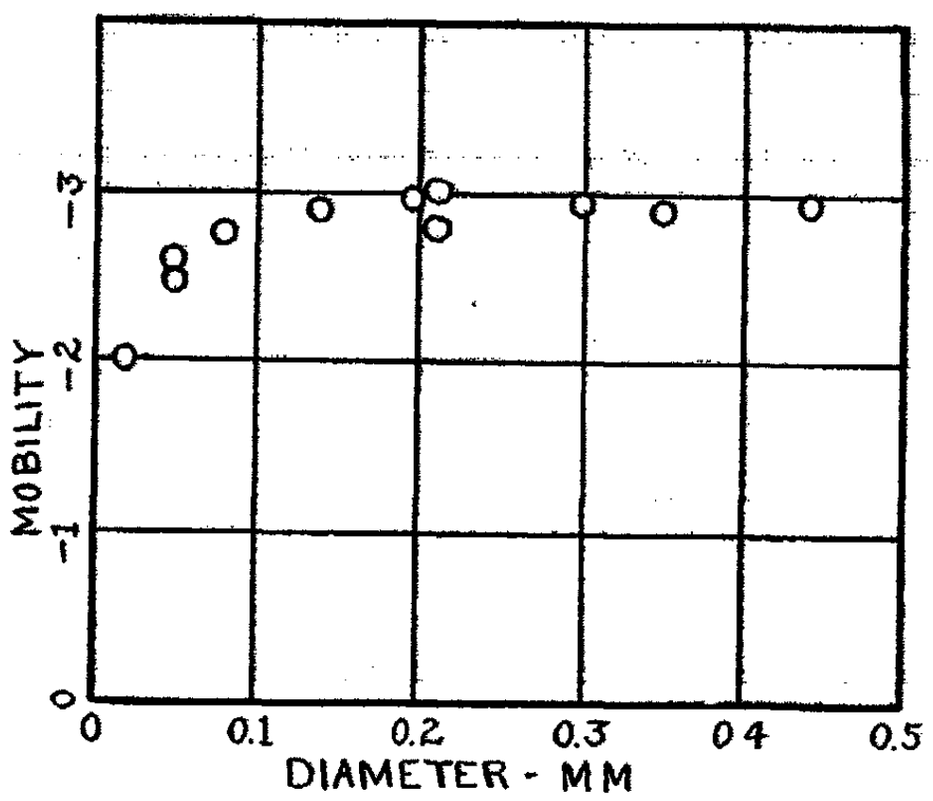

FIG. 1

Cataphoretic mobility of Red Oil and benzyl chloride measured in distilled water.

The nature of the mobility-diameter curve in distilled water is shown in Fig. 1. Alty[2] has reported that the mobility curve[3] of air bubbles in distilled water passes through a maximum at a diameter of about 0.2 mm; and he suggested that, if the author's measurements had been extended to larger diameters, there would have been found a maximum in the mobility curve for oil-drops also. The measurements plotted in Fig. 1 extend to diameters of nearly 0.5 mm; but they indicate only an asymptotic approach of the mobility to an upper limit.

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[1] Mooney: Phys. Rev., 23, 396 (1924).

[2] Proc. Roy. Soc., 112A, 235 (1926).

[3] The theory that will be outlined in the present paper cannot be tested with these data of Alty's, for two reasons; first, because his gas bubbles were not in equilibrium but were dissolving and decreasing continuously in diameter, and second, because all of his observed velocities require a correction for the electro-osmotic mobility, which was not determined.

Since the publication of the article just referred to, the effects of electrolytes on the mobility-diameter curve have been investigated in more detail; and a theory purporting to explain the experimental results has been developed. It is the purpose of the present paper to give a brief outline of the theory and to compare it with some of the experimental data. More details of the theory and the experiments will be given in a series of papers to be published elsewhere.

Current Theory

Up to the present time there have been published two theoretical formulas for electrophoretic mobility: the Helmholtz formula,[4] later modified by Lamb[5] and by Smoluchowski;[6] and the Debye-Hückel formula.[7] Since neither formula suggests or explains any variation in mobility with particle size, let us consider the necessary assumptions underlying these formulas. They are:

A—Helmholtz

1. The particle is rigid and non-conducting.
2. D, the dielectric constant and η, the coefficient of viscosity, have the same values within the electric double-layer as in the liquid in bulk.
3. The charge distribution in the double-layer is unaffected by the impressed field or by the relative motion of the particle and the suspension medium.
4. The thickness of the double-layer is small in comparison with the radii of curvature of the particle surface.

B—Debye-Hückel

1. The particle is rigid and spherical.
2. Identical with A2.
3. The spherical symmetry of the charge distribution in the double-layer is unaffected by the impressed field or by the relative motion of the particle and the suspension medium.
4. The thickness of the double-layer is large in comparison with the radius of the particle.

The formulas obtained on these assumptions are:

$$\mu_e = \frac{v}{E} = \frac{D\varphi}{4\pi\eta} \quad (1)A \qquad\qquad \mu_e = \frac{v}{E} = \frac{D\varphi}{6\pi\eta} \quad (1)B$$

in which μ_e is the electrophoretic mobility, v the velocity, E the impressed field, D the dielectric constant, η the coefficient of viscosity of the liquid, and φ the potential at the surface. The difference between the assumption A4 and B4 accounts for the difference between the two resulting formulas.

[4] Helmholtz: Ann. Physik, 7, 337 (1879); Mem. London Phys. Soc. (1888); Ges. Abhandl. Kenntnis Kohle, 1, 855 (1922).

[5] Lamb: Brit. Ass. Adv. Sci. Repts., 495 (1887); Phil. Mag., 25, 52 (1888).

[6] Smoluchowski: Bull. intern. acad. sci. Cracovie, 182 (1903).

[7] Debye and Hückel: Physik. Z., 25, 49, 204 (1924).

The assumption B_4 is not mentioned in the Debye-Hückel articles; and indeed no one seems to realize that such an assumption is involved. In fact, however, this condition is necessary to the validity of the Debye-Hückel analysis, the reason being that those authors neglected the electric polarization of the particle under the influence of the impressed field. In doing so they necessarily neglected also the interaction between the polarization charges and the mobile charge of the double-layer; and this interaction would produce an appreciable effect on the mobility if an appreciable fraction of the mobile charge were situated close to the particle.

Assumption A_2, or B_2, concerning the constancy of D and η, has been subjected to criticism,[8] and it is certainly reasonable to expect some change in the values of these "constants" due to the special forces within one or a few molecular diameters from a surface. However, if we consider the tendency of the mobile ions to diffuse away from the surface, we arrive at a picture, first drawn for us by Gouy,[9] in which the thickness of the double layer often far trancends the limits of these surface forces. Furthermore, present day knowledge concerning the nature of adsorbed layers leads us to reject as very improbable any surface slip such as was considered by both Helmholtz and Lamb.

Theory of Electrophoresis based on the Diffuse Layer

In the author's attempts to improve the theory of electrophoresis, assumption A_2 has been retained and assumptions A_3 and A_4, B_3 and B_4 have been rejected as being much less acceptable. The rejected assumptions are replaced with a quantitative theory of the charge distribution in the outer, mobile part of the double-layer, hereafter termed the ionic atmosphere or the diffuse layer. Specifically, it is assumed:

a. The particle is spherical, non-conducting, or surrounded by a non-conducting surface, and is rigid—at least to the stresses involved in electrophoresis. The liquid in which the particle is suspended contains in solution a single di-ionic electrolyte.

b. The ions in the diffuse layer move in accordance with established physical laws, under the influence of 1, the velocity of the water; 2, the local electric field; 3, diffusion.

c. D, η, and also m_1 and m_2, the absolute mobilities of the positive and negative ions, respectively, are constant up to the spherical surface enclosing the particle and any rigidly adsorbed material.

As in previous analyses of electrophoresis, the inertia terms in the hydrodynamic equations are neglected in comparison with the viscosity terms. The formulas obtained are consequently valid only for small velocities.

It is obvious that, on the basis of assumption *b*, the mean thickness of the Helmholtz double-layer will vary with the concentration and valence of the electrolytic ions, the conditions reducing to Gouy's theory in the special

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[8] Harkins: Colloid Symposium Monograph, 6, 17 (1928).

[9] Compt. rend., 149, 654 (1909); J. Phys., 9, 457 (1910).

simple case of an infinite sphere (plane surface) with zero impressed field. The mobility of a finite spherical particle will be shown to depend theoretically upon the ratio of its radius to the mean thickness of the diffuse layer.

The system of differential equations representing my assumptions is too complicated to allow any hope for a complete solution; but I have succeeded in obtaining the first two terms of the solution in the form of a power series in χ, the surface curvature:

$$\mu_e = -\left\{\frac{D\varphi}{4\pi\eta} + \chi F_1(\varphi) + \sum_2^\infty{}^i \sum_2^\infty{}^j F_{ij}(\varphi)\chi^i E^j\right\} \qquad (2)$$

in which χ is the surface curvature, or $1/r$, r being the radius of the sphere; F_1 is a known function of φ, and the F_{ij}'s are undetermined functions of φ. The first term in this formula is the familiar Helmholtz mobility formula. The second term gives the first order correction for the curvature of a finite sphere. The remaining terms all involve higher powers of χ and E.

For purposes of comparison with experiment it is convenient to differentiate equation (2) with respect to χ, thus obtaining an expression for S_0 the limiting slope at zero curvature,

$$S_0 = \left(\frac{\partial\mu_e}{\partial\chi}\right)_0 = -\frac{2l\mu_0}{\varphi}\left(\lambda_1 + \frac{2DA}{\pi\eta}\lambda_2 + \lambda_3\right) \qquad (3)$$

in which

$$\lambda_1 = 6\int_0^\omega \ln\frac{1+x}{1-x}\cdot\frac{dx}{x} - \frac{8\omega}{3(1+\omega)}\ln(1+\omega) - \frac{8\omega}{3(1-\omega)}\ln(1-\omega)$$

$$\lambda_2 = \frac{1}{m_1}\ln(1+\omega)\left[\ln\frac{1+\omega}{1-\omega} - \frac{2\omega}{1+\omega}\right] + \frac{1}{m_2}\ln(1-\omega)\left[\ln\frac{1+\omega}{1-\omega} - \frac{2\omega}{1-\omega}\right]$$

$$\lambda_3 = 4\omega\frac{1-\omega^2}{1+\omega^2}$$

$$\omega = \sinh\frac{\varphi}{2A} \qquad A = \frac{kT}{\nu e}$$

$$l = \sqrt{\frac{DkT}{8\pi ne\nu^2}}$$

μ_0 is the limiting (extrapolated) mobility at zero curvature, k is the Boltzmann constant, T the absolute temperature, n the number of ions of one kind per ml of solution, ν the valence of the ions, and e is the electronic charge. The definitions of the other terms are the same as have already been given.

The term λ_3 does not occur in these equations if it is assumed that the surface potential, φ, is independent of χ; but it does occur if it is assumed that it is σ, the surface charge, that is independent of χ. It can be argued on very reasonable grounds that these assumptions represent the two extreme possibilities and that the actual situation lies somewhere between the two. Fortunately, λ_3 is found to be small in comparison with the other terms in

equation (3); and in view of the present inaccuracy in electrophoresis measurements, we do not need to concern ourselves further with the exact variation of φ or σ with χ.

In testing equation (3) with experimental data, the value of φ is calculated from μ_0 by means of the Helmholtz formula. ω and the λ's are thereby determined; and the right member of equation (3) is evaluated by inserting the proper values of the parameters.

Experimental Procedure

The electrophoretic mobilities of oil drops suspended in various solutions of electrolytes were determined, the microscopic method being used. The electrophoresis cells employed were thin-walled, cylindrical glass U-tubes immersed in a small water bath. The oil phase in the suspensions was always quite small, 1 per cent or less. The suspensions were formed in some cases by shaking a few drops of oil with 100 or 200 ml of water or aqueous solution in a separatory funnel; in other cases by squirting into the water or solution a fine stream of oil under high pressure. The following oils were used, either singly or combined in mixtures of the same density as the solution used:—phenyl chloride, phenyl bromide, anisol, anethol, Stanolind and Red Oil, the last two being commercial paraffin hydrocarbon oils manufactured by the Standard Oil Company.

Measurements at room temperature were made without any thermostatic control. The data thus obtained were recalculated to the standard basis of 20°C on the assumption that all mobilities would merely be changed inversely as the viscosities of the water at the two temperatures considered.

The precision attained in this work was better than that in most measurements of electrophoresis, the mean error being 1 per cent or less under favorable conditions. Nevertheless, this precision is obviously not at all what it should be for testing a theory which predicts only the limiting slope of the mobility curve at zero curvature; that is, at infinite radius.

A still greater hindrance to accuracy in determining the limiting slope was found to lie in the suspensions themselves. They were difficult to reproduce; and in the more concentrated electrolyte solutions they seldom gave smooth mobility curves. Generally many drops of the same diameter were found with widely different mobilities. Consequently, all that can be done with the experimental data is to determine very roughly the limiting slope of the mobility curve and see whether or not the theoretically predicted slope is correct in its order of magnitude.

Comparison of Experimental Results with Theory

In Fig. 2 are shown some electrophoretic mobilities, plotted against curvature, in various concentrations of KOH. Extrapolation to zero curvature gives us μ_0, from which we calculate the limiting slope of the mobility curve as χ approaches 0. These theoretical slopes and the values assumed for μ_0 are indicated by the straight lines in the figure. It is seen that the theoretical

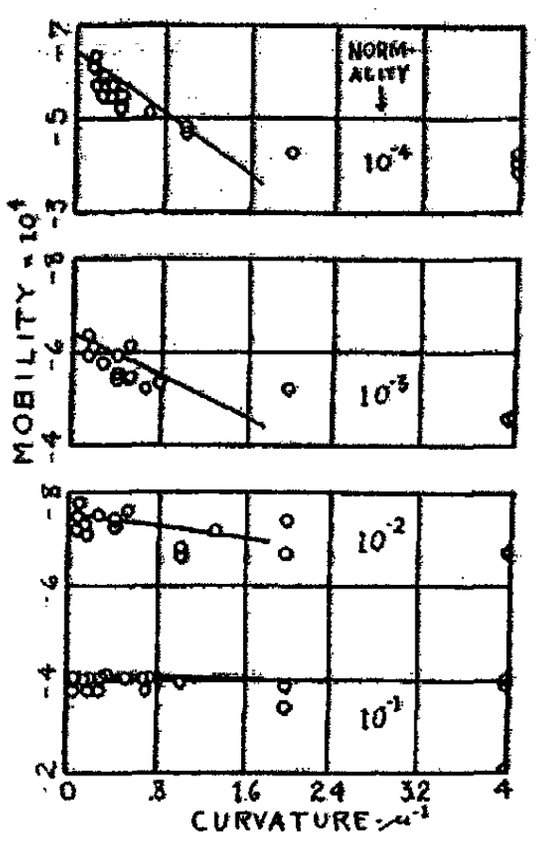

FIG. 2
Cataphoretic mobilities in cm/sec/volt/cm, measured in KOH.

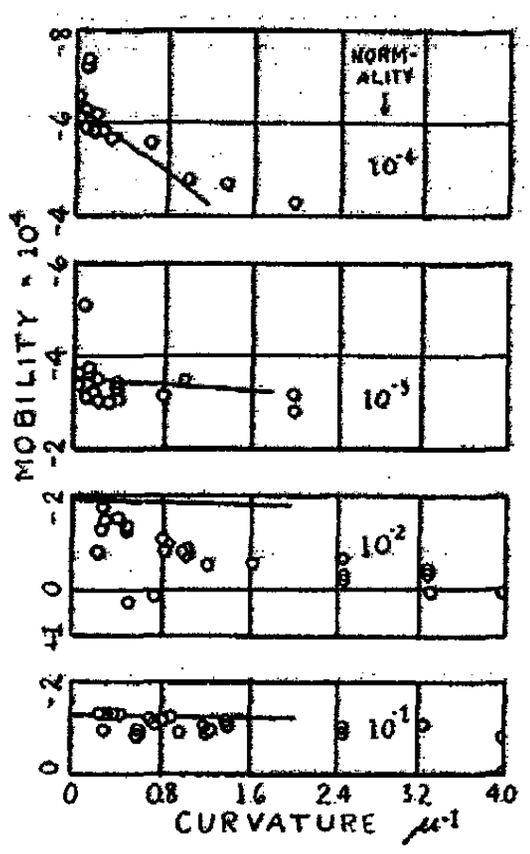

FIG. 3
Cataphoretic mobilities in cm/sec/volt/cm, measured in KCl.

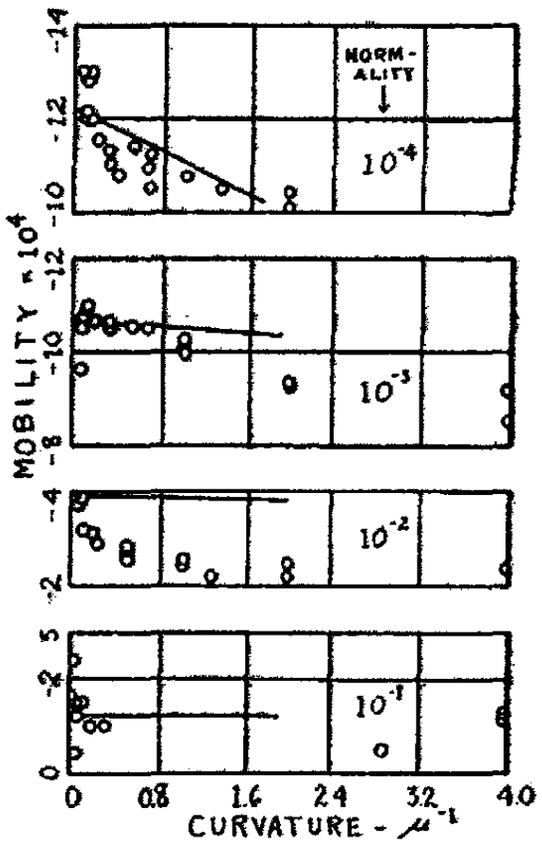

FIG. 4
Cataphoretic mobilities in cm/sec/volt/cm, measured in KCl.

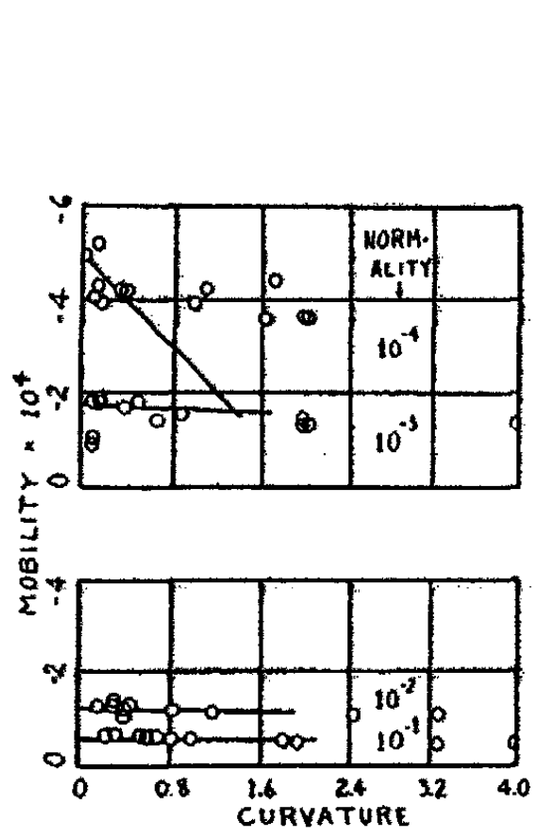

FIG. 5
Cataphoretic mobilities in cm/sec/volt/cm, measured in $CuSO_4$.

slope rapidly approaches zero as the concentration increases and is in rough agreement at all concentrations with the experimental slope.

Figure 3 shows a series of measurements made in KCl solutions. The agreement between theory and experiment is satisfactory with concentrations up to 10^{-3} molar; but at the higher concentrations definite disagreement appears. The difference between the theoretical and experimental slopes in 10^{-1} molar KCl is not large; but their ratio appears to differ considerably from unity. In the next series, Fig. 4, with HCl as the electrolyte, the agreement between theory and experiment is still good with the dilute solutions; but with the concentrated solutions the disagreement is more pronounced than with concentrated KCl. In Fig. 5 are shown the results obtained with $CuSO_4$, a salt with bivalent ions; and the agreement here seems to be good throughout the entire series. The calculations in this case are based on the assumption that the $CuSO_4$ is partially ionized but not hydrolyzed at all. Fig. 6 shows some cataphoretic mobilities at 75°C. The theory agrees with the experimental results except in the case of 0.5×10^{-2} molar $CuSO_4$.

To summarize these results, it can be said that the theoretical slope of the mobility-curvature curve agrees fairly well with the experimental data for dilute solutions up to concentrations of 10^{-3} molar and in some cases for the more concentrated solutions. Assuming that such agreement as is obtained is not accidental, but results from the essential soundness of the theory, we have yet to explain the lack of agreement for concentrated neutral and acid solution.

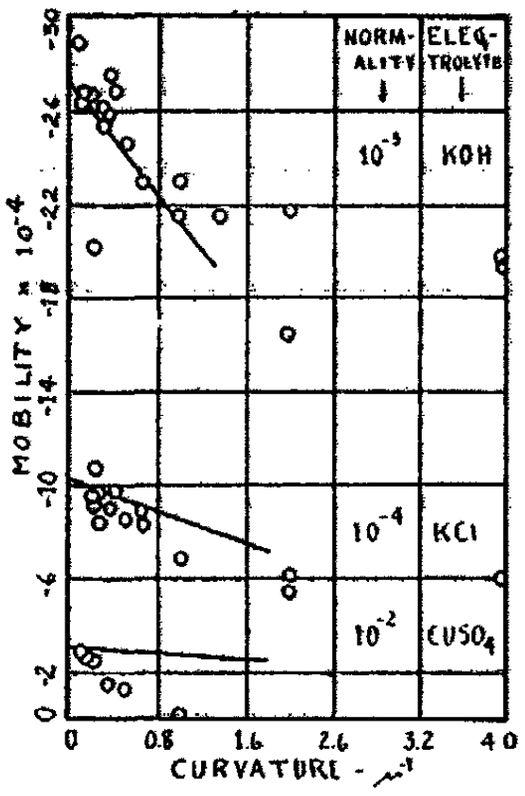

FIG. 6
Cataphoretic mobilities in cm/sec/volt/cm, measured at 75°C.

Early in this program of research the question was examined as to how soon equilibrium is established between the surface charge and the ionic atmosphere surrounding the drop. Suspensions of oil in distilled water, in 10^{-3} molar KOH and HCl and in weaker solutions of KOH, were examined when formed and also after ageing for several days; but no significant changes in electrophoretic mobilities were found. Extended ageing experiments with more concentrated solutions were attempted but failed, because of the instability of the oil suspensions. On the basis of the results in dilute solutions, it was assumed that in all cases an oil-water interface attains its equilibrium surface charge practically as soon as it is formed.

However, certain other experimental results in addition to those already shown led to a re-examination of the question of equilibrium. Greater stability of the suspensions was attained by using mixtures of oils having

practically the same densities as the electrolytic solutions in which the oils were suspended. Fig. 7 shows some data obtained with 10^{-2} molar HCl. The "hot" suspensions were made by atomizing the oil in boiling hot solution. The suspension was then allowed to cool slowly—in an hour or two—to room temperature before filling the electrophoresis cell. It is obvious that the cold suspension on the second day had changed from what it was when fresh, but had not yet reached the state of the "hot" suspension, which appears to be more stable. A series of such experiments indicated that, in all cases in which

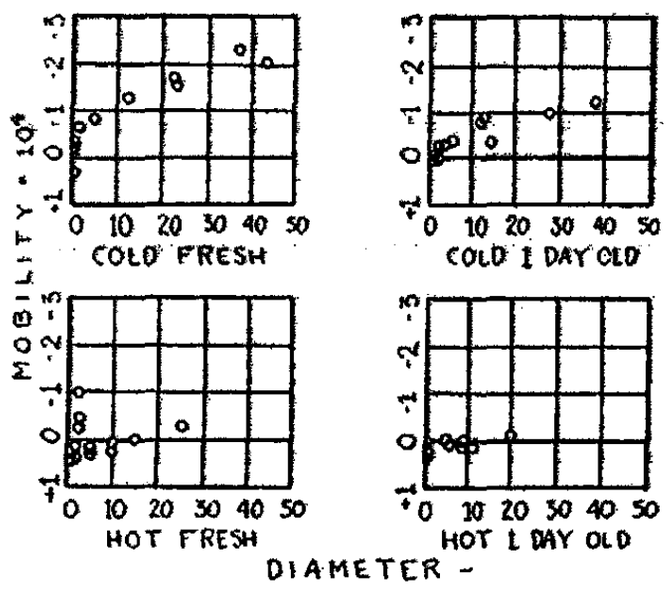

Fig. 7

Cataphoretic mobilities in cm/sec/volt/cm, measured in 10^{-2} molar HCl. "Hot" indicates a suspension formed in boiling hot solution and cooled slowly to room temperature. "Cold" indicates a suspension formed at room temperature.

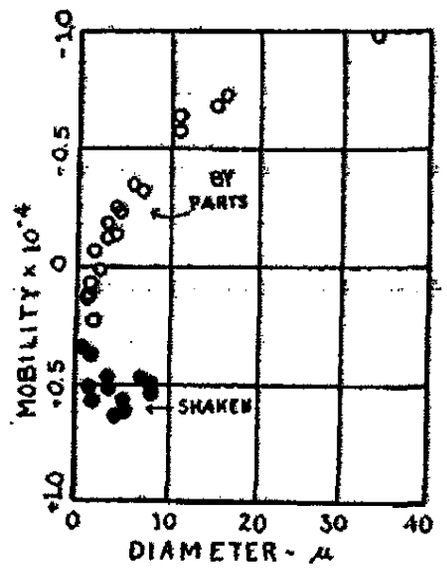

Fig. 8

Cataphoretic mobilities in cm/sec/volt/cm, measured in 10^{-1} molar HCl. "Shaken" indicates suspension formed by shaking oil with the acid solution. "By parts" indicates suspension formed by shaking oil with water and then adding the acid.

the theoretical slope of the mobility-curvature curve departed notably from the experimental curve, the suspension was not in its equilibrium state.

Logically the next step in the experimental procedure would be to produce suspensions that are in equilibrium; but this seems to be very difficult to do, at least if we assume as one criterion of equilibrium that all drops of the same diameter must have the same electrophoretic mobility. Since the oil drops coalesce, extended ageing cannot be used; and no method of preparing the fresh suspensions was found which gave reproducible, smooth and stable mobility curves. This difficulty is much greater with acid than with neutral or alkaline solutions. It is illustrated in Fig. 8, which shows the different results obtained, when the suspension is formed by shaking the oil in a 10^{-2} molar solution of HCl, in the usual manner, and when it is formed "by parts", by shaking the oil in distilled water and adding the acid afterwards. The latter method is the only one that gives a definite curve, but ageing and other tests show that the suspension thus formed is further removed from equilibrium than the one formed by the first method.

Anomalous Effects

Considerable effort was spent in trying to determine the disturbing factor that was interfering with the establishment of equilibrium. In addition to the effect just mentioned, depending upon the method of preparing the suspension, a variety of other anomalous effects were thus discovered. Either ageing or temporary heating may sometimes increase and sometimes decrease the mobility. There are both permanent and temporary changes in mobility with the duration of the impressed field; and the mobility sometimes varies with the intensity of the impressed field. By coating the wall of the electrophoresis cell with the oil used in the suspension, the ratio of electrophoretic mobility of the large drops to the electro-osmotic mobility was determined. This ratio was found to vary considerably. For suspensions which were normal in other respects, it was 1, which is the theoretical ratio on the basis of the Helmholtz theory. For suspensions which were abnormal in other respects, the ratio was usually greater than 1, the largest observed ratio being 2.

All these and several other anomalous effects taken together can scarcely be said to establish the underlying cause of the anomalies. Nevertheless, they all seem to indicate or allow an explanation based on the following "slow motion" picture of the formation of the Helmholtz double-layer:

1. As soon as an oil-water surface is formed, adsorption of ions from the water begins. In general, ions of opposite sign will not be adsorbed equally; and a net surface charge will result.

2. The surface charge attracts ions of the opposite sign and repels ions of the same sign and thereby causes the development of a diffuse ionic layer in the water near the surface.

3. The surface forces, including that due to the surface charge, generally cause strong adsorption of water and electrolyte molecules. These adsorbed molecules sometimes form a semi-rigid crust or plastic layer between the surface and the diffuse layer. The plastic layer may be many molecules deep and its growth may occupy seconds, minutes or even hours; but as soon as it begins to form, it interferes with the further adsorption of ions by the surface and hence tends to stabilize the surface charge before true equilibrium has been reached.

In order to make this picture consistent with experimental results, it is necessary further to postulate that the plastic layer has a volume charge of the same sign as that of the diffuse layer, that it can be more or less disrupted by mechanical or electric forces, and that in electrokinetic processes it is more easily dislodged from a finite sphere than from a plane surface.

The first two elements of this picture, the adsorbed surface charge and the diffuse ionic layer, have already been depicted in many of the recent discussions of electro-kinetic phenomena. The third element, also, the layer of adsorbed molecules, enters into some of these discussions;[10,11] and its existence is further indicated by a large number of phenomena other than electro-

[10] Gyemant: Z. Physik, 17, 190 (1924); "Kolloidphysik," (1925).

[11] Stern: Z. Elektrochemie, 30, 508 (1924).

kinetic, such as the hydration of colloids, precipitation under conditions that permit peptization, thixotropy, plastic oil-water surfaces which the author has observed in the presence of $FeCl_3$, and the lack of adhesion[12] in some cases between the particles of a suspension and a glass surface. There is thus plenty of precedent for postulating this third element in the picture of the double-layer. The novel features suggested here are the susceptibility of this molecular or poly-molecular layer to external forces and its interference with ionic diffusion and interchange between the surface and the diffuse ionic layer.

Surface Charge

Preliminary to analyzing the diffuse ionic layer around a sphere, it was necessary, among other things, to find the relationship between the electrokinetic potential and the surface charge of a plane surface. This relationship is

$$\sigma = \frac{DA}{\pi l} \cdot \frac{\omega}{1 - \omega^2} \tag{4}$$

In Fig. 9 are plotted on a logarithmic scale values of σ calculated from μ_0, the limiting electrophoretic mobilities of oil drops.

Surface Conductivity

As a consequence of the tangential motion of the mobile ions in the double-layer, there will be an increment in the conductivity of the liquid near a surface. The value of this increment per unit area of a plane surface, or the specific surface conductivity, κ, will be expressed by an integral of the form

$$\kappa = \int_0^\infty \left[(\rho_1 - \rho\ ) (m_1 + w) + (\rho_2 - \rho_\infty) (m_2 - w) \right] dx \tag{5}$$

or

$$\kappa = \int_0^\infty \left[(\rho_1 - \rho_2)w + (\rho_1 - \rho_\infty)m_1 + (\rho_2 - \rho_\infty)m_2 \right] dx \tag{6}$$

in which ρ_1 and $-\rho_2$ are the charge densities due to the positive and negative ions, respectively; ρ_∞ is the charge density outside the diffuse layer due to the positive ions; w is the velocity of the water under unit field; m_1 and m_2 are the absolute mobilities of the positive and negative ions, respectively; and x is the distance from the surface. The term, $(\rho_1 - \rho_2)w$, expressing the current due to the net charge carried by the water, is the only term included in Smoluchowski's formula for surface conductivity.[13] The other two terms in the integrand of equation (6) represent the current due to the motion of the ions with respect to the water.

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[12] Buzágh: *Kolloid-Z.*, 51, 105 (1930).

[13] Smoluchowski: Physik. Z., 6, 529 (1905).

The indicated integration can be accomplished without difficulty in the case of a di-ionic electrolyte, yielding

$$\kappa = \sigma\mu_e\left(1 - \frac{2\omega A}{\varphi}\right) + \sqrt{\frac{2DkTn}{\nu}}\left(-\frac{m_1\omega}{1+\omega} + \frac{m_2\omega}{1-\omega}\right) \qquad (7)$$

in which μ_e is now the electro-osmotic mobility. The rest of the notation is the same as in previous sections. We can test this formula with the measurements of absolute conductivity of plane surfaces recently reported by McBain and Peaker.[14] They found $\kappa = 4.3 \times 10^{-8}$ mhos for polished glass in contact with 10^{-3} molar KCl at 25°C, and $\kappa = 3.5 \times 10^{-8}$ mhos for a stearic acid film on distilled water. For the electro-kinetic potential of glass against the salt solution we can use the figure 0.8 millivolt, reported by Powis.[15] Equation (7) then gives us $\kappa = 8.5 \times 10^{-10}$ mhos, which is only 0.02 of the experimental value. No figure is available for the electro-kinetic potential of stearic acid in water; but from the order of magnitude of all such potentials we know that in this case also equation (7) will give a value for κ many times too small. From these discrepancies we must conclude that there are other factors contributing to the surface conductivity in addition to what we have considered. What they may be can only be surmised; but it is noteworthy in this connection that Bancelin[16] found that a glass surface adsorbs 14×10^{-8} g/cm² of NaCl from a 10^{-4} molar solution. If the surface was plane, this adsorption figure corresponds to 1.1 molecular layers with the molecules normal to the surface; that is, 1.1 double ionic layers. If we assume that these molecules are oriented, some with their chlorine atoms and some with their sodium atoms towards the glass, that some of them are completely ionized, and that many of them are partially ionized in such a way that the ion on the water side of the surface is free to move parallel to the surface, but not normal to it—then we have a picture which meets all the requirements of the theory of the diffuse layer and of the experimental measurements of surface conductivity and of electro-osmotic mobility.

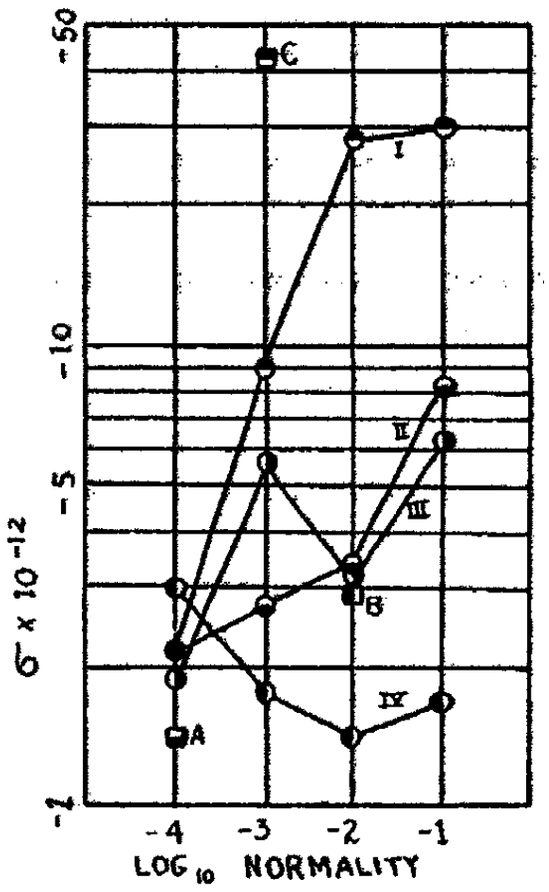

FIG. 9

Surface charge expressed as the number of elementary charges per cm².

[14] Proc. Roy. Soc., 125A, 394 (1929).
[15] Z. physik Chem., 89, 91 (1915).
[16] J. Chim. phys., 22, 518 (1925).

The conductivity of the stearic acid-water surface presents a different problem; for in this case we know that practically all of the acid molecules are turned the same way, with the $-COOH$ group towards the water. In order to explain the large surface conductivity in this case, it is necessary to assume either that impurities in the water are adsorbed and behave like the NaCl in the preceding picture or that the ionization of the water itself is increased in the neighborhood of the surface.

The plastic adsorbed layer, postulated in section 6, has not entered into this discussion of surface conductivity, because NaCl or KCl are not very active in forming a plastic layer. Among the electrolytes which were used in the author's work the most active in this respect were $FeCl_3$, $Zr(NO_3)_4$, and $Th(NO_3)_4$, all of which are salts with poly-valent cations. Recently Briggs[17] has measured the relative surface conductance of cellulose fibers (filter paper) in several electrolytic solutions; and he found that the surface conductance is increased by HCl and KCl, but very little affected by $ThCl_4$. We cannot avoid the suggestion here that the activity of $Th(NO_3)_4$ in building up a plastic adsorbed layer and the inactivity of $ThCl_4$ in promoting surface conductance are closely associated phenomena.

Discussion

The present state of the theory and general understanding of electro-kinetic phenomena is deplorably chaotic. Some writers are using the Debye-Hückel formula for calculating electro-kinetic potentials, while others stick to the Helmholtz formula. Those who are trying to determine experimentally which of the two formulas is "right" do not consider the difference in the derivations of the formulas or discuss adequately the significance of an experimental discrimination. Recently Thon[18] has questioned whether the electro-kinetic potentials as determined by electrophoresis and by streaming potential are essentially the same thing, as has always been assumed; and both Harkins[8] and McBain[19] have argued that the "electro-kinetic potential" does not exist or mean anything, anyhow. In this rather extended discussion an attempt will be made to clarify and settle some of these cloudy questions.

The original Helmholtz conception of a very thin electric double-layer of atomic dimensions is frequently criticized, usually on the basis of Gouy's theory of the diffuse ionic layer; and sometimes the conclusion is drawn that the Helmholtz analysis of electro-kinetic phenomena must be discarded. However, it has been shown in this paper that when we make a quantitative analysis of the effect of the diffuse layer, considering also its distortion during electrophoresis, we find that the first approximation to the electrophoretic mobility of a large sphere is the familiar Helmholtz formula. It can likewise be shown that the Helmholtz analysis is valid for any surface in water or aqueous solutions, so long as the radii of curvature are large in comparison with the thickness of the double-layer.

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[17] Colloid Symposium Monograph, 6, 41 (1928).
[18] Z. physik. Chem., 147, 147 (1930).
[19] J. Phys. Chem., 28, 706 (1924).

Furthermore, barring mathematical blunders, there can be no question concerning the fundamental validity of the theory of the diffuse ionic layer as it has been outlined in this paper; for the theory is based upon well-established physical laws which have their origin and proof in lines of experiment entirely outside of electro-kinetic phenomena. The only assumption *ad hoc* is that the moving particle has an electric charge, and that is really a conclusion necessitated by the visible motion of the suspended particle. Consequently, even if the theory is found to disagree completely with the data obtained under any particular experimental conditions, we cannot conclude that the theory is false. We have only proved that it is incomplete or that incorrect values have been assigned to the parameters involved.

As for the incompleteness, a number of experimental results in electrophoresis have already been interpreted in this paper as being due to the strange behavior and interference of a plastic or semi-solid adsorbed crust which was not contemplated in the theory.

Concerning the values of the parameters close to a surface, we do not have entirely satisfactory information; but it is yet to be proved that the values there are much different from what they are in the liquid in bulk. Kallmann and Dorsch[20] have measured the dielectric constant of films of liquids about $1\mu_0$ thick; and they found no perceptible difference from the normal values. No variation in dielectric constant less than their mean error, about 0.2 per cent, could have any important effect on the charge distribution in a diffuse layer that extends several $m\mu$ from the surface.

Concerning the viscosity near a surface, if there is any deviation at all from the normal value, current theories of surface structure would lead us to expect an increase, associated with more or less molecular orientation. Any electro-kinetic phenomenon would tend to disturb this special orientation of the molecules, if it exists; and we would anticipate some lack of proportionality between cause and electrokinetic effect. For example, Ettisch and Zwanzig[21] found a variation in streaming electro-kinetic potential with pressure when forcing mixtures of methanol and water containing a trace of KCl through glass capillaries; and a variation in cataphoretic mobility with impressed field in some of my own measurements has already been mentioned. But in the absence of such abnormal effects there is no reason for doubting that in dilute and moderately concentrated solutions, the viscosity is constant throughout the greater part of the double-layer. In view of these considerations the conclusion seems justified that, with limitations of the kind that have been discussed, the Helmholtz analysis of electro-kinetic phenomena is applicable whenever the curvature of the surface involved is small in the sense previously indicated.

Unfortunately, the situation is quite different in regard to surfaces of large curvature. The system of differential equations resulting from the author's set of assumptions can probably be solved for the mobility as a power series in φ, the electro-kinetic potential; and such a solution would be

[20] Z. physik. Chem., 126, 305 (1927).
[21] Z. physik. Chem., 147, 151 (1930).

valid for a sphere of any size, provided that φ were sufficiently small. But the development of this solution still remains for the future.[22] The Debye-Hückel mobility formula can be used for a small sphere in a very dilute solution; but the assumptions B_3 and B_4 of section 2 are such severe restrictions that the applicability of the formula is limited to very dilute solutions and to ultramicroscopic micelles, composed of only a few molecules and carrying only a few elementary charges. In between the regions covered by the Helmholtz and the Debye-Hückel theories there is a large region in which the radii of surface curvature are of the same order of magnitude as the Gouy diffuse layer. This region is a "no-man's land," not yet belonging to either theory. Obviously, ignoring these limitations of the theories will lead to false deductions and to confusion. This fact is illustrated in Thon's suggestion that electrophoresis and electro-osmosis are different in some fundamental way not yet understood. The indiscriminate application of Stokes' law and the treatment of all colloids as electrolytes are violations of the restrictions upon the Debye-Hückel electrophoresis theory. Some of the discrepancies that result in this case have already been discussed by Pauli and Valkó.[23]

Summary

1. The theory of the diffuse ionic layer and its influence on the electrophoresis of a sphere is outlined and a theoretical formula for the limiting slope of the mobility-curvature curve is given.

2. Experimental data are reported which are in rough agreement with the theory as applied to dilute aqueous solutions. In concentrated solutions there is definite disagreement in some cases.

3. Formulas are given for surface charge and surface conductivity. The latter formula does not agree with measured values.

4. Various anomalous effects in cataphoresis suggest the existence of a plastic adsorbed layer which seems to have a profound effect on the electrokinetic potential in concentrated acid and neutral solutions.

5. It is pointed out that the validity of the Debye-Hückel cataphoresis formula is limited to conditions in which the colloidal particle is much smaller than its diffuse ionic layer.

The experimental work reported in this paper was done at the Ryerson Physical Laboratory of the University of Chicago. I am greatly indebted to Professor A. C. Lunn and other members of the faculty for their assistance and interest. I feel quite incapable of expressing my gratitude to the University for the facilities placed at my disposal, especially as an appreciable part of the work was done during my spare time after I was no longer officially connected with the Laboratory, and at a time when space was very much in demand for full-time research workers. To the National Research Council, I am greatly indebted for their long-continued support in a baffling problem.

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[22] The corresponding analysis of electro-osmosis in a straight capillary tube of small radius has recently been published by Komagata: Bull. Chem. Soc. Japan, 4, 255 (1929).

[23] "Elektrochemie der Kolloide," 268 (1929).

POTENTIAL DIFFERENCES AT AIR-LIQUID INTERFACES

BY JOHN WARREN WILLIAMS AND V. A. VIGFUSSON

It is well known that the electrical phenomena with which we have to deal in colloidal chemistry are quite different from those which may be treated thermodynamically to form what we know as electrochemistry. Indeed, in colloidal chemistry it is necessary to consider just those electrical phenomena which are neglected in ordinary electrochemistry. The relationship between the electrokinetic potential and the thermodynamic potential has been the subject of much investigation, yet, in spite of this fact, there remains much to be learned about the electrokinetic potential.

There exists an electrokinetic potential at the various types of interface, solid-liquid, liquid-liquid, liquid-gas, etc. This potential, called the ζ-potential, is measured *tangentially* to the interface between the two phases. In other words, it is necessary to assume that a layer of the more mobile phase adheres to the surface of the less mobile phase in order to measure it. The most familiar methods for this purpose are electroendosmose and cataphoresis.

More recently there have been reported in the literature determinations of potential differences which have been measured *vertically* to the interface. Since in the case of both the tangential and vertical measurements adsorption exerts such a pronounced influence it might have been suspected that the two potential differences were at least quite intimately related to each other. As yet, however, the meagre experimental data indicate that such is not the case. It is not the purpose of the present article to make this comparison, rather, we shall limit the discussion to the potential differences which have been measured in a vertical direction across the liquid-air interface. These potentials are found to be absolutely dependent upon the composition of the surface layer of molecules limiting the liquid phase. This layer is definitely an adsorption layer whose composition may be determined more or less exactly by noting the changes in surface tension caused by dissolved substances in accordance with the well-known equation of Gibbs.

Because of these facts it appears that it should be possible to calculate from the magnitude of the observed potential difference the electric moment of any molecule which does not dissociate and which is adsorbed in the surface layer. This calculation necessarily involves the assumption that the molecules be imagined as arranged in a parallel layer perpendicular to the interface. The following relation may be shown to hold between the potential difference, E, and the electric moment of the molecule, μ.

$$E = 4\pi N\Gamma\mu,$$

$$\text{or } \mu = \frac{E}{4\pi N\Gamma}.$$

In this equation N is the Avogadro number and Γ is the surface concentration in gram mols per square centimeter. The quantity $4\pi N\Gamma$ may be found from surface tension measurements.

Using this equation Rideal[1] calculates the electric moment of the butyric acid molecule to be

$$\mu = 0.3 \times 10^{-18} \text{ e.s.u.}$$

In recent years the Debye modification of the Clausius-Mosotti relation has made it possible to determine the electric moment of a molecule either from the temperature coefficient of the dielectric constant of its vapor or from dielectric constant and density data for a binary liquid mixture composed of a non-polar solvent and the molecule in question as solute. The values of the electric moments of molecules determined in this way are now universally considered to be quantitatively correct, provided, of course, that complicating chemical influences are not operative in the vapors or solutions.

There has been reported recently a value for the moment of butyric acid by Wolf[2], $\mu = 0.7 \times 10^{-18}$ *e.s.u., obtained from dielectric constant and density data for its benzene solutions.* It is therefore evident that the value calculated from the observed potential difference across the interface is too low by a factor greater than two. Indeed there is every reason to believe that this factor should be even greater than two, since the value reported by Wolf is undoubtedly too low due to an association of butyric acid molecules when dissolved in benzene. The effect of this association is to lower the electric moment of a dissolved molecule. It was previously mentioned in the case of benzoic acid[3] and in the case of cyclohexane carboxylic acid.[4] Since the group moment[5] of the C – OH linkage is 1.7 and that of the C=O linkage is 2.8 a simple spatial consideration for the carboxyl group indicates that its characteristic moment will be greater than the difference between the moments characteristic of its components, that is, 1.1. In other words the moment of the butyric acid molecule may well be taken as being greater than $\mu = 1.1 \times 10^{-18}$ e.s.u., that is, approximately four times the value calculated from the potential difference data.

To cite a single other case, the change of potential difference when chloracetic acid is substituted in the interface for acetic acid can depend only on the value of the electric moment characteristic of the C–Cl linkage. In this way the value, $\mu = 0.5 \times 10^{-18}$ e.s.u., is found. However, the moment for methyl chloride is $\mu = 2.0 \times 10^{-18}$ e.s.u.,[6] so that again the moment calculated from the potential difference at interface data is too small by a factor of something like four. In fact, it seems that any electric moment calculated by a method similar to the one outlined by Rideal will be too small by a factor of this order of magnitude.

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[1] Rideal: "Surface Chemistry" (1926).
[2] Wolf: Physik. Z., 31, 277 (1930).
[3] Williams and Allgeier: J. Am. Chem. Soc., 49, 2416 (1927).
[4] Williams: J. Am. Chem. Soc., 52, 1831 (1930).
[5] Williams: J. Am. Chem. Soc., 50, 2350 (1928).
[6] Sänger: Physik. Z., 27, 556 (1926).

Frumkin and Williams[7] have recently sought to account for the reason, or reasons, why the electric moment of a molecule cannot at present be calculated from potential difference at interface data. Four possibilities were suggested, as follows:

1. Incomplete orientation of the molecules at the interface.
2. A disturbing influence of the neighboring water molecules or ions.
3. Differential nature of the measurements of potential difference.
4. The polarization of the oriented molecules by the neighboring molecules, assuming the orientation to be always complete.

It was shown that there are certain objections to most of these possibilities. If, however, the oriented molecules are polarized by the presence of the neighboring molecules a dielectric constant of the order of magnitude three or four instead of unity might be accounted for. Since the equation relating electric moment and potential difference involves the assumption that the dielectric constant of the molecules at the interface is actually unity it is evident that a higher dielectric constant of magnitude three or four would account for the larger part of the discrepancy. It will, however, be very difficult to make any statements concerning the dielectric constant of the surface layer, so in order to accept this as an explanation experimental data must be made available.

Careful examination of factors 1 and 2 indicates that if they are operative the potential difference at the interface should be a function of temperature. Furthermore, it follows from our modern ideas concerning the factors which contribute to the dielectric constant of a system that if the oriented molecules are polarized by the presence of neighboring solvent molecules this polarization, and therefore the potential difference at the interface, calculated for equal amounts adsorbed, should be practically independent of temperature. Therefore, if data giving the temperature coefficient of this potential difference were made available it should lead to an elimination of either possibilities 1 and 2 or of possibility 4. We sought to obtain data of this character.

In view of papers published by Kenrick[8], Guyot[9], Frumkin[10], Bühl[11] and Garrison[12] it appeared as if this might be achieved, since in these articles there are described three distinct methods to measure the interfacial potential difference. However, the general agreement between the results of these methods and the agreement between the results of different observers leaves much to be desired. In our experiments we used both the method of Kenrick and the method of Guyot and Frumkin, and many modifications of each in the attempt to reproduce the results which have been reported.

The experimental arrangement of Kenrick makes use of a single vertical glass tube down the inner surface of which the reference liquid is allowed to

[7] Frumkin and Williams Proc. Nat. Acad. Sci., 15, 400 (1929).
[8] Kenrick: Z. physik. Chem., 19, 625 (1896).
[9] Guyot: Ann. Phys., (10) 2, 506 (1924).
[10] Frumkin: Z. physik. Chem., 111, 190 (1924); 116, 485 (1925); 123, 321 (1926).
[11] Bühl: Ann. Physik, (4) 84, 211 (1927); (4) 87, 877 (1928).
[12] Garrison: J. Phys. Chem., 29, 1517 (1925).

flow. The second liquid is passed from a fine glass tip in the form of a narrow jet down the axis of the tube. The two solutions are connected through calomel electrodes to a quadrant electrometer which is calibrated to read the electromotive force of the cell. This method is claimed by Kenrick and also by Frumkin to give very satisfactory results in the case of inorganic electrolytes and readily soluble derivatives of shorter chain hydrocarbons. There are however, several serious sources of error, namely

1. Streaming potential developed by the second liquid in case of dilute solutions.

2. Balloelectric effect associated with the formation of fine drops and spray by the liquid jet.

3. Liquid-liquid junction potentials.

4. Electrostatic effects of unknown origin and magnitude.

We have demonstrated experimentally that these liquid junction potentials may easily be as large as the potential difference across the interface which has been reported in various cases.

A second method, which is subject to less error than the method just described, was developed by Guyot and by Frumkin for determining the change in the potential difference when capillary active substances are present. In this arrangement a stationary liquid surface is used. A platinum electrode which has been coated with a radioactive material is placed directly above

TABLE I

Solution	Conc. N.	Kenrick Dropping Electrode	Frumkin Dropping Electrode	Garrison Condenser Method	Bühl Dropping Electrode	Authors Ionization Method (Modified)
H_2O				+40	−5.5 ±0.5	−9
KCl	1.0		−2			−56
KCl	0.1			+70		
KBr	1.0		−10			−82
KI	1.0		−34	+125		
KSCN	1.0		−57	+70		
NaCl	2.0		−4			
NaCl	1.0		− 1	+80	±0	
HNO_3	1.0	−53	−48	+265		
HCl	2.0		−55	+100		
HCl	1.0	−29	−23	+185		−50
HCl	0.5			+230		
HCl	0.1	− 8		+170	±0	
H_2SO_4	1.0		−13.5			
KOH	1.0		0			+158
NH_4OH	1.0		+78			

this surface. The ionization of the air produced in this manner is sufficient to permit a determination of the potential difference between this air electrode and the body of the liquid. The activated electrode is directly connected to the isolated pair of quadrants of an electrometer, while the liquid is joined by a potassium chloride bridge to a calomel electrode connected to the other pair of quadrants.

In our experiments with the method of Guyot and Frumkin we were successful only to the extent of a partial agreement with the results obtained by these investigators. We did not obtain the same absolute magnitudes, but values which were shifted by a more or less constant factor from them, in spite of the fact that we tried to compare them to the same reference solution. In Table I we have shown a comparison of the results of the various investigators with our own for several solutions of inorganic electrolytes.

Thus it appears that before we can hope to calculate electric moments of molecules from interfacial potential difference data a number of experimental difficulties will have to be solved. *It appears that in addition to the* possibility already mentioned, a difficulty due to the differential nature of the measurements of potential difference, there may be involved other factors in the experimental procedure which have not been properly controlled. To determine the value of an electric moment it will certainly be necessary to know the *single* potential difference. It seems probable that any experiment will always give a differential effect which is related to a layer of pure solvent molecules or to some other quite arbitrary zero point. Represented schematically the cell whose potential difference is measured is as follows:

Pt + Radioactive Material	Air	Molecule AB (Conc. C, in conducting solution)	Hg_2Cl_2 KCl (sat'd)	Hg

The measured electromotive force of such a cell will evidently not be the

single potential difference	Air	Molecule AB (Conc. C, in but a conducting solution)

combination of several potential differences; in other words it appears that the potential difference observed will be related to some arbitrary, even if practically constant, reference. Thus, our values differ from those of Frumkin, although we tried to reproduce them exactly. We believe that this difference can be explained, (at least in part), by the difference in radioactivity of the substances used to ionize the air in the two experiments.

It appears also that even had we used the same radioactive substance in exactly equivalent amount we could have reproduced the earlier results only if we could have adjusted the electrode to exactly the same height above

the surface in our experiments. It is evident from Fig. 1 that the measured electromotive force is a function of the distance of any given radioactive electrode from the stationary liquid surface. For comparable results it will always be necessary to use equivalent amounts of radioactive materials on an electrode which is always accurately adjusted to a predetermined height. These results will not be absolute in nature, rather they will be referred to a constant which appears at the present writing to be indeterminable.

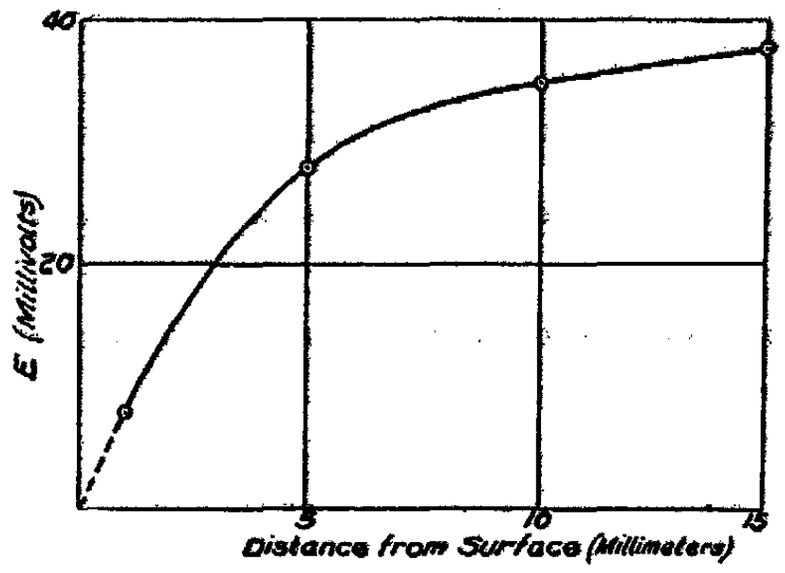

FIG. 1
Variation of potential with distance of electrode from surface of solution.

It should not be necessary to mention that serious errors may affect the results if the apparatus and leads to the electrometer are not properly shielded and insulated. In our experiments every known precaution was taken.

As stated, our original intention was to study the temperature coefficient of the potential difference at several interfaces to see if there could be eliminated any of the possible reasons why the electric moment of a molecule cannot at present be calculated from interfacial potential difference data. Because of the time involved in the study of the various experimental methods described in the literature which do not give concordant results and in the construction of an apparatus which does give a reproducible result our data on this particular point are too meagre to report at the present time except to say that there appears to be a real temperature effect. We are not at present willing to commit ourselves as to whether this temperature effect is due simply to the change in the junction potentials involved, or is really caused by either a decrease in the degree of orientation of the molecules at the interface as the temperature is increased or a change in the disturbing influence of the neighboring water molecules or ions.

We do feel it to be worth while, however, to point out that in spite of the tremendous difficulties involved in this type of measurement something has been and is being accomplished by workers in this field. It has been shown that there is a striking difference in the *order of magnitude* of the electric moment calculated from the potential difference data and that calculated according to the now familiar dielectric constant methods, yet there are a

number of marked parallelisms between the results of the two types of study. Both indicate very definitely that polar molecules of the organic type are made up of polar parts and non-polar parts. In the simpler molecules which have but a single polar group the length of the hydrocarbon chain appears to have little or no effect. These are conclusions whose importance need not be discussed further.

Agreement is also generally found when the conclusions concerning the sign of the charge on definite linkages is considered. Thus in the case of the carbon to oxygen linkage the carbon is charged positively with respect to the oxygen; in the case of the carbon to chlorine linkage the carbon is charged positively with respect to the chlorine; and in the case of the carbon to nitrogen linkage the carbon is positively charged and the nitrogen negatively charged. This conclusion is more definite from potential difference data than it is from electric moment data in the case of the linkages to oxygen and nitrogen because of the structures which have to be assigned to the water and ammonia molecules and to what may be considered to be their derivatives. The two valence bonds of the oxygen atom are not extended as has usually been assumed in the discussion of molecular orientations at interfaces, but make an angle of considerably less than 180° with each other. Thus if the alcohol, ROH, be considered to be oriented at the interface water-benzene the oxygen atom is the hydrophilic part of the molecule just as it has always been considered to be in the case of ether molecules, ROR′. Likewise, the three valences of the nitrogen atom are directed toward the corners of a tetrahedron with the nitrogen atom situated at the apex.[13]

If, however, allowances are made for the stereochemistry of the various atoms involved it is found that the order of magnitude of the electrical effects for the alcohols, ketones, ethers, esters, and amines is relatively the same as the dipole effects, in order. The influence of the change when bromine is substituted for chlorine, or iodine is substituted for bromine is readily comparable in both cases. From the remarks made in an earlier part of this article it is evident that the effects in the case of the acids cannot be compared because of the difficulty in obtaining electric moment data for this type of compound.

Before leaving this particular discussion it is well to note that the interpretation of the electric moment data is not as simple as might be wished because the molecules must be considered as non-rigid in practically every case. There is even in some cases evidence in favor of rotation about valence bonds which is quite unrestricted by other parts of the molecule in the case of both aliphatic and aromatic derivatives. The electric moment as measured must be considered to be an average moment, and nothing more. If it were possible to calculate the electric moment of a molecule from interfacial potential

[13] See Debye: "Polare Molekeln," (1929); Sack: Ergebn. exakt. Naturwiss., 8, 307 (1929); Williams: Fortschritte Chem., Physik, physik. Chem., 20, und No. 5. (1930); Chem. Rev., 6, 589 (1929).

difference data this moment might be quite different because it could only be the moment of a molecule fixed in position because of the proximity of its neighbors.

There is another comparison between data from two types of study which make it appear that, at least in a relative way, the interfacial potential difference data which now exist in the literature are not without significance. If one compares the results of a study of the electrocapillary curves with those obtained from the potential differences measured according to the methods described above there is a definite, even if qualitative, agreement between them. Experiments show[14] that the position of the maximum of the electrocapillary curve changes strongly with the composition of the solution. Gouy showed that these effects could be explained on the basis of an adsorption of ions or molecules at the interface, and it has developed that considerable information about the orientations of molecules at this mercury-water interface may be obtained by observing the changes produced in the rising and falling branches of the curves obtained when the interfacial tensions are plotted against the applied potentials. The observed shift in the maximum of this curve indicates the existence of an adsorbed layer of molecules which produces a potential difference between the mercury and the solution, such that if the positive end of the molecule is turned toward the mercury the maximum will be shifted in one direction, and if it is turned toward the water the maximum will be shifted in the other direction. Since the potential difference data discussed and described in this article are attributed to an adsorption of these compounds at the air-water interface and since this adsorption gives rise to similar electric effects Frumkin[14] has compared the results of the two types of study and has found it necessary to assume that at the mercury-water interface there exists the same orientation which is known to exist at the air-water interface. This means again that the polar group is attracted by the water and the non-polar group by the less active substance.

The result of this comparison of data may be stated by saying that except in the cases where there is reason to believe that there exists a specific interaction between the mercury surface and definite constituents of the molecules in question there is good agreement between the conclusions which have to be drawn from the data in both these cases. It seems probable, too, that when the potential differences across the air-water interface can be measured more accurately this agreement will become even better.

It might be mentioned that it would perhaps have been easier to study the effect of a change in temperature on the position of the maximum in the electrocapillary curve in order to account for the reason, or reasons, why the electric moment of a molecule cannot be calculated from interface potential difference data. It was because of the fact that these specific interactions between the mercury surface and certain constituents of molecules had been previously recognized and would have complicated the situation that measurements at the mercury-water interface were not made. Furthermore, in

[14] Frumkin: Colloid Symposium Annual, 7, 89 (1929).

that event it would have been necessary to reason by analogy rather than by direct inference from the experimental data which were made available. Measurements of this type are now being made upon systems designed to avoid these specific interactions.

Finally, it is clear that if we are to increase our knowledge concerning the orientation and structure of molecules at interfaces the electrical properties of these interfaces must be studied as a function of temperature. While a method which seems to be suitable for this study in the case of the mercury-water interface is available it appears that considerable work still remains to be done before a technic will be developed which can be depended upon to give reproducible and comparable results in the case of the air-liquid interface. Two methods, the air ionization method of Guyot and Frumkin, and the electrostatic method of Garrison can be considered to be correct in principle, but as yet they have not given results in any agreement whatsoever, even at a single temperature.

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SOME UNUSUAL PROPERTIES OF COLLOIDAL DISPERSIONS[1]

BY R. V. WILLIAMSON

We have been studying the viscous and plastic properties of dispersions for several years in order to increase our knowledge of their structure. During this time we have collected several dispersions that show rather striking characteristics when caused to flow under different conditions. The structural characteristics of these dispersions are only partially known, but their flowing properties are of considerable interest to the manufacturer of colloidal dispersions, and a description of them may also interest those who are studying the problem of colloidal structure in a theoretical way.

The Flowing Properties of Paints and Similar Suspensions. The paint manufacturer has known for a long time that the practical flowing and brushing behavior of paints cannot be estimated for their viscosities as ordinarily determined. This fact may be demonstrated with dispersions made by grinding 11 to 14 parts by volume of zinc oxide in 100 parts of alkali-refined raw linseed oil, blown linseed oil, and blown linseed oil thinned with turpentine until it has the same viscosity as the raw oil. The dispersions in the raw oil and in the thinned blown oil have the same apparent viscosity when stirred or when allowed to flow through an ordinary viscosity cup. Blown linseed oil is considerably more viscous than the raw oil; and the blown oil dispersion similarly exhibits a very much higher apparent viscosity than the other two.

The flowing characteristics of these dispersions may be compared by painting glass plates with each of these dispersions, placing small cylinders (approximately one centimeter high and one-half centimeter inside diameter) open at both ends on the freshly painted glass plates, filling each cylinder with the paint that was used to paint the glass plate upon which the cylinder rests, and then gently raising the cylinder and allowing the paint to flow out. The raw-oil dispersion flows out to a much smaller area than the other two although its apparent viscosity is comparatively low. The blown-oil and thinned blown-oil dispersions flow out to approximately the same area in spite of the difference in the viscosities of the two dispersions. The time required for the blown-oil dispersion to flow out is greater, however, than that required by the thinned blown-oil one.

If the apparent viscosities of these dispersions are determined at different rates of flow through a capillary tube, the raw-oil dispersion shows a very high apparent viscosity at low rates of flow, but at high rates of flow its apparent viscosity is about the same as that of the thinned blown-oil dispersion. In other words, this dispersion shows marked plasticity. The other

[1] Contribution No. 39 from the Experimental Station, E. I. du Pont de Nemours and Co., Inc., Wilmington, Delaware.

two dispersions do not show much if any change in viscosity at different rates of flow; *i.e.*, they flow like ordinary viscous liquids.

Photomicrographs of the specimens reveal a highly flocculated condition of the particles in the raw-oil dispersion, whereas the particles are highly dispersed in the other two dispersions. The areas covered by the dispersions as they flow out on the painted glass plates appear to be a function of the size of the flocculates. The degree of plasticity of the dispersions is also directly related to the sizes of the flocculates. One may say, therefore, that the flowing properties of a dispersion can be estimated from its plastic properties.[2] This is qualitatively true, but unfortunately scientists have not been able to find a satisfactory method for quantitatively expressing the plastic properties of dispersions.

A mental picture of some of the factors that determine the areas of the flow-outs may be drawn as follows: As the oil film advances the largest flocculates settle to the bottom first, and the friction on the glass plate prevents them from advancing farther. The smaller flocculates, however, are carried still farther. Finally the film advances until the friction of the smallest flocculates between the glass plate and the air-oil surface is great enough to overcome the "head" or stress due to the thickness of the oil film. If the forces of flocculation are sufficiently great to prevent the flocculates from being broken into smaller ones under this stress, the advance of the particles in the film is stopped.

The control of the plastic characteristics of paints is important to the paint manufacturer because to a large extent they determine the character of the surface of the paint film. In enamels, the plasticity must be very low so that brush marks and any uneven surface characteristics will disappear, and the paint will flow out to a mirror-like surface. In flat wall-paints, printing inks, and paints for printed linoleum, a certain amount of plasticity is essential.

Thixotropic Dispersions. The term thixotropy has been used by Freundlich[3] and others to describe that property of dispersions that enables them to change repeatedly from a gel form to a liquid form under the stress of agitation and then to revert to the gel form again when allowed to remain at rest. The first thixotropic dispersion that I observed was prepared by Marion Veasey at the University of Wisconsin in 1922. This was an aluminum hydroxide dispersion. Freundlich and his co-workers have described the conditions for preparing thixotropic dispersions of ferric oxide and aluminum hydroxide. I have observed several thixotropic dispersions of pigments. One of these was presented to me by C. K. Sloan of this laboratory. It is a dispersion of gas black in petroleum hydrocarbon which contains an organic dispersing agent. This dispersion remains very fluid for an hour or more after shaking, but it sets to a solid gel in a few hours. The time re-

[2] For further discussion of this point, see Williamson: Ind. Eng. Chem., 21, 1108; Williamson, Patterson, and Hunt: 1111 (1929).

[3] Freundlich: Kolloid-Z., 46, 289 (1928).

quired for gelation can be shortened by reducing the amount of volatile vehicle until the dispersion will set immediately after shaking. This dispersion has been kept in the laboratory for a year, and the thixotropic property has been demonstrated many times without any apparent change in this property of the dispersion.

A dispersion with similar properties may be prepared by mixing zinc oxide (such as is used as a paint pigment) with gasoline in the proper proportions. If such a dispersion, contained in a small can, is shaken vigorously, it produces a sound resembling that produced by a very fluid liquid under similar circumstances. The dispersion does not flow out, however, if the shaking is stopped, the lid immediately removed, and the can turned bottom side up. In this case, the effect is probably due to the highly flocculated condition that results from the poor wetting of the zinc oxide by the vehicle. This effect can be completely changed by adding a few drops of some good wetting agent, such as blown linseed oil. The dispersion then remains perfectly fluid after shaking, but the pigment settles rather rapidly to the bottom of the container.

Inverted Plasticity. The thixotropic dispersions described above are examples of highly plastic dispersions. Such dispersions are characterized by a very high apparent viscosity when stirred slowly and a lower viscosity when stirred rapidly. Several dispersions have been brought to my attention that show an inverted form of plasticity, compared to that described above. These dispersions flow readily when stirred slowly, but become quite stiff when stirred rapidly. I have used the term "inverted plasticity" in referring to this property. Victor Cofman called my attention to the fact that a dispersion of corn-starch and cold water in approximately equal proportions by weight shows this property to a marked degree. A striking demonstration can be made by inserting the finger into the dispersion, moving it around slowly to show the fluid character of the dispersion, and then jerking it out quickly, whereupon one receives the impression that the dispersion has solidified around the finger. If the concentration is right and the beaker is held firmly on the table, the whole mass of the dispersion will tend to be lifted as a solid. As soon as the violent agitation is stopped, the whole mass becomes fluid again.

The peculiar properties of this dispersion can also be demonstrated by replacing the cylinder on a Stormer viscometer with a double-pronged stirrer[4] and determining the rates of stirring of the dispersion with different weights on the stirring device. For ordinary viscous liquids or dispersions the rate of stirring is proportional to the load on the stirring device. If the concentration of the starch dispersion is adjusted properly (approximately 1:1 by weight) and the same test is applied to it, the stirrer rotates at a uniform rate with only the weight of the pan on the stirring device. If a thousand-gram weight is added to the pan, the stirrer continues to rotate at the same rate.[5]

[4] The Stormer viscometer was modified in this way by Booge and Steinbring in the duPont Laboratories.

[5] The properties of this dispersion are described in greater detail in a paper with Heckert: Paint Oil Chem. Rev., 89, 9 (1930).

The same property has been found in a number of dispersions of ordinary paint pigments in organic vehicles by Heckert and Sloan at the du Pont Experimental Station. Since the effect appears only within certain concentration limits, it is probably related to the increase in volume that occurs when granular masses are deformed, owing to differences in the relative pore-space for different arrangements of the grains or particles. This phenomenon was named "dilatancy" and explained by Reynolds.[6] Inverted plasticity is not, however, determined simply by the relation of the volumes of dispersed solid and vehicle, for it occurs only in those dispersions in which the vehicle has a high dispersing action on the particles or, in other words, wets the particles well.

Sodium Silicate Dispersions. The viscous, plastic, and elastic properties of sodium silicate dispersions vary greatly with the relative proportions of sodium, silica, and water. A dispersion that exhibits properties similar to the inverted plasticity described above can be prepared by evaporating the water from an ordinary water-glass solution until the proper concentration of sodium silicate is reached. The proper concentration can be readily determined by removing a piece of the dispersion from the mass by means of a spatula, drawing it out very slowly with the hands, and laying it on the table to show that it has no tendency to return to its original shape, and then cutting a fresh piece from the original dispersion, rolling it into a ball, and throwing it to the floor with considerable force. If it has a suitable concentration, it bounces from six to ten feet in the air. If an attempt is made to stretch the ball rapidly, it breaks with the conchoidal fracture characteristic of a non-crystalline solid. Different types of flow are shown by other sodium silicate dispersions. For example, one may prepare a dispersion (with a higher ratio of sodium to silica and a lower proportion of water) which appears to flow under low stresses in much the same manner as the one described above, but which behaves quite differently under high sudden stresses. The similarity as well as the difference in properties of the two dispersions can be shown by wrapping a sample of each dispersion in tin-foil and applying the following tests. If the samples are squeezed gently between the thumb and finger, both of them feel soft and flow slowly and in much the same manner. But if the samples are thrown to the floor, the difference in properties is revealed. The first sample bounces like a rubber ball, and the second sounds like a brick instead of the soft sodium silicate dispersion. If the sample that bounces is subjected to a sudden pull, it breaks with a conchoidal fracture, whereas the one that strikes like a brick stretches like a good grade of pulling taffy.

A slight modification of the above demonstration serves very well to illustrate how much alike different dispersions may be under one set of conditions and how different under another. For example, the two sodium silicate dis-

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[6] Phil. Mag., 20, 496 (1885); Proc. Roy. Inst., (1886); "Scientific Papers," 2, 203, 217 (1901).

persions described above may be placed in rubber bags made from toy balloons and a third specimen added containing a paste of ordinary molding clay and water. If the concentrations of these dispersions are properly adjusted, they all feel soft and deform to about the same degree when squeezed gently. But when they are thrown to the floor, the first bounces like a rubber ball, the second does not bounce but sounds like a rock hitting the floor, and the third squashes like a bag of wet meal.

The first sodium silicate dispersion exhibits the property of inverted plasticity described above in connection with starch and water suspensions. Attention was there called to the similarity of the conditions of concentration necessary for producing inverted plasticity and "dilatancy". The same similarity exists in the case of the sodium silicate dispersions, for the property is noticeable only within a limited range of concentration. Attention was called, however, in the case of the starch and water suspensions to the difficulty of accounting for the property of inverted plasticity on the basis of the volume relation of starch and water alone, because the property is specific for given liquids. The difficulty is even more pronounced in the case of the sodium silicate dispersion, for the dispersion has no obvious suspended particles. Also, the second sodium silicate dispersion is several times as concentrated as the first, yet it does not exhibit inverted plasticity.

I am indebted to James G. Vail of the Philadelphia Quartz Company for the sodium silicate demonstrations.

Liquefaction of Viscose Gels by lowering the Temperature. Most materials become more fluid as the temperature is raised and become solid or freeze when the temperature is lowered sufficiently. Viscose is rather unusual in this respect inasmuch as freshly prepared viscose sets to a gel within a few minutes when heated to the temperature of boiling water and liquefies again when placed in an ice bath. Liquefaction of the gel does not take place, however, unless it is placed in the ice bath immediately after gelation occurs. The phenomenon is probably due to changes in hydration of the components of the dispersion brought about by lowering the temperature. If the chemical changes that produce gelation proceed too far, the changes in hydration produced by lowering the temperature are not sufficient to redisperse the gel again. It is essential that only a small amount of viscose is used for demonstrating this property so that the time required to change the temperature of the whole mass is short. We ordinarily use about five cubic centimeters contained in a test tube. The test tube is placed in a glass vessel that contains boiling water. The viscose is stirred with a glass rod, and the heating is continued until the material shows a definite crack that does not flow together when the stirring rod is drawn through the material while the end of the rod is in contact with the wall of the test tube. This is considered to be the point of gelation. If the gel is then taken out and immediately placed in an ice bath, it returns to a fluid condition.

Summary

A number of experiments are described to show the marked changes in the plastic and elastic properties of dispersions which may be produced simply by changes in temperature or in the magnitude and the rate of application of stresses. The experiments may be useful to the manufacturer of colloidal materials because they illustrate some of the unexpected results that may occur from simple changes in the physical environment of the materials. They should also be useful to those interested in the fundamental study of structure in colloidal dispersions because they furnish a number of facts which must be explained by any comprehensive theory of colloidal structure.

E. I. du Pont de Nemours and Company,
Wilmington, Delaware.

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SOME CHEMICAL REACTIONS OF COLLOIDAL CLAY

BY RICHARD BRADFIELD

At the first Colloid Symposium seven years ago, the author had the privilege of presenting a paper on the same subject[1] as the above. In preparing this paper the first was reread with considerable interest and amusement. A friend, noted for his frankness, once remarked that the best part of the earlier paper was the discussion which followed! As this discussion was reread I wondered if our committee had acted wisely in abandoning the policy adopted by Professor Mathews of publishing at least a résumé of the discussions in the Symposium Annual. An opinion the earlier paper shared by many was that it was rather futile to attempt to obtain an understanding of the reactions of a substance as complex as a clay. "Simple" substances like silicic acid, aluminum and iron hydroxides, pure carbon, and pulverized soil-forming minerals were suggested as being much more suitable objects of study.

The author was not completely indifferent to this advice and at times has used all of these "simple" substances in comparative studies with clays; nor was he convinced that it was wise to abandon clays completely for these simpler systems. The economic importance of clays to both agriculture and industry seems sufficient to justify some study of this material in spite of its complexity. Most comparisons of the behavior of natural clays with these simpler, supposedly similar substances, have served but to show how different the two really are. For every property found in common, several can be found in which they are very different. This has led to the feeling that the only way to find out about clays is to study clays. Synthesis is often the capstone of a chemical research problem but analysis logically precedes it. If we learn enough about the behavior and properties of clays we may eventually be able to make synthetic imitations. But first we must know a little more about what we are trying to imitate.

The term clay means very different things to different people. To the soil scientist a clay is that inorganic fraction of the soil whose particles are less than 2 microns in diameter. Colloidal clay is that fraction of the clay whose particles have an effective diameter of less than 100 millimicrons. Since it represents a fractionation based solely on size of particle it may be applied to fractions which differ greatly in both chemical composition and in mineralogical make up.

Since the classic work of Odén and Svedberg many attempts have been made to determine the size-distribution of clays. The chief difficulty encountered is to secure suspensions of stable unit particles. Most of the clay exists naturally, fortunately for the farmer, in the form of rather stable aggregates. The various methods of deflocculation commonly used were not

[1] Bradfield: Colloid Symposium Monograph, 1, 369 (1923).

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100 per cent efficient and consequently the older mechanical analyses represented neither the size-distribution of the naturally occurring aggregates nor of the unit particle, but something in between these extremes.

Recent studies of base-exchange phenomena and their effect upon the electrokinetic potential of clays, which will be discussed later, have pointed out the way to obtain more efficient deflocculation. It is now quite definitely proven that the amount of colloidal material in clays is much larger than earlier workers believed. Most of them, Schloesing, Ehrenberg, Gedroiz, et al, felt that the amount of truly colloidal material in clays was at most only a few per cent. Recent work has revealed clays with 80-90 per cent colloidal material, while from 20-50 per cent is quite common. In fact there is a decided tendency to regard all clay particles under 2 microns in diameter, as defined by the International Society of Soil Scientists, as being colloidal. The Bureau of Soils' workers were the first to suggest that the limit should be placed at 1 micron. Joseph, working on African clays, came to the same conclusion. Some experiments made by DeYoung in the author's laboratory furnished strong evidence that practically all the particles, in certain clays at least, that are under 2 microns in diameter are in reality made up of aggregates which may be broken down to particles about 10-20 millimicrons in diameter by merely churning with distilled water, centrifuging out particles larger than 20 millimicrons by means of the supercentrifuge, resuspending the coarser particles in distilled water, recentrifuging, etc. The original purpose of this experiment was to prepare a series of fractions of clays with different specific surfaces and to study the absorptive power as a function of external surface. It proved a very easy matter to secure large quantities of clay with particles between 2000 and 10 millimicrons; but it did not prove possible to make satisfactory fractionations of this material. After 8-10 fractionations all of the original kilogram of clay with particles under 2000 millimicrons was reduced to a fraction with particles from 10-20 millimicrons in diameter.

The amount of stable particles between 1000 and 20 millimicrons was negligibly small in this clay. The 2-5 microns fraction was very stable and easily washed free from all smaller particles. It possessed, however, none of the properties usually associated with clays but was decidedly silt-like in nature. Thomas, working in Utah, and Joseph, working in Africa, have observed that the smallest clay particles in the samples studied by them were of the same order of magnitude as those found above. The almost total absence of particles of the intermediate sizes may prove quite significant if found to be generally true. It is hoped that the investigation can be extended to other clays using an improved technique.

Shape of Particles. A large proportion of the particles of most clays are plate-like in form. The stream lines observed when a clay sol is gently stirred is evidence of this. The particles can be oriented also by means of an electric field. The number of particles visible in the ultramicroscope can often be increased from 20-40 per cent by applying an electric field perpendicular to the direction of the illumination. These oriented sols are strongly doubly re-

fracting, the amount and sign of the double refraction varying with the nature of the cation saturating the clay. The surface of clays is tremendously increased as a consequence of this plate-like shape. Variations in plasticity may frequently be associated with the extent of this plate-structure development.

X-ray and Chemical Analysis. Results obtained by the X-ray analysis of clays were discussed before this symposium last year. Kaolinite which many used to consider the predominant mineral in clays seems to be rather rare in agricultural soils. Minerals of the nontronite, beidellite, and montmorillonite types seem to be much more abundant. Chemical analyses of the colloidal fraction of clays have revealed the rather interesting fact that clays formed under similar climatic conditions tend to be very much alike in spite of great differences in the origin and nature of the parent material. The colloidal fraction of most of the soils of the corn belt regions of this country has a silica-sesquioxide ratio of about 3 to 1. Other ratios are found, of course, but this one is most common. As we approach the tropics the proportion of sesquioxides increases and in extreme cases, the so-called lateritic clays, the silica disappears almost completely. All gradations between these extremes can probably be found. These considerations render extremely improbable the view held by some, that there is a single base-exchange complex or a single alumino-silicate responsible for soil acidity phenomena.

Thus far an attempt has been made to portray the physical and chemical make-up of some of these colloidal clays as a preface to a discussion of some of their chemical reactions. All the studies to be considered were made on the colloidal fraction of clays with particles all under 100 millimicrons which apparently were rather instable and capable of being broken down easily into particles from 10-20 miilimicrons in diameter. These particles are crystalline and are for the most part plate shaped. Mineralogically they seem to belong to either the montmorillonite or beidellite group.

Cation Exchange Reactions. The long-known ability of soils to exchange a certain definite amount of their cations for the cations of neutral salts is associated largely and in some soils almost exclusively, with this colloidal fraction. This exchange capacity varies commonly from 0.30-1.00 milliequivalents per gram. The clays differ from the synthetic permutits, with which they are so often compared, in that a much smaller percentage of their total cations are easily exchangeable. In the permutits which have the general formula 1 base.$Al_2O_3-3SiO_2.xH_2O$ almost 100 per cent of the cations present can be rather readily exchanged for the cations of a neutral salt. This corresponds to from 3.2 to 4.5 milliequivalents per gram depending upon the amount of hydration. The total amount of cations in the permutit and clay are almost identical. The exchangeable fraction constitutes then from but 10-30 per cent in clays ordinarily in comparison with 95-100 per cent in permutits.

This difference is commonly explained by assuming a much more porous structure in the case of the permutit, the so-called permutoid structure of Freundlich in which the entire interior surface is readily accessible to the ions

of the common salts. The clay particle is apparently denser in structure and the rapid exchange of ions is limited to those situated near the surface. Given sufficient time, suitable concentrations, and higher temperatures, the exchange can go to completion also in the case of certain closely related ions which are capable of fitting into the crystal lattice of the particle, as was shown over 50 years ago by the studies of Lemberg.

Kelley[2] has found that the percentage of readily exchangeable cations in a bentonitic clay could be greatly increased by prolonged grinding. The effect of the grinding was apparently due to the opening of fresh surfaces. The additional base obtained was largely Mg. There is some evidence that this may be rather generally true. Ca and H on the other hand constitute the largest proportion of the exchangeable cations of the soils of the humid regions. In the alkaline soils of arid regions Na appears in the place of H and, in extreme cases, of Ca also.

The proportion of total Ca which is readily exchangeable is usually quite high, in many cases almost 100 per cent, indicating that it may be the product of a secondary exchange reaction rather than a part of the surface of the original particle. The fact that Ca occurs in the drainage waters of our soils of the humid region in greater abundance than the other cations, makes such an hypothesis probable.

Acid Clays. In humid climates any reserve of $CaCO_3$ which may have been present in the soil material is eventually leached away. After this reserve is exhausted the bases on the surface of the colloidal particles are gradually replaced by hydrogen ions supplied by the carbonic and other acids which are formed largely as a result of bacteriological activities. The extent to which this replacement of the basic ions by hydrogen ions has proceeded is a measure of the degree of weathering of the clay. Natural clays are found in which exchangeable hydrogen constitutes over 60 per cent of the total exchangeable cations. The division between exchangeable and non-exchangeable cations is not an extremely sharp one but in most cases it is sufficiently well defined that comparable values can be obtained by very different replacement methods. Almost identical values can be obtained, for example, by extracting the clay with tenth-normal solutions of strong acids, or normal solutions of appropriate neutral salts. Within reasonable limits the amount of cations replaceable is independent of the concentration of the replacing solution provided the extraction is continued to completion.

Electrodialysis. If most clays are subjected to electrodialysis a rather definite quantity of bases can be removed. The endpoint is usually rather sharp. The amount removed is found to be identical with that which can be removed by the acid or neutral salt extraction methods. The resulting clay is saturated with hydrogen ions. It is free or practically so from soluble salts and non-colloidal acids. Any ion which may have been present which was small enough to pass through a parchment membrane has been removed by the prolonged application of the electrical potential. This electrodialyzed

[2] In a paper presented before Am. Soc. Agron., Chicago, Nov. (1929).

colloidal clay represents an attempt to obtain a simpler system by methods which are not sufficiently drastic to cause any deep-seated change in the colloidal particle. As evidence of this, it has been found possible to put an electrodialyzed clay through a cycle of chemical reactions, for example, to neutralize it with $Ca(OH)_2$, replace the Ca by prolonged leaching with a neutral NaCl solution, and then electrodialyze again, obtaining a product apparently identical with that with which we started. It has the additional advantage that it can be brought easily to any desired degree of saturation with any of the important cations by the addition of the proper amount of the appropriate hydroxide.

Characteristics of Hydrogen Clays. 1. Influence of the solid phase upon the hydrogen-ion concentration of clay sols.

It has been long known that the potential of the hydrogen electrode, when immersed in a suspension of a carefully washed acid clay, was markedly influenced by the concentration of the suspension. The colloid-free aqueous extract of such soil was frequently found to be almost neutral. In earlier studies on the acidity of a very acid colloidal clay it was found that the relationship between the pH value of the clay sol and its concentration was very similar to that observed with weak acids such as acetic.[3]

On the basis of these and other experiments the hypothesis was advanced that the bulk of the acidity found in soils was due to acids whose anions were of colloidal dimensions on using the terminology of Michaelis, to acidoids. As the clay used in these earlier experiments were natural clays, only 50 per cent of whose exchangeable cations were hydrogen, it seemed that further work should be done on the clays saturated with hydrogen ions. The studies served naturally to magnify the differences between the clay and its aqueous extract. With an electrodialyzed bentonite, for example, it has been found that while the clay-paste collecting on the membrane of an ultrafilter and containing about 10 per cent of oven dry clay had a pH value of 2.2 as measured with the quinhydrone electrode, the clear ultrafiltrate had a pH value of 5.2.

In a second experiment a 1.5 per cent electrodialyzed bentonite sol was placed in a collodion bag and the bag set in a volume of distilled water equal to that of the clay. After standing 24 hours so that equilibrium might be established it was found that the bentonite sol on the inside of the bag had a pH value of 2.8 while the water on the outside gave a pH value of 5.4. The hydrogen, quinhydrone, and antimony electrodes all gave pH values in satisfactory agreement, with these sols.

It is felt that the function of the membrane in these experiments was merely mechanical, preventing the diffusion of the colloidal clay anions. Any Donnan effect resulting from traces of any diffusible acids which might have been present would serve to decrease the differences in hydrogen ion concentration observed on the two sides of the membrane. Any other mechanism for separating colloidal clay from the medium in which it was

[3] Bradfield: J. Phys. Chem., 28, 170 (1924).

suspended would probably give identical results. Similar results have been obtained by using centrifugal force for the separation. The differences in pH value between the clay thrown down and the supernatant liquid were not as great as in the case of the ultrafiltration experiments due to the fact that all of the clay particles could not be thrown down with the centrifugal force available. The simplest explanation of these observations is that a part of the hydrogen on the surface of the acid-clay particle is ionized and is far enough removed from the particle to act as an ordinary "free" hydrogen ion when brought in contact with the electrode, but these ions are restrained by electrostatic forces from moving farther than this distance.

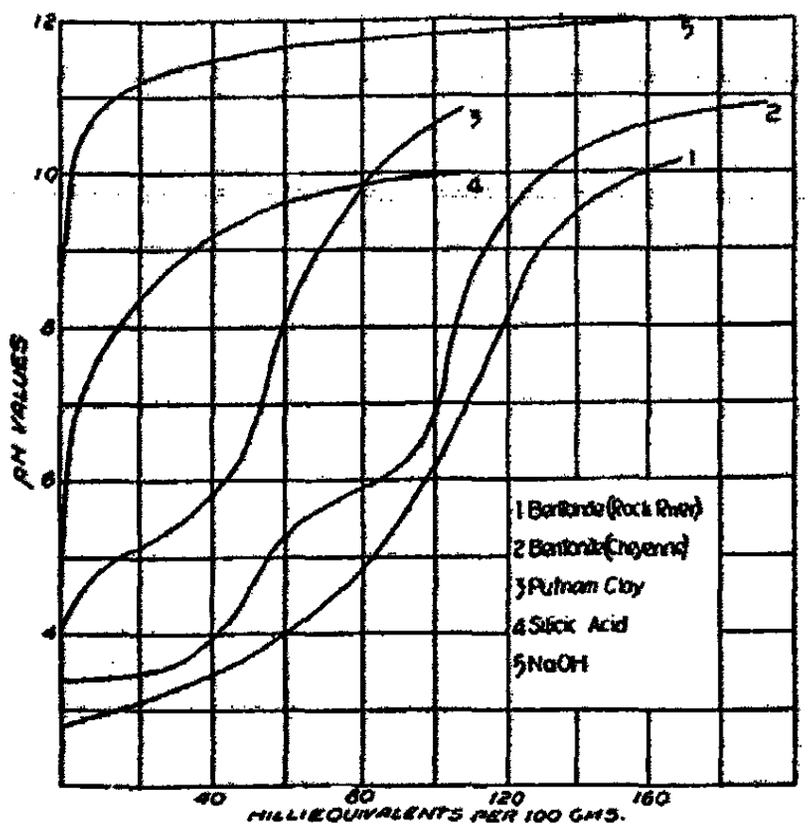

FIG. 1

Titratable Acidity of Electrodialyzed Clays. As has been shown earlier, even the natural clays give fairly distinct inflection points when titrated potentiometrically or conductometrically with solutions of standard hydroxides. The use of electrodialyzed clays tends of course to make these endpoints more distinct. A group of curves obtained by titrating 100 cc of 1 per cent electrodialyzed clay sols with 0.1 N NaOH using the hydrogen electrode are shown in Fig. 1. The curve for Putnam clay is of the type most commonly found in agricultural soils of the corn belt section. It resembles the monobasic type in having but one endpoint. This endpoint is not as sharp as those commonly obtained with simple monobasic acids. The reason for this, of course, is that these clay acids are very complex. For example, if we calculate the number of hydrogen ions that must be supplied by a particle with a radius of 10 mμ in order to account for the amount of NaOH neutralized up to pH 7.0,

we find 7.50. To account for this observed titratable acidity the particles of a true monovalent acid must have a radius of only 0.5 μ, a value much smaller than those observed.

One clay has been found, and so far as the author has been able to ascertain this is the only one reported which gives a curve having two rather distinct inflection points. (Fig. 1, curve 2). In appearance this bentonite from Cheyenne, Wyoming, was, superficially at least, very similar to the one from Rock River. The SiO_2 content of the two is almost identical—56 per cent. Minerals having two distinct types of crystal patterns have been found in bentonites. It may be that the dibasic character of the Cheyenne bentonite curve can be correlated with its mineralogical composition. The marked similarity between curves 2 and 3 at pH values above 6.5 indicates that these clays may have some constituents in common. A comparison of the silicic acid curve 4 with any of the clays shows how little they have in common and consequently how futile it is to attempt to obtain an understanding of the acidity of clays by studying "pure substances" which are so different from clays. The colloidal acids were prepared in a similar way, namely, the electrodialysis of their salts until all possible bases were removed. The curve for silicic acid shows a strong buffer action between pH values 9 and 11, indicating dissociation constants of the order of 10^{-10}: a value in satisfactory agreement with those found in the literature. It has, however, no buffer capacity in the acid region. Attempts have been made to prepare aluminosilicic acids by combining sodium aluminate and sodium silicate in the same ratios that they are found in clays, then converting the sodium salts into the acid by prolonged electrodialysis. The resulting product had no appreciable buffer action at pH values less than 7. Every other attempt made thus far to prepare synthetic substances analogous to clays has resulted in failure when subjected to this acidity test, even though the base-exchange reactions of clays and permutits are quite similar. Some have claimed that the differences in pH values of electrodialyzed permutits and electrodialyzed clays were due to the much finer particles of the latter. This might be true as far as pH measurements are concerned but the ability to neutralize NaOH in an acid medium should not be affected by particle size in substances as permeable to Na ions as are permutits, especially if sufficient time is allowed for the reaction.

Since clays which are made up predominantly of silicates and aluminosilicates are so different from any pure artificial substances we have been able to prepare, the question naturally arises as to whether or not other acid-forming substances might not be present in sufficient quantity to account for the results obtained.

The most common substances in clays other than SiO_2 that might contribute to the acidity are C, N, S, and P. The analyses of a series of electrodialyzed colloidal clays are shown in Table I. The bentonites are very low in all of these elements. The nitrogen content is not given but in clays it is usually only one-tenth as abundant as carbon. If one considers that all of the carbon is present as carboxyl groups, all the S as H_2SO_4, and all the P as

TABLE I

Content of Acid-forming Elements in some Typical Electrodialyzed Clays[4]

	Colloidal Clay	C	S	P
1.	Bentonite—Cheyenne. Finest	0.073	0.011	Trace
2.	Bentonite—Cheyenne. Regular	0.198	0.005	Trace
3.	Bentonite Rock River	0.055	0.019	Trace
4.	Putnam	0.977	0.014	0.040
5.	Putnam (H_2O_2 treated)	0.184	0.010	0.129
6.	Susquehanna	0.667	0.014	0.065
7.	Boone	0.566	0.015	Trace
8.	Sharkey	0.591	0.025	Trace

H_3PO_4, which represents the maximum possible contributions of these substances to the acidity of the clays, we find that their combined acidity equals only about 10 per cent of that found by the titration curves. This seems to force us to the conclusion that the acidity of these clays is due to alumino-silicic acids. The differences in properties between the natural clays and the common synthetic alumino-silicates must be due to differences in structural arrangement.

Characterization of the Clay Acids. Many studies have been made of the quantitative factor of soil acidity, or amount of exchangeable hydrogen, but the intensity factor has received scant attention. The most obvious way of getting at this intensity factor is by the use of some expression which is analogous to the dissociation constants of ordinary weak acids, which the author has termed the apparent dissociation constant or, if expressed in the form of the negative logarithm, as the apparent pK value of the acid. It is obtained from the mass law equation:

$$pK = pH + \log \text{salt/acid}$$

At the point of half neutralization the last term becomes 0 and the apparent pK value is numerically equal to the pH value at that point. Such a treatment is of course not strictly rigid but it has the virtues of simplicity and usefulness and enables us to make comparisons with other acids.

By inspection of the titration curves we see that the apparent pK value of the Putnam clay is about 5.6, that of the Rock River bentonite 3.8, the Cheyenne bentonite 3.6 and 5.9, while that of silicic acid is of the order of 10.

It has been pointed out in an earlier paper that the relationship between the hydrogen ion concentration of a clay and its concentration is similar to that observed with weak acids such as acetic and that by the use of the simplifying assumption that the concentration of the unionized acid is equal to the total titratable acidity, the relationship can be calculated with a fair degree of accuracy from the mass law. The pK values calculated from the titration curve and from the pH concentration relationship are in satisfactory agreement.

[4] Analyses obtained through the kindness of Mr. C. S. Schollenberger.

Distribution of a Base between Two Acids. If the apparent pK value has the significance attached to it above, it should be possible to calculate the pH value that would result when an acid clay is treated with an equivalent amount of the salt of a second acid of known pK value. Under these conditions[5] the relationship, $\frac{x}{1-x} = \sqrt{\frac{K_1}{K_2}}$ holds, in which x represents the amount of base combining with the acid, whose dissociation constant is K_1, and $1-x$, is the amount combining with the second acid. It is very easy to test this equation in the case of the colloidal clay acids because they can be separated from the second acid formed by merely centrifuging and titrating the clear supernatant liquid.

The results of a series of such experiments are shown in Table II. The agreement between the calculated and measured pH values are in most cases as good as one could expect. It is possible then, to calculate (1) the relationship between the pH value of clay suspensions and the concentration of such

TABLE II

Distribution of a Base between an Electrodialyzed Bentonite and Certain Organic Acids

Concentration of Salt Millimols per liter	Monochloracetic pK = 2.81				Lactic pK = 3.85			
	pH		Acid freed		pH		Acid freed	
	Found	Calcd	Found	Calcd	Found	Calcd	Found	Calcd
10	3.50	3.42	2.13	2.01	4.03	3.97	3.60	4.33
25					4.57	4.36	5.58	5.90
50	3.93	3.88	4.14	3.96	4.73	4.65	6.10	6.80
100	4.29	4.11	5.12	4.95	5.11	4.96	—	5.75

Concentration of Salt Millimols per liter	Acetic pK = 4.74			
	pH		Acid freed	
	Found	Calcd	Found	Calcd
10	4.70	4.50	5.10	5.82
25	5.09	4.97	5.54	7.38
50	5.44	5.47	7.00	7.80
100	5.75	5.87	7.02	7.90

suspensions, (2) the pH values resulting when clay acids are treated with various increments of standard hydroxide solutions, and (3) the reaction resulting when clay acids of known combining weight are treated with the salts of acids of known pK value. This use of the pK value as an expression of the intensity factor of the acidity relations of clay acids is admittedly only an approximation but we are aware of no other method of treatment which enables us to predict as many of the reactions of clays.

[5] W. C. McC. Lewis: "A System of Physical Chemistry," 2nd Ed., 1, 237.

There is unfortunately one complicating condition, the value of the apparent dissociation constant obtained from titration curves is influenced noticeably by the nature of the base used. This is shown by the curves in Fig. 2 which are taken from a recent study made by Baver[6] in the author's laboratory. The curves were obtained by adding increments of the hydroxide solutions to fixed amounts of electrodialyzed Putnam clay. After standing for several days the pH value was measured with the quinhydrone electrode. The usual lyotropic series is quite evident. In the experiments cited above the

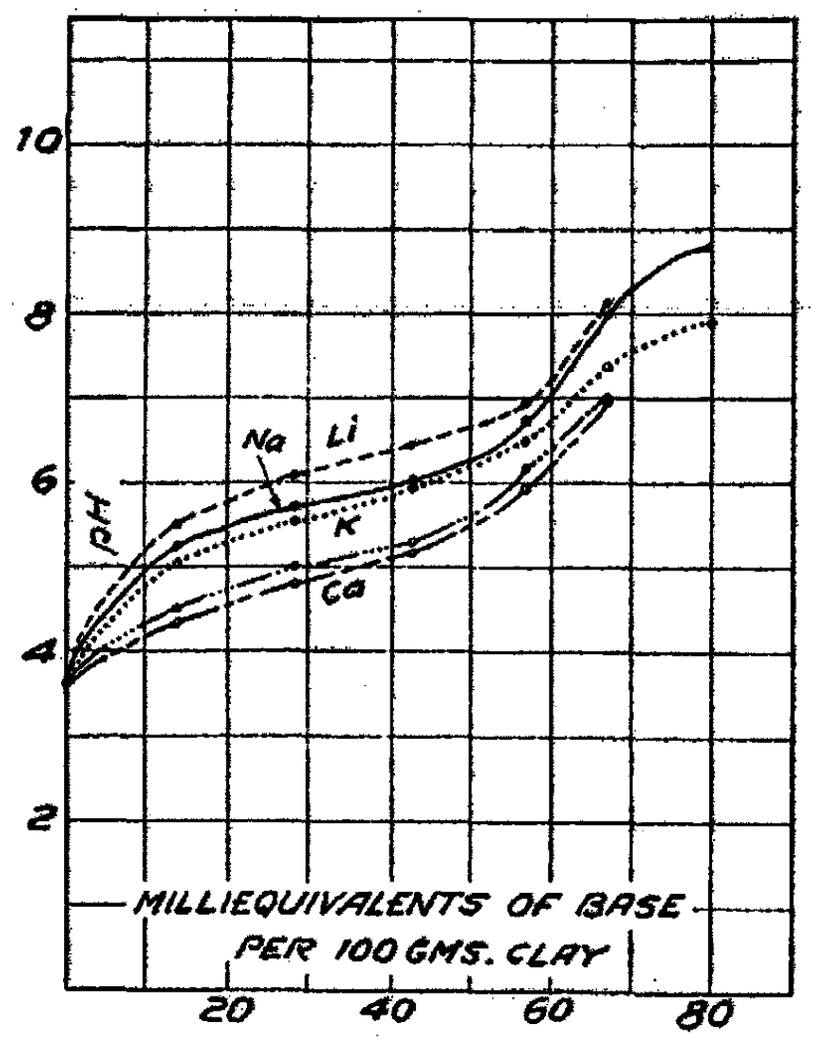

FIG. 2

The change in reaction of clays containing various amounts of different cations. (After Baver).

pK values obtained with KOH were used and K salts were used in the distribution studies. Natural clays contain more exchangeable Ca than any other ion. The calcium pK value would probably more nearly represent natural conditions.

The Effect of the Amount and Nature of the Exchangeable Cations on the Physical Properties of Colloidal Clays. It has long been known that the physical properties of clays were greatly influenced by the nature of the exchangeable cations. Homoionic clays have usually been prepared in the past by prolonged leaching with a neutral salt of the desired cation. Two objections may be raised against this method: (1) It is difficult to obtain a

[6] Missouri Agr. Expt. Sta. Research Bull. 129 (1929).

definite predetermined amount of replacement and (3) it is difficult to remove the last traces of the neutral salt. These objections may be overcome by preparing a stock sol of the hydrogen clay by electrodialysis and then adding the proper amount of the desired cation in the form of the hydroxide. Time does not permit a discussion of all the work that has been done in this field in the last few years but attention will be called to the work of Baver whose results are in general quite typical.

As changes in the physical properties of clays seem to be correlated usually with changes in electrophoretic potential let us first consider the effect of

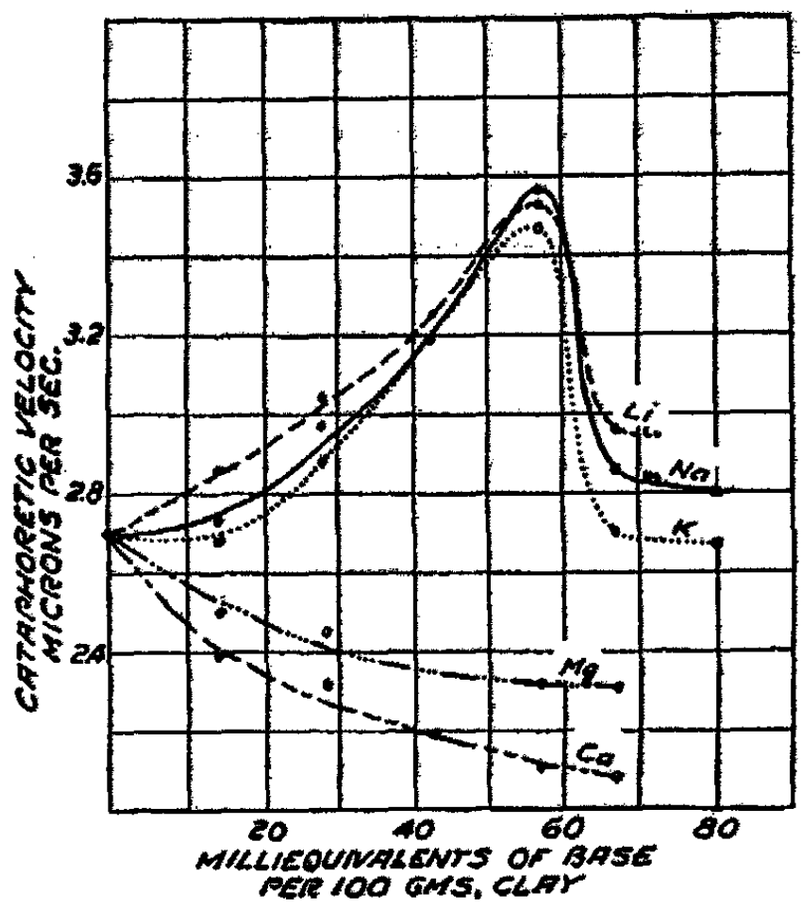

Fig. 3

The migration velocities of clay sols as affected by the amount and nature of exchangeable cations. (After Baver).

adding increments of different bases to an electrodialyzed clay (Putnam) on the migration velocity, expressed as v/sec/volt/cm. The measurements were made ultramicroscopically in a cell of the Tuorilla type. The most striking thing in the curves shown in Fig. 3 is the great difference in effects of the monovalent and divalent cations. With the monovalent ions there is a gradual increase to a maximum, then a sharp decline. The maximum comes at the same concentration with each cation and it is identical with the saturation values obtained by conductometric and potentiometric titrations. There is some overlapping of the curves of the monovalent series but in most cases the relationship is what one would expect. The sharp decline in the curves is probably a common ion effect. With the divalent ions a gradual retardation of the velocity is obtained.

There is a marked similarity between the electrophoretic velocities and the viscosities of the sols. The rate of flow of the 2.35 per cent suspensions through the Washburn modification of the Ostwald viscometer is shown in Fig. 4. The relative viscosity of the hydrogen clay was 1.42. For some reason as yet unknown, the maximum of the viscosity curves occurs at a lower concentration of the bases than the maximum of the electrophoresis curves. This may be due to the differences in concentration. It was necessary to use a high dilution, less than 0.01 per cent, in the cataphoresis studies.

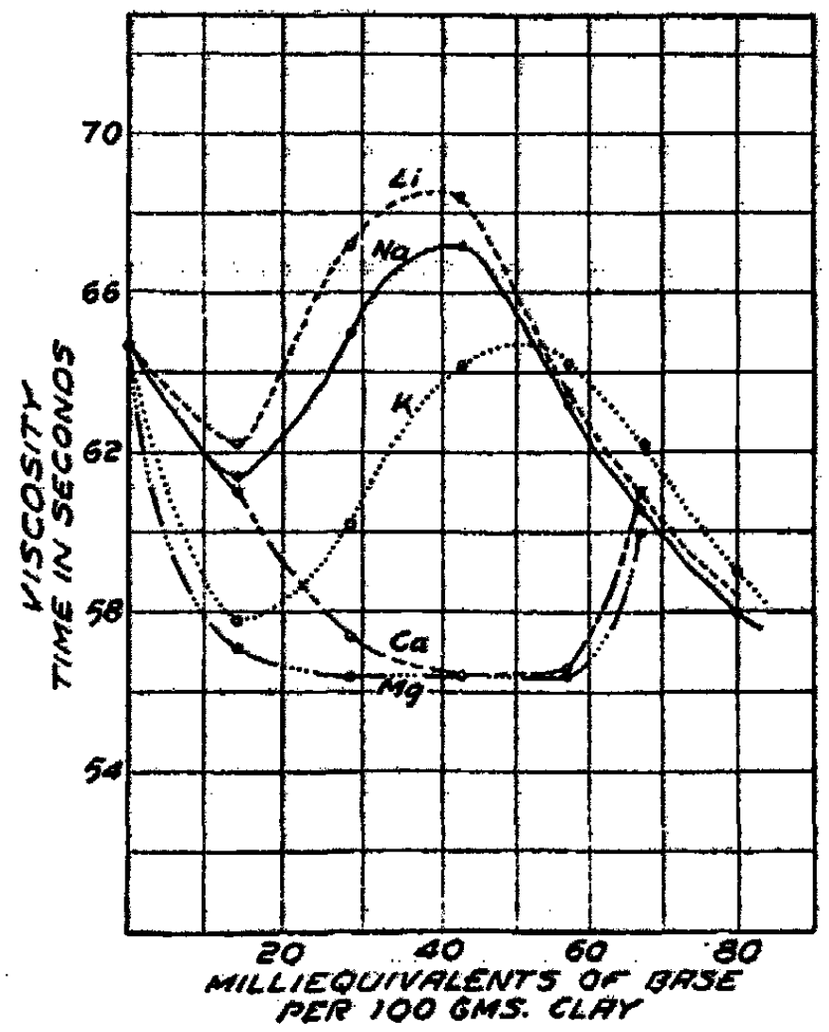

FIG. 4
Viscosity of clay sols containing different amounts of bases. (After Baver).

The initial drop observed with the monovalent cations is due to a dispersion of the aggregates of the hydrogen clay. This effect is most marked in the case of the K sol. The initial increase is undoubtedly associated with the hydration of the cation as pointed out earlier by Wiegner and others. The divalent cations cause a decrease in viscosity up to the saturation point. Further additions cause incipient flocculation. The relative magnitudes of the changes in viscosity caused by the hydration of the particles and by the increase in volume of aggregates due to water entrapped in the micells, can be seen in Fig. 5.

An estimation of the particle-sizes in the clays in the Na and Ca series was made by the ultramicroscopic method. The particles were very large due

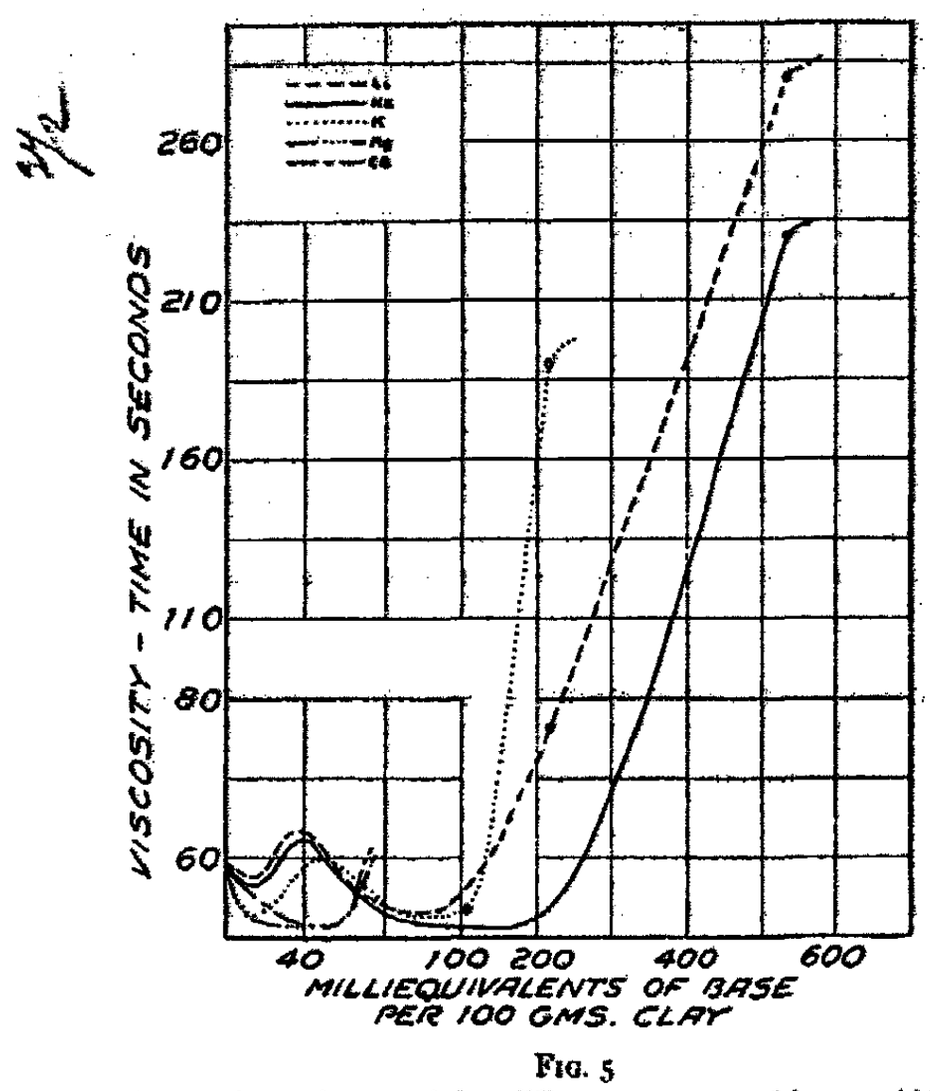

FIG. 5
Viscosity of clay sols containing different amounts of bases. (After Baver).

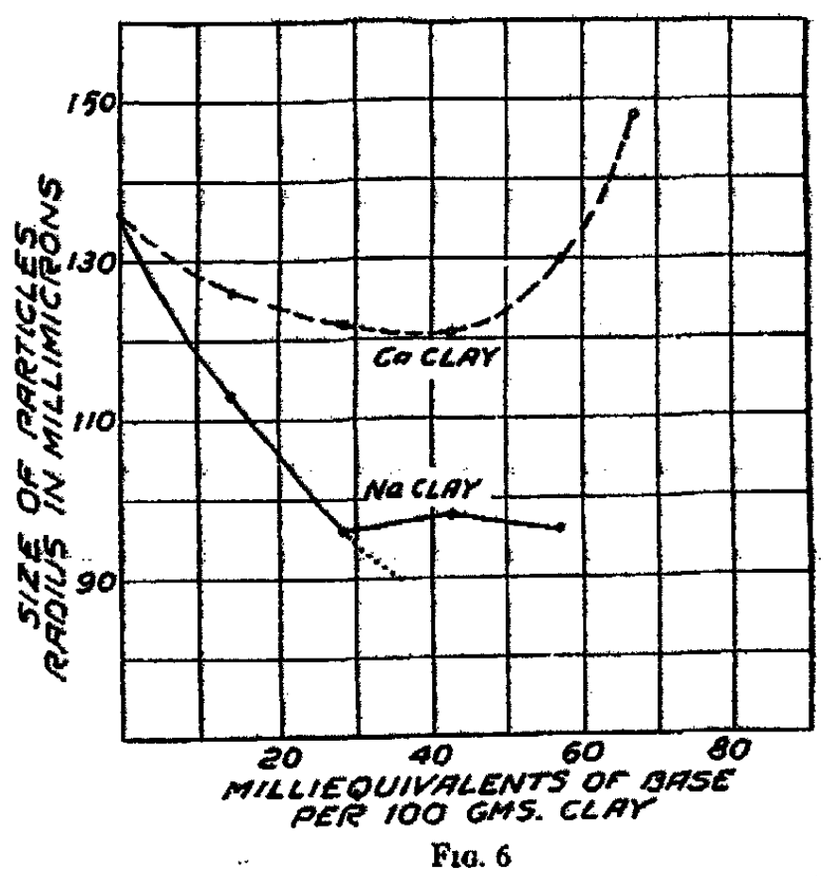

FIG. 6
The effect of exchangeable Ca and Na upon the size of particles of colloidal clay. (After Baver).

in part to the failure to remove all of the particles over 100 μ in the preparation of the clays. Satisfactory counts could be made with the Ca-clay but with the Na-clay it was quite evident that all the particles were not sufficiently visible to permit accurate counts. The shape of the Na-clay curve in Fig. 6 is additional evidence of this. It is not the smooth type to be expected in the light of the other studies.

Another striking illustration of the difference in size between the particles of the Na-clay and the Ca-clay is shown in Fig. 7. These curves represent the velocity of ultra filtration through a collodion membrane under a pressure of

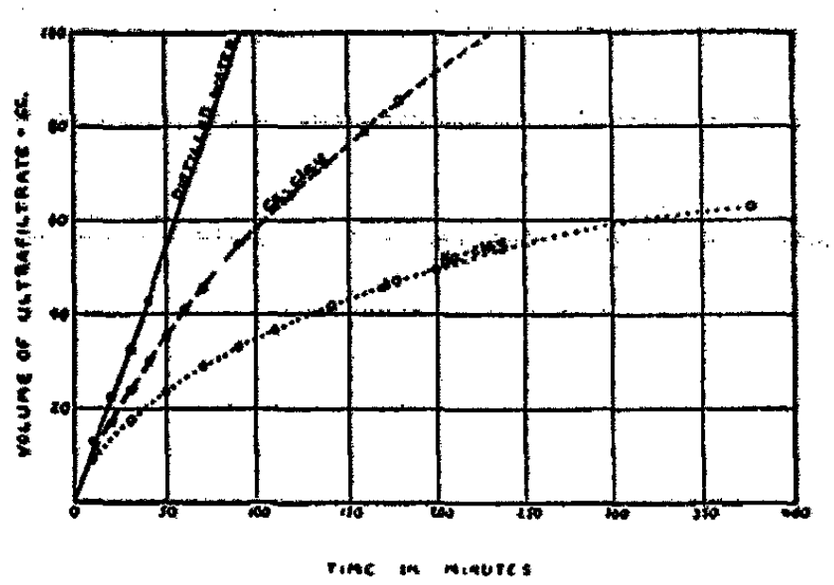

FIG. 7

The effect of exchangeable Ca and Na upon the filtration velocity of clays. (After Baver).

100 pounds per square inch. The Ca-clay is much more permeable. An attempt to calculate the size of the pores in the clay membrane by the formula of Bjerrum and Manegold[7] indicates that the cross section of the pores of the Ca-clay are about eight times as large as those of the Na-clay.

The greater permeability of Ca-clays has long been observed in the field. The unproductiveness of many of our irrigated soils in arid regions has been found to be due to a bad physical condition caused by the replacement of Ca by Na in the colloidal fraction. The formation of clay pans in the humid region, which reduces the productivity of the soils over them to less than 50 per cent of the normal expectation of the region is likewise to be attributed to a replacement of Ca by H. The study of the colloidal behavior of clays is admittedly bristling with difficulties but the results obtained in the last decade seem to justify a continuance of the work in spite of the dire predictions of many prominent colloid chemists, made at the first Colloid Symposium seven years ago.

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[7] Kolloid-Z., 43, 5 (1927).

MEASUREMENTS OF THE PLASTICITY OF CLAYS

BY G. W. SCOTT BLAIR

Introduction

The conception of that property of materials which we call *Plasticity** must have been a fairly important one, even in very early times. This is especially true in the case of clay, where the plastic properties of the material were of so great importance to the craftsman; but although the craftsman was able to judge the quality of his clay with considerable precision, Brongniart[1] was right when he said of plasticity in 1844, "On a souvent parlé de cette propriété, on semble la connaître, mais on n'en a qu'une vague idée." Ever since the time of Brongniart, scientific minds have been trying to define an exact conception of plasticity, and to measure it. An excellent summary of these attempts is to be found in Mellor's Treatise on Inorganic Chemistry, which it is not the purpose of this paper to attempt to reduplicate, but it seems that in spite of all the work that has been done, Brongniart's remark is almost as true today as it was eighty-six years ago.

There can be no doubt that the term "plasticity" has been used by different writers to mean very different things. In some cases the conception may be that of a single physical property, but more often a convenient combination of properties, describing a workable condition of the material, is implied. Without being too dogmatic, we can agree with Mellor to exclude from our conception of plasticity those properties which do not belong to the wet material (in the case of an aqueous two-phase plastic such as clay.) "It is assumed [by certain authors] that the tenacity of the dried clay is proportional to the plasticity of the wet clay. This is generally, but not always true. No known property of the *dry* clay can be used as an infallible index of the plasticity of the *wet* clay," (p. 485). We can scarcely agree that the proportionality is even generally true. Although more circumscribed definitions of plasticity have been suggested (e.g. Karrer[2]) it is thought that the most convenient formula is that of Wilson,[3] which is believed to combine an accurate description of the age-long meaning of the word with a comparatively simple scientific conception. Wilson says "Plasticity is that property which enables a material to be deformed continuously and permanently without rupture, during the application of a force which exceeds the yield value of the material." It is this general conception of plasticity that will be used throughout this paper. It will be seen that such "plasticity" is not *necessarily* related

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* Plasticity, from the Latin, plasticus, Greek πλαστικός = deformable, mouldable. Plasso (πλάσσω) = I mould.

[1] "Treatise on the Ceramic Arts" (1844). See also J. W. Mellor: "Treatise on Inorganic and Theoretical Chemistry," 6, 485 (1925).

[2] Ind. Eng. Chem., 21, 770 (1929); Anal. Ed., 1, 158 (1929); Rheology, 1, 290 (1930). (This paper contains an interesting discussion on the relation of plasticity to flow-data).

[3] "Ceramics—Clay Technology," 55, etc. (1927).

quantitatively either to the binding power of the dried material, as pointed out by Mellor, or to the amount of water which the material will absorb in order to attain its maximum plasticity. The latter property has so often been confused with plasticity, consciously or unconsciously, that many erroneous methods for measuring plasticity have not only been suggested, but have received a fairly wide popularity. This has been particularly true in the case of attempts to relate the plasticity of various colloidal systems to constants derived from curves relating volume of flow to shearing stress, when the material is caused to flow under shear. It seems likely that some such relationship should exist, but previous attempts to define it have invariably resulted in the measurement of a property dependent on the amount of the dispersed phase present, or, where different materials are compared at the same concentration, on the amount of the dispersed phase remaining free; or in other words, on the amount of solvation of the material.

It seems generally to have been accepted at one time that plasticity is measured by flow data of this type. Bingham,[4] who showed that for many two-phase systems at high rates of shear, the curve relating flow to shearing stress is a straight line which on extrapolation gives an intercept on the stress axis, headed his first discussion on the obtaining of these curves and evaluation of the slope and intercept "The Measurement of Plasticity." Wilson[5] states that the plasticity depends on a combination of both the properties measured by slope and intercept, and that plasticity can be measured comparatively by arranging that the materials are identical with respect to one of these constants, the other then defining the relative plasticity of the materials. (Ref. 3. p. 108.) Bleininger[6] is rather less definite, speaking of "plastic properties" rather than "plasticity" itself.

It is the object of the present paper to discuss the relationship between flow-stress curves and the plasticity of aqueous clay pastes, and then to consider how flow curve data can be used to investigate the causes and control of the plasticity of such clay pastes.

Some Empirical Plasticity Tests

In order to compare flow constants with the plasticity of a clay, it is necessary to have some simple tests of plasticity depending fairly strictly on the definition, or accepted by the experts as giving on the whole a good rough measure of plasticity, as a standard of comparison. The author has developed a test for this purpose which will be described first, as it seems the most satisfactory of those used.

Atterberg[6] has described a test in which a plastic mass of clay in water is rolled out into a fine "wire," the moisture content at which the wire or thread just tends to crumble being recorded. This is called the "Lower Plasticity Limit" of the clay, and gives a measure of its hydration capacity. To measure

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[4] "Fluidity and Plasticity," 320 (1922).

[5] J. Ind. Eng. Chem., 121, 436 1920).

[6] Internat. Reports on Pedology (1911) etc. See also Kinnison: U. S. Bur. Standards. Tech. Papers, No. 46 (1925); Wilson: Ref. 3, p. 114.

plasticity roughly, this test has been modified in the following way. A small pellet of plastic clay is rolled into a thread or wire very carefully with the finger, on a piece of smooth paper. This is done at that water content which gives the thinnest possible thread before crumbling takes place. The determination of the right moisture content is done by trial and error in the hands, and with a little practise becomes fairly easy. The moisture content need not be measured, but the diameter of the thinnest "wire" of clay that can be rolled is measured with a gauge. This test is believed to give a good rough indication of the extent to which the most plastic mass which can be made from the clay can be "deformed without rupture", and appears to correlate well with other information about the plasticity of clays. For convenience this will be referred to as "The Wire Test".

Two other empirical tests have been used which give some measure of the plastic properties of a clay. The first, called "The Slaking Test", has been used a good deal by practical ceramists. (It has also been called "The Bancroft Test.")[7] In this test, a mass of clay is kneaded under the thumb into a ball at what is termed the concentration of maximum plasticity, (though actually this is rather drier than the concentration of maximum plasticity as used for the wire test), allowed to dry out at room temperature over night, and then placed in distilled water in such a way that the material which falls away as the water replaces the cementing material in the ball, is able to fall clear of the mass of the clay. The time taken for a ball made from a given weight of clay to disintegrate completely is termed the "Slaking-Time", and it has been claimed that this gives a good measure of the plasticity of the clay.

In view of what has been said earlier in this paper, it is not surprising that although in many cases this test measures something so near to plasticity as to make it highly useful, experiment shows that in certain cases the slaking-time does not depend directly on plasticity at all, but rather on other properties of the material.*

The second, the "Oil Filtration Test", depends on the phenomenon investigated by Nutting,[8] who claims that the extent to which a clay is able to remove coloured impurities from a heavy oil by filtration, depends on the presence of hydroxyl groups, and open bonds in the clay. Dr. Nutting suggested to the writer of this paper that this property might be related to the plasticity of clay, and although the method is quite indirect, and although the author has not been able to obtain such regular and reproducible results as has Nutting, yet there does appear to be a very close correlation between the oil filtration capacity of a clay and its plasticity. Since work on this test is still in an early stage, no detailed technique will be described.

Having described a few rough tests by which some idea of the relative plasticity of a batch of clays may be obtained, we can now proceed to give an

[7] Bancroft and Jenks: J. Phys. Chem., 29, 1215 (1925); Jenks: 33, 1733 (1929); Boyd: J. Am. Soc. Test. Mat., 22, 337 (1922); Middleton: U. S. Dept. Agri. Tech. Bull., No. 178 (1929).

* Bancroft and Jenks are quite clear on this point.

[8] J. Washington Acad. Sci., 18, 409 (1928). See also Haseman: J. Phys. Chem., 33, 1514 (1929).

account of the way in which flow-constants are obtained. The modified Bingham plastometer used in this work has already been described.[9] A paste of the clay is caused to flow between two pipette bulbs through a glass capillary tube of known dimensions at a series of different pressures, the volume of material flowing through the capillary at each pressure being determined by means of a flowmeter somewhat similar to that described by Green.[10] The shape of the flow curve thus obtained has been much discussed, both from the theoretical and experimental points of view (for references see (9)), but in general, the following is a brief outline of its character.

Up to a certain small, but quite definite pressure (a), there is no flow at all (Fig. 1. stage I.); then follows a stage (II) in which the material flows as a solid plug through the tube, the flow-curve being rectilinear. This plug may

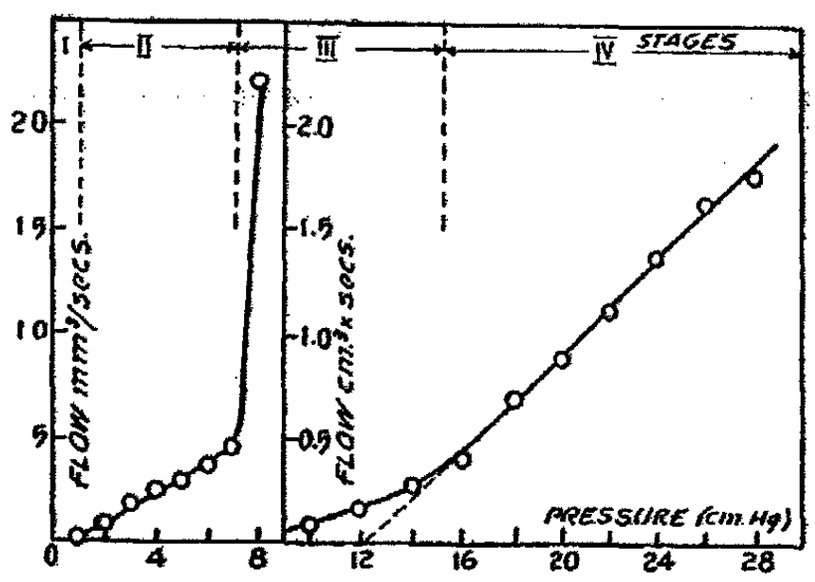

FIG. 1

be regarded as sliding through a water-envelope of constant thickness. The intercept (a) may be regarded as the shearing-strength or yield value of this water-envelope, or as a measure of the adhesion of the plug to the wall of the tube. It appears that these water films show rigid properties up to a thickness of at least 10^{-4} cm. (minimum value).* When another critical pressure (b) is reached, the curve slopes sharply upwards, and streamlining takes place near the wall of the tube (stage III.), the material still moving as a plug in the centre. As pressure is still further increased this plug diminishes at the expense of the streamlining sheath surrounding it, until finally almost the whole of the material is streamlining, the flow curve being again rectilinear (stage IV.). The extrapolated intercept (c) of this last straight line to the pressure axis gives Bingham's "yield value",* or as we prefer to call it, the shearing strength of the material.

[9] G. W. Scott Blair: Rheology, 1, 127 (1930); G. W. Scott Blair and E. W. Crowther: J. Phys. Chem., 33, 321 (1929); G. W. Scott Blair: J. Phys. Chem., 34, 1505 (1930); R. K. Schofield and G. W. Scott Blair: 34, 248 (1930); B. A. Keen and G. W. Scott Blair: J. Agric. Sci., 19, 648 (1929).

[10] J. Am. Soc. Test. Mat., 20, 450 (1920). A detailed description of the apparatus and technique are given in the paper by Keen and Crowther, listed under Ref. 9.

* This is calculated on the assumption that at concentrations where the water-film is only just thin enough to show rigid properties, its viscosity is of the same order as that of ordinary water. Compare Weber and Lewin: Kolloid-Z., 50, 197 (1930).

Experimental

A preliminary attempt was made to correlate mobility (slope of stage IV of curve) and the shearing strength of five clays with the order of their plasticity as determined by the rough tests described above, and alternatively with their water-absorbing capacity (moisture content at maximum plasticity). It will be apparent from Table I that these plastic constants depend on the water-absorption capacity rather than the plasticity. The clays were compared in the plastometer at a constant concentration by weight.

TABLE I

Clay	Slaking time mins. (2.5g.)	Wire test diameter mm.	%ge dry matter at condition of maximum plasticity.	Shearing strength (c) (pressure) cm. Hg.	Mobility
1	3.6	2.0	71.0	12.5	0.95
2	4.3	1.0	79.5	0.3	2.5
3	18.5	0.6	77.0	1.6	1.3
4	>50.	<0.6	72.5	3.3	1.25
5	9.0	0.8	75.0	3.3	1.1

Order of oil filtration capacities:—1 <2 <5 <3 <4.

An attempt to compare mobility and shearing strength of clay pastes made up to equivalent concentrations in free water by allowing for water absorption capacity differences was unsuccessful. It is also found that the slope and intercept of the "plug"-curve (stage II) depend on hydration rather than plasticity, when comparisons are made at the same concentrations either by weight or volume.

A Relationship between Plasticity and the Flow Curve

After a very careful study of all the data available, it was found empirically that *when clays are compared at concentrations such that their a-values (adhesions to the wall of the tube) are the same, in tubes made of the same kind of glass, then under these conditions, the shearing strengths of the materials give a good measure of the relative plasticity of the clays.*

TABLE II

Clay*	B_A	Diam. of "wire" mm.	Clay*	B_A	Diam. of "wire" mm.
A	2.82	0.6	H	1.64(?)	2.1
B	2.66	0.6	I	1.59	1.8
C	2.36	0.7	K	1.59	2.0
D	2.21	0.8	L	1.58	2.5
E	2.05	1.1	M	1.38	3.0
F	1.85	1.0	N	0.82	5.0
G	1.69	2.0—	O	0.56	9.0

B_A is the value of B, when $aR/2L$ is 0.21 dyne/mm²

* These materials are not all strictly "clays."

Table II shows the relationship between B, the critical shearing stress per unit area at the wall, (which is bR/2L, where R is the radius of the tube and L its strength), to the diameter of "wire" from the wire test. A fairly good correlation for a large number of materials is shown.

In these cases, the concentration which would give the arbitrarily fixed value of "a" was first determined for each material by trial and error, but when it was observed that for different concentrations of the same material, a and b were at any rate roughly linearly related, it was found much simpler first to do a test at a value of "a" slightly higher than is required, and then to dilute to a slightly lower value, calculating the value of b for the intermediate arbitrary "a" value by means of an interpolation formula. The a/b curves do not pass through the origin, and the question arises as to whether plasticity determined in this way is really independent of the arbitrary value of "a" chosen. Actually the relative values are not quite independent of "a", if the clays are compared at very widely different "a" values. Plasticity probably depends in some complex way on the entire a/b curve; but for practical purposes, the simple test, taking a suitable value of "a", is considered as giving a fairly reliable figure, though a complete and much more complicated test could easily be devised if greater accuracy were required. For ordinary purposes, a flow curve derived from a single capillary is adequate, but it is best to define the constants as stresses per unit area at the wall, in this way making the values independent of the dimensions of the tube.* It has been found (9) that there is a modification in the flow properties of clay pastes in the immediate vicinity of the wall of the tube. This means that B is not really a true measure of the critical shearing stress of the whole bulk of the material. However, at high concentrations this effect is small, and the correction not serious; for this reason the arbitrary "A" value should be taken as high as is convenient. If a slightly less simple test is no disadvantage, the extrapolated intercepts of the stage IV part of the curve can be taken instead of B. We will then define *the critical shearing stress at the wall in a paste of a clay having an adhesion at the wall equal to one dyne per square millimeter as the Flow-plasticity* (B_{A1}). One dyne/mm^2 is quite a convenient value for "A" for the less plastic clays. For very plastic clays, a lower value may be used (as in Table II). The word "Flow-plasticity" is used in order not to be too dogmatic about the exact nature of plasticity. Flow-plasticity is at least something very much like the Wilson definition of plasticity, and can be measured quickly, easily and with fair accuracy.

The Mechanism of the Test

It is not understood exactly why plasticity can be measured in the way described. It is not surprising that the critical shearing stress of the material should be related to plasticity, but why it should be necessary to compare

* If the force per unit area of the cross-section of the capillary is p, the total force, $p\pi R^2$, must be equal to the total stress on the wall of the capillary. Since the area of the wall is given by $2\pi RL$, the stress per unit area on the wall is given by $pR/2L$. Throughout this paper, pressures are written with small letters, and stresses per unit area with capitals. Thus $A = aR/2L$, and $B = bR/2L$.

clays at the same wall-adhesion is not at all clear. One must remember that the idea of a water envelope surrounding the plug is conventional, each particle of clay being hydrated. The hydration layers round the particles may be distorted at the wall, but in any case the thickness of the water envelope refers simply to the mean distance between the outermost particles forming the moving plug, and the wall of the tube. The clays are compared at such concentrations that the shearing strength of this thick layer of water molecules is the same in all cases. That this procedure should give results which yield comparable plasticity figures for different clays is a fact which must at present be regarded as empirical, but it is hoped that some explanation will shortly be forthcoming.

The Performance of the Test

The following is an account of the exact way in which the test is carried out. Clay is mixed with distilled water into a thick paste,* forced through a

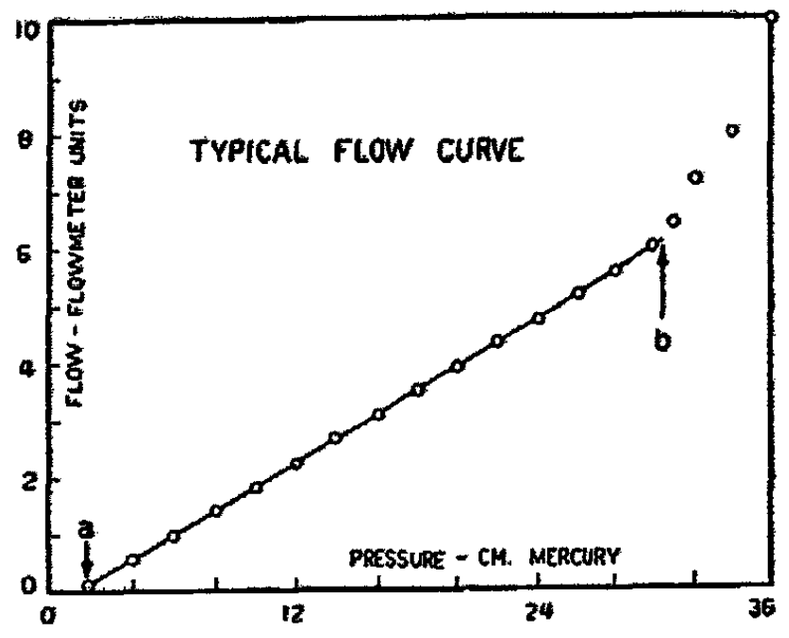

FIG. 2

100-mesh-per-inch sieve, diluted to a concentration slightly greater than that required, (with a little practice this is quite easily done,) then placed in the plastometer in the thermostat. The paste is first forced rapidly through the capillary to eliminate thixotropic structure, and ensure good mixing, and is then forced backwards and forwards by compressed air as previously described[9] at a series of pressures ranging from zero to a point where streamline flow has begun. The flow curve is then plotted (a typical curve is given in Fig. 2), and A and B are calculated. These we will call A_2 and B_2.

The paste is then removed from the plastometer, diluted slightly, mixed thoroughly, and the test is repeated, the constants A_1 and B_1 being evaluated. The arbitrary A value, (normally 1 dyne/mm^2.), should lie between A_2 and A_1. Then we have;—

* *It is sometimes necessary to work the material for some time before a really smooth paste is obtained.*

$$B_{A1} = \frac{(B_2 - B_1)(1 - A_1)}{(A_2 - A_1)} + B_1$$

an equation which assumes only that A and B are linearly related over a small range of concentration—which is certainly true. Should there be any doubt as to the accuracy of a test, a third concentration, or even a different capillary may be used. The whole test normally takes rather less than one hour to complete. Attempts to use a simpler type of plastometer for this test, (the Bingham-Murray for example,)[11] have not proved encouraging so far.

The Causes and Control of Clay Plasticity

Having developed a test for measuring the plasticity of clay, it is of interest to find out how far the use of this new test substantiates or refutes earlier theories on the ways in which plasticity may be produced or increased in a clay. Bancroft and Jenks[7] have suggested that a clay may be rendered more plastic by treating it with a flocculant in the presence of a peptizing medium, and have shown that this is actually the case, if the slaking test is taken as a measure of plasticity. Table III shows the effect of treating a kaolin sample with (1) NaOH (2) NaCl (3) NaOH + NaCl, the material being boiled on a water-bath to dryness for about four hours, and then once more made into a paste, and tested by the flow-plasticity test. It is clear that the combined action of the NaOH and NaCl has a very marked plasticizing effect.

The use of solutions of potassium tartrate and sodium citrate as peptizing media give a similar, but less marked effect.

TABLE III

Treatment	B_{A1}	% increase B_{A1} on control
Control	6.4	—
1% NaOH	2.15	−66
5% NaCl	7.4	+16
1% NaOH + 5% NaCl	10.2	+59
5% Potassium Tartrate	6.1	− 5
5% Potassium Tartrate + 5% NaCl	8.5	+33
5% Potassium Tartrate + 5% KCl	8.0	+25
5% Sodium Citrate	7.2	+12.5
5% Sodium Citrate + 5% NaCl	8.7	+36

(All concentrations are given as percentages of dry clay.)

However, kaolin can be rendered more plastic in a number of other ways as well as by the action of a flocculant in the presence of a peptizing medium. The mechanism of the processes is not quite clear, but if kaolin is treated

[11] J. Am. Soc. Test. Mat., 23, 655 (1923).

with increasing quantities of HCl, the plasticity is increased up to an optimum concentration, after which it falls again. Sulphuric acid, or mixtures of sulphuric acid and aluminium sulphate plasticize kaolin to an enormous extent. The results of these preliminary experiments are given in Table IV.

TABLE IV

Treatment	B_{41}	% increase B_{41} on control
Control	6.4	——
0.18% HCl	8.3	+ 30
0.37——	11.0	+ 72
0.44——	14.2	+122
0.55——	10.4	+ 63
1.1 ——	6.4	0
0.73% H_2SO_4	17.0	+166
0.73% HS_2O_4 + 2% $Al_2(SO_4)_3$	21.9	+242

Experiments on the effect of mixed electrolytes are in progress. It is of interest to note that whereas the slaking test shows an increased plasticity on the addition of NaOH to clay alone, both the flow-plasticity test, and the wire test show a decrease. This is much more in accordance with general experience. These investigations are still in a preliminary stage, and are being continued.

Summary

The meaning of the term plasticity is discussed, and various simple, rough tests for the plasticity of a clay are described. It is shown that when different clays are caused to flow through a capillary tube under stress at the same concentrations, the ordinary flow constants, mobility and shearing strength (or yield value) depend on the hydration capacity of the clay rather than on its plasticity. By comparing the flow of clay pastes at such low shearing stresses that the material flows as a solid plug, and arranging the concentrations so that the water envelope surrounding the plug has a constant shearing strength, it is possible to get values for the critical shearing stress of the material, which depend on a property very closely allied to plasticity, to which the term "Flow-plasticity" has been applied. Preliminary work on the effect of electrolytes on the flow-plasticity of kaolin is described, with special reference to the Bancroft-Jenks theory of mixed peptizing and flocculating action.

The author is much endebted to Professor Wilder D. Bancroft for his constant help and advice throughout the progress of this work, and to the Norton Company of Worcester (Mass.) for their kindness in supplying some of the clays used.

Cornell University.

32-81

STUDIES IN THE PLASTICITY OF PAINTS

BY F. H. RHODES AND W. J. JEBENS[1]

The plasticity of paints has been extensively studied in connection with their brushing characteristics. Among the various factors that affect the plasticity, the following are some of the more important ones—the volume concentration of pigment, the size and shape of particles, the extent to which the pigment is wetted by the vehicle, the extent to which the pigment is flocculated in the paint, the viscosity of the vehicle, the presence of soap, the presence of water, and the age of the paint. As the concentration of the pigment in the paint is increased, the mobility of the material is decreased and yield value is increased. Rhodes and Wells[2] found this to be true with paints made with the following pigments: zinc oxide, lithopone, Dutch process white lead, basic sulphate white lead, electrolytic white lead, and titanox. Although theoretically the yield value is zero for values of concentration lower than that required for cubical packing of the pigment particles, a small yield value is obtained experimentally. The mobility of the suspension decreases linearly with the concentration of the pigment in the paint.[3,4]

For particles of fairly uniform size and shape the yield value increases and the mobility decreases with a decrease in the average diameter of the particles. Einstein[5] in deriving his formula for the viscosities of dilute suspensions neglected the effect of the size of the particles as modified by adsorption. Hatschek[6] called attention to the error introduced by this omission. However for paints prepared from zinc oxide and linseed oil, Green and Haslam[7] have shown that the yield value increases as the particle size decreased. Odén[8] found an increase in the viscosity for sulphur sols with increased dispersion of the sulphur, the effect being more pronounced the higher the concentration of the sulphur. It has also been noted that the form of the size distribution curve for the pigment affects the plastic characteristics of the paint.[9]

A third factor that may affect the plastic characteristics of a paint is the ease with which the solid is wetted by the liquid. Both the nature of the pigment and the nature of the vehicle affect the ease of wetting. In general, an increase in the ease of wetting causes an increase in the mobility and a decrease in the yield value. In some instances, the wettability of the pigment varies greatly with apparently minor changes in the composition of the vehicle.

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[1] DuPont Fellow in Chemistry at Cornell University.
[2] Ind. Eng. Chem., 21, 1273 (1929).
[3] Bingham, Bruce, and Wolbach: J. Franklin Inst., 195, 303 (1923).
[4] Bingham and Jacques: Ind. Eng. Chem., 15, 1033 (1923).
[5] Ann. Physik, (4) 34, 591 (1911).
[6] Kolloid-Z., 1, 301 (1910).
[7] Ind. Eng. Chem., 19, 53 (1927).
[8] Z. physik. Chem., 80, 709 (1912).
[9] Ingalls: Am. Paint Var. Mfg. Assocn. Circ. 135.

For instance, a small increase in the concentration of free fatty acids may cause the oil to wet the pigment much more readily. It is well known that linseed oil will displace water from pulp-mixed white lead only if the acid value of the oil is above a certain minimum limit.[10]

The extent to which the pigment in the paint is flocculated depends upon the nature of the pigment and upon the character of the vehicle. In general, the deflocculation of the pigment is more nearly complete when the solid is readily wetted by the liquid. In some cases, the effect of the degree of flocculation upon the consistency of the suspension is very pronounced. The effect of the addition of a deflocculating agent upon the plastic characteristics of a suspension may be illustrated by adding a small amount of oleic acid to a mixture of lithopone and mineral oil. If dry lithopone is mixed with a considerable amount of mineral oil, the pigment remains in a highly flocculated condition, and the resulting mixture is a stiff paste which can be shaped and moulded like clay. If a few drops of a deflocculating agent—as, for example, oleic acid—are added, the lithopone is wetted and dispersed, and a mobile suspension results. The addition of the dispersing agent greatly increases the mobility but decreases the yield point only slightly. The flocculating power of a liquid is one of the important factors in determining its characteristics as a thinner for paints. All of the commonly used thinners—benzol, petroleum naphtha, and turpentine—have viscosities of the same general order of magnitude. Turpentine, however, tends to flocculate certain pigments, and therefore in reducing the paint to the desired consistency it is necessary to add more of the turpentine than of any of the other thinners.[2,11]

A decrease in the viscosity of the medium increases the mobility of the suspension but has little or no effect upon the yield point. In many cases the effect of the viscosity of the liquid is small in comparison with that due to its wetting power.

The addition of soaps to a paint results in "false" body. Bingham and Jacques[4] found that the addition of aluminum stearate to a paint made with lithopone and linseed oil increased the yield value markedly, but lowered the mobility only slightly. The effect of soaps in lubricating greases is much better known than their effect in paints, and it may be of interest to give some of the facts concerning them. The structure of a soap in a lubricating oil is probably much the same as that given by McBain for water solutions of soap.[12] If the soap is quite soluble in the oil there is little increase in the consistency of the grease. This is true with greases made with calcium oleate where in order to obtain proper consistency it is necessary that water should be incorporated in the solution of soap in oil. Sodium soaps incorporated in a grease are practically completely dehydrated and are able to give a very stable structure in this state. Lead soaps are very much less soluble in the oil and tend to precipitate out if too much water is present. Zinc soaps are

[10] Smith: "The Manufacture of Paints" (1915).
[11] Wolff: Chem.-Ztg., 48, 647 (1924).
[12] Kleingard: "Lubricating Greases" (1927).

never used alone in the manufacture of greases as they have little ability to thicken the oil and are very unstable in the presence of moisture. The effect due to soaps in paints if similar to their effect in greases will vary widely depending on the type of soap and the conditions.

Bingham and Jacques[4] found that the addition of small amounts of water to a paint made with dry lithopone and linseed oil increases the yield value and decreases the mobility. It does not follow, however that the presence of water always injures the brushing qualities of a paint; in fact, it is common experience that in many cases paints which contain small amounts of water "brush out" much better than do those made from absolutely dry materials.[13] The superior working qualities which are claimed for pulp-mixed white lead may be due in part to the fact that this material always contains a small amount of moisture.[14]

In many instances, ready mixed paints tend to undergo changes in texture and plasticity on standing. The oil may hydrolyze to some extent, and the free acids thus formed may react with the pigment to form soaps.[15] In certain cases, the formation of these soaps may tend to cause "skinning" and "puttying." Furthermore, the slow reactions that occur during ageing may change, and in some instances may improve, the plastic characteristics. Sabin[16] states that "The fluidity and working characteristics of white zinc paint are considerably improved with age." Bingham and Jacques[4] found that with continued grinding the yield value at first decreases and then remains constant, while the mobility at first rises and later decreases. The effects may be due in part to changes which are analogous to those which occur during ageing.

Experimental Procedure

The linseed oil used in preparing the paints was pure refined linseed oil from North American seed. The two lots of oil which were used were analyzed by the methods recommended by the A. C. S. Committee on Analysis of Commercial Fats and Oils with the following results:

	Lot 1	Lot 2
Acid number	0.459	0.280
Saponification number	189.800	194.500
Iodine number	194.300	182.700
Specific gravity	0.9275	0.9276

The pigments were zinc oxide, Dutch process white lead, aluminum powder, and iron oxide.

In the preparation of the paints, the following procedure was adopted: The required amount of pigment was weighed into a mortar, and sufficient

[13] Toch: "Chemistry and Technology of Paints" (1925).
[14] Sabin: "White Lead: Its Uses in Paints" (1920).
[15] Ware and Christman: Ind. Eng. Chem., 8, 897 (1916).
[16] "Technology of Paints and Varnishes" (1917).

linseed oil was added to form a thick paste. The mixture was ground for thirty minutes. The remainder of the oil required to give a paint of the desired composition was then added slowly and with constant grinding, and the grinding was continued until the pigment was thoroughly incorporated in the vehicle and a homogeneous paint was obtained. The paint was passed through a 200-mesh sieve and was then placed under a vacuum for several hours and stirred at intervals to eliminate bubbles of air.

Paints free from moisture were prepared from dry linseed oil and pigment which had been dried for two hours at 120°C. In the preparation of the paints which contained water, the required amount of water was weighed into a mortar and a portion of the dry paint was added. The mixture was ground until homogeneous, then the rest of the dry paint was added with constant grinding and the grinding was continued until thorough incorporation of the water was attained. To remove any air which may have been introduced during this operation, the wet paint was again evacuated for thirty minutes with almost constant stirring. Some of the water in the paint was vaporized during the second evacuation. The water content could not therefore be calculated from the proportions used in preparing the paint and was determined by analysis.

The same apparatus and procedure was used to measure the plasticity of the paints as was used by Rhodes and Wells.[2] The capillary used in this work was 6.05 cm long and 0.0247 cm in radius. The pressures were measured in centimeters of mercury, and are so expressed in all of the following tables. With the particular capillary which was used, a pressure of one centimeter of mercury is equivalent to a stress of 27.06 dynes per square centimeter. All yield points, as given, may be converted to the absolute basis by multiplying by this factor. The mobilities, as given, are expressed in terms of the slopes of the graphs obtained by plotting rates of flow, in cubic centimeters per minute, against the corresponding pressures in centimeters of mercury. While these units are perfectly satisfactory for purposes of comparison, they may be converted into absolute units by multiplying by the factor, $8L/R^4Dg$, in which, L is the length of the capillary in centimeters, R is the radius of the capillary in centimeters, D is the density of mercury (13.596), and g is the gravity constant (980.4). The numerical value of this constant, for the capillary used, was 52.03.

Experimental Results

Effect of Water. Paints were prepared from dry neutral linseed oil (Lot 1) and each of the following pigments: zinc oxide, white lead, mixtures of white lead and zinc oxide, and iron oxide. To each of the dry paints, various amounts of water were added, and the plasticities of the resulting paints were determined. The results are summarized in Table I.

The addition of water to paints made with oil of low acid value increases the yield and lowers the mobility—*i.e.*, it renders the paint considerably stiffer and less fluid. In general, the effect of the addition of water upon the mobility appears to vary qualitatively with the relative ease with which the

TABLE I

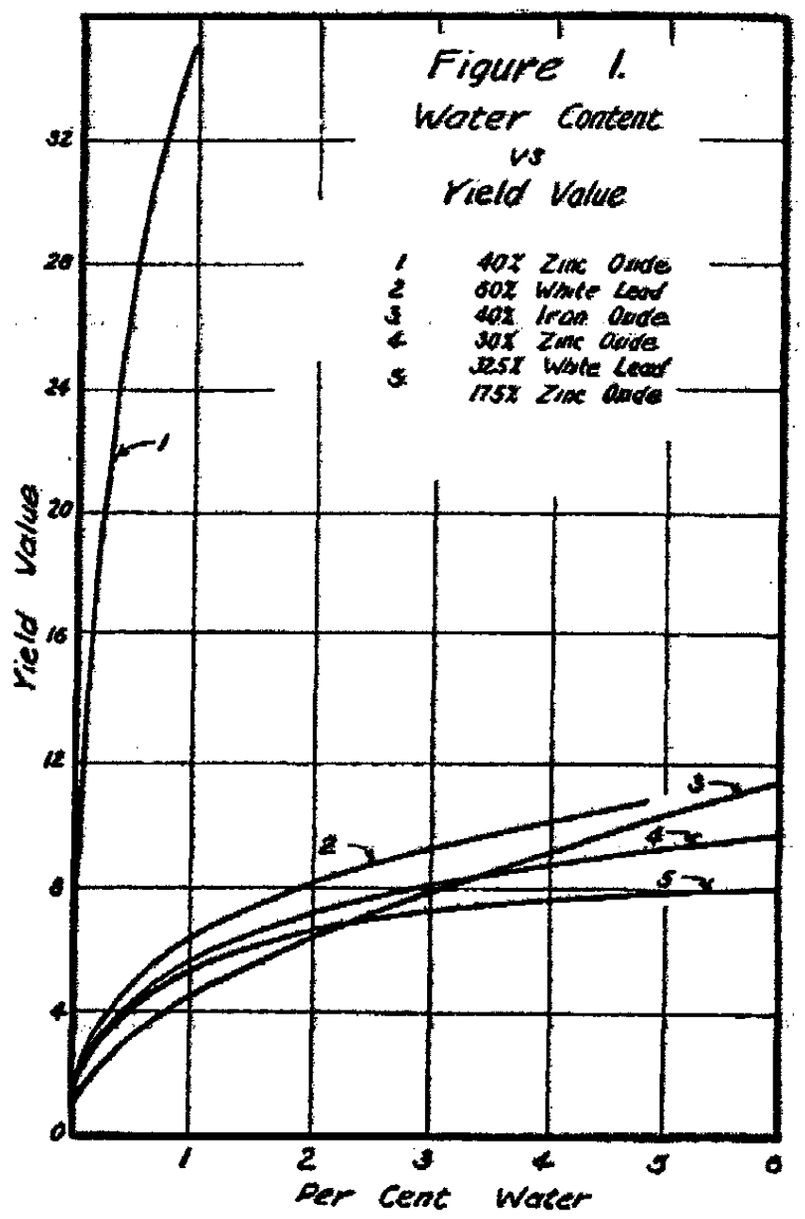
Effect of Water on Paints prepared from Neutral Linseed Oil

Pigment	% by weight of Pigment	Water Content	Yield Value	Mobility
Zinc Oxide	30%	0.00%	1.5	0.0306
		0.40	4.3	0.0190
		0.89	5.4	0.0190
		1.84	6.9	0.0168
		4.75	8.2	0.0168
		7.77	10.0	0.0147
Zinc Oxide	40	0.00	4.9	0.0240
		0.99	35.2	0.0147
White Lead	60	0.00	1.0	0.0226
		0.42	4.5	0.0139
		0.76	6.0	0.0127
		1.83	7.0	0.0116
		4.87	10.8	0.0089
Mixture:	50	0.00	1.5	0.0272
65% white lead		0.50	4.3	0.0138
35% zinc oxide		1.02	5.5	0.0126
		1.86	6.7	0.0120
		4.92	7.8	0.0110
		7.78	10.2	0.0114
Iron oxide	40	0.00	1.0	0.0221
		0.44	2.1	0.0212
		0.96	5.0	0.0196
		1.79	6.2	0.0188
		4.54	9.8	0.0160
		7.38	12.2	0.0126

The results are shown graphically in Figs. 1 and 2.

pigment is wetted by water. In the paints made with white lead, which is very much less readily wetted by water than by oil, the first small additions of water very greatly decrease the mobility; with larger amounts of water the effect is still apparent, although much less pronounced. Somewhat similar results were obtained with the paints made with mixtures of white lead and zinc oxide. Paints containing zinc oxide alone, which is somewhat more readily wetted by water than is white lead, also showed a rather marked decrease in mobility with the first additions of water, but the effect was somewhat less pronounced. With iron oxide, which is rather readily wetted by water, the decrease in mobility was less pronounced and was more nearly linear throughout the entire range of concentrations.

With each of the paints, the first small additions of water increased the yield values markedly, further increase in the content of water had relatively less effect. All of the dry paints except that one which contained forty per cent of zinc oxide had yield values of the same general order of magnitude, and with all of these paints the effect of the addition of water was quite similar. The initially high yield value of the paint which contained forty per cent of zinc oxide was increased very rapidly indeed by the addition of small amounts



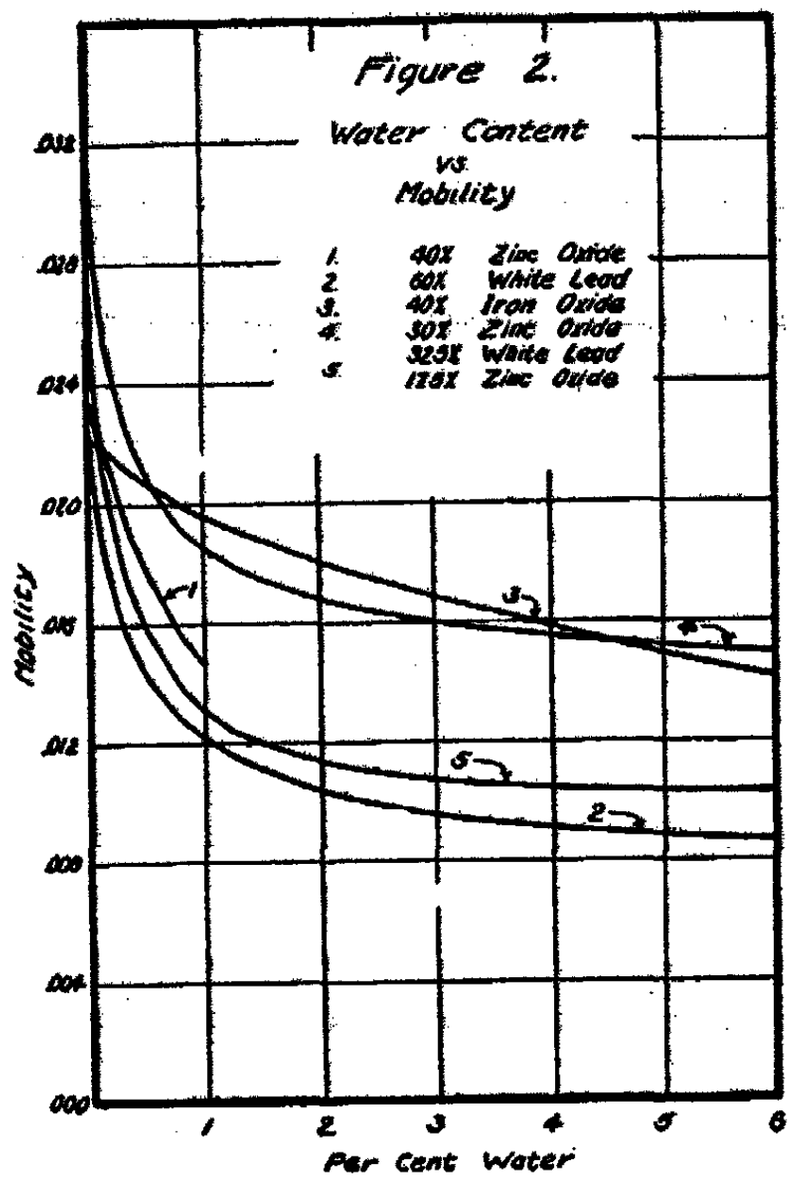
of water, so that at first glance it would seem that the effect of water upon the plasticity of this paint is unusually great. It will be observed, however, that the proportional increase in yield value which is brought about by the addition of water to the dry paint is approximately the same with all of the paints.

The increase in the consistency of all these paints is probably due to the action of the water in tending to flocculate the pigment and to form an emulsion of water in the paint. In either case a structure is built up in the paint with the resulting increase in yield value and decrease in mobility.

The Effect of Soaps. The effect of the addition of soap upon the plastic characteristics of paints was studied for the two soaps, sodium oleate and

calcium oleate. These particular ones were selected because they are typical of the two principal classes of soaps: sodium oleate is soluble in water and tends to aid in the formation of emulsions of oil in water, while calcium oleate is soluble in oil, and tends to produce emulsions of water in oil.

In preparing these paints, an amount of soap equal to ten per cent of the weight of the combined oil and pigment was placed in a mortar, and to it was added a small amount of the linseed oil. After grinding the soap and the oil



together thoroughly, the pigment and the remainder of the oil were added and the paint prepared in the usual way. All of the paints contained thirty parts by weight of zinc oxide to seventy parts of linseed oil (Lot 2). Mixtures containing less than ten per cent of soap were made up by blending portions of this paint with the proper quantities of paint which contained no soap. The results of the plasticity determination are given in Table II and are shown graphically in Figs. 3 and 4.

These results are qualitatively significant, but may not be extremely accurate quantitatively. The soaps—and particularly the sodium oleate—probably exist in the paint in the form of micelles or minute threads which give the mass a "false body". The mere stirring of the solution, or the dis-

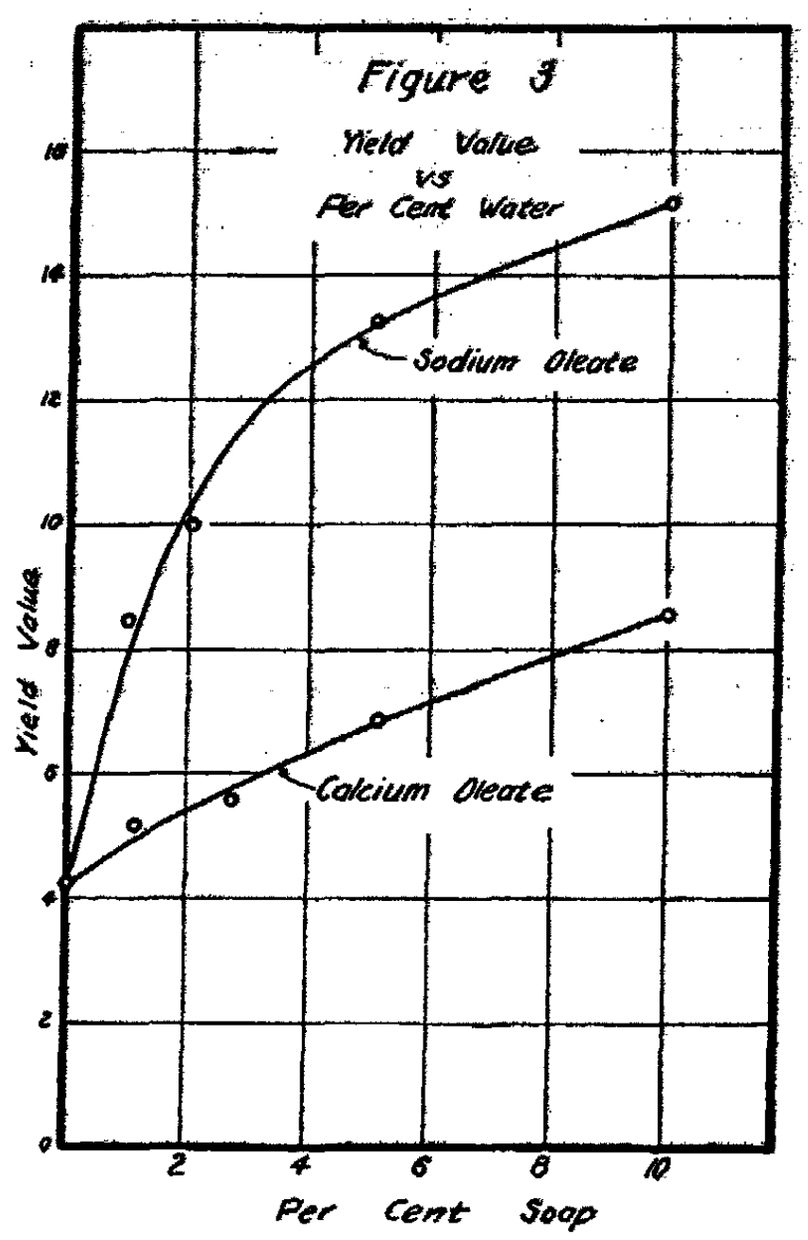
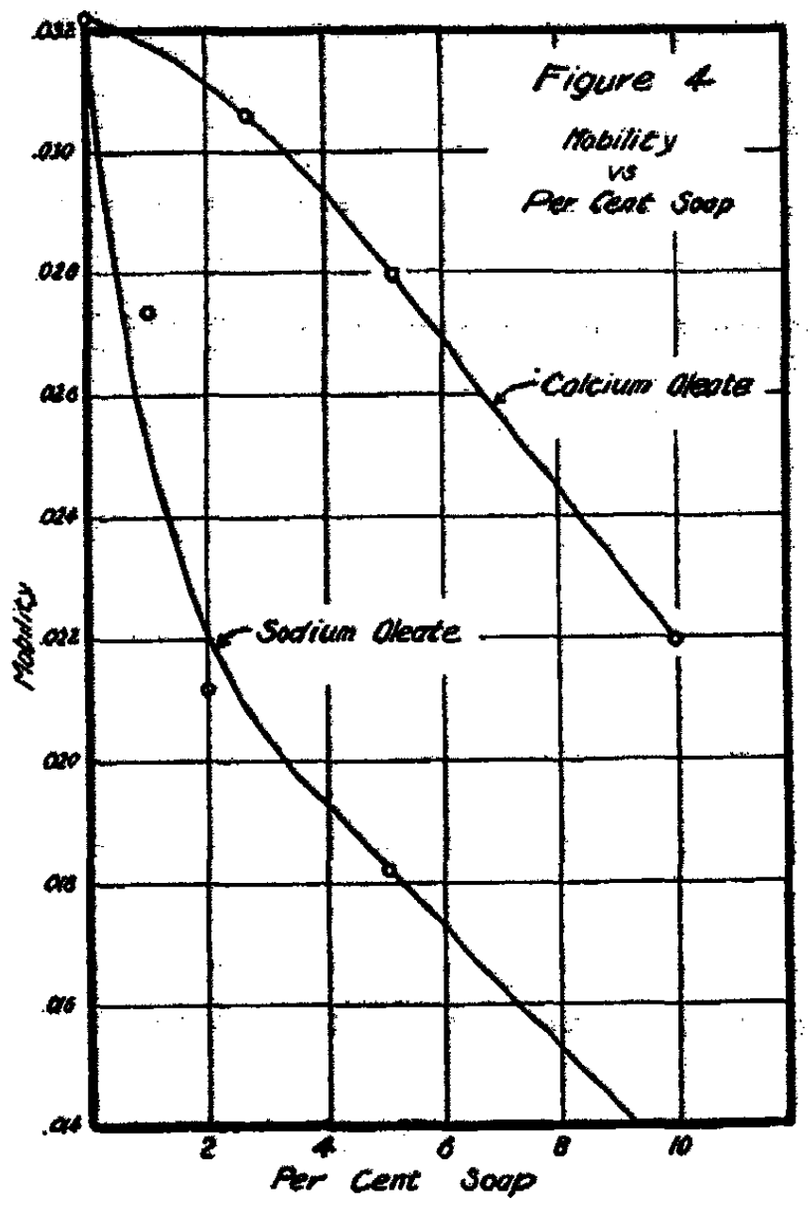


TABLE II

Effect of Soaps on Paints prepared from Neutral Linseed Oil

Soap	Per Cent of Soap	Yield Value	Mobility
Calcium Oleate	0.00	4.3	0.0322
	1.18	5.2	0.0318
	2.72	5.6	0.0306
	5.19	6.9	0.0280
	10.00	8.5	0.0220
Sodium Oleate	0.00	4.3	0.0322
	1.02	8.5	0.0274
	2.01	10.0	0.0212
	5.10	13.3	0.0182
	10.00	15.2	0.0132

tortion which occurs when the mass flows through the outlet tube of the plastometer, may disrupt this structure to some extent, and may therefore cause a change in plasticity during the determination. It is well known that a change in the plasticity of a lubricating grease—a suspension of soap in mineral oil—does occur when the grease is passed through a capillary tube, and it is to be expected that a similar change will occur with a suspension of a soap in a vegetable oil.



The addition of either sodium oleate or calcium oleate increases the yield point and decreases the mobility of the paint, but the effects are much more pronounced in the case of the sodium soap. This is to be expected. The calcium oleate is quite soluble in the soil, and probably exists either in true solution or in a highly dispersed condition, while the sodium oleate is much less soluble in linseed oil, and probably exists principally in the form of thread-like micelles.

Joint Effect of Soap and Water. Various amounts of water were added to paints which were made u· vith 30 parts of zinc oxide, 70 of linseed oil and 2 of soap. The results arc ·.own in Table III and Figs. 5 and 6.

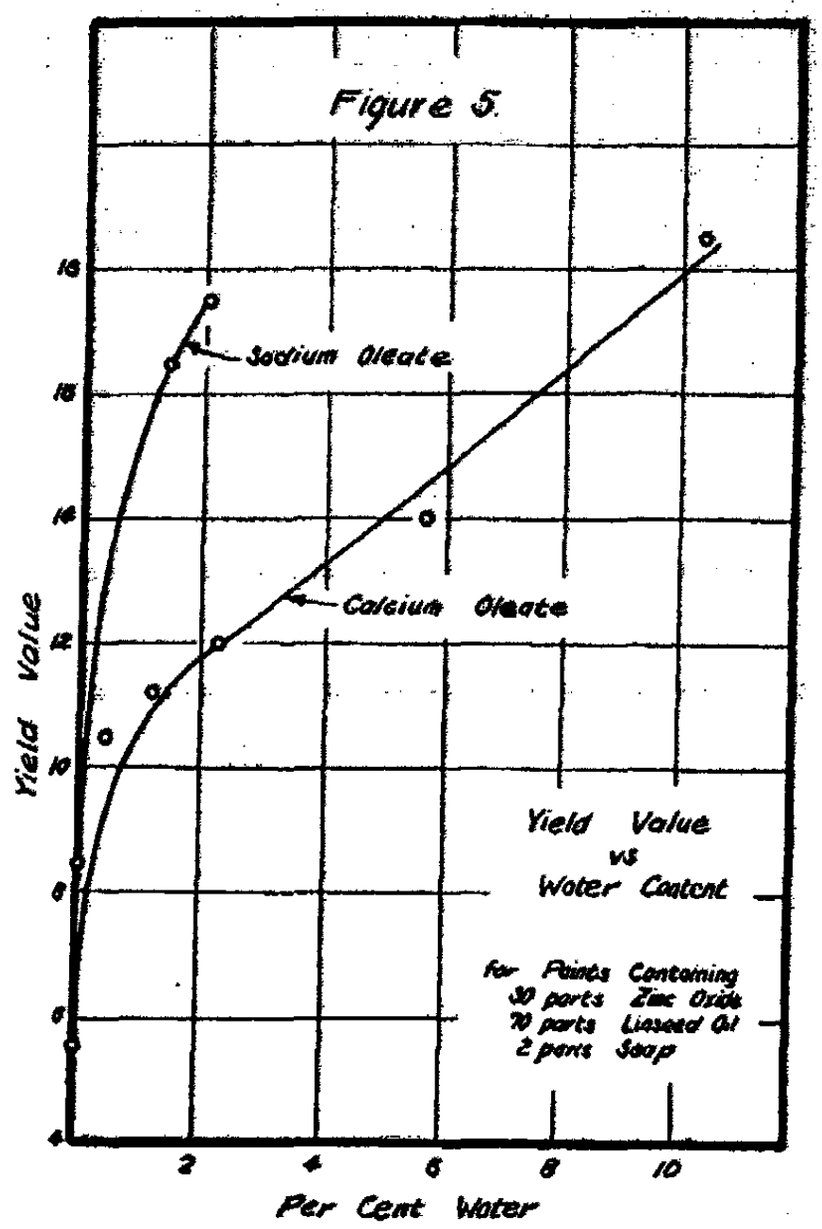
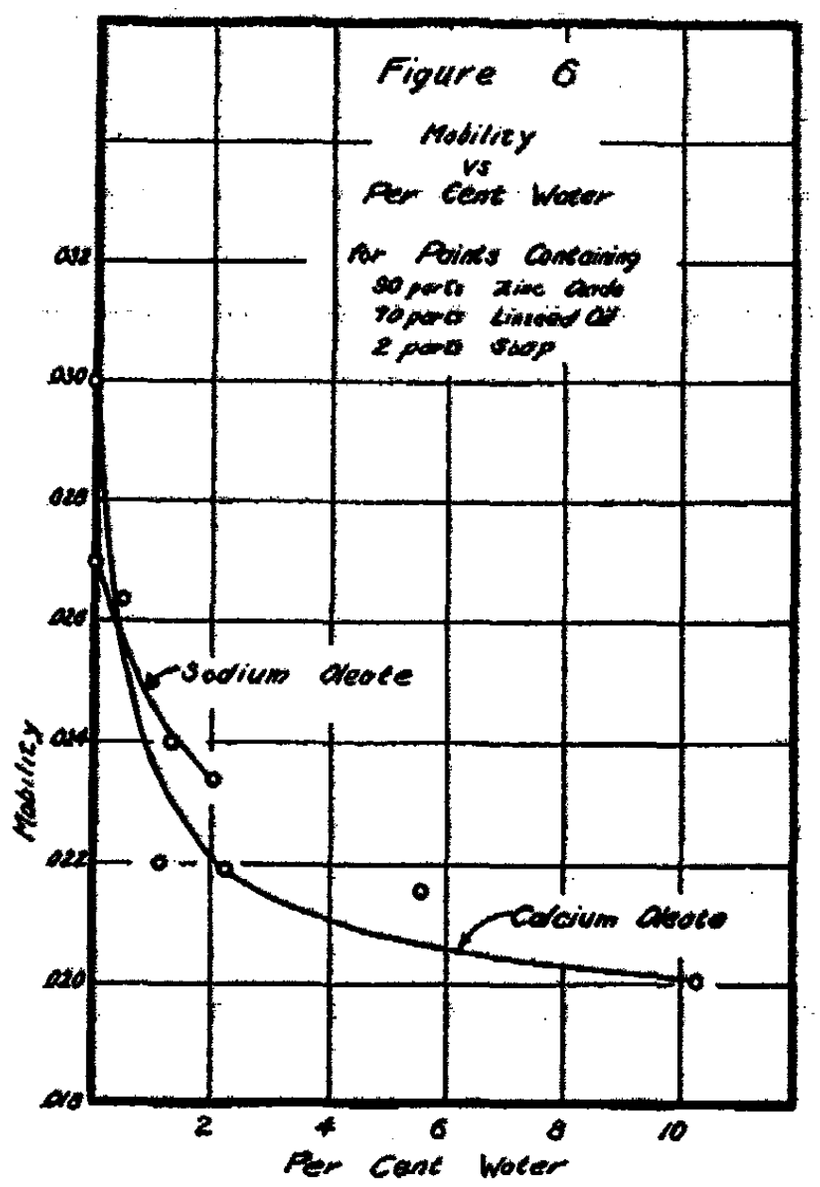


TABLE III

Joint Effect of Soap and Water on Paints prepared from Neutral Linseed Oil

Soap	Per Cent of Water	Yield Value	Mobility
Calcium Oleate	0.00	5.5	0.0300
	1.19	11.2	0.0220
	2.25	12.0	0.0219
	5.62	14.0	0.0216
	10.31	18.5	0.0200
Sodium Oleate	0.00	8.5	0.0270
	0.48	10.5	0.0264
	1.36	16.5	0.0240
	2.05	17.5	0.0234

With the paints containing sodium oleate, difficulty was experienced in obtaining complete and permanent emulsification when the water content was over two per cent. A very thick mixture was obtained when the water was first emulsified but in a few minutes the zinc oxide agglomerated in curdy masses which settled very quickly. Sodium oleate tends to give emulsion of oil in water and it is not surprising therefore that emulsions of water in oil are rendered less stable. On the other hand, water could be very readily

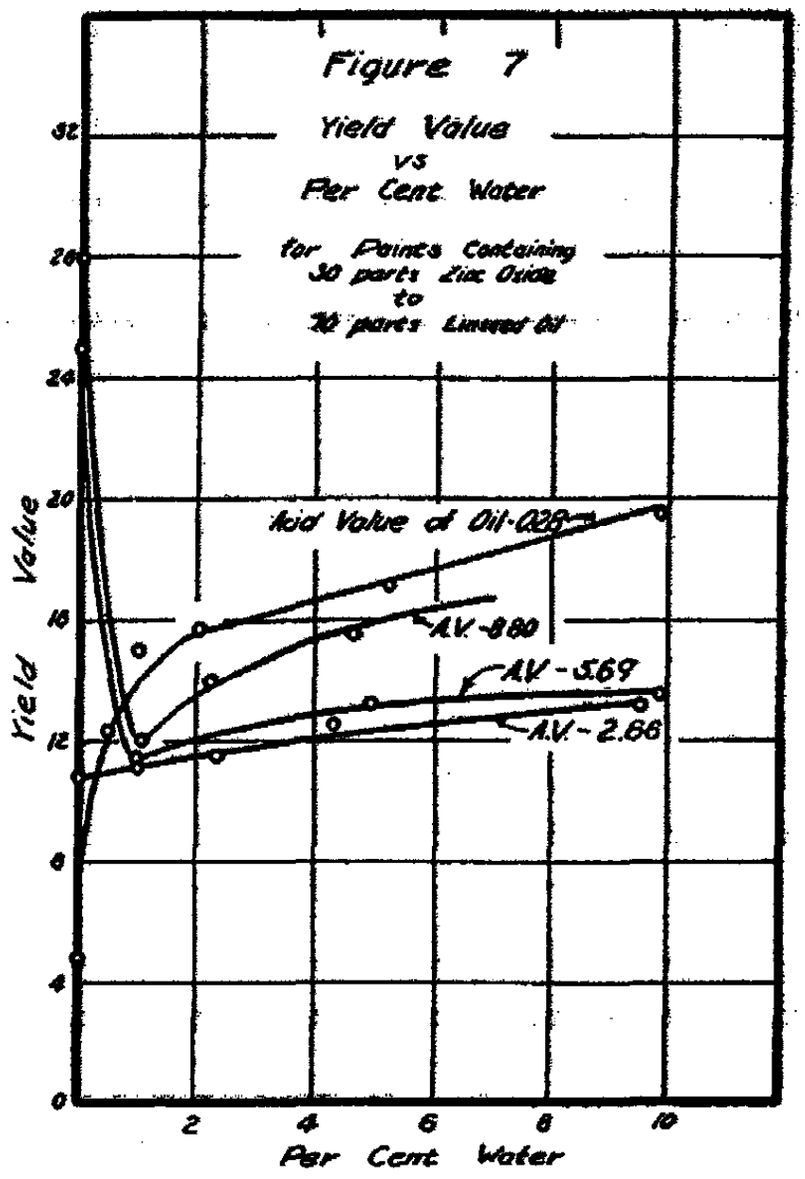


emulsified in the paints containing calcium oleate. In this case, both the paint and the calcium oleate tend to give emulsions of water in oil with the result that a stable emulsion is formed.

The water increases the yield value of these paints. The effect is qualitatively similar to that observed with paints which contained no soap. The first additions had a greater effect than later ones. For the same water content, the paints made with soap have a greater yield value than those without. That is, the effect due to the water and that due to soap are qualitatively additive. The mobilities of these paints are lowered by water, the effect being more pronounced with the first additions. The water does not have

such a large effect as it does in those paints free of soap. The soaps counteract some of the drop in the mobility due to water, sodium oleate being more effective than the calcium oleate.

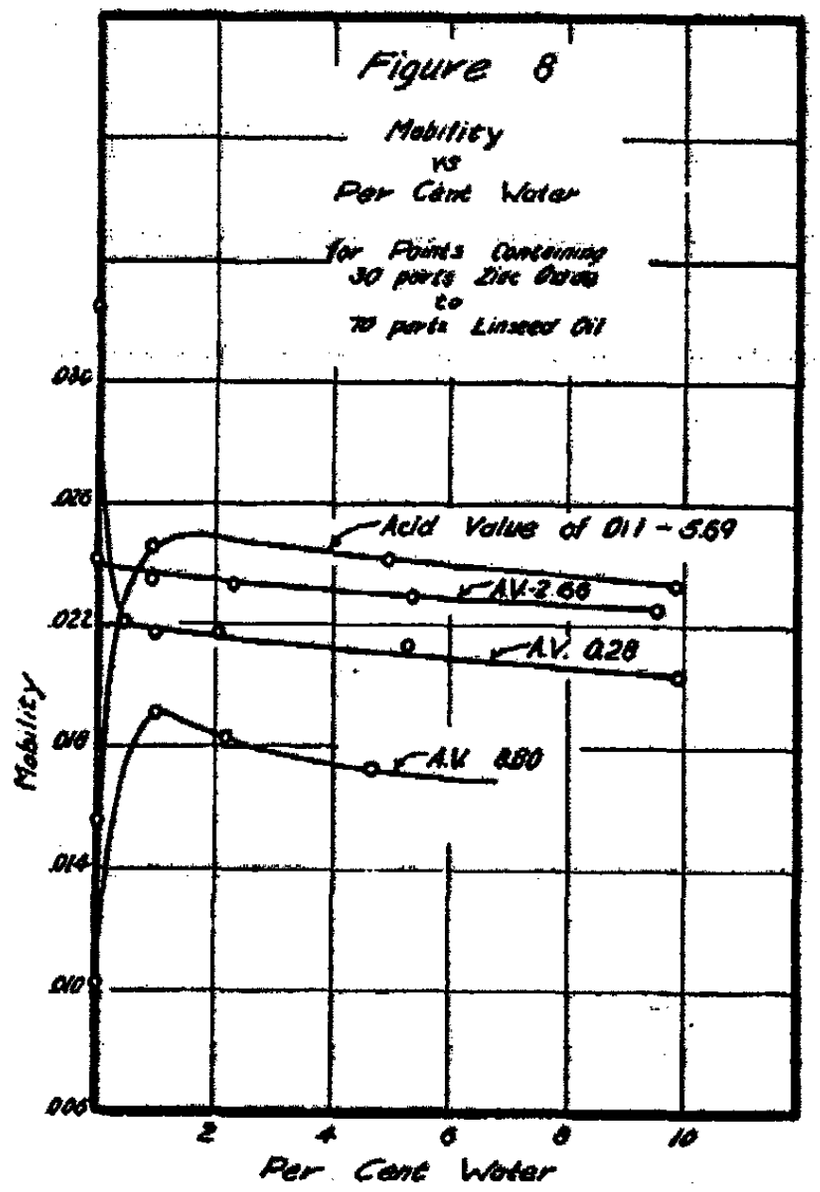
Joint Action of Water and Free Fatty Acids. Free fatty acids were prepared from linseed oil by saponifying the linseed oil by heating with alcoholic potash, distilling off the alcohol, liberating the free fatty acids by adding dilute sulphuric acid, and washing the separated acids thoroughly with water.



The acids thus obtained were but slightly darker than the original oil and had an acid value of 197.1. This free fatty acid was mixed with various portions of the linseed oil to give oils of the desired acid values. The pigment used for this work were: zinc oxide, white lead, and aluminum powder. The paints made with zinc oxide contained 30 parts of the pigment to 70 of the vehicle, those with white lead contained 60 parts of the pigment to 40 of the vehicle, while those made with aluminum powder contained 30 parts of the pigment to 70 of the oil.

The first method of incorporating the water was found satisfactory if the water was readily emulsified in the paint and was therefore adopted in the first part of the experimental work. It was found, however, that water could

be emulsified somewhat more readily by shaking the mixture of paint and water than by merely grinding the two together. Accordingly, the following procedure for introducing water into these paints was adopted: About 30 to 40 cubic centimeters of the paint was placed in a 100 cc bottle, the desired amount of water was added, the mixture thoroughly shaken, and then allowed to stand for about one hour before being tested in the plastometer. The effect



due to the air that may have been introduced into the paint during the shaking process was assumed to be negligible and paints prepared in this way were not evacuated a second time. The results are shown in Table IV and in Figs. 7 to 12.

The effect of water in these paints is more complex than in those paints made with the practically neutral linseed oil. Paints made with zinc oxide and low acid value oil showed an increase in the yield point and a decrease in mobility as the water content was increased. The effect of the free fatty acid alone in the linseed oil is to increase the yield value greatly. The presence of both water and free fatty acid results in changes in the plasticity depending on the conditions. If the acid value of the oil is 2.66, the effect of water is

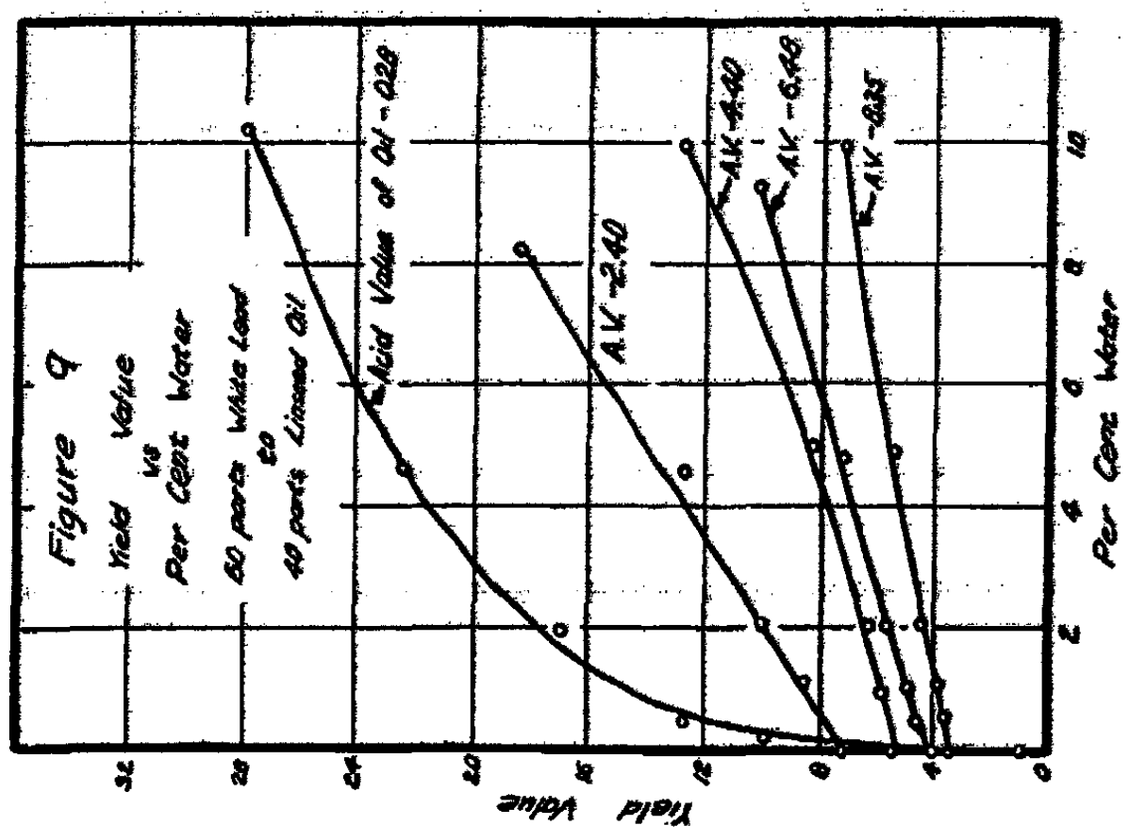


Figure 9
Yield Value
vs
Per Cent Water
60 parts White Lead
to
40 parts Linseed Oil
Acid Value of Oil - 6.48
A.V. -2.40
A.V. -4.40
A.V. -6.48
A.V. -8.35
Yield Value
Per Cent Water

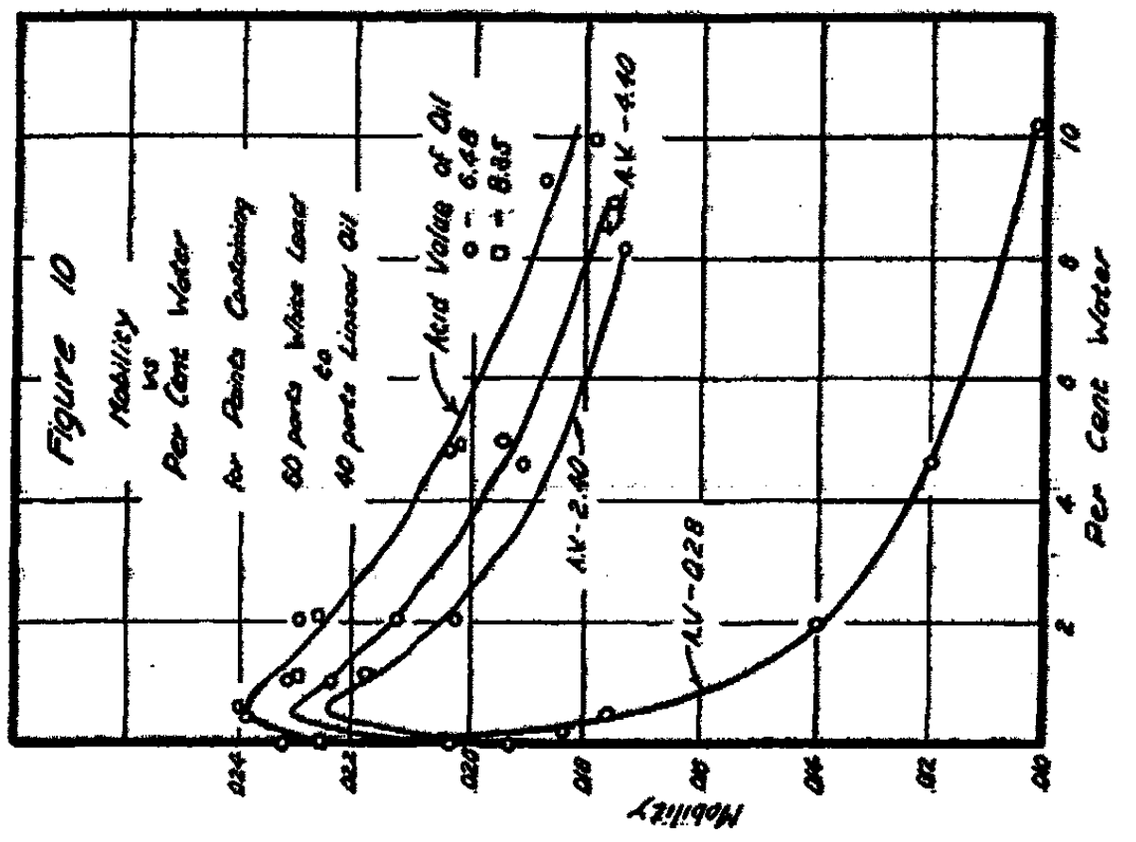


Figure 10
Mobility
vs
Per Cent Water
for Paints Containing
60 parts White Lead
to
40 parts Linseed Oil
Acid Value of Oil
0 - 6.48
0 - 8.35
A.V.-4.40
A.V.-2.40
A.V.-.028
Mobility
Per Cent Water

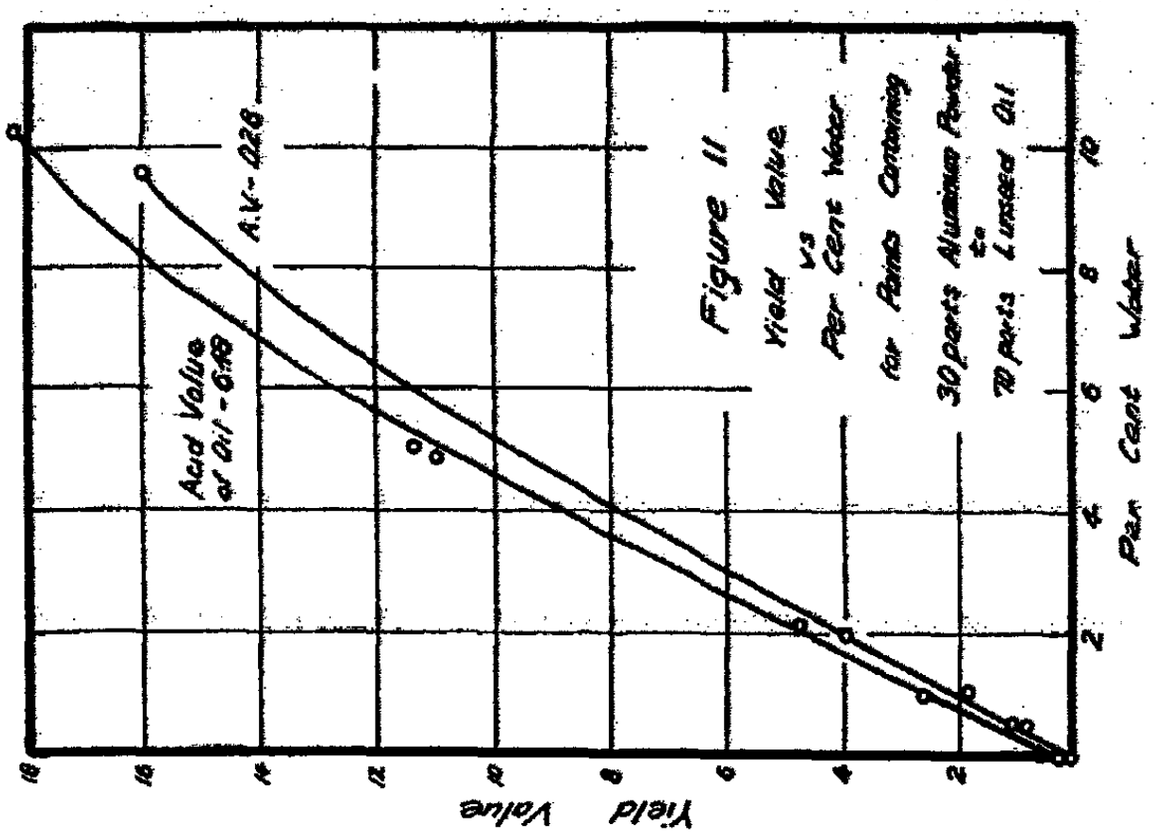


Figure 11
Yield Value
vs
Per Cent Water
for Paints Containing
30 parts Aluminum Powder
to
70 parts Linseed Oil
A.V.- 0.26
Acid Value
of Oil - 6.48
Yield Value
Per Cent Water

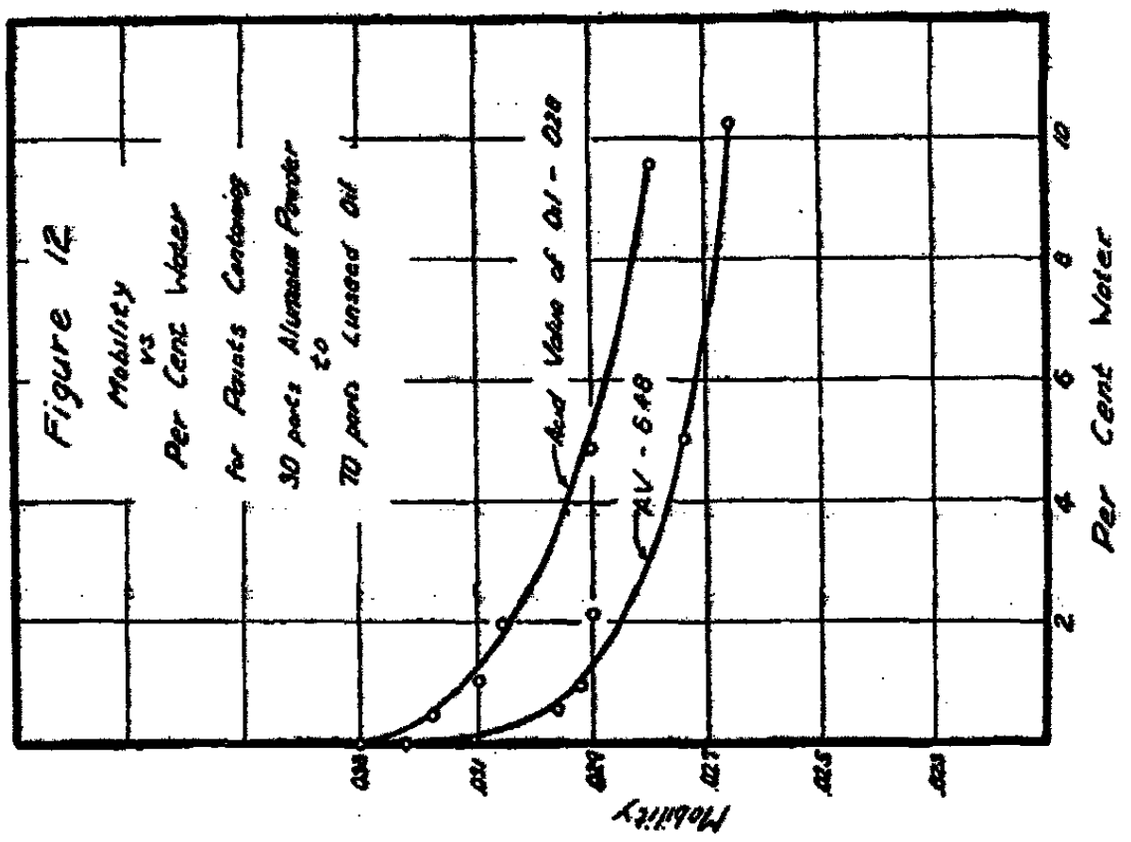


Figure 12
Mobility
vs
Per Cent Water
for Paints Containing
30 parts Aluminum Powder
to
70 parts Linseed Oil
Acid Value of Oil - 0.26
A.V. - 6.48
Mobility
Per Cent Water

TABLE IV

Effect of Water on Paints prepared from Linseed Oil of Varying Acid Value

Pigment	Acid Value of Oil	Per Cent of Water	Yield Value	Mobility
Zinc Oxide	0.28	0.00	4.8	0.0324
		0.51	12.4	0.0222
		1.03	15.0	0.0218
		2.00	15.8	0.0218
		5.27	17.2	0.0214
		9.89	19.6	0.0204
	2.66	0.00	10.9	0.0242
		1.00	11.3	0.0235
		2.23	11.6	0.0234
		4.32	12.5	0.0230
		9.57	13.2	0.0226
	5.69	0.00	25.0	0.0156
		0.99	11.5	0.0246
		4.91	13.2	0.0242
		9.90	13.4	0.0234
	8.80	0.00	28.0	0.0102
		1.06	12.0	0.0192
		2.24	14.0	0.0184
		4.65	15.5	0.0174
White Lead	0.28	0.00	1.0	0.0236
		0.22	10.0	0.0184
		0.49	12.8	0.0176
		2.00	17.0	0.0140
		4.62	22.5	0.0120
		10.22	28.0	0.0102
	2.40	0.00	7.2	0.0194
		1.14	8.5	0.0218
		2.06	10.0	0.0203
		4.59	12.7	0.0192
		8.21	18.5	0.0174
White Lead	4.40	0.00	5.4	0.0204
		1.01	5.8	0.0224
		2.06	6.2	0.0213
		5.00	8.3	0.0195
		9.95	12.8	0.0176

TABLE IV (Continued)

Effect of Water on Paints prepared from Linseed Oil of Varying Acid Value

Pigment	Acid Value of Oil	Per Cent of Water	Yield Value	Mobility
White Lead	6.48	0.00	4.0	0.0226
		0.49	4.5	0.0238
		1.03	4.8	0.0232
		2.02	5.6	0.0230
		4.81	7.2	0.0204
		9.28	10.2	0.0188
	8.35	0.00	3.4	0.0226
		0.58	3.6	0.0240
		1.08	4.0	0.0230
		2.10	4.4	0.0226
		4.92	5.4	0.0202
		9.94	7.2	0.0179
Aluminum Powder	0.28	0.00	0.0	0.0330
		0.51	0.8	0.0318
		1.04	1.8	0.0310
		2.00	4.0	0.0306
		4.90	11.0	0.0290
		9.60	16.0	0.0280
	6.48	0.00	0.2	0.0322
		0.57	1.0	0.0296
		0.98	2.6	0.0292
		2.16	4.8	0.0290
		5.09	11.4	0.0274
		10.25	18.2	0.0266

to increase but slightly the relatively high yield value due to the free fatty acids. However for paints made with linseed oil with an acid value of 5.69 and 8.80, the first addition of water has a very pronounced effect in lowering the yield value. A minimum value is obtained at about one per cent of water and further additions increase the yield value.

For paints made with zinc oxide and a practically neutral linseed oil, the effect of the water alone or of fatty acids alone is to increase the mobility. With an acid value of 2.66 for the oil, the mobilities are decreased but slightly on addition of water with the result that the mobilities are higher for these paints for the same water content than with those made with the low acid value oil. When the acid value of the oil is 5.69 the first additions of water tend to increase the mobility to a maximum value when about one per cent of water is present. Further additions lower the mobility again slightly. The paints made with this concentration of free fatty acid show the highest

mobilities for any given content of water. When the acid value of the oil is 8.80, there is again a maximum in the mobility curve when about one per cent of water is present, but these paints all show a relatively low mobility.

With paints made with white lead, the effect of free fatty acids alone on the yield point is to increase it to a maximum at an acid value of 2.40 and then to decrease it continuously on addition of more free fatty acid. The lowest yield value is shown by the paint made with neutral oil and no water. For acid values of the oil of 2.40 and above, the effect of the water is to increase the yield value slightly, and for the same concentration of water, the yield value decreases as the acid value increases.

The effect of free fatty acids on the mobility of paints made with dry white lead is to decrease it to a minimum with an oil of acid value of 2.40 and then to increase it slightly with further additions of free fatty acid. For paints made with linseed oil of 2.40 and higher, the mobility increases to a maximum on addition of about one-half of one per cent of water and then decreases again. The mobilities are higher for the same water content in those paints made with oil of higher acid value.

The paints made with aluminum powder had practically the same yield value for the same amount of water when made with linseed oil of acid value of 0.28 or 6.48. Water increased the yield value in both cases. The mobilities of these paints decrease as more water is added, the values for the paints made with oil of acid value of 0.28 being slightly higher than those made with oil of acid value of 6.48.

Effect of Heating the Paint. The effect due to heating the paint was studied with mixtures made up with 30 per cent of zinc oxide and 70 of linseed oil (Lot 2). The paints were prepared as described and then heated for half an hour in an oil bath kept at a temperature of 150 to 160°C. To prevent any oxidation of the oil during the heating, a slow stream of nitrogen was passed through the flask. The following results were obtained.

TABLE V

Effect of Heating the Paint

Acid Value of Oil	Heat Treated	Yield Value	Mobility
0.28	No	4.8	0.0324
0.28	Yes	5.4	0.0332
8.35	No	31.0	0.0136
8.35	Yes	6.0	0.0274

With the paints prepared from the neutral linseed oil, the effect of heating the paint resulted in a slight increase in yield value and mobility. A very pronounced change occurs however with paint made with the oil of acid value of 8.35. The yield value is reduced almost to that for the paint made with the neutral oil while the mobility is increased to double its initial value.

That this effect is not due to any change in the linseed oil was shown by preparing paints from linseed oil that had been heated as described, cooled, and then used in preparing these paints. The plastic constants of these paints differed but little from those of paints prepared from untreated linseed oil of the same acid value.

As described in the first part of the experimental work, the effect of adding one per cent of water to a paint made with 30 parts of zinc oxide and 70 of linseed oil with acid value of 8.35 was to decrease the yield value and increase the mobility. This effect is very similar to that due to heat although not as marked. If the effect due to the water is the same as that due to heating the paint, the addition of water to a paint that has been heated should not result in lowering of the yield value and an increase in the mobility when approximately one per cent water is added. Water was added to a paint made with linseed oil of acid value of 8.35 and zinc oxide and heated as described above. The water had a similar effect in increasing the yield value and decreasing the mobility as in those paints made with the neutral oil.

Effect of Zinc Sulphate. The effect due to zinc sulphate in paints made with zinc oxide was studied with mixtures prepared with one part of anhydrous zinc sulfate, thirty of zinc oxide, and seventy of linseed oil of various acid values. The plastic constants for these paints were found to be practically independent of the zinc sulphate content for paints made with linseed oil of acid value as high as 8.35.

Effect of Free Fatty Acid and Soap. Paints were prepared with thirty parts of zinc oxide, seventy of oil, and two of calcium oleate as described previously. The results are shown in Table VI.

TABLE VI

Effect of Calcium Oleate on Paints prepared from Linseed Oil of Various Acid Values

Acid Value of Oil	Parts of Soap added	Yield Value	Mobility
0.28	0.0	4.8	0.0324
0.28	2.0	5.5	0.0300
2.40	0.0	10.4	0.0250
2.40	2.0	6.0	0.0308
8.35	0.0	31.0	0.0136
8.35	2.0	6.2	0.0288

The effect of the soap in the paint made with the oil of low acid value is to increase the yield value slightly and lower the mobility. However in the paint made with the oil of acid value of 2.40 the soap decreased the yield value and increased the mobility. The same thing was true in the case of the paints

made with the oil of 8.35 although the effect was very much more marked. When this last paint is heated, the yield value is lowered still more and the mobility increased to practically the same value as those for the paints made with neutral oil and no water.

Discussion of Results

The results obtained with paints made with practically neutral linseed oil can be readily explained qualitatively. The effect of the water in always increasing the yield value and lowering the mobility is due to its tendency to emulsify in the paint and thus build up a structure in the paint. The amount of the increase in consistency depends on the type of pigment, the concentration of the pigment, and the concentration of water. The effect of sodium oleate and calcium oleate is to increase the yield value and decrease the mobility due to their gel structure in the paints. The sodium oleate has a more pronounced structure than the calcium oleate and so has a greater effect in increasing the consistency.

The presence of free fatty acids in the vehicle may affect the plasticity of the paints in various ways. With paints made with zinc oxide, the effect of the free fatty acids in the linseed oil is to increase the consistency of the paint very markedly. This is probably due to the interaction of the zinc oxide and the free fatty acids to give zinc soaps. The addition of anhydrous zinc sulphate to these paints has no appreciable effect; although as this is a soluble zinc salt, one would expect it to form soaps more readily than the zinc oxide and thus increase the consistency to a greater extent. Apparently the free fatty acids are able to react with the dry zinc oxide rather completely.

When the acid value of the oil is 8.35, there are several factors that can decrease the initial high consistency due to the free fatty acid. Water in small amounts tends to do this. Heating the paint for thirty minutes at a temperature of 150°C brought the plastic constants very close to that for the paints made with the neutral oil. The addition of two parts of calcium oleate was also found to have approximately the same effect as that due to heat. Another factor that tends to do the same thing is ageing which lowers the consistency.

With paints made with zinc oxide and linseed oil of high acid value, soaps are formed in relatively large amounts. The zinc soaps are insoluble in the linseed oil, but are probably dispersed to some extent by the free fatty acids present. That free fatty acids are adsorbed by the soap micelles has been shown by Arsen.[17] The high consistency of paints made with a high acid value oil is due to the soap micelles which are present as loose ramifying aggregates. Anything that will tend to precipitate out the soap and thus destroy the structure of the soap should result in a lowering of the viscosity of the paint.

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[17] Ind. Eng. Chem., 18, 157 (1926).

With time more of the free fatty acids react with the zinc oxide to form soaps. The result is a gradual decrease in the concentration of the free fatty acids. The vehicle then loses its power to disperse the soaps which are precipitated out. The gel structure of the soap in the paint is thus broken down with a resulting decrease in the yield value and increase in the mobility. This is probably the change that occurs during the ageing of paints prepared with zinc oxide. Water is known to precipitate soaps from solution in organic liquids and its action in reducing the consistency of paints prepared from linseed oil of high acid value and zinc oxide can be explained on this basis. Thus calcium soaps are precipitated out as a flaky material from a clear benzene solution in the presence of a trace of moisture.[14] Also lead and zinc soaps in greases are unstable and will tend to precipitate out if water is present. The effect of heating the paint is due to the increase in the rate with which the free fatty acids react with the pigment to form soaps. The action is thus similar to that which occurs during ageing. The calcium oleate is effective in lowering the concentration of the free fatty acid due to its ability to adsorb these acids. The calcium soaps apparently have but little effect in changing the consistency even when dispersed in the vehicle.

This change in the structure of the soap micelles may also explain why turpentine is less effective in reducing the consistency of paints than some of the other thinners. It is known that zinc soaps are insoluble in neutral linseed oil and in naphtha and are soluble to some extent in free fatty acids and in turpentine.[15] The turpentine apparently has the power to disperse the zinc soaps into loose ramifying aggregates which tend to enmesh the vehicle and thus increase the consistency.

With paints prepared from white lead, the effect due to any free fatty acid is very much less marked than with paints made with zinc oxide. An increase in the acid value of the oil from 0.28 to 2.40 resulted in a slight increase in consistency probably due to the formation of a small amount of soap. Any further increase in the acid value of the oil resulted in a decrease in consistency due to the better wetting and dispersing power of the vehicle. Moreover the lead soaps differ from the zinc soaps in that they do not have the same tendency to coagulate or "lump".[15]

The result is that no very marked structure is built up in the paint with a resulting increase in consistency. Some soaps are however formed. With paints prepared with linseed oil of acid value of 2.40 or higher, the addition of one-half of one per cent of water results in an increase in mobility while further additions lowered the mobility. The ability of water to increase the mobility of these paints is substantiated by the fact that paints prepared from pulp-mixed white lead are said to have better working properties than those prepared from pan-dried white lead.

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[14] Wellman and Tartar: J. Phys. Chem., 34, 379 (1930).

Summary

1. Water added to a paint prepared from a practically neutral linseed oil increases the yield value and decreases the mobility; the amount of the effect depending on the type and concentration of pigment.

2. Sodium oleate and calcium oleate increase the yield value and decrease the mobility of a paint prepared from a neutral linseed oil, the effect being more pronounced for the sodium oleate.

3. Water added to a paint prepared from a practically neutral linseed oil and two parts of sodium oleate or calcium oleate increases the yield value and decreases the mobility.

4. With paints prepared from linseed oil and dry zinc oxide, the effect of free fatty acid is to very markedly increase the consistency. Small additions of water tend to offset part of this increase in consistency, the effect being most marked when one per cent of water is present and the acid value of the oil is relatively high.

5. With paints prepared from dry white lead and linseed oil, the effect of free fatty acids is relatively small. With paints prepared with oil of acid value of 2.40 or higher, the mobility has a maximum value when about one-half of one per cent of water is present; while the yield value increases slightly but continuously with water content.

6. The presence of anhydrous zinc sulfate has but little effect on the plastic constants of paints prepared from zinc oxide.

7. The increase in consistency in a paint prepared from zinc oxide due to the free fatty acids present in the vehicle can be practically completely offset by heating the paint for one-half hour at 150°C. The same result can also be obtained by the addition of two parts of calcium oleate in the paint.

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THE CATALYTIC OXIDATION OF CARBON MONOXIDE

BY J. C. W. FRAZER

Introduction

The catalytic oxidation of carbon monoxide is of interest largely because of the unusual and interesting properties of carbon monoxide. My interest in this subject began with the development some years ago of a catalyst which would bring about the complete oxidation of this gas at 0°C and below at an extremely rapid rate. The first catalyst which we developed consisted of manganese dioxide and silver oxide. Shortly after this we found it possible to prepare a catalyst equally good from manganese dioxide and copper oxide.[1] In both mixtures the manganese dioxide was readily recognized as the more active of the two constituents. Finally we found it possible to prepare an equally good catalyst from manganese dioxide alone[2] by using a method for its preparation which eliminated the possibility of contamination with adsorbed materials, particularly alkalies which manganese dioxide is so prone to adsorb from solution and from which it cannot be freed by ordinary methods of washing. Subsequently it was found possible to prepare finely divided cobaltic oxide[3] in a state of purity and of equal catalytic activity for the oxidation of carbon monoxide. Finally, Bennett[4] working in this laboratory, has succeeded in preparing so-called "nickelic oxide" finely divided and free from adsorbed materials and again the metallic oxide so purified has been found to be an extremely active catalyst for the reaction under consideration. In all three of these cases the essential characteristics of the catalyst are the existence of the metallic oxide in finely divided condition and free from adsorbed materials. In all three cases the use of other oxides and so-called "promoters," originally thought by many necessary to obtain catalysts of high catalytic activity, has lost its significance, freedom from "poisoning" impurities being much more important. Having carried the experimental work this far it became at once a matter of interest to see what degree of success would attend the preparation of catalysts from other metallic oxides in a pure and finely divided condition.

For this purpose a method was devised for electrolysing the impurities from the finely divided oxides suspended in water.[4] This was the only method which could be relied on to free many of these oxides from adsorbed materials. None of the seventeen oxides as prepared was found to be in the same class as catalysts for this reaction as the three already mentioned, although some of them as for example ferric oxide show some activity below 100°C.

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[1] Roger, Piggot, Bahlke, and Jennings: J. Am. Chem. Soc., 43, 1973 (1921).
[2] Whitesell and Frazer: J. Am. Chem. Soc., 45, 2841 (1923).
[3] Williams: Dissertation, Johns Hopkins University (1928).
[4] Dissertation, Johns Hopkins University (1930).

It appears on studying the properties of these highly active oxides that they are characterized by one common property which distinguishes them from the other oxides and to which we are inclined to ascribe their high catalytic activity. This property is their indefinite composition. They all behave as mixtures of more than one oxide which mutually dissolve to form solid solutions. This appears not to be true of the other oxides tested under the conditions of their use in these experiments. This property enables these oxides to function as catalysts over a wide range of oxygen pressure allowing them to give up or take on oxygen with great readiness, the oxygen as given up

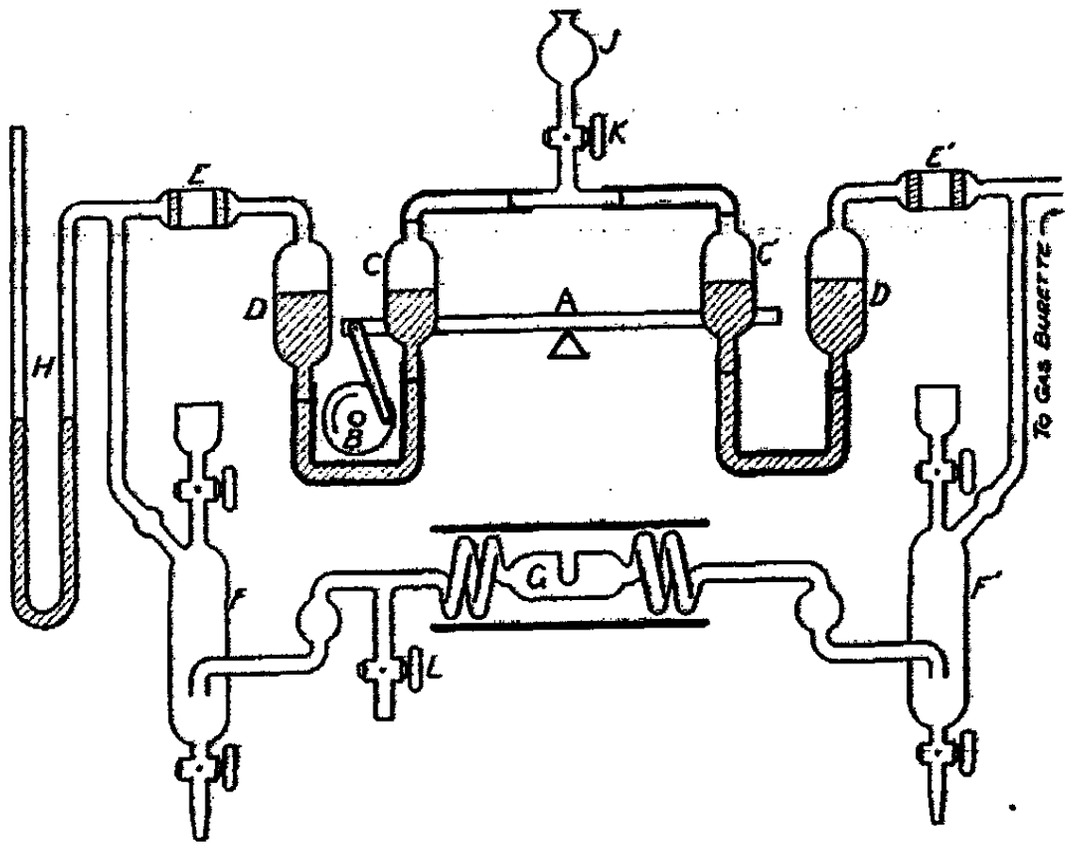

FIG. 1

amounting essentially to nascent oxygen is activated and readily reacts with the carbon monoxide which is likewise probably activated by adsorption on the catalyst.

This peculiar property was first studied in the case of finely divided manganese dioxide. English,[5] in an unpublished investigation, showed in this laboratory that finely divided manganese dioxide readily dissociated and the oxygen pressure in equilibrium with the oxide depended on the composition of the oxide.

English's apparatus shown in Fig. 1, consisted of a closed system. The part of this system containing the sample of oxide under investigation was kept in an electric furnace the temperature of which was regulated. At the beginning of the experiment the system was filled with pure nitrogen which was passed backward and forward at regular and frequent intervals over the oxide in the furnace. The mechanism by means of which this was accom-

[5] Dissertation, Johns Hopkins University (1922).

plished is shown in the illustration referred to. Provision was made for keeping the temperature of the gas in contact with the oxide the same as that of the oxide and also for removing the water vapor given off from the oxide.

In order to follow the course of the reaction it is only necessary to know the capacity of the gas space, the original composition and weight of the oxide used. At intervals a sample of the gas was removed for analysis and the partial pressure of oxygen therein determined. After the oxygen determination the nitrogen was returned to the system or this could be done after restoring the amount of oxygen it contained when it was removed from the

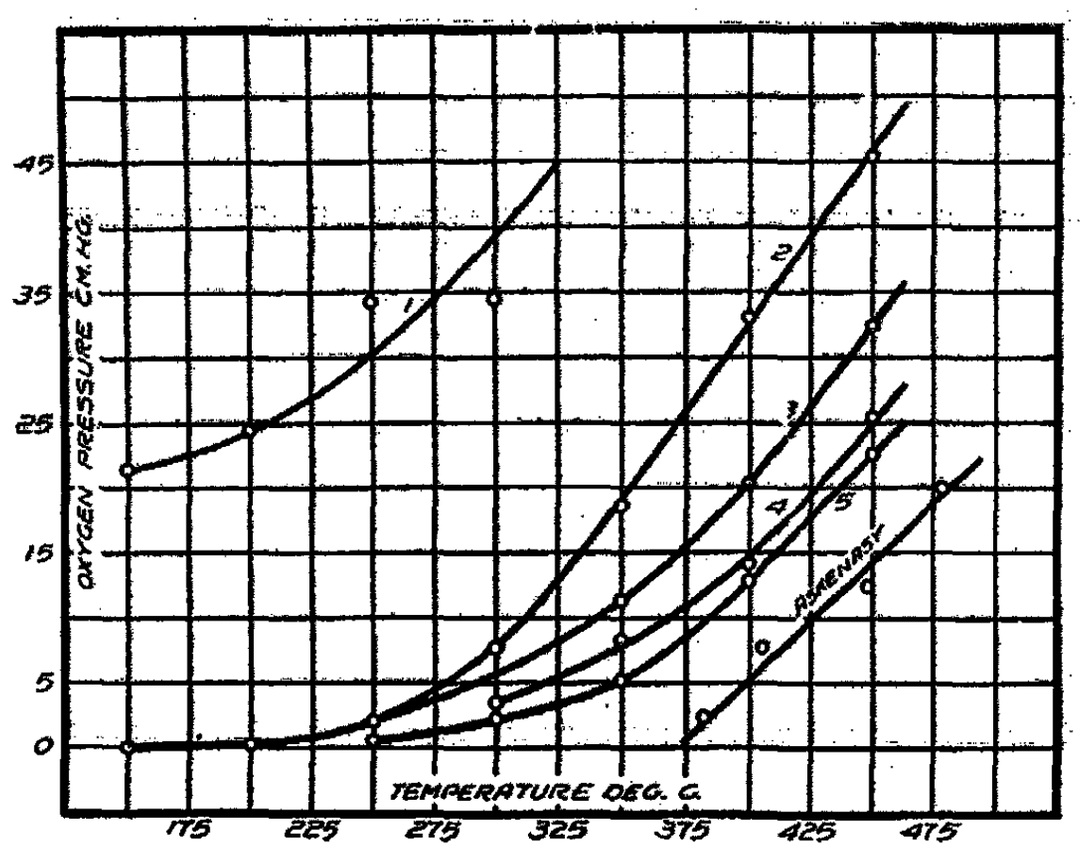

FIG. 2
Oxygen Pressure over 20 Gm. Fremy Oxide

system. In this way the results given in the following series of curves, Fig. 2, were obtained. It will be seen that as oxygen is removed from the system and the oxygen content of the oxide diminished the dissociation pressure of the oxide diminishes. With each removal of oxygen the dissociation-pressure curve drops and finally approaches the lowest curve which is that of Askenasy[6] for the dissociation of pyrolusite after it has been strongly heated.

In 1924, Weld[7] working in this laboratory made a much more careful study of the dissociation of manganese dioxide using a static method. The apparatus used is shown in Fig. 3. The oxide was kept for long periods of time at constant temperature, especially at the low temperatures. This was accomplished simply by using various pure liquids with appropriate boiling points

[6] Askenasy and Klonowski: Z. Elektrochemie, 16, 107 (1910).
[7] Dissertation, Johns Hopkins University (1924).

to fix and maintain the desired temperatures. The results obtained are shown for manganese dioxide of a certain known composition in the following series of curve, Figs. 4 and 5.

The two remaining oxides, "nickelic" oxide and cobaltic oxide have been more recently studied by Le Blanc and Sachse.[8] In both cases there is ample evidence that both of these oxides show a similar variable oxygen content and give up or take up oxygen continuously according to conditions.

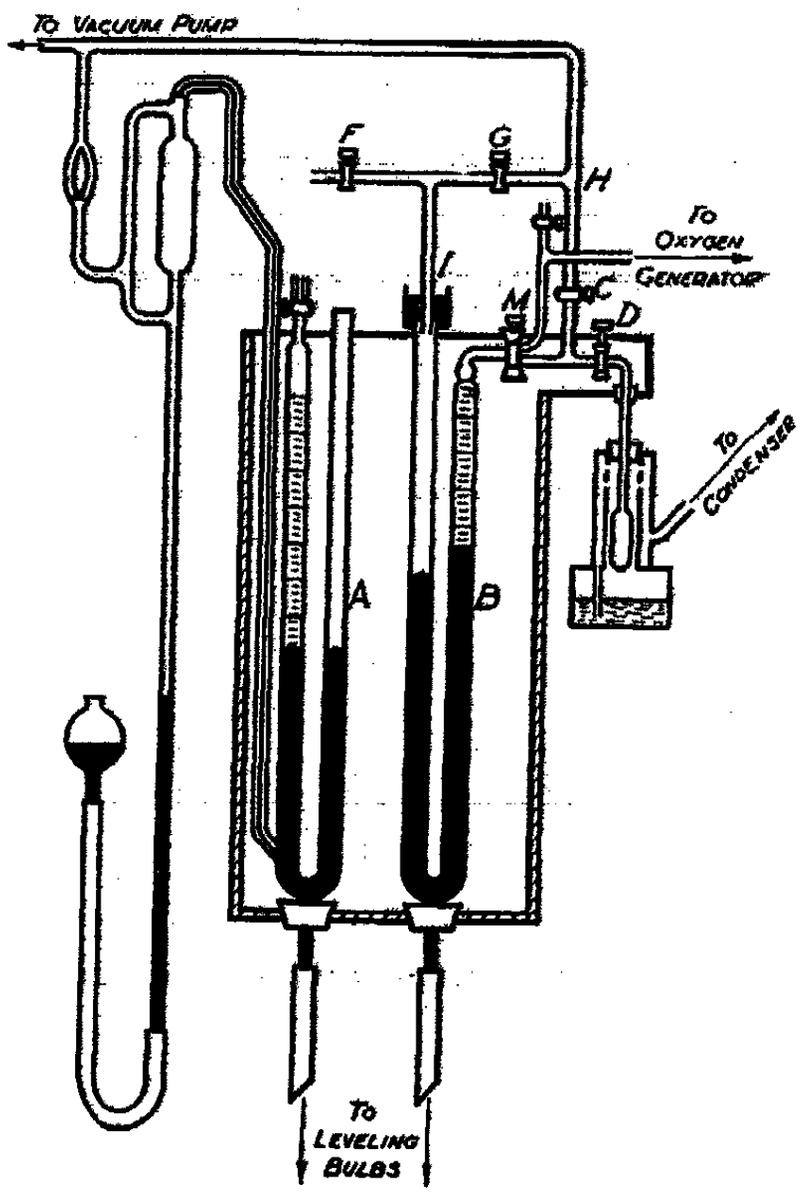

Fig. 3

It is assumed that this property is responsible for the very great catalytic activity of these oxides and distinguishes them in their catalytic behavior from other metallic oxides investigated and gives a mechanism by means of which oxygen is activated at such a surface.

Owing to the fine porosity of these oxide catalysts they are also characterized by their ability to condense vapors within their pores. For example, unless water vapor is removed from the gases in contact with them these

[8] Z. Elektrochemie, 32, 58, 204 (1926); Z. physik. Chem., 142, 151 (1929).

catalysts lose their catalytic properties through capillary condensation of water within the porous oxide. In testing the catalytic properties of these oxides they and the gases passing over them are carefully dried.

The effect of traces of water vapor on many reactions is well known. This effect on the oxidation of carbon monoxide has been noted and carefully studied by Dixon and others.[9]

The investigations of greatest interest to us here are those which show the effect of small traces of water vapor on the explosibility of a mixture of carbon monoxide and oxygen and also on the rate of flame propagation in such an explosive mixture.

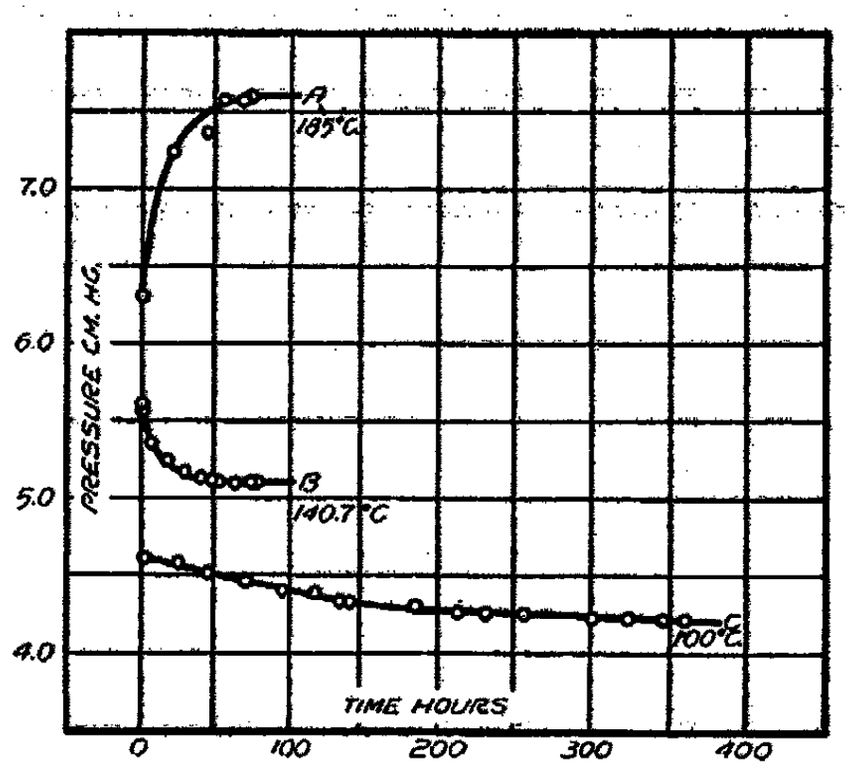

FIG. 4

It was thought that a trace of water on these catalysts might exert a similar effect on their activity. In 1925 Blitch[10] in this laboratory undertook to investigate this point. A sample of active manganese dioxide was heated for one week in an all glass apparatus in a current of oxygen dried over phosphorus pentoxide. At the end of this time the sample showed its former activity. It was then dried similarly for another week at 240°. At the end of this time it still retained its activity. It was then dried continuously for another week at 300° and at the same time the apparatus frequently evacuated. At the end of the experiment it had apparently lost none of its original activity.

More recently Bone[11] has investigated the effect of extreme drying on the catalytic oxidation of carbon monoxide using such substances as copper and

[9] Dixon: Brit. Assocn. Adv. Sci. Repts., 503 (1880); Phil. Trans., 175, 617 (1884); Baker: J. Chem. Soc., 47, 349 (1885); Phil. Trans., 179, A 571 (1888); Bone and Weston: Proc. Roy. Soc., 110A, 615; Bone, Frazer, and Newitt: 634 (1926); Fenning: Phil. Trans., 225A, 31 (1926).

[10] Dissertation, Johns Hopkins University (1925).

[11] Proc. Roy. Soc., 112A, 474 (1926).

nickel oxides and metallic gold and silver. In all the cases the first effect of drying was an increase of catalytic activity due to the removal of the water condensed by capillarity as discussed above. In the experiments with gold (at 250°) and silver (at 365°) the drying was carried to great extremes and the remarkable fact was observed that the catalytic action practically ceased. The introduction of small amounts of water was sufficient to restore the high catalytic activity. The velocity constant in the case of gold was 0.0155 (moist) and 0.00045 (dry). In the case of the experiment with silver the constant varied from 0.1208 to 0.0039. This apparent discrepancy in the effects of extreme drying on the catalytic activity of extremely active catalysts such as manganese dioxide on the one hand and poor catalysts such as metallic

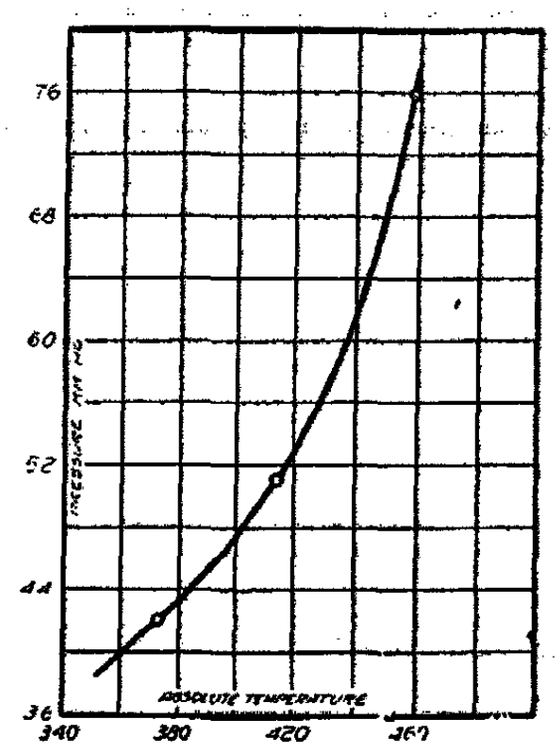

FIG. 5

silver and gold on the other may be reconciled if we assume that in the one case oxygen is activated and the reaction catalysed is $_2CO + O_2 \rightleftarrows CO_2$ and where the effects of extreme drying are negligible while in the other case which is almost completely inhibited by extreme drying the reaction catalysed is the water-gas reaction

$$CO + H_2O \rightleftarrows CO_2 + H_2$$
$$H_2 + O_2 \rightleftarrows H_2O$$

The catalytic oxidation of carbon monoxide is of technical interest in connection with the risks which industrial workers in several fields run from exposure to dangerous concentrations of this gas. A great step forward in this direction was taken during the war by the production of catalysts of the Hopcalite type for use in gas masks. When properly used these masks give complete protection against carbon monoxide. Many suggestions have been made to eliminate carbon monoxide from the exhaust gases of internal com-

bustion engines. At the present time, however, there is no device of this kind available, but we have demonstrated that it is possible to produce a catalyst which will completely remove carbon monoxide from the exhaust gases of automobiles and some of these catalysts have been tested in a temporary device through which all of the exhaust gases were passed. The longest of these was a regular road test covering a distance of 1500 miles. Whether the possibilities of such catalysts can be fully utilized and applied in a commercial way remains shortly to be seen as work on the mechanical applications are now well under way.

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A STUDY OF THE INFLUENCE OF HYDROLYSIS TEMPERATURE ON SOME PROPERTIES OF COLLOIDAL FERRIC OXIDE

IV. Variation of Density and Relative Viscosity with Sol Concentration

BY GILBERT H. AYRES AND C. HARVEY SORUM*

Introduction

References in the literature to the relation between density and concentration in colloidal systems are not numerous. Linder and Picton[1] studied some of the physical properties of As_2S_3 sols and found that the relation between specific gravity and dilution was linear, which is not the case with solutions of metallic salts. Dumanskii[2] prepared ferric hydroxide sols by the dialysis of ferric chloride solution saturated with ammonium carbonate. After standing for one year and then filtering through collodion, the density of the dispersed phase was determined by the use of the formula:

$$A = B + C - C/xd$$

where the symbols have the following significance:

A = weight of solution
B = weight of solvent
C = weight of colloid
x = density of colloid
d = density of filtrate

Dumanskii found that at 0°, x = 4.704, and since this was not the same as the value for the density of precipitated iron oxide, he concluded that the colloid was a mixture of oxide and chloride. He apparently took no consideration of the possibility of hydration of the disperse phase.

Wintgen[3] studied the density and refraction of colloids; he found the density (or its reciprocal, the specific volume) to be a linear function of the concentration. For colloidal iron hydroxide he gives the equation:

$$v = 1.00296 - (0.0065071\ C)$$

where v is the specific volume and C is the weight percent of dispersed phase. When C = 100%, v = 1.00296 − 0.65071 = 0.35225, and d (the density) = $1/v = 1/0.35225 = 2.84$ for the disperse phase. This value is smaller than the density of the precipitated material, the difference being ascribed to the hydration of the dispersed particles.

* The authors wish to express their thanks to Dr. J. H. Walton for many valuable suggestions during the course of this investigation.

[1] Linder and Picton: J. Chem. Soc., 67, 71 (1895).

[2] Dumanskii: Kolloid-Z., 8, 232 (1910).

[3] Wintgen: Kolloidchem. Beihefte, 7, 251 (1915).

Since the sols with which this study is concerned had given pronounced evidence of hydration[4], it was deemed advisable to study the density of the sols prepared at different temperatures, as well as the variation of density and relative viscosity with concentration.

Experimental Methods

For this study samples of the original stock solutions were diluted with distilled water to make series of varying iron oxide content (concentration expressed in grams of iron oxide per liter).

The relative viscosity of these diluted sols was determined following the same technique as previously described.[4]

Density determinations were made by means of a 10 cc. pyknometer; the pyknometer was filled with the sol which had been brought previously to the temperature of the thermostat, and the filled pyknometer allowed to stand in the thermostat for ten minutes; it was then removed, dried with a clean towel, and allowed to stand in the balance case for ten minutes, at which time the weighing was made. The pyknometer was calibrated with distilled water following the same procedure. The method just described was used in making all of the density determinations which were required in calculating the relative viscosity.

Results

Tables I to VI show the results of some typical determinations.

TABLE I

Variation of Density and Relative Viscosity with Concentration

Sol No. 42

Conc. g./l.	Density	Rel. Viscosity	Conc. g./l.	Density	Rel. Viscosity
0.5	0.9975	1.003	2.0	.9984	1.019
1.0	.9979	1.009	2.5	.9992	1.025
1.5	.9983	1.012	3.0	.9998	1.030

TABLE II

Variation of Density and Relative Viscosity with Concentration

Sol No. 45

Conc. g./l.	Density	Rel. Viscosity	Conc. g./l.	Density	Rel. Viscosity
1.0	0.9975	1.002	3.5	1.0002	1.009
1.5	.9983	1.004	4.0	1.0005	1.012
2.0	.9990	1.006	4.5	1.0009	1.013
2.5	.9993	1.006	5.0	1.0014	1.015
3.0	.9998	1.007			

[4] Ayres and Sorum: J. Phys. Chem., 34, 2826 (1930).

TABLE III

Variation of Density and Relative Viscosity with Concentration

Sol No. 58

Conc. g./l.	Density	Rel. Viscosity	Conc. g./l.	Density	Rel. Viscosity
0.5	0.9974	1.004	2.5	.9993	1.018
1.0	.9980	1.007	3.0	.9998	1.021
1.5	.9984	1.011	3.5	1.0001	1.025
2.0	.9988	1.014			

TABLE IV

Variation of Density and Relative Viscosity with Concentration

Sol No. II

Conc. g./l.	Density	Rel. Viscosity	Conc. g./l.	Density	Rel. Viscosity
1.0	0.9979	1.003	3.5	.9999	1.019
1.5	.9983	1.007	4.0	1.0003	1.023
2.0	.9987	1.012	4.5	1.0007	1.026
2.4	.9990	1.013	5.0	1.0011	1.030
2.8	.9993	1.015	5.84	1.0018	1.038
3.0	.9994	1.017			

TABLE V

Variation of Density and Relative Viscosity with Concentration

Sol No. III-C

Conc. g./l.	Density	Rel. Viscosity	Conc. g./l.	Density	Rel. Viscosity
1.0	0.9978	1.003	4.0	1.0005	1.013
2.0	.9988	1.007	5.0	1.0014	1.016
3.0	.9998	1.010			

TABLE VI

Variation of Density and Relative Viscosity with Concentration

Sol No. IV

Conc. g./l.	Density	Rel. Viscosity	Conc. g./l.	Density	Rel. Viscosity
1.0	0.9976	1.003	6.0	1.0026	1.050
2.0	.9987	1.005	8.4	1.0049	1.099
4.0	1.0010	1.019			

Fig. 1 shows the plot of density against sol concentration for two sols which represent the maximum variation observed; these two sols were prepared at the same temperature, namely, 100°. All of the sols studied showed a linear relation between density and concentration. The temperature of

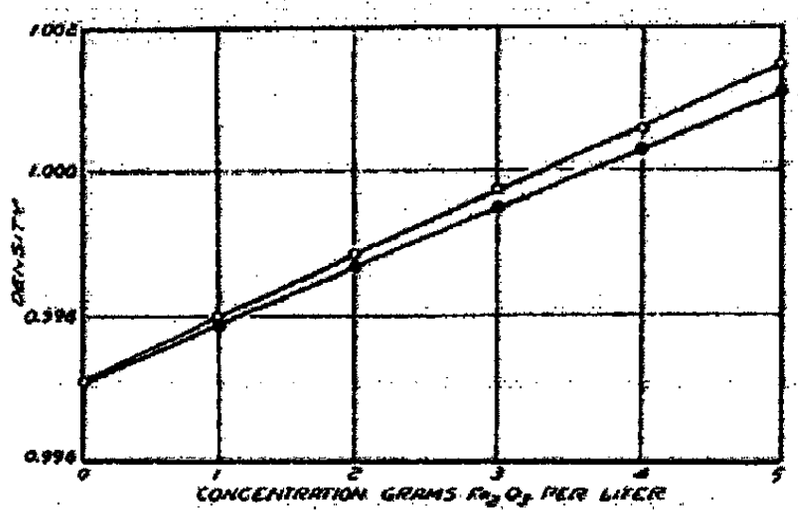

FIG. 1
○ Sol No. III-C
● Sol No. II.

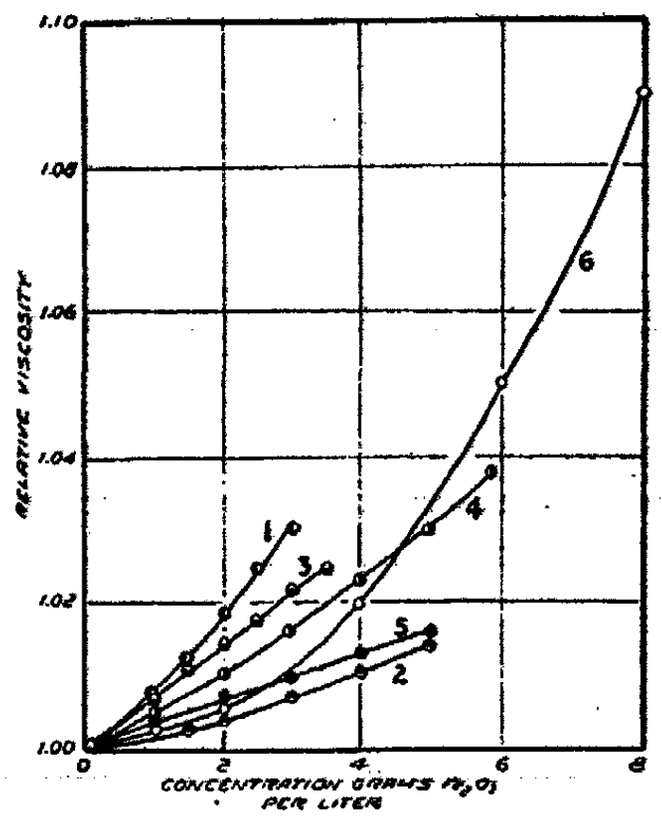

FIG. 2

preparation of the sol had no detectable influence on the density of the system. The densities of 17 different sols, prepared at temperatures ranging from 100° to 140° and containing 2.0 g. of ferric oxide per liter, were determined; the mean density (25°) was 0.9988, the maximum deviation from the mean being ± 0.0002.

The curves in Fig. 2 are plotted from the data of Tables I to VI.

Discussion

In speaking of sols such as those of Fe_2O_3 and Al_2O_3 Freundlich[5] says: "In all cases the viscosity increases in the region of small concentration *linearly with the content of the disperse phase*. The linear rise is confined to small concentration. For higher ones the viscosity-concentration curve is decidedly convex towards the axis of concentration."

Inspection of the curves in Fig. 2 shows that a linear relation is not observed in all cases. Of the six curves shown, only two exhibit the linear relation; in three other cases the viscosity-concentration curves are slightly convex towards the concentration axis, while in the other case the convexity towards the concentration axis is very pronounced.

It is of interest to note that the sols indicated as Nos. II, III-C and IV were prepared and dialyzed under conditions as nearly identical as possible; yet the curves are quite different in form: Sol No. II gives a curve which is slightly convex; Sol No. IV gives a curve which is decidedly convex; while the curve for Sol No. III-C shows a linear relation. It would seem, therefore, that a generalization as to the form of the viscosity-concentration curve in the case of colloidal ferric oxide is impossible.

It is somewhat difficult to interpret what Freundlich means by the "region of small concentration." The most concentrated sol used in these concentration studies contained 8.4 grams of iron oxide per liter, which is only 0.84% of disperse phase. In the case of Sol No. IV the curve shows a decided convexity even between the concentration of 2.0 and 4.0 grams per liter, corresponding to 0.2% and 0.4% of disperse phase.

Summary

1. The density of ferric oxide sols varies linearly with the concentration of the dispersed phase.

2. The density is not influenced by the temperature of preparation of the sol.

3. No generalization can be drawn regarding the shape of the viscosity-concentration curve, even at low concentrations of dispersed phase, say up to 0.5%. In some cases the relation is linear, while in others the curve is slightly or markedly convex towards the axis of concentration.

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[5] Freundlich: "Colloid and Capillary Chemistry," 367 (1926).

SOLUBILITIES IN THE SYSTEM WATER-IODINE TO 200°

BY F. C. KRACEK

1. Iodine dissolves in water to a limited extent only, but in aqueous solutions of iodides, particularly in KI, and RbI, its solubility is unusually high. This apparently abnormal solubility, taken together with other criteria, has led to a wide acceptance of the view that iodine combines with these salts in solution to form polyiodides. Such compounds, when they exist, should be capable of crystallizing from their solutions under the proper conditions, and hence, a phase rule study is obviously the most direct way of attacking the problem. The system water-iodine-potassium iodide was selected, principally because potassium "polyiodides" have figured extensively in the literature,[1] and secondly, because potassium iodide can be obtained in abundance, and in a state of high purity. The first measurements made have dealt with the three binary systems water-iodine, water-potassium iodide and iodine-potassium iodide, which form the boundaries of the ternary system. The results for the binary system water-iodine are communicated in this article.

2. Previous measurements of the solubility of iodine in water, summarized in Table I, end at 60°. The solubility is small, and increases moderately

TABLE I

Previous Reliable Values for the Solubility of Iodine in Water

t°C	Per cent Iodine		Reference
	weight	mol	
0.0	0.0162	0.00115	Jones and Hartmann: J. Am. Chem. Soc., 37, 241 (1915).
18.0	.02764	.001962	Hartley and Campbell: J. Chem. Soc., 93, 741 (1908).
25.0	.03394	.002409	Hartley and Campbell: op. cit.
25.0	.03403	.002416	Sammet: Z. physik. Chem., 53, 641 (1905).
25.0	.03386	.002404	Jakovkin: Z. physik. Chem., 18, 585 (1895).
25.0	.03403	.002416	Noyes and Seidensticker: Z. physik. Chem., 27, 357 (1898).
35.0	.04660	.003309	Hartley and Campbell: op. cit.
45.0	.06472	.004596	Hartley and Campbell: op. cit.
55.0	.09220	.006549	Hartley and Campbell: op. cit.
60.0	.10560	.007503	Sammet: op. cit.

[1] See article by Grinnell Jones in J. Phys. Chem., 34, 673 (1930) for a summary of published work on this question; see also Briggs, Greenawald and Leonard: J. Phys. Chem., 34, 1951 (1930), which was published while this paper was in proof.

rapidly with temperature, but it is evident that the solubility curve must be of a special type in order to reach 100 per cent at 113.7°, the melting point of iodine. A preliminary experiment confirmed the supposition that two liquid layers are formed at higher temperatures, and subsequent measurements have established the course of the solubility curve for solid iodine to 112.3°, the quadruple S-L_I-L_{II}-V invariant points, and the curves for the mutual miscibility of the liquid layers from 112.3° to beyond 200°. The critical solution temperature, estimated to be about 300°, could not be reached because of the extremely high vapor pressure developed by the system.

Experimental

3. *Method of Solubility Determination.* Because of the volatility of both water and iodine, the usual methods of measuring solubility can not be applied to this system at the higher temperatures. The method adopted for this work was that of rotating, in a regulated air bath, tubes in which known amounts of the constituents were sealed up, and noting the temperature at which the last trace of the dissolving phase disappears. The temperatures were kept constant at each stopping point long enough to assure equilibrium being attained, particularly in the neighborhood of the point of disappearance of the phase which is dissolving in the solution. This equilibrium method of solubility determination is analogous with the quenching method used so extensively in this Laboratory in silicate work, and can be recommended as an excellent method for all cases in which the solubility exceeds a certain arbitrary minimum value, since the method depends upon visual detection of the last traces of the dissolving phase; in the case of crystals, the uncertainty is of the order of less than 0.1 mg of material. The refinement of the method depends upon accurate knowledge of the weights of substances sealed in the tube, and on sufficiently sensitive temperature control. With modern facilities, neither of these requirements offers any difficulties.

4. The tubes employed were made from Pyrex tubing 11 mm outside diameter, 1.2 mm wall thickness. No attack on the glass was noticeable, and the mechanical strength of such tubes appears to be sufficient to withstand in excess of 40 atm internal pressure. A constriction was blown in the tubes to facilitate sealing when filled, the open end serving as a funnel for the introduction of the materials.

Iodine was weighed into a tared tube in the desired amount, water was then added and the tube sealed. The drawn-off portion was then weighed together with the sealed tube, to obtain the weight of water. All weighings were made to 0.1 mg purely as a matter of routine.

The electrically-heated air bath was regulated by a special potentiometer controller of a standard commercial type, using a five-junction copper-constantan thermocouple. The sealed tube was attached by clips to a fan, rotated at about 40 r.p.m., which kept the air in the bath in motion. Double-walled glass windows provided a means of observing the tube during the course of an experiment. The temperature inside the air bath was read on a

separate potentiometer, with a calibrated copper-constantan single junction thermocouple. The temperature control was sensitive to ±0.1° at all temperatures employed; small erratic fluctuations of temperature, due to eddies in the current of air in motion past the bare thermocouples, were of relatively small consequence in view of the great differences in heat capacity between the solubility tubes with their contents, and the air.

5. *The Method of Determination of the Fixed Points*, namely, the melting point of iodine, and the temperature at which solid iodine is in co-existence

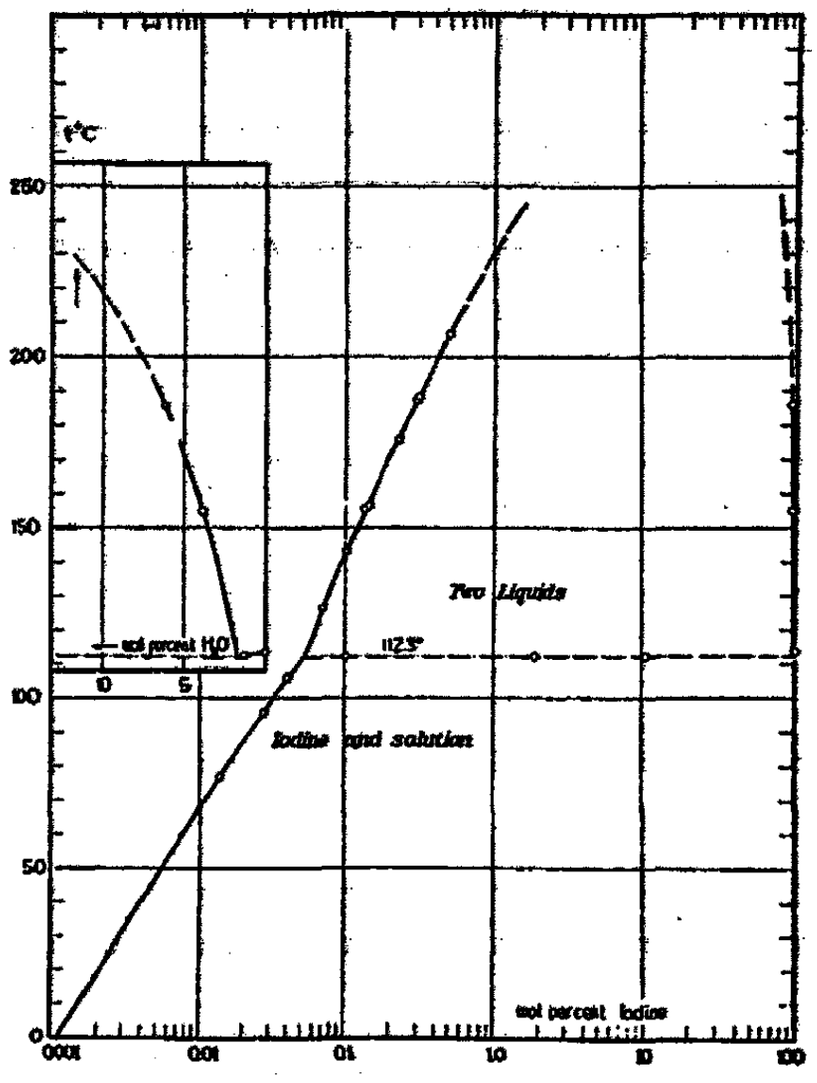

FIG. 1
Logarithmic graph of the solubility relations in the system water-iodine.
Inset figure: Solubility relations in the iodine end of the system.

with the two liquid phases and vapor, differed from that just described. These two temperatures are only a little over 1° apart, and since liquid iodine is a very dark, relatively viscous liquid, totally non-transparent, the rotating tube method can not give correct results.

It was advantageous to determine these points by thermal analysis in sealed tubes, since iodine is appreciably volatile at its melting point, and the S-L_I-L_{II}-V temperature is above the normal boiling point of saturated iodine solutions. The tubes selected for this purpose were of the type previously employed in the study of the polymorphism of potassium nitrate,[1] being pro-

[1] F. C. Kracek: J. Phys. Chem., 34, 225 (1930).

vided with a re-entrant well for the insertion of the thermocouple. To obtain good temperature distribution the tubes were supported within a heavy copper block placed in the furnace, with a uniform air space between the copper block and the tube, the heat being carried to the tube only by radiation and air convection. A reference couple was placed in a well in the copper block, and differential heating curves at a controlled rate of *ca* 0.5° per minute were taken, alternately reading the temperature of the charge in the tube, and the differential temperature of the charge with reference to the block. The thermocouples used were of copper-constantan, calibrated with accepted standards.

6. *The Experimental Results.* The results obtained with solutions are collected in Table II.

TABLE II

Determined Values of Solubilities in the System Water-Iodine

Expt. No.	Iodine g	H_2O g	rw^1	rm	Per cent Iodine wt	Per cent Iodine mol	t°C
			A. Solid Phase: Iodine				
7	0.0091	4.6561	0.00195	0.000139	0.195	0.0139	77.1
6	.0136	3.5071	.00388	.000275	.386	.0275	96.0
5	.0258	4.5805	.00563	.000400	.560	.0400	106.1
11	17.2313	0.0161			.093*	1.30*	113.
			B. Two Liquids; Aqueous Layer				
4	0.0423	4.2915	0.00986	0.000700	0.976	0.0699	126.5
3	.0530	3.6732	.01443	.001024	1.422	.1023	143.2
1	.0757	4.0712	.01859	.001319	1.825	.1317	155.4
8	.0733	3.6907	.01986	.001409	1.947	.1407	156.4
2	.0973	3.0594	.03180	.002257	3.082	.2252	175.9
10	.1630	3.9170	.04161	.002953	3.995	.2944	187.4
9	.1731	4.0224	.04303	.003054	4.125	.3045	188.4
15	.2764	3.9182	.07054	.005006	6.589	.4981	206.7
			C. Two Liquids; Iodine Layer				
14	16.3529	0.0472			0.288*	3.91*	155.
13	21.1455	.0998			.470*	6.24*	186.
12	15.1964	.1407			.917*	11.54*	>225.

[1] rw = grams of iodine per gram of water.
rm = mols of I_2 per mol of water; H_2O = 18.0154, I_2 = 253.86.
* weight and mol per cent of water.

7. The melting point of iodine was determined to be 113.7°, and the invariant S-L_I-L_{II}-V temperature 112.3°. The composition of the aqueous layer at this temperature, 0.0517 mol per cent iodine, equivalent to 7.29 g iodine per 1000 g water, was determined with sufficient precision by noting the point at which the solubility curve for solid iodine intersects the immiscibility curve, in a large scale logarithmic plot, shown in Fig. 1. The logarithmic plot is to be preferred in this case, since it separates the points on the aqueous solubility curves, and since it serves as a check on the relative

accuracy of determination of the data in this region. Moreover, the slope of the solubility curves above and below the S-L_I-L_{II}-V point in the logarithmic plot is such that the point of intersection is more definite than in the usual percentage graph. It will be seen that the data obtained in this investigation form a smooth continuation of the previously known curve.

8. The composition of the iodine-rich layer at the invariant S-L_I-L_{II}-V temperature was deduced graphically, as shown in the inset diagram in Fig. 1. The immiscibility curve meets the liquidus curve of iodine at 1.7 mol per cent H_2O (corresponding to 0.12 weight per cent H_2O), at a sharp angle. The liquidus curve of iodine then rises from this point to 113.7° at 100 per cent iodine.

9. The location of the water-iodine eutectic can be estimated from the known value of the solubility at 0°. If we take Jones and Hartmann's (op. cit.) value of 0.000638 mols I_2 per liter, and 1.86° for the molar freezing point depression, we obtain the temperature of the eutectic as −0.00119°. This is so near the melting point of ice that no experimental determination of the point can be realized, principally because iodine dissolves very slowly at 0°.

Table III contains a summary of the invariant points in the system.

TABLE III

Invariant Points in System Water-Iodine

Type	Solution, mol per cent Iodine	t°C
Ice → water, melting	0.0	0.0
Ice + solid iodine eutectic	0.00115	−0.0012
S-L_I-L_{II}-V, aqueous layer	0.0517	112.3
S-L_I-L_{II}-V, iodine layer	98.3	112.3
Critical solution point	——	*ca.* 300.
Iodine, melting	100.0	113.7

Discussion

10. These results are of interest from more than one viewpoint. First, and perhaps the more fundamental point of interest is, that aside from the intrinsic value of these data in establishing the previously uninvestigated formation of liquid layers in the system, we have here a plausible explanation for the anomalous behavior of polycomponent aqueous systems containing salts and iodine. It is a necessary consequence of the phase relations that the region of immiscibility must extend into the polycomponent systems, and since the immiscibility extends practically across the whole binary system, the effect in any polycomponent system will be large. Such solutions deviate so largely from ideal behavior that the ordinary laws of solutions lose much of their significance, and many deductions hitherto made from them for such systems must fail completely. In a ternary system, the S-L_I-L_{II}-V surface slopes down from the horizontal line at 112.3° in the binary system, and meets the liquidus curve of iodine at concentrations dependent upon the third component present. Thus, it is not surprising to find that at 25°, according

to Parsons and Whittemore,[1] the aqueous solution saturated with iodine and KI contains only *ca.* 6 wt per cent water.

11. A somewhat minor interest attaches to the extension of solubility studies into regions above atmospheric pressure, by the use of the sealed tube method. The method is old,[2] but very little use has been made of it in the past for exact work, principally for lack of facilities in maintaining constant temperatures in the neighborhood of any given point within the region studied. Granted that this requirement is satisfied, the method is convenient, moderately rapid, and more accurate than any other widely applicable method suitable for investigations at temperatures above the normal boiling point in the system studied.

12. Another point of interest lies in the relation of this system to the systems water-chlorine and water-bromine, studied by Bakhuis Roozeboom,[3] who showed that in both systems there are formed immiscible liquid layers, but that the solid phase in contact with the immiscibility region in each case is a hydrate instead of crystals of the element. The quadruple S-L_I-L_{II}-V point in the chlorine system is at 28.7° (m. p. of chlorine −103°), in the bromine system it is at 6.2° (m. p. of bromine −7.3°); in the iodine system the solid phase is pure iodine, and the temperature is 112.3°, just below the m.p. of iodine. The aqueous layer at the invariant point contains 0.915, 0.407 and 0.0517 mol per cent Cl_2, Br_2 and I_2 respectively, whereas the halogen-rich layers contain 99.5 mol per cent Br_2 and 98.3 mol per cent I_2 respectively (the composition is unknown for the chlorine system). The immiscibility region extends almost entirely across each of these systems. Of particular importance is the magnitude of the vapor pressures in these systems. In the chlorine system the vapor pressure of the saturated solutions is much less than the vapor pressure of chlorine; in the bromine system it exceeds the sum of the vapor pressures of bromine and water; so we may predict that in the water-iodine system the vapor pressure also exceeds the sum of the vapor pressures of the components.

Summary

Water-iodine solutions above 112.3° form two liquid layers, the mutual solubility increasing with temperature. The solubility curves were determined to temperatures above 200°. Below 112.3° the solutions are saturated with solid iodine. The composition of the liquid layers at the invariant temperature is 0.0517 and 98.3 mol per cent I_2 respectively.

Geophysical Laboratory,
Carnegie Institution of Washington,
July, 1930.

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[1] Parsons and Whittemore: J. Am. Chem. Soc., 33, 1933 (1911).

[2] F. Guthrie: Phil. Mag., 18, 105 (1884); W. Alexejeff: Ann. Physik, 28, 305 (1886); more recently used extensively by N. V. Sidgwick and co-workers, see J. Chem. Soc. from 1911 on.

[3] Bakhuis Roozeboom: Rec. Trav. chim., 3, 59, 73 (1884); 4, 69, 71 (1885); Z. physik. Chem., 2, 449 (1888).

NOTE ON A SIMPLE ONE-PIECE ELECTRODIALYSIS APPARATUS

BY L. REINER

Since electrodialysis has developed into a widely used laboratory method, a simple apparatus may have general interest. The apparatus previously used generally has been put together from three pieces corresponding to the three chambers of the common type of electrodialysis apparatus. This procedure is time consuming and also has the disadvantage that one must depend on rubber washers, and use some kind of clamp or device to keep the parts together. A simple apparatus has been described[1] which avoids these inconveniences. Practice with this apparatus, however, suggested the need of a membrane support. Dr. Prausnitz (Jena) suggested the use of Jena-glass

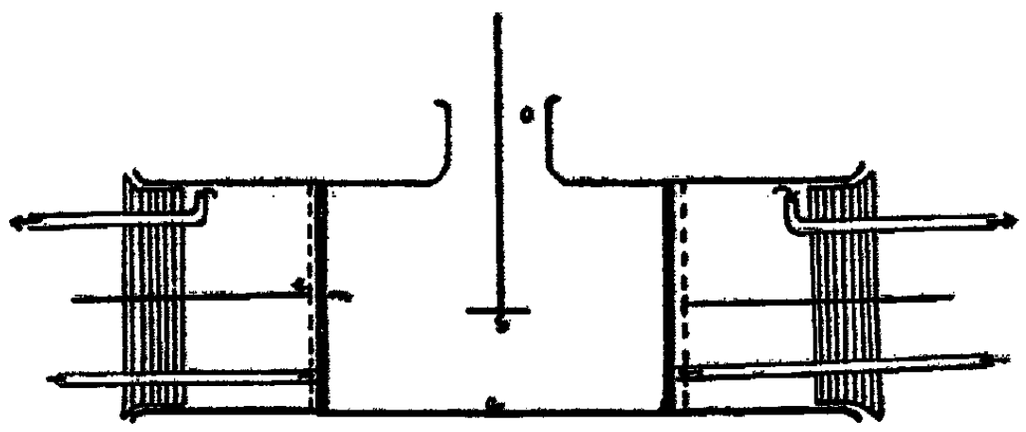

FIG. 1

filter plates as a support for collodion membranes. I then designed the apparatus described below. It was prepared in different sizes by the Schott works in Jena.

A glass cylinder (c) has two filter plates (m) (medium porosity) sealed in at a distance of 8-10 cm. from each other, thus forming a cell, which is the middle cell of the electrodialysis apparatus. This middle cell has an opening (neck) at O to receive the stirrer (s). The two ends of the cylinder are closed with rubber stoppers containing the electrodes (e) and inlet and outlet for circulating water. Platinum gauze or platinized glass can be used as anode, and copper or nickel gauze as cathode. Stirring in the electrode chambers does not seem to be necessary, because the circulation of water can be made fast enough to provide the necessary mixing and quick diluting of the alkali and acid produced. If metal gauze is used the mesh should be wide enough not to prevent mixing. In the case of platinized glass electrodes, a daisy shape, i.e., a petal-like aster of blades, was used for the same purpose.

As membrane, ether-alcohol collodion or acetic acid collodion was used. Coating is made in the usual manner as for the preparation of ultra-filters.

[1] Reiner: Kolloid-Z., 40, 123 (1926).

It is advisable to coat both membranes at the same time, filling the whole apparatus with the collodion solution and pouring it off only when the first drops of the solute appear on the back sides of filter plates. After sufficient drainage the whole apparatus is put in water for about 5 minutes, then the collodion is scraped off from the glass wall. This is necessary because the shrinking of the collodion connecting the two membranes may tear it off the filter plates. If biological products are to be electrodialysed (serum) it is useful to keep the whole apparatus 24 hours in horse serum or other protein solution (hemoglobin) instead of water. The protein "coats" the membranes and transforms them from negative membranes into amphoteric membranes. (Very old and dried membranes cannot be coated readily in this way.)

If the membranes must be changed, the glass part of the apparatus is put in a sulphuric acid-bichromate solution and is ready for use after one or two days. The apparatus can be prepared in any size up to 100 mm. diameter, which, if the membrane distance is 80-100 mm., corresponds to 600-700 c.c. content.

The only disadvantage of the apparatus may be the large electro-osmotic effect sometimes seen, due to the filter plates, viz. thickness of the membranes. This may lead to a water movement, which usually occurs from the anode to the cathode, the membranes usually being negatively charged. Migration of the acid into the middle chamber can be avoided by increasing the rate of water circulation. If the membranes have different charges, owing to the difference of hydrogen ion concentration around or in the membrane, the water-flow into the middle chamber may be less or more than the outflow, which may lead to a dilution or concentration of the fluid in the middle chamber. In practice only the latter has been observed, which is usually desirable.

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OBSERVATIONS ON THE MECHANISM OF FORMATION OF COLLOIDAL SILVER*

BY HELEN QUINCY WOODARD

The earliest theory of the formation of colloidal metals by the Bredig[1] method postulated a simple thermomechanical process of evaporation of the metal in the arc, and subsequent condensation of the vapor to particles of colloidal size in the surrounding fluid. The work of Beans and Eastlack[2] and of subsequent workers in Beans' laboratory[3,4,5,6,7], showed this explanation to be inadequate, and established the formation of a gold-anion "complex" as necessary to the formation of colloidal gold. The work of Pennycuick[8] on colloidal platinum and of Eirich and Pauli[9] on colloidal gold shows that in the preparation of Bredig sols of these metals complex acids are formed through the action of the electric arc. In the present paper evidence is presented to show that the formation of colloidal silver by the Bredig method involves the reaction of silver with the electrolyte present according to the ordinary laws of physical chemistry simultaneously with the formation of a metal-anion "complex". No assumptions are made as to the nature of this "complex".

Apparatus and Materials

These were the same as those reported in previous papers[10,11].

Method

The sols were made, centrifuged, and analysed in the same manner as previously described[11]. pH determinations were made colorimetrically with suitable indicators to ±0.2 pH. Titrations for acid and alkali were made against N/100 NaOH or HCl, and were accurate to ± 7%. Thiocyanates were determined by titration against standard $AgNO_3$ to ± 2%. Sulfates were estimated to ± 10% by the turbidity produced with N/10 $Ba(NO_3)_2$. Nitrites were determined to ± 4% by titration at 35°C. against standard $KMnO_4$. Nitrates were estimated colorimetrically to ± 5% with diphenylamine reagent. Oxalates were estimated to ± 10% by titration against standard $KMnO_4$. (All precisions are given for determinations made on 3 cc. of .0015N reagent. Where the concentration was less the precision fell accordingly).

Results

As explained in a previous paper, when an arc is maintained between silver electrodes in a suitable solution, colloidal silver is formed, increases to a maximum of concentration as arcing continues, and then, upon further arcing, falls to zero. Table I gives the results of examination of the liquid

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

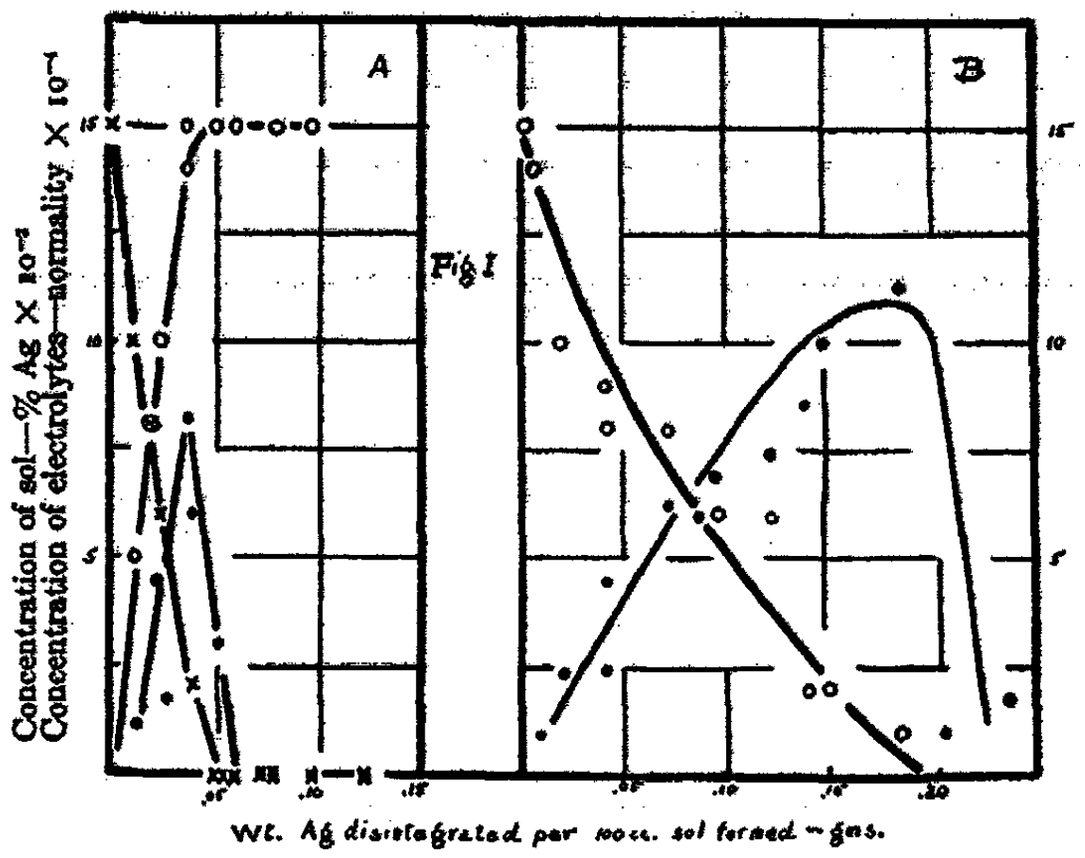
remaining after this final precipitation of the sol. The fate of the cation of the initial solution was followed by titration or pH determinations. Direct tests were made for some of the anions. Other anions were not determined directly, but are reported as silver salts because of the recovery of dissolved silver in sufficient amount to satisfy the anion originally present. Sol formation is reported as "+" when stable sols were formed regularly; "++" when the sols formed were concentrated and stable over a long arcing time; "−" when sols were never formed; and "±" when the sols formed were extremely dilute, unstable on standing, or very sensitive to slight changes of technique.

An examination of the table suggests the following theory of sol formation:—In nearly all cases when arcing takes place in distilled water or in an electrolyte solution, silver reacts with the water sufficiently to saturate the solution with AgOH. This is shown by the fact that, except in certain special cases, the liquid remaining after a sol has been arced to precipitation has a silver concentration of .0002N − .0003N, and a pH of about 9.5. Two other processes take place at the same time. During arcing in a suitable electrolyte solution, a sol forms and precipitates according to the "complex" theory. In addition, silver combines with the anion present to form a silver salt. If the silver salt is highly insoluble, as AgCNS, AgCl, or Ag_2S, then the available anion is removed so fast from the solution that little can be used to stabilize the sol, and the sol is dilute. Qualitative evidence in favor of this hypothesis is furnished by the presence of a white deposit, presumably silver salt, in the sludge thrown down when sols prepared in NaCNS and NaCl solutions are centrifuged. If the silver salt is sparingly soluble, as Ag_2CO_3 or Ag_2CrO_4, then the anion is removed slowly from the system, and is available in considerable concentration long enough to stabilize concentrated sols. (Data for silver sols stabilized by K_2CrO_4 are not given in the table because the chromate ion is so good a stabilizing agent for colloidal silver that very prolonged arcing was necessary to precipitate the sols. This rendered quantitative work impossible). If the silver salt is moderately to highly soluble, as $AgNO_3$, CH_3COOAg, or Ag_2SO_4, then the disintegrated silver reacts with the electrolyte instead of dispersing, and no sol, or an exceedingly dilute sol, is formed. In this case the anion remains approximately constant in concentration during arcing (NO_3^-), or decreases slowly ($SO_4^=$). The decrease is probably due to adsorption on the sludge. This is evidently an electrolytic process, since only minute traces of silver (.00004N) are dissolved when the electrodes are left in contact with the arcing solution with the current not flowing.

Interesting results are obtained when arcing takes place in the solution of an electrolyte whose anion is capable of forming a highly soluble silver salt. When the electrolyte is an acid, as H_2SO_4 or CH_3COOH, silver salt forms. The final solution is slightly alkaline, and contains sufficient silver to neutralize the acid and to saturate the solution with AgOH. When the electrolyte is an ammonium salt, replacement takes place, the silver goes into solution as silver salt, and the ammonium appears as hydroxide (NH_4NO_3 and $(NH_4)_2SO_4$). This is in contrast to the condition when arcing takes place in

solutions of $NaNO_3$ or Na_2SO_4. Here the silver can not replace the sodium as it does the ammonium, and only dissolves sufficiently to saturate the solution with AgOH.

As the anion is removed from the solution as salt or precipitated "complex", the cation is set free to form hydroxide almost wholly (KOH, NaOH, NaCNS, Na_2CO_3, NH_4Cl, NaCl, NH_4NO_3, $(NH_4)_2SO_4$, $K_2C_2O_4$, CH_3COONa), or in part (Na_2SO_4, Na_2S). The sodium from Na_2SO_4 which is not recovered as hydroxide apparently remains in the solution as $NaHSO_4$, since there is



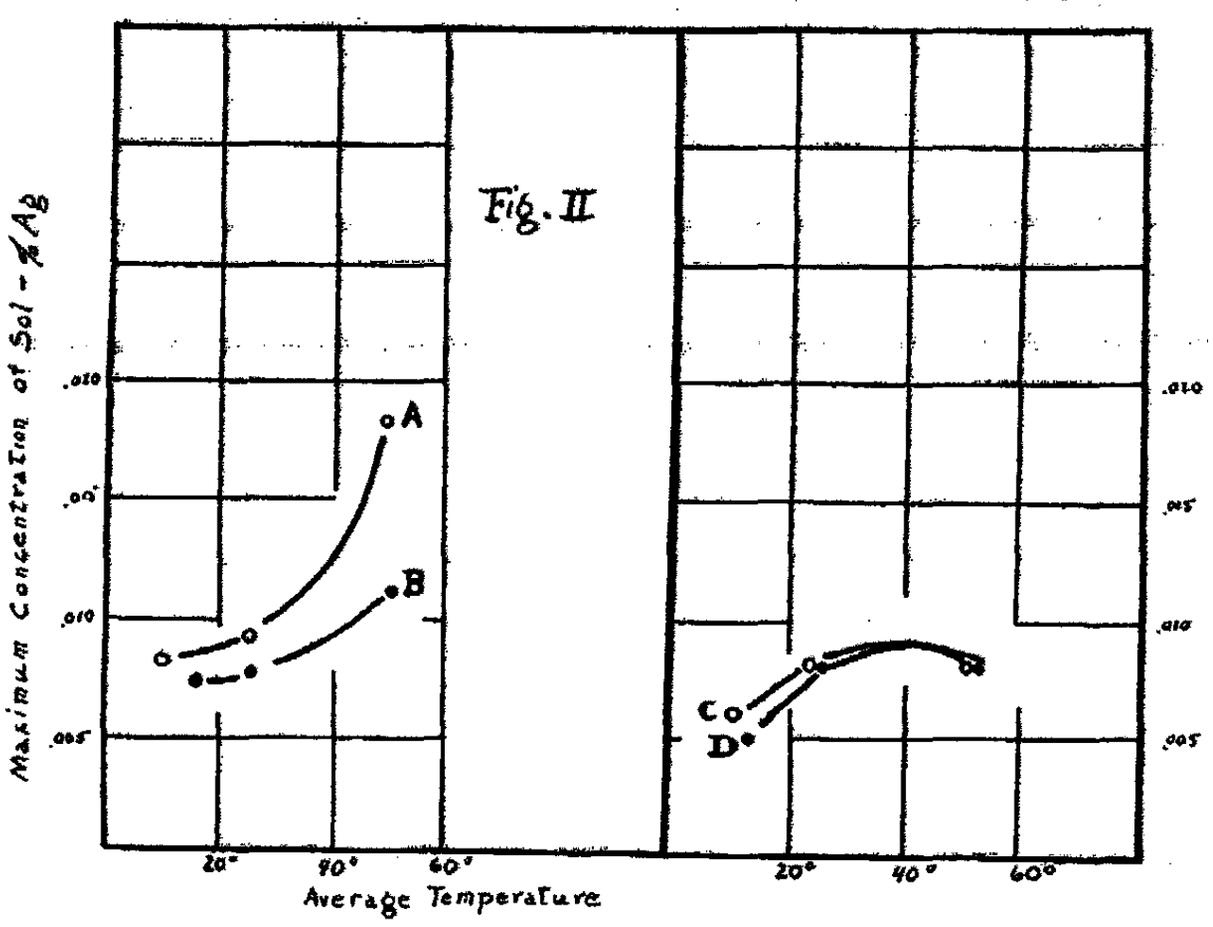
Change in Electrolytes during Arcing

A – Sols stabilized by .0015 N NaCNS.
B – " " " .0015 N HCl.
● = concentration sol silver in percent.
x = " thiocyanate in normality.
O = Alkalinity in Fig. 1 A; acidity in Fig. 1 B.

sufficient sulfate ion in the solution to account for this. The fate of the portion of the sodium from Na_2S which is not recovered as hydroxide remains unexplained, although it might possibly be accounted for by preferential adsorption of NaHS on the sludge. If the electrolyte in the initial solution is an acid, the released H^+ disappears as H_2O (HCl, H_2SO_4, CH_3COOH).

This process was followed directly with two electrolytes, NaCNS and HCl. Samples were withdrawn at intervals during sol formation. The samples stabilized by NaCNS were precipitated by solid $NaNO_3$, centrifuged, and the thiocyanate in the supernatant liquid was determined. The samples stabilized by HCl were titrated against N/100 KOH, the sols being diluted sufficiently so that a fair end-point was obtained. As no other acid was present, this gave a good indication of the concentration of HCl in the sol. A few direct determinations of the chloride content of the supernatant liquid remaining after

the precipitation of these samples with $NaNO_3$ were also made. These checked the results of direct titration within the limits of experimental error. The results are given in Fig. I. It will be seen that the anion of the original solution disappears at about the same time as the precipitation of the sol in each case, while the alkalinity of the solution reaches its maximum at about the same point. This confirms the findings of Shear[5], Amsden[7], and Eirich and Pauli[9] for colloidal gold.



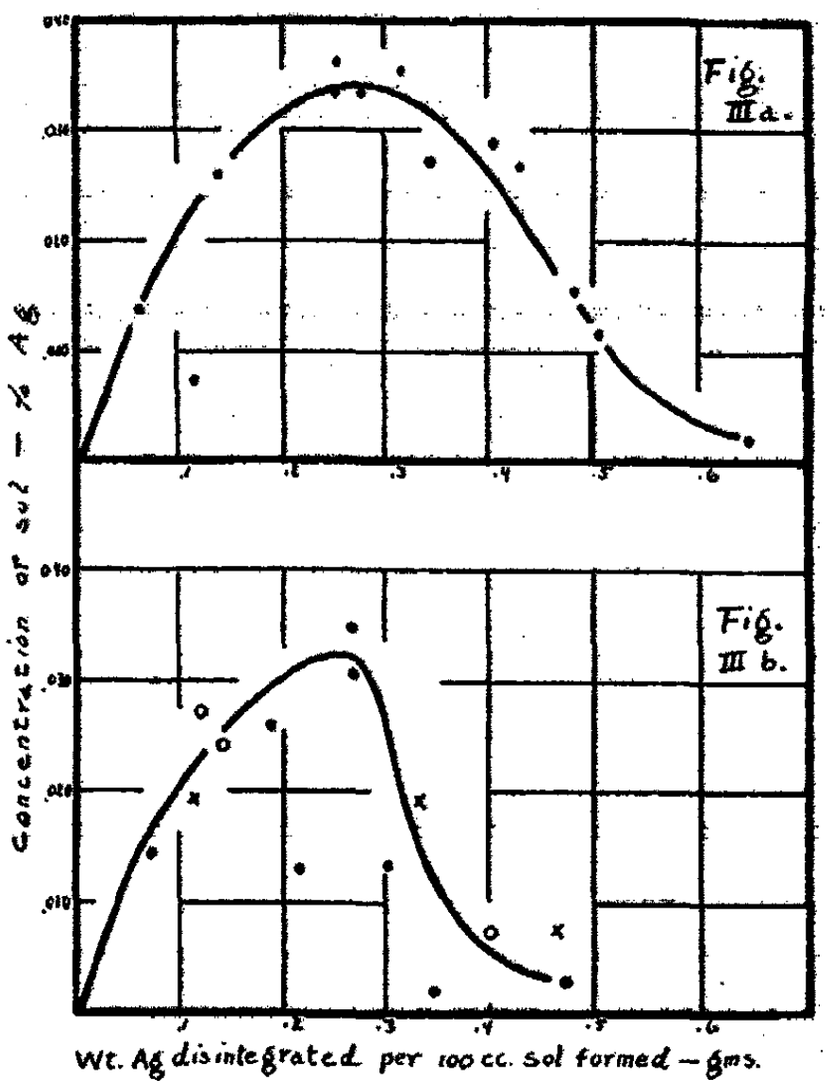
Change of Maximum Concentration of Sols with Temperature.

A = sols stablized by .0015 N NaCNS.
B = " " " .0015 N HCl.
C = " " " .0015 N H_2SO_4.
D = " " " .0015 N CH_3COONa.

As the solubility of most silver salts increases markedly with temperature, it was possible to make direct tests of the influence of the solubility of the salt which silver is capable of forming with the anion of the stabilizing electrolyte, as is shown in Fig. II. Silver sols were made at the temperature ranges 5°—15°C., 15°—35°C., and 40°—60°C., in H_2SO_4 and CH_3COONa, and in NaCNS and HCl. The first two yielded anions whose silver salts are above the most favorable solubility for sol formation; the silver salts with the anions of the second two electrolytes are below the most favorable solubility for sol formation. In Fig. II the maximum concentrations of the sols formed are plotted against the average temperature. Two effects are evident in the curves. Rise of temperature in itself evidently favors sol formation, as is shown by the initial rise in all the curves. The favorable effect of rise in temperature is largely offset by the increasing solubility of the highly soluble

Ag_2SO_4 and CH_3COOAg. On the other hand, the increase in the low solubility of AgCNS and AgCl causes a marked rise in the curves for sols stabilized by NaCNS and HCl. The difficulty of maintaining an arc below 5°C. or above 60°C. rendered it impossible to follow these curves further.

Several points in the data remain unexplained by the theory presented above. The most important of these relates to the behavior of silver sols stabilized by KOH and NaOH. The alkalinity of these sols remains nearly



FIGS IIIa and IIIb
Successive Sols made in the same Solution
a = first sols stabilized by .0015 N NaOH.
b = second sols stabilized by .0015 N NaOH
● = sols in NaOH remaining after arcing in .0015 N NaOH.
○ = sols in NaOH remaining after arcing in .0015 N NaCl.
x = sols in NaOH remaining after arcing in .0015 N Na_2CO_3.

constant during arcing and after the precipitation of the sol. If the cation is released during arcing and reforms the hydroxide as fast as released, then the electrolyte remains essentially unchanged. There is thus a constant supply of hydroxyl ion available for sol stabilization. One would therefore expect that the concentration of sol silver would remain constant at its maximum even after prolonged arcing. This is not the case, however, since silver sols stabilized by KOH or NaOH may readily be arced to precipitation. Further, KOH is formed during arcing in solutions of $K_2C_2O_4$, and NaOH

TABLE I

Initial Electrolyte	Sol Formed	Cation recovered in final liquid	Anion recovered in final liquid	Final Ag conc.
.0009 N Na_2CO_3	++	100% as alkali	Trace	.0003 N
.0015 N "	++	100% "	"	.0002 N
.00075 N Na_2S*	+	45% as alkali		.0001 N
.0012 N "	+	50% "	o	.0001 N
.0025 N "	+	55% "		.0001 N
.00086 N KOH	++	100% as alkali	100% as alkali	.0003 N
.0013 N "	++	100% "	100% "	.0002 N
.0009 N NaOH	++	100% "	100% "	.0002 N
.0015 N "	++	100% "	100% "	.0003 N
H_2O	−	pH 9.2		.0002 N
.0015 N NaCNS	+	70% as alkali	o	.0002 N
.0015 N HCl	+	pH 9.5	o	.0005 N
.0015 N NH_4Cl	+	80% as alkali	o	.0001 N
.0014 N NaCl	+	95—100% as alkali	o	.0002 N
.0005 N $NaNO_3$	±	pH 9.5		.0002 N
.0014 N "	±	pH 9.5	.0014 N	.0002 N
.0025 N "	±	pH 9.5		.0016 N
.0015 N NH_4NO_3	−	80% as alkali	.0014 N satisfied as $AgNO_3$	.0002 N
.0015 N $K_2C_2O_4$	±	100% as alkali	Rapid decrease during arcing	.0002 N
.0015 N $NaNO_2$	−	pH 9.5	Slow decrease during arcing	.0003 N
.0015 N CH_3COONa	+	100% as alkali		.0018 N
.0013 N CH_3COOH	−	pH 8.0	Satisfied as CH_3COOAg	.0017 N
.0015 N H_2SO_4	±	pH 7.2	Satisfied as Ag_2SO_4	.0003 N
.0015 N Na_2SO_4	±	50% as alkali	.0015 N	.0017 N
.0015 N $(NH_4)_2SO_4$	−	100% "	.0015 N satisfied as Ag_2SO_4	

* Concentrations of Na_2S are given with respect to S content. Owing to hydrolysis, the Na content was about 20% higher. This is allowed for in calculating the percent of cation recovered.

remains in solutions of NaCNS, NaCl, and Na_2CO_3 from which the anions have been removed by sol formation and precipitation, yet prolonged arcing in these alkaline solutions does not result in the formation of sols stabilized by hydroxyl ion.

It seemed possible that the explanation of this anomaly lay in the presence of temporarily suspended sludge in the solution after the precipitation of the sol. This might provide nuclei for the condensation of metal vapor from further arcing, and so prevent the formation of stable colloid. That this explanation is correct is shown by the following experiment.

Sols were prepared in .0015 N NaOH, .0015 N NaCl, and .0015 N Na_2CO_3, and were arced to precipitation. The liquid remaining was then centrifuged to remove sludge. After centrifuging, the liquid was colorless, or retained a faint green color from traces of colloidal silver. This liquid was then used for the preparation of further sols. Sols so prepared were poorly reproducible, probably owing to the presence of traces of suspended silver. They had, however, approximately the same maximum of concentration and position of maximum as original sols made in .0015 N NaOH. This is shown in Fig. III. It was possible to repeat the process a third time with the liquid remaining after the precipitation of the second sols.

Further evidence in support of the above explanation was obtained by arcing to precipitation sols stabilized by .0015 N HCl. The liquid remaining after the precipitation of these sols only contained sufficient hydroxyl ion to bring the pH to 8.3—8.8, and no further sols could be formed in it even after prolonged arcing.

An observation which remains unexplained is that $K_2C_2O_4$ and $NaNO_2$ are not good stabilizing agents for colloidal silver, although their anions form salts with silver which are in the range of solubility favorable to sol formation. The theory in its present form is inadequate for these cases.

Summary

Evidence has been presented to show that the formation of colloidal silver by the Bredig method involves the effect of the laws of physical chemistry.

Bibliography

[1] Bredig: Z. angew. Chem., 11, 951 (1898).
[2] Beans and Eastlack: J. Am. Chem. Soc., 37, 2667 (1915).
[3] Beaver: Diss. Columbia (1921).
[4] Davidson: Diss., Columbia (1924).
[5] Shear: Diss., Columbia (1925).
[6] Layton: Diss., Columbia (1926).
[7] Amsden: Diss., Columbia (1926).
[8] Pennycuick: J. Chem. Soc., 1927, 2600.
[9] Eirich and Pauli: Kolloidchem. Beihefte, 30, 113 (1930).
[10] Woodard: J. Am. Chem. Soc., 50, 1835 (1928).
[11] Woodard: J. Phys. Chem., 34, 138 (1930).

THE REVERSIBILITY OF COUPLED REACTIONS IN BIOLOGICAL SYSTEMS AND THE SECOND LAW OF THERMODYNAMICS

BY DEAN BURK

The problem of the general applicability of the second law of thermodynamics to biological systems has of late years received attention of substantial character (1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12, 13, 13a). The two following different but hardly conflicting views summarize the present position. Lewis and Randall (8, p. 120) state, "The second law of thermodynamics is a principle which has never failed to satisfy the severest test of experiment." Donnan (12) states, as a result of probability calculations, "It seems, therefore, that there exist biological systems of such minute dimensions that the laws of classical thermodynamics are no longer applicable to them." It is the purpose of the present paper to offer some rather exact support for the first of these statements, without, however, detracting in any way from the suggestiveness of the second.

Both proof and disproof of the biological applicability of the second law, according to which no isothermal biological machine may spontaneously yield more free energy than it receives, have been difficult to establish experimentally in any particular instances. There is only one general class of biological reactions where, so far as experiment has been capable of deciding, it is certain that the second law is operating. This class may be designated as "the entire life processes of an organism." It has been universal experience that the thermodynamic work done by any organism has always been considerably less than the free energy consumed by that organism, i.e., in net effect heat has always been given to, and not taken from, the environment in amount greater than that minimum required by the second law. No perfectly reversible "whole life process" of an organism has ever been observed; the chemical free energy of the oxidizable organic matter supplied heterotrophic organisms or the radiant energy or oxidizable inorganic matter supplied autotrophic organisms has always been gradually, continuously, and often completely dissipated into heat.

The aforementioned class of biological reactions is, however, obviously extremely limited in number compared to the total number of biological reactions, when it is considered that the life process as a whole of any one organism is made up of an almost infinite number of more or less independent specific reactions. This opens the question of whether in some one or more of these specific reactions the law does not obtain but the infraction is not usually observed owing to the relatively overwhelming irreversible effects in the remaining specific reactions. The net reversibility of a life process as a whole is rarely greater than 50% and is generally only 10% or less, hence the free energy efficiency of any particular specific reaction under investigation has always been to a certain extent considerably obscured by the free energy

losses in other simultaneous independent life processes. It has not been easy to exclude the frictional, and other irreversible, similarly irrelevant losses consequent upon life processes from the free energy balance sheets, so that only empirical "machine" efficiencies have been measurable, rather than what may be termed "second law" efficiencies.* The best review of the data concerning such machine efficiencies has been given by Baas-Becking and Parks (11) for the autotrophic processes whereby CO_2 is reduced by living forms by means of chemical energy supplied by the oxidation of sulfur, ammonia, carbon monoxide, hydrogen, etc. Machine free energy efficiencies give serviceable information regarding the fraction of useful work (i.e., CO_2 reduction) obtained in one process intricably and necessarily bound to many other useful chemical processes (i.e., growth, maintenance, etc.) which also consume free energy reversibly or irreversibly, as the case may be. Unfortunately they give no indication as to the degree of irreversibility of the isolated process itself, and can not, therefore, be employed as a test of the second law with respect to the isolated process (as has upon occasion been assumed) but only with respect to all life processes as a whole. The necessity for experimental, as distinguished from *a priori*, proof of the validity of the law has always been clearly recognized, particularly by its early formulators

*The machine free energy efficiency is defined by the writer as the work done in any specific reaction occurring in a biological system divided by the free energy consumed by the system as a whole. The second law free energy efficiency is defined as the efficiency obtained upon correcting the machine free energy efficiency for the irrelevant losses involved in simultaneous extraneous metabolism (i. e., the work done in any specific reaction is divided by the free energy dissipated by that reaction only); specifically, it measures, in per cent, the real reversibility of an isolated reaction. Where reversibility is perfect and the second law operates, the efficiency attains one hundred per cent, but values higher than this may result in event that the second law does not obtain. When on the other hand, reversibility is not perfect (i. e., stoichiometric yields are not obtained, see nitrate reduction case), but where the second law operates, the efficiency is then less than one hundred per cent. In other words, there is one condition where the efficiency may be less than one hundred per cent, one condition where greater. The writer was for some time uncertain as to the nomenclature most suited to distinguishing the two efficiencies. Both efficiencies, as will be more evident upon consideration of specific cases, are "second law efficiencies" in the sense that they deal with relations of phenomena which take place in accordance with, or in exception to, the second law. The second law efficiency has been designed as a *test* of the law in cases where there might be considerable expectation as to the failure of its operation, and has been so named accordingly. In the case of the machine efficiency, on the other hand, more than one independent free energy consuming process is concerned, but only one is evaluated with respect to the free energy consumed in all processes and hence no test of the operation of the law in the one process is possible except in the unique event that the independent process so far disobeys the law as to more than cover the amounts of free energy disappearing in the other processes. But even here the quantitative extent of the disobeyal would be masked so long as the amounts thus disappearing in the other processes were unknown. The following contrasting terms have been considered as possible alternative nomenclature: (1) "machine efficiency" and "corrected machine efficiency"; (2) "overall efficiency" and "efficiency of isolated step"; or, in the case of autotrophic processes, (3) "efficiency as a machine for storing CO_2" and "efficiency as a machine for reducing CO_2". Each of these distinguishing designations has its objections, however. It is believed that the two terms finally chosen are fairly accurate descriptions of what they are intended to represent, especially when, as has been the case throughout this paper, an attempt has been made to point out that for the more fundamental applications of thermodynamics to life processes a great deal more is to be gained by isolating each process for consideration than by lumping together a number of generally chemically independent but physically inseparable processes. The proposed nomenclature therefore receives justification from its usefulness as an arbitrary convention based upon the proposed *principle of isolation*. This isolation may amount to either a physical reality, or, more often, to merely a mathematical convenience.

(14, 15, 16, 16a*). In view of the historical interest attached to the various and almost solely theoretical discussions of the subject during the past hundred years, it has appeared desirable to present an experimental proof of applicability accurate to an order of about one per cent. This is now possible in a fundamental case (autotrophic hydrogen oxidation) involving a highly endothermic biochemical energy transfer process, only one important, but entirely probable, assumption obtaining.

Autotrophic Hydrogen Oxidation

We shall consider the non-photochemical reduction of carbon dioxide by the autotrophic hydrogen bacterium, *Bacillus pycnoticus*. This organism derives its energy from the oxidation of hydrogen. Its metabolism has been exhaustively investigated by Ruhland (17). Under the most favorable conditions only six and eight-tenths volumes of hydrogen are consumed for every volume of carbon dioxide finally changed to organic carbon. Calculations show that this ratio corresponds to a maximum machine free energy efficiency of $(105140 \times 100\%)/(54230 \times 6.8)$, or 28.4%, where 105140 and -54230 are the respective molal free energies of reduction of carbon dioxide and oxidation of hydrogen under the conditions of Ruhland's experiments (see below). However, such a machine free energy efficiency does not take into consideration the carbon dioxide reduced and then lost subsequently through respiration processes. Therefore, since it is not based upon the total carbon dioxide reduced, it can not be employed as a test of the second law with respect to autotrophic reduction of carbon dioxide by hydrogen.** The second law

*Clausius (16a) says, "I can not but think that when it is asserted that heat never passes from a colder to a warmer body (however complicated the process) without some permanent change occurring which may be regarded as an equivalent thereof, this theorem ought not to be treated as self-evident."

**It will perhaps clarify matters further to illustrate the difference between the two efficiencies in the case of some purely non-biological system of energy transfers. Let us imagine a single motor arranged to perform simultaneously in an isothermal system a number of types of mechanical work, such as (a), moving a house, (b), sawing wood, (c), running a watch, etc., and that the amounts of work done in each case are respectively u, v, and w, and that the total mechanical work is $u + v + w = M$. Let the motor be driven by free energy supplied from a galvanic cell, and A be the total amount of free chemical energy lost as heat and work from the galvanic cell. We note that in the whole system there are five possible sources of irreversible production of heat, viz., m, n, o, p, and q, in respectively (a), (b), (c), in the running of the motor (d), and in the operation of the galvanic cell (e), the sum of the five heat losses being equal, let us say, to N, so that $A = (M + N)$. The machine free energy efficiencies in the cases of (a), (b), (c), (d), and (e) are then respectively u/A, v/A, w/A, $(u + m + v + n + w + o)/A$, and $(u + m + v + n + w + o + p)/A$; in each case the work done in any arbitrarily isolated process is divided by the work done and heat liberated in all five processes. The whole system, involving five processes (and therefore four energy transfers), is considered as a machine in which, in any one process, both the heat and the *work* used in the other processes before it and adjacent to it in the transfers are considered dissipated and unavailable with respect to the one process except the actual work done in that process. The corresponding second law free energy efficiencies are $u/(A - v - n - w - o - p - q) = u/(u + m)$, $v/(A - u - m - w - o - p - q) = v/(v + n)$, $w/(A - v - n - u - m - p - q) = w/(w + o)$, $(u + m + v + n + w + o)/(A - q) = (M + N - p - q)/(M + N - q)$, and $(u + m + v + n + w + o + p)/(A) = (M + N - q)/(M + N)$; in each case the work done in any arbitrarily isolated process is divided by the work done and heat liberated only in that *same* process, i. e., here the denominators are not all the same, but are all different. Comparing, in any one process, such as (a), the machine efficiency u/A with the second law efficiency $u/(u + m)$, it can be

(*Footnote continued on next page*)

efficiency may, and probably ordinarily should, be independent of the observed ratio of hydrogen to carbon dioxide used, variations in the ratio depending upon the relative amounts of respiration to organic carbon formed, i.e., upon the amount of energy expended to produce a given dry weight of organism.

Fortunately, in addition to measuring the hydrogen and carbon dioxide changes, Ruhland determined the oxygen consumption. The oxygen consumption provides a measure of the metabolic energy. Owing to this opportune circumstance, it is possible to determine the "second law" (as distinguished from the "machine") free energy efficiency and thereby test the law with respect to CO_2 reduction.

Ruhland gives eleven experiments with complete and unambiguous data concerning hydrogen and oxygen consumed and organic carbon produced, Nos. 2, 3, 4, 15, 19, 22, 28, 29, 30, 31, 32, as shown in Table I. Cultures of the organisms were grown at constant volume in approximately half liter, mercury sealed, flasks containing fifty cc. of mineral nutrient solution free from organic matter. Ammonium salts were employed as a source of fixed nitrogen. After gas evacuation the culture flasks were filled with varying amounts of oxygen, hydrogen, carbon dioxide and nitrogen, and immersed in a constant temperature bath at 32°C. Gas analyses were made at the beginning and at the end of the experiments. These usually lasted about ten days. Organic carbon was determined by wet combustion.

When the organisms are supplied suitable organic compounds of carbon no hydrogen is consumed.[1] On this account and others[1] it may be concluded that the process of carbon dioxide reduction and hydrogen oxidation can not be dissociated and that no reaction between hydrogen and ordinary[2] oxygen to form water takes place directly,[3] and that a high order of reversibility

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** *Footnote (continued from page 434)*

seen why the former is no test of the law as applied to the process (a), since A contains a great many terms in addition to, and obscuring, (u + m); only so far as (a) may disobey the law in such a manner that u > A would the disobeyal be detected, and then, only qualitatively. We may note also the arbitrary nature of the principle of isolation, that, just as the system as a whole (described above) can be divided into various processes, so each of these processes might be divided into sub-processes of energy transfer more or less indefinitely; thus in (c), for example, we might isolate and determine the second law free energy efficiency of the transfer of the free energy of the motor to the stem of the watch, and then from the stem to the mainspring, and then from the mainspring to the minute hand, and then from the minute hand to the air currents set in motion, and so on. In the case of hydrogen bacteria, it may be considered that the free energy available in hydrogen oxidation, corresponding, let us say, to the free energy given to the motor above by the galvanic cell, is transferred, in effect, into (1) storing reduced CO_2 (corresponding to the u + m terms) and into (2) heat by reacting directly or indirectly with oxygen (corresponding to the p term), but to no other process (i. e., there are no corresponding v, n, w, or o terms); we shall be interested in distinguishing chiefly between the machine efficiency u/(u + m + p) and the second law efficiency u/(u + m). Here the number of terms is small, and all terms are experimentally measurable with but little uncertainty; in other biological cases, as will be shown, a greater number of terms (corresponding to v, n, w, o, etc.) are often involved and generally are difficult if not impossible to measure experimentally, and it is for this reason that it is so difficult to prove or disprove the application of the second law to the overwhelming majority of biological processes.

(*Footnotes 1, 2, and 3 on next page*)

probably obtains. All the hydrogen consumed being used to reduce carbon dioxide, all the oxygen consumed is therefore used in respiration, i.e., in metabolism, and oxygen consumption is a measure of metabolic energy. Oxygen consumption measures that fraction of the H_2 used for reducing the CO_2 which is later reoxidized back to CO_2 in the metabolic processes of the

(*Footnotes for page 435*)

[1] Ruhland neither gives data nor mentions a single experiment showing hydrogen consumption to take place under heterotrophic conditions otherwise favorable for hydrogen consumption. However, he describes some dozen or more experiments wherein organisms were maintained heterotrophically in the presence of H_2 in .5% and 1% glucose with and without $CaCO_3$ or $MgCO_3$ without showing a trace of H_2 consumption although growth took place. In the cases without $CaCO_3$ or $MgCO_3$ the pH sank from 7.4 to 6.1 in 3 days and to 4.8 in 5 days. Ruhland was inclined to believe that this change in hydrogen ion concentration accounted for the lack of hydrogen consumption (in spite of growth occurring), yet his own data show that even in short time autotrophic experiments where the pH was initially low relatively large amounts of H_2 were consumed (many times the maximum experimental error of about .5 cc.), as reported in Table II. The experiments of Table II show that a certain amount of H_2 oxidation might have been expected in the heterotrophic experiments without $CaCO_3$ or $MgCO_3$ (taking place *at least* during the time that the pH was not inhibitory but only becoming so, which required about four days), provided that any H_2 could have been consumed at all. The experiments with $CaCO_3$ and $MgCO_3$, where presumably the pH was maintained constant at a favorable value, about 7.0, would seem to show conclusively, however, that no H_2 and CO_2 consumption takes place under truly heterotrophic conditions. A number of other experimental facts confirm this view. (1) The addition of sugar to an autotrophic culture actively and rapidly consuming H_2 (which was easily accomplished in Ruhland's apparatus without disturbing the gas mixture therein except momentarily) immediately stopped H_2 consumption but the oxygen consumption proceeded at practically the same rate (as shown by the behaviour of the manometer attached to the apparatus). (2) Mannite was observed to have the same effect as glucose. (3) In the system $H_2 + CO + O_2$, no CO is reduced by H_2, indicating that CO_2 must be reduced in order for H_2 to react. (4) Formate is not used as a source of carbon in the absence of H_2 or other organic matter, and yet H_2 may be used in its presence (CO_2 being present also), indicating that H_2 oxidation is resorted to only when a source of *sufficiently available* reduced carbon is not at hand. (5) Even H_2-consumption in the presence of sugar (and CO_2) under certain circumstances would not necessarily mean direct reaction with oxygen. In the case of normal inhibition of H_2-consumption there obviously must nevertheless be a certain low concentration of sugar which is not sufficient to completely inhibit H_2-consumption, and it is conceivable that the normal completely inhibiting concentration (i. e., about .5% at most) may not, under certain circumstances, be entirely effective. From any or all of these numerous reasons it appears to be reasonably safe to conclude that hydrogen never reacts to a measurable extent directly with ordinary oxygen.

[2] The designation "ordinary" oxygen is used to distinguish it from oxygen which might appear in such an equation as $CO_2 + H_2O \rightleftarrows CH_2O + O_2'$, where O_2' is *not* in equilibrium with the ordinary oxygen supplied in the reaction chamber but is activated in the sense that hydrogen may react with it. It actually may be a gas, or a peroxide form, etc., hydrogen acting as an oxygen accepter.

[3] Cultures of washed heavy cell suspensions of the organisms in a medium from which carbon dioxide and carbonate were excluded yielded a ratio of hydrogen to oxygen consumed of less than 2, about 1.8, but this can throw no light on the possibility of the direct water reaction taking place since a respiratory quotient of carbon dioxide to oxygen of less than 1 under these conditions could account for the result. Under such conditions of carbon dioxide—and therefore carbohydrate compound—starvation, a value of less than 1 is quite possible since bacterial proteins, and possibly to a very small extent fats, would be attacked, no compounds of the nature of organic acids being present, as Ruhland showed. Another explanation of the low $H_2:O_2$ ratio might be that the CO_2 derived from such respiration could then have been reduced again by the hydrogen, but not entirely, because of a partially efficient CO_2-absorbing alkali cup suspended in the reaction chamber which would have tended to remove some of the CO_2. With a respiration coefficient of 1, the observed ratio of $H_2:O_2$ of 1.8 would be accounted for if one eighth of the respired CO_2 was absorbed in the alkali, whereas if the respiration coefficient were less than 1, as suggested, alkali-absorption of even more than one eighth of the respired CO_2 could still leave the $H_2:O_2$ ratio of 1.8 accounted for. Using the Warburg apparatus Ruhland showed in fact that in the absence of H_2, CO_2, and HCO_3, but in the presence of O_2, large amounts of CO_2 were respired, the organic material being derived from the bodies of the organism themselves; in one experiment lasting only 5 hours, 6.4 mg. of bacterial dry matter gave off 2.1 mg. of CO_2.

organism. The remaining H_2 is a measure of the H_2 required to reduce the CO_2 to organic C found in the cells at the end of the experiment (Table I, Column 3). We see from Table I, Column 7 that this latter ratio, $(H_2-2O_2)/2CO_2$, is $(1169.22-(2\times455.21))/(2\times134.02)$, or $.966 \pm .012$.* The probable error has been calculated by means of the usual formula P. E $= (.6745\sqrt{\Sigma d/n})/\sqrt{n-1}$ on the ratios $(H_2-2O_2)/2CO_2$ obtained from each of the eleven individual experiments, without, however, making a slight additive correction of several per cent for the fact that only eleven experiments are involved. This ratio is to be compared with the theoretical free energy efficiency ratio calculated from thermodynamic data, and then yields a measure of the second law efficiency and reversibility of the reaction.

Fortunately the thermodynamic data for the involved coupled reactions in their standard states is of the highest order of accuracy, owing, no doubt, to the general importance of the reactions. The coupled reaction in the standard state

$$2H_2(g) + CO_2(g) = 1/6\ C_6H_{12}O_6(s) + H_2O\ (l) \qquad (1)$$

$$\Delta F^\circ = 1184 \qquad (2)$$

may be divided into its two components and the actual states of the reacting substances indicated.

$$2H_2(.35\ \text{atm}) + O_2(.06\ \text{atm}) = 2H_2O\ (l) \qquad (3)$$

$$\Delta F = \Delta F^\circ - RT\ \ln(.35)^2 - RT\ \ln(.06) - RT\Delta N$$
$$= (2 \times -56560) + 1250 + 1630 + 1780 = -108460 \qquad (4)$$

where $\Delta F^\circ = (2 \times -56560)$; $RT\Delta N$ is a factor correcting for the circumstance that the reaction takes place at constant volume (i.e., without external work), N being the mol volume change, in this instance -3; and the stated pressures of the gases are the averages between the initial and final pressures in each of the eleven experiments.

$$CO_2(.06\ \text{atm}) + H_2O\ (l) = 1/6\ C_6H_{12}O_6(10^{-6}M) + O_2(.06\ \text{atm}) \qquad (5)$$

$$\Delta F = \Delta F^\circ - RT\ \ln(.06) + RT\ \ln(.06) + RT\ \ln(10^{-6})^{1/6}$$
$$= 114300 + 1630 - 1630 - 1365 = 112935 \qquad (6)$$

where $\Delta F^\circ = 114300$, and the activity of glucose is considered to be that of about 1/1000 the average cell carbon in 50 cc. of medium (and the maximum solubility of glucose 5M), i.e., (1/1000) (10 cc. /2) (1/22400) (1000/50 cc.) (1/5 M) = ca. 10^{-6} M per $(C_6H_{12}O_6)$.

*The same value might have been obtained in a more roundabout manner by dividing the total hydrogen consumption by twice the total carbon dioxide reduced as obtained from the observed reduction (as organic carbon) plus that amount corresponding to the loss through oxygen consumption. The latter amount is equal to the oxygen consumption multiplied by the factor of about 1.03 obtained from stoichiometric considerations. Other ratio arrangements of known quantities in the three equations (1), (3), and (5) also yield the same result. See also footnote p. 439.

However, from the experimental data, the empirical formula of the reduced CO_2 as in equation (5) is not $(C_6H_{12}O_6)$ but $(C_6H_{12x}O_6)$ where x is slightly less than unity, $(1169.2-(2\times455.21) - 134.02)/134.02$, or .931, i.e., (cc. H_2 actually consumed, minus cc. H_2 appearing as H_2O as a result of combining with the O_2 lost from the gas phase of the system, minus cc. H_2 appearing as H_2O as a result of combining with one half the O_2 in CO_2 as in equation (1))/(cc. H_2 theoretically combined with C as in glucose). This gives for the true free energy of reduction of CO_2, $.931 \times 112935 = 105140$. This assumption involving the method of deriving a conversion factor for obtaining the free energy of reduction of $C_6H_{.931\times12}O_6$ from $C_6H_{12}O_6$ is the most uncertain element in the second law efficiency calculation.* What is indicated literally is that equation 5 should read

$$CO_2(.06\text{ atm.}) + .931\ H_2O(l) = 1/6\ C_6H_{.931\times12}O\ (10^{-6}M) + 1.931/2\ O_2(.06\text{ atm.});\ \Delta F = 105140 \qquad (5')$$

i.e., that $(100 \times (1.000-.931))$, or 6.9%, less H_2O must be decomposed to yield the necessary H_2 to reduce the CO_2.

In accordance with Equation 4 the oxidation of 2 mols of H_2 can furnish 108460 cal. of free energy. In accordance with Equation 5' the reduction of one mol of CO_2 requires a slightly smaller amount. Hence we should expect the following relation between the numbers of mols (or cc.) involved,

$$\frac{(\text{No. of mols } H_2 \text{ needed})}{2 \times (\text{No. of mols } CO_2 \text{ reduced})} = \frac{105140}{108460} = .970$$

On the other hand, as has been shown, in accordance with Table I Column 7, the experiments gave

$$\frac{(\text{No. of mols of } H_2 \text{ used})}{2 \times (\text{No. of mols } CO_2 \text{ reduced})} = .966 \pm .012$$

Hence there was apparently very slightly less hydrogen oxidized than was necessary to produce the available energy needed for the reduction of CO_2, the efficiency of the process being

$$100 \times \frac{.970 \pm .000}{.966 \pm .012} = 100.4 \pm 1.2\%,$$

if one assign a probable error (in distinction to any other type of error) of $\pm .000$ to the thermodynamic data.

We see thus that (1) the reduction of carbon dioxide by hydrogen is a highly reversible, and if the figures be taken literally, perfectly reversible

*Ruhland showed that no more than traces of fats or anaerobic carbohydrate decomposition products such as organic acids were detectable in culture of *B. pycnolicus* growing under autotrophic conditions. Burk and Lineweaver (18) have shown that the energy change from ammonia and glucose to bacterial protein involves only a small fraction of the combustion energy of the glucose, one to two per cent, ordinarily.

process,* and (2) the second law is not transgressed,** since the free energy efficiency is not significantly greater than 100%. The exact agreement can not, of course, be taken too literally, both on account of the experimental and probable errors involved in Ruhland's work and the thermodynamic calculations,† and the important assumption made that the free energy of reduction

*By perfect reversibility is here meant the perfect reversibility of the isolated process of stored carbon dioxide reduction, and that *all* of the free energy of hydrogen oxidation concerned has been stored in the free energy of the stored reduced CO_2, rather than being converted irreversibly into a certain amount of heat. A certain amount of heat is of course given off in the isolated process since ΔF of Equation (3) is considerably smaller than ΔH.

It is important to note that the ratio $(H_2 - 2O_2)/2CO_2$ gives no indication as to the possible extent of any direct reaction of hydrogen with ordinary oxygen; evidence on this point must be derived from other experimental sources (see footnote p. 436). The independence of this ratio from the amounts of hydrogen which might react directly with ordinary oxygen may be shown as follows:

Let us assume that the major reactions which accompany the life processes of the bacteria are

$$1.93\ H_2 + CO_2 = 1/6(C_6H_{12}O_6) + H_2O \qquad (a)$$

$$1/6(C_6H_{12}O_6) + 1.93/2\ O_2 = CO_2 + .93\ H_2O \qquad (b)$$

$$2H_2 + O_2 = 2H_2O \qquad (c)$$

Let x = no. cc. H_2 used in (a)
y = no. cc. reduced CO_2 used in (b)
z = no. cc. H_2 used in (c)

Then the total no. of cc. of H_2 used is $H_2 = x + z$

The total number of cc. O_2 used is $O_2 = \frac{1.93}{2} y + \frac{z}{2}$

The net no. of cc. of reduced CO_2 is $CO_2 = \frac{x}{1.93} - y$

Combining we obtain

$$\frac{(H_2 - 2O_2)}{2CO_2} = \frac{x + z - 1.93y - z}{2/1.93x - 2y} = \frac{x - 1.93\,y}{2/1.93\,x - 2y}$$

with the complete elimination of z, the number of cc. of H_2 reacting directly with ordinary O_2. The value of the fraction $(x - 1.93y)/(2\,x/1.93 - 2y)$ is, of course, by experiment .966, from thermodynamic data .970.

**It might be thought that perhaps the value of the ratio $(H_2 - 2O_2)/2CO_2$ is approximately unity merely as a necessary consequence of the major reactions that accompany the life of the bacteria. This is true, however, only so far as the second law *holds*. It is just this circumstance which permits the data to become a test of the law. Let us conceive of a case of transgression. If the organisms were able to make some such reaction as Equation 5, which requires a large amount of free energy, proceed spontaneously by means of heat energy taken from the surroundings in temperature equilibrium with themselves, they could then either store up free energy potentially as cell material or use the energy by recombustion. In the latter case no chemical change would be evident. In the former case, in addition to the chemical change involved in the cell material appearing, a certain amount of "ordinary" oxygen would have appeared which would not react with hydrogen. What the efficiency of 100% indicates is that the amount of CO_2 actually reduced is not greater than that permitted by the free energy of oxidation of hydrogen after all extraneous but perfectly clearcut losses of hydrogen (in this instance by indirect reaction with oxygen) have been accounted for. In other words, no reaction such as $CO_2 + H_2O = CH_2O + O_2$ has taken place spontaneously. Had it occurred the experimental ratio would have sunk below .966. We must conclude from the fact that the observed second law efficiency is 100% either that (1) the second law is not transgressed, or that (2) another chemical reaction (in the case under discussion one involving hydrogen) occurs in such a manner as to be exactly compensating with respect to both sign and magnitude. The latter possibility, which would involve reduction by hydrogen of the inorganic salts or the production of highly hydrogenated gaseous organic compounds, was not observed to take place.

†The free energy required in concentrating the salts from the culture medium into the cells would be negligible, calculations indicating that probably .1%, at most, of the free energy of CO_2-reduction would be involved, in such a direction, if at all, as to increase the efficiency from 100.4% to 100.5%. There are a number of other similar very minor factors involved such as changes in surface tension, pellicle formation, etc.

of carbon dioxide is exactly 105140 cals. per mol, whereas a value even two or three per cent different is conceivable. In any case, there can be no question but that the reaction is highly reversible and that an enormous difference obtains between the maximum machine efficiency and the second law efficiency, namely, a difference of between 28.4% and 100.4%. This difference, it may be stated again, is owing to the energy required to produce a given weight of dry matter (see Buchanan and Fulmer, 11a).

TABLE I

Ratio of Gases consumed by *Bacillus pycnoticus*. (From Ruhland).

Column / Exp. No.	1 H_2	2 O_2	3 CO_2*	4 H_2/CO_2	5 H_2/O_2	6 $O_2:CO_2$	7 $(H_2-2O_2)/2CO_2$
2	137.82	52.75	16.90	8.15	2.63	3.12	.956
3	111.48	44.72	10.40	10.72	2.50	4.30	1.060
4	89.48	39.06	6.20	14.42	2.29	6.30	.916
15	87.92	41.15	3.00	29.31	2.14	13.7	.937
19	91.21	40.71	5.30	17.20	2.24	7.68	.924
22	103.20	39.39	13.10	7.88	2.62	3.01	.932
28	29.51	10.58	4.31	6.84	2.79	2.45	.969
29	85.20	30.64	10.89	7.84	2.78	2.82	1.098
30	113.13	40.71	17.01	6.65	2.78	2.39	.932
31	94.93	34.12	13.87	6.85	2.78	2.46	.962
32	225.34	81.38	33.04	6.83	2.78	2.46	.947
Total	1169.22	455.21	134.02				
Average	106.29	41.38	12.18	8.71	2.56	3.40	.966 ± .012
Relative	8.71	3.40	1				

* This refers to the C in the cells; i.e., reduced CO_2.

Indeed, an independent roughly quantitative demonstration of the operation of the second law might be based upon the dry matter requirement of *B. pycnoticus*. In the case of most bacteria and yeasts, etc., deriving their metabolic energy from respiration, three to six grams of glucose (or about 12000 to 24000 cals. of free energy) are required under the most favorable conditions to produce one gram of dry matter. The figures in Table I Column 6 show that these limits quite neatly cover the requirements of *B. pycnoticus*, which, of course, likewise obtains its energy of growth directly from respiration quite comparably to the bacteria and yeasts. In other words, since the machine efficiency is 29%, 29 + 71 cc. of reduced CO_2 are required to produce 29 cc. of stored reduced carbon dioxide, or 29 + 71 grams of sugar are required to produce approximately 29 grams of hydrogen bacteria, or a ratio of 3.4, which agrees with the best values derived from Column 6, where (O_2 :

CO_2) + CO_2 = 2.4 + 1 = 3.4, showing that the inefficiency of the bacteria considered as a machine for storing reduced CO_2 is entirely taken care of by its normal metabolic needs as judged by the needs of comparable organisms, and hence that the reversibility of the hydrogen-carbon dioxide reaction must be fairly high. Conforming to this view, the reason why the other known types of autotrophic bacteria all have much lower machine efficiencies (11, p. 104) is with little doubt owing to the fact that they also require much more energy to produce a given weight of dry matter.

It must be remembered in regard to the experimental data that the probable error of the mean, ± .012, is quite small in view of the facts that in the different experiments the H_2 consumed varied 8-fold (225 to 29 cc.); O_2 consumed 8-fold (81 to 10 cc.); organic carbon produced 11-fold (33 to 3 cc.); initial pH from 7.5 to 6.5; duration 11-fold (34 to 3 days); ratio of H_2 to O_2 used 2.79 to 2.14; ratio of H_2 used to CO_2 reduced 4-fold (29.1 to 6.6); and the rate of growth (final amount of organic matter produced per total time) 58-fold (5.2 to .09 cc. of organic C from CO_2 per day), as is shown for the most part by Table I. This shows that the wide variations in the ratio of total hydrogen to total carbon dioxide as given in Table I Column 4 are owing to variations in conditions of cell metabolism processes and not to variations in conditions of the efficiency or reversibility of the isolated coupled reaction of hydrogen oxidation—carbon dioxide reduction.

Attention should be drawn to the fact that the theoretical ratio based upon standard rather than actual free energies (as given in Equations 4 and 5[1]), uncorrected by the factor .931, is .990, not greatly different from .970; also to the fact that were the experimental ratio calculated from the five best experiments where the highest machine efficiencies were obtained (i.e., Nos. 28-32 where the ratio of H_2 to CO_2 was only about 7 to 8) it would be .968 ± .020, or little different from .966 ± .012 except for an increased probable error.

Finally, additional support for the second law is to be found in the opportune circumstance that the theoretical ratio is much smaller when based upon heats of reaction rather than upon free energies. The heats of reaction corresponding to Equations 3 and 5 are (2 × −68270) and 112300. Hence

$$\frac{\text{(No. of mols } H_2 \text{ needed)}}{2 \times \text{(No. of mols } CO_2 \text{ reduced)}} = \frac{112300 \times .931}{2 \times 68270} = .762.$$

In other words, if the entropy considerations of the second law be neglected, then, on the basis of heats of reaction, the biological machine could use (.970−.762)/.970, or 22% less cc. of H_2 per cc. of CO_2 consumed than calculated previously. We see, however, that the observed ratio is not significantly less than the minimum allowed by the second law, and hence the actuality of the latter's operation is somewhat strikingly indicated. Here is an interesting refutation of the Thomsen-Berthelot principle supplied by experimental observations on a living process rather than by *a priori* generalizations such as those of Guldberg and Waage, etc.

Summarizing,* we may say that it has been shown to within an accuracy of about 1% that (1) the second law of thermodynamics operates during the reduction of carbon dioxide by hydrogen,** granting the one assumption regarding the exact free energy of reduction of carbon dioxide, and (2) the reversibility is one hundred per cent (i.e., all the consumed H_2 reacts with CO_2 and none of the free energy of the isolated reaction is irreversibly converted into heat), granting further that the writer has given sufficient proof that the oxygen consumption is totally accounted for by respiration. There seems to be no reason to suppose that both the assumption in the first case and the proof in the second case do not hold rather exactly. In any event it is hardly conceivable that they are quantitatively inexact to such an extent as to affect the order of accuracy to more than a few per cent, possibly ten per cent,† rather than one per cent as stated. Even so, an experimental accuracy of to within 10% in the determination of the operation of the second law is far better than obtains in the cases of other known comparable coupled biological reactions involving large amounts of free energy.

*It may be well now to briefly summarize the chief experimental data. (1) and (2), the hydrogen and carbon dioxide consumptions are known, which permit calculation of the machine free energy efficiency. (3), the oxygen consumption is known, which permits calculations of the second law free energy efficiency by correcting for the irrelevant losses of simultaneous extraneous metabolism. (4), hydrogen does not react with ordinary oxygen, which indicates high reversibility. (5), the difference between the machine and second law efficiency is confirmed as to order of magnitude by the probable free energy requirement of dry matter formation. In addition (6), it is to be observed that the chemical free energy of the hydrogen oxidation can be transferred consequentially only into either chemical free energy in reduced CO_2 compounds, or into heat.

**It is possibly an interesting observation that particularized proof of the second law for animate nature as given here is about a century less advanced temporally than particularized proof of the first law for inanimate nature. It is, of course, just one hundred years since Carnot first stated that the quantity of energy (motive power) in nature is invariable and *indestructible*, however much it may be changed from one form into another, and determined the mechanical equivalent of heat, some fifteen years before Sequin, Mayer and Joule. Although Rumford determined the mechanical equivalent of heat about 1798 to within twenty per cent of the correct value, he apparently did not correlate this with the idea of the *indestructibility* of energy, which is the essence of the first law as announced by Carnot, and a little later by Mayer, Grove, Helmholtz, Joule, Colding, and others. The equality, as distinguished from the proportionality (or some other function), between heat and work appears to have escaped conception and particularized proof until the later years of Carnot's life. Newton's Query 30 "Are not gross Bodies and Light convertible into one another?"can hardly be considered an anticipation of either of the laws of Conservation of Energy or of Mass, since neither the query nor the discussion following it imply a quantitative (as distinguished from a qualitative) convertibility, which, again, is the essence of these laws, just as by the Atomic Theory is meant Dalton's quantitative demonstration. Newton (Opticks, 2nd Ed., 1718, p. 373) unconsciously portrays the conception of the destructibility of energy maintained for centuries previous to the last one in his statements, "there is not always the same quantity of Motion in the World—Motion is always upon the Decay—if two equal Bodies meet directly *in vacuo* they will lose all their Motion (if elastic they will lose all but what they recover from their Elasticity) . . . .". While these clauses are possibly true, there is no implication that the lost motion is quantitatively converted into something else; it has been considered destroyed. For the same reason it can hardly be said that the Second Law is anticipated by the second very suggestive clause quoted, nor by the similar one (p. 375), "the variety of Motion in the World is always decreasing". Unusefulness is very different from total destruction. For an excellent historical review of work on the first and second laws between the years 1830-1880 see Planck "Das Princip der Erhaltung der Energie" (1921).

†See previous remarks concerning the energy requirement of growth. The growth energy must be derived from the reaction between oxygen and organic matter, i.e., from respiration, and it has been shown that in the case of *B. pycnoticus* the oxygen consumption no more than covers the approximate growth energy requirement, i.e., little or none is directly available for direct oxidation of hydrogen. See also footnote, page 436.

Autotrophic Methane Oxidation

The methane-oxidizing organisms are very similar to the hydrogen-oxidizing organisms, being facultatively heterotrophic and apparently yielding, under autotrophic conditions, fairly high machine free energy efficiencies as large as 30% (11). If the available data (17a) be taken literally the second law is not obeyed, however. In one experiment (in which the organisms were grown in an inorganic medium containing ammonium salts as a source of nitrogen and in an atmosphere of one part of methane to two parts of air), 225 cc. of methane and 148.7 cc. of oxygen were consumed, producing 99 cc. of CO_2 and an unmeasured amount of organic carbon, according to the equation:

$$225\ CH_4 + 148.7\ O_2 = 99\ CO_2 + 126\ CH_{2x}O_y + x'\ H_2O \qquad (10)$$

where x, x', and y are unknown constants, $(x+x') = 225$, and the value 126 has been derived from $(225-99)$. Now 99 cc. CO_2 correspond to 99 cc. O_2, leaving only $(148.7-99)$ or 49.7 cc. O_2 to have formed both the water and organic matter. If no water were formed, the organic matter would have the formula (with respect to C, H, O, neglecting N, S, P etc.) $C_{126}H_{900}O_{99.4}$, or approximately $C_5H_{36}O_4$. If any water were formed the organic matter would still possess closely the same degree of reduction with respect to the valence of carbon. Such formulas, or degrees of reduction, while not experimentally disproven, are not only practically inconceivable, physiologically, but correspond to a second law efficiency of about 170%,[1] if it be assumed, as in the case of other bacteria, that the degree of reduction of carbon corresponds to glucose or thereabouts. Either the second law has really been transgressed or some unobserved reaction has taken place, probably a gaseous one involving H_2, N_2, CO, etc. The production of hydrogen gas, or its incorrect estimation as methane could entirely account for the discrepancy, not to mention, of course, sheer mistakes in determining oxygen and carbon dioxide or the undetected appearance of hydrocarbons such as C_2H_6, etc. The rather meager data on methane bacteria are discussed here not so much with respect to proof or disproof of the second law, but to show how, granting the applicability

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[1] Even considering no water formed in Equation (10) we have, after neglecting the respiration CO_2 formed which yielded only heat energy,

$$126\ CH_4 + 49.7\ O_2 + 26.6\ H_2O = 126\ CH_2O + 152.6\ H_2 \qquad (11)$$

In other words, some of the oxygen used to oxidize the methane to CH_2O is not atmospheric gaseous oxygen but must be conaidered as derived from bound oxygen, as in water, at no expense of energy and therefore contrary to the second law. Without troubling to distinguish between standard and actual free energies, Equation (11) may be split into two components

$$126\ CH_4 + 126\ O_2 = 126\ CH_2O + 126\ H_2O;\ \Delta F^\circ = (126 \times -80700) \qquad (12)$$

$$49.7\ O_2 + 152.6\ H_2O = 126\ O_2 + 152.6\ H_2;\ \Delta F^\circ = (152.6 \times 113120) \qquad (13)$$

yielding a second law free energy efficiency of $(152.6 \times 113120)/(126 \times 80700)$, or 170%. The increase of 70% over 100% is owing to the fact that $((152.6 \times 113120) - (126 \times 80700))/126$, or 56200 cal. of heat energy in the environment are employed contrary to the second law in changing a mol of CH_4 and H_2O to CH_2O and H_2.

of the latter, the second law efficiency calculations may be very useful in detecting impossible, improbable, or incomplete experimental biological data.[1]

In the only other experiment performed by Söhngen for which data are given, 161 cc. CH_4 and 193 cc. O_2 were consumed and 90.8 cc. of CO_2 were formed, yielding a second law efficiency very much less than one hundred per cent. Here, as may be shown, far too much oxygen is consumed, unless the organic material formed be assumed to correspond to an average degree of oxidation of practically HCOOH instead of CH_2O (even with no H_2 being produced), which circumstance, while not inconceivable, is most improbable. The machine efficiencies for both experiments were respectively 33.8 and 25.8% (11); yet, because they take no account of oxygen consumption, they give no inkling that (granting the second law) the data are incomplete as they stand, if not incorrect. This point is especially interesting when it is considered that the two experiments are unsatisfactory in opposite directions.

TABLE II

Effect of Initial pH upon Hydrogen Consumption (From Ruhland).

Exp. No.	Length of Exp. (days)	H_2 Consumed (cc.)	Initial pH
25	3	5.51	6.3
26	5	16.01	6.5
24	5	45.52	6.9
28	3	29.51	7.2
27a	4	35.49	—

The inaccuracy and extent of the experiments in the case of methane bacteria are not to be compared in any sense with those of hydrogen bacteria, and the poor data in the former case cast no reflection on those in the latter case. Consideration of the methane oxidation case has illustrated some common difficulties met with in attempting to apply the second law to any particular biological case.

Heterotrophic Nitrate Reduction

The non-photochemical reduction of nitrate to ammonia by the green alga Chlorella has been studied by Warburg and Negelein (19). In this case the energy is derived from the oxidation of carbohydrate, rather than from the oxidation of hydrogen. The free energy of the nitrate-ammonia reaction under Warburg and Negelein's experimental conditions

$$NO^-_3(0.1M) + H_2O\ (l) + 2H^+(0.01M) = NH^+_4(0.005M) + 2O_2(0.2\ atm) \quad (7)$$

[1] The showing by the writer (13), for example, that the free energy of glycogen-lactic acid breakdown in muscle is considerably smaller than the theoretical maximum work of muscle as obtained by the tension length diagram area method has led, in part, to the discarding of this method of measurement of the theoretical maximum work, in favor of the heat liberated in relaxation.

is +68000 cal. (19). The energy relations are, interestingly enough, approximately the same as those obtaining in the case of the reduction of nitrogen to ammonia (i.e., nitrogen fixation) by carbohydrate, where the free energy required is +73800 (18).

The approximate maximum possible yield obtainable in the coupled nitrate reduction and carbohydrate oxidation reactions, employing Warburg's value for the free energy of combustion of glucose (−690000), calculates to be (690000/6)/68000, or a ratio of 1.69 mols of NH^+_4 per mol of CO_2 formed. The observed ratio (Table III, Protokolle 12, 13, 14) was, under *optimum* conditions, i.e., after about the third hour, .193 (Table III, Protokoll 13C), or a maximum machine free energy efficiency of ammonia production of .193/1.69, or 11.5%. Under infra-optimal conditions, i.e., during the first and second hours, the efficiency was also found to be zero independently of time under any conditions of high pH, i.e., greater than pH 2; no ammonia was produced by cells maintained in (a) 0.1 N $NaNO_3$, (b) 0.1 N Na_2SO_4 − 0.01 N H_2SO_4, (c) 0.1 N KH_2PO_4, or (d) Knop's solution containing nitrate (Table III, Protokolle 3, 4, 5, 6). In these latter solutions the respiration quotient was 1, within experimental error, although under conditions of ammonia formation the quotient ordinarily rises to about 1.7 (Table III, Column 5).

The efficiency thus calculated has included the energy represented by the CO_2 of normal metabolism as well as that involved in NH^+_4 formation, and is therefore the machine efficiency by definition. When the CO_2 of resting or normal metabolism (i.e., that amount given by the oxygen consumption since the normal respiration quotient is 1) is excluded, the maximum observed ratio of (mols NH^+_4)/(mols extra-CO_2) reached .532 (Table III, Protokoll 13C) corresponding to a maximum second law efficiency of ammonia production of .532/1.69, or 32%.* Here again the second law efficiency may decrease to zero under the same two conditions governing the decrease of the machine efficiency to zero.

Warburg and Negelein (19, Protokoll 7) show that the rate of oxygen consumption is increased about 40% during the first hour when the organisms are maintained in .1 N $NaNO_3$ − .01 N HNO_3 instead of in Knop's solution. Strictly speaking, this might mean that the maximum second law efficiency of about 32%, as calculated, should be about 48% less (i.e., $\frac{(.4 \times 100)}{(1.4 \times 1.6) - 1.4}$, where .4 is the relative increase in oxygen consumption, 1.4 is the relative total oxygen consumption, and 1.6 is the respiration quotient), were it not for the fact that the oxygen consumption rate decreases (see Table III,

*The second law efficiency here calculated to be 32% was approximately that given by Warburg and Negelein (19, p. 383) and Meyerhof (20, p. 95). These workers did not calculate the machine efficiency (reaching a maximum of 11%), and failed to indicate that the efficiency they obtained was not to be compared with the efficiencies for autotrophic processes where, so far as the writer is aware, the efficiencies given in the literature have always been machine and not second law efficiencies. For example, the nitrate-ammonia second law efficiency of 32% is not to be compared with the machine efficiency of nitrification found by Meyerhof (20) to be 6%.

TABLE III

Data concerning Nitrate-Ammonia Reduction (from Warburg and Negelein).

Col. 1	2	3	4	5	6	7	8	9	10	11	12
Proto-koll	Expt.	Time (hr)	O_2 cmm. consumed	$\frac{CO_2}{O_2}$	Total CO_2 (cmm.)	Extra-CO_2 (cmm.)	NH_3 10^{-6} mols	Mols NH_3 to mols total CO_2	Mols NH_3 to mols extra-CO_2	Machine efficiency %	Second law efficiency %
12[v]	a	1st	365	1.74	635	270	1.0	.0352	.0823	2.09	4.90
	b	2nd	293	1.81	530	240	3.0	.127	.280	7.55	16.6
	c	3rd	258	1.63	815	320	6.0	.164	.420	9.8	25.0
		4th	241								
13[v]	a	1st	233	1.70	396	163	1.2	.0565	.165	3.36	9.82
	b	2nd	201	1.74	350	149	1.2	.0767	.180	4.56	10.7
	c	3rd	178	1.57	279	101	2.4	.193	.532	11.5	31.6
14[v]	a	1st	253	1.62	409	156	0.9	.0493	.129	2.93	7.68
	b	2nd	226	1.62	365	139	1.3	.0798	.209	4.75	12.4
	c	3rd	201	1.43	288	87	1.8	.140	.464	8.34	27.6
3[w]	a	1st	102	1.03	105	1	0	0	0	0	0
4[x]	a	1st	102	1.04	106	0	0	0	0	0	0
5[y]	a	1st&2nd	65	1.03	67	2	0	0	0	0	0
6[z]	a	1st&2nd	38	1.00	38	0	0	0	0	0	0

[v] Low pH (i.e., 2) with nitrates (.1N $NaNO_3$ – .01N HNO_3).
[w] High pH (i.e., >2) with nitrates (.1N $NaNO_3$).
[x] Low pH without nitrates (.1N Na_2SO_4 – .01N H_2SO_4).
[y] High pH without nitrates (.1N KH_2PO_4).
[z] High pH with nitrates (Knop's solution).

Column 2) by the third hour (when the maximum efficiencies are obtained) to about normal so that the correction is probably unnecessary (but see later discussion). It is obvious that the second law is obeyed so far as ammonia production is concerned, since the second law efficiency is considerably less than 100%.*

It is practically impossible to derive any satisfactory proof of the second law in the case of nitrate reduction as a whole, as will now be shown. Too many assumptions would be involved, in the absence of experimental data. The chief difficulty lies in the fact that Warburg and Negelein give no data to show that the ammonia produced under optimum conditions of efficiency corresponds stoichiometrically with the nitrate disappearing (nor did they analyze the cells for increase in organic nitrogen). Such determinations would be very difficult to carry out, of course, since it would mean measuring decreases of roughly 10^{-5} to 10^{-6} mols out of 10^{-1} mols of nitrate per liter of

* The writer would venture to suggest a means of predicting the probable maximum second law efficiencies to be expected in cases of isolated coupled reactions, making the assumption, of course, that the second law holds. In the case of nitrate reduction, we have, approximately,

$$H^+ + HNO_3 + H_2O = NH^+_4 + 2O_2;\ \Delta F = 68000$$
$$X\,O_2 + X\,CH_2O = X\,CO_2 + X\,H_2O;\ \Delta F = -X\,115000$$

where with perfect reversibility X would equal 68000/115000, or .59. It will be observed, however, that experimentally the mechanism proceeds corresponding to X equals at least 2, the least number of oxygen molecules in the equation requiring energy.

Similarly, in the case of hydrogen oxidation we have approximately,

$$CO_2 + .93\,H_2O = 1/6CH_{1.33}O + 1.93/2\,O_2;\ \Delta F = 105140$$
$$X\,O_2 + 2X\,H_2 = 2X\,H_2O;\qquad \Delta F = -X\,108460$$

where the perfect reversibility X would equal 105140/108460 = .97 and again it will be observed that experimentally X actually equals at least .97, the least number of oxygen molecules in the equation requiring energy.

In other words, in both cases, the maximum amount of free energy-yielding reaction taking place is possibly determined not only by the amount of free energy demanded in the free energy-requiring process in accordance with the second law, but also by the stoichiometry of the latter. Expressed in more strictly chemical terms, *all* the incidental compound produced in the free energy-requiring reaction (in the above particular cases oxygen) must, by virtue of the mechanism chosen by the organism, be consumed in the free energy-yielding reaction.

This "biochemical reversibility principle" stands in much the same relation to the second law as the second law does to the first, namely, as conditioning the convertibility of energy from one form into another, and states that of the free energy available in the free energy-yielding reaction of a coupled reaction taking place in a biological system only a fraction of this is available under biological conditions, the loss of availability being determined by stoichiometric considerations. The greater the free energy of the free energy-requiring reaction in proportion to the free energy of the properly stoichiometric free energy-yielding reaction, the greater will be the maximum reversibility and second law efficiency, up to 100%. An analogous, but not in all respects similar principle is employed by Warburg in explaining the varying efficiencies of different wave lengths of visible light in the photosynthetic reduction of carbon dioxide, where $N_0h\nu$ grows proportionally to ν, while U, the energy required remains constant, so that the efficiency must vary with wave length. While the "biochemical reversibility principle" has been proposed upon the experimental basis of only two cases, it is to be observed that the two cases present widely different reversibilities (namely 32 and 100 per cent), which is in favor of the principle. It is not anticipated that invariable applicability will necessarily obtain. The word principle has been used in the sense of being a generalization of experience applying in a number of cases, in distinction to the word law, which is a relation of phenomena invariable under given conditions. Without going into detail it may be stated that according to this principle the reversibilities of isolated autotrophic reductions of carbon dioxide should approximate perfection, whereas the reversibilities of heterotrophic consumptions of organic carbon compounds should usually be fairly low i.e., 0 – 50%, and, so far as is known, this is the case.

solution. Without either this information or calorimetric measurements (see later) it is impossible to properly account for the (100 − 32%), or 68%, efficiency loss, i.e., to know whether the loss can be explained upon the basis of other reduction products (involving storage of chemical free energy) or heat evolution; we know the second law efficiency of ammonia production but not of nitrate reduction as a whole (i.e., reduction to ammonia and other nitrogenous compounds).

It was shown that normally no appreciable amount of ammonia is to be found inside the cells, and that NO, N_2, and NO_2 were not produced. The possibility of numerous other likely intermediate nitrogen compounds was, however, not experimentally excluded (i.e., by chemical analysis) and there can be no question that during the first hour or two of ammonia production part of the reduction products do not appear as ammonia but are built into the cell tissue (Table III, Protokolle 12, 13, 14), since it was shown that cells which had been previously starved for nitrate and then placed in nitrate solution at pH 7 gave high respiratory quotients of 1.7 etc., without, however, producing ammonia (19, Protokolle 16, 17). The total extra cellular ammonia nitrogen content never rose much above 5×10^{-6}M whereas the concentration of organic cell nitrogen in algal cultures may attain values one thousand times as great. Judging from this evidently small percentage of nitrogen appearing as ammonia, it is possible therefore that even under conditions of maximum observed efficiency there are nitrate-reduction products which do not appear as ammonia but disappear in assimilation, the observed concentrations of ammonia merely representing balances between ammonia production and assimilation. Now the aforementioned decrease in rate of oxygen consumption to normal by three hours might have occurred because the organisms were able to make some such reaction as Equation 7 take place spontaneously without any corresponding expenditure of energy upon their part; the oxygen given out by such a reaction would tend to lower the observed rate of oxygen consumption (the decrease might be owing, of course, to any number of factors, such as decreasing concentration of respirable carbohydrate, lowered vitality of the cells, etc.). It should be pointed out also that the oxygen consumption continues to decrease to values much below normal (19, Table 19). On account of the unknown reason for both the initial increase and the subsequent marked decrease in rate of oxygen consumption, it is therefore unfortunately true that until it can be shown that the nitrate disappearing corresponds stoichiometrically either with the ammonia appearing or other reduction products of nitrate the possibility exists that the second law does not operate in nitrate reduction as a whole.

Still another possible difficulty arises from the fact that no efficiency data are available for periods of time later than the third hour, at which period the efficiency is increasing at a marked rate; indeed not only the first differential but also the second differential of efficiency with respect to time is increasing (Table III, Protokolle 13 and 14, Column 12). It is true that the decrease in oxygen consumption after three hours may explain how the

efficiency might increase after three hours, as it promises to do; i.e., after three hours the reaction may not take place according to

$$HNO_3 + H_2O + 2/6(C_6H_{12}O_6) = NH_4^+ + 2CO_2 - 162000 \text{ cal. (heat, see below)} \quad (8)$$

Some of the oxygen may then appear as gas, causing the observed decrease in rate of oxygen consumption, rather than reacting with carbon in carbohydrate. This explanation involves a sudden change of mechanism at the point where a 32% second law efficiency is attained and is therefore improbable. Warburg and Negelein offer an explanation for the increase of oxygen consumption when the cells are placed in the nitrate mixture at pH 2, but they take no note of the difficulties offered by the subsequent decrease, nor the difficulties presented by the promised increased efficiency after the third hour. The possibilities that either (1) some of the extracellular ammonia after the third hour is derived from breakdown of cell organic nitrogen (i.e., ammonification) or (2) the carbon oxidized corresponds to a reduction stage considerably different from that in carbohydrate, do not seem very probable, but must also be taken into consideration.

It is to be observed that the uncertainty in regard to proof of the second law consequent upon not knowing the stoichiometric relations in the case of nitrate reduction does not obtain correspondingly in the case of carbon dioxide reduction by hydrogen. Here, even if it had been true that the reversibility was not 100% (i.e., that some hydrogen reacted directly rather than indirectly with oxygen to form water), the proof of the second law would have been in no way affected since all the reactants of the then irreversible reaction, hydrogen and oxygen, would have nevertheless been accounted for, having disappeared in the ratio 2:1 as in water (see also footnote p. 439).

A fair approximation to proof of the applicability of the second law might be obtained from calorimetric measurements, i.e., it might be possible to show that the difference between 32% and 100% could be accounted for entirely as heat, providing ammonia was the only nitrogenous reduction product of nitrate. According to Equation (8), all of the oxygen given out according to Equation (7) has reacted according to Equation (5) (taking place in the reverse direction however), and that of the approximately 230000 cal. available per $2O_2$ only 68000 cal. have been converted into chemical work, the rest, about 162000 cal., appearing as heat. The measurement of this 162000 cal. has not been carried out calorimetrically, as yet however.[1]

[1] Meyerhof (20) performed a somewhat similar experiment in the case of autotrophic nitrification for the reaction $NO_2 + \frac{1}{2}O_2 = NO_3$. The machine efficiency as determined chemically was about 6%, and Meyerhof found as the average of a series of calorimetric experiments that the heat given off per mol of nitrate formed actually corresponded to about (100−6) or 94% of that given by the heat of reaction. Owing to the small efficiency yield, and the accuracy of calorimetric determinations in general, and, indeed, a number of other experimental uncertainties, this proof of the second law can not be considered very accurate, altho it is possibly as accurate as for any comparable coupled reaction case apart from autotrophic hydrogen oxidation. The calorimetric measurements in the nitrification case correspond to the oxygen consumption measurements in the hydrogen oxidation case; they determine directly or indirectly the metabolic energy. The nitrification case really presents a much better demonstration of the first law than the second, since all but approximately 5% of the chemical energy was converted into, and obtained as, heat, as required. Here it is not determining a quantity as a small difference between two large quantities, but rather comparing two large and nearly equal quantities.

Summarizing, we see that in the nitrate-ammonia reaction it is possible to calculate both the machine and second law free energy efficiencies (and therefore the reversibility and the applicability of the second law) as in the case of autotrophic hydrogen oxidation, but, owing to lack of certain data (i.e., data accounting for the difference between the maximum observed second law free energy efficiency and an efficiency of 100%), it is as yet impossible to test the applicability of the second law of thermodynamics to nitrate reduction as a whole. It has been found again that a large difference (about 3-fold) obtains between the two types of efficiencies. In other cases to be mentioned below such large differences will not always exist.

The Reversibility of Other Coupled Reactions

a. Partially Reversible Reactions

The non-reconversion of the potential energy of tension in isometric muscular contraction presents a case where the second law free energy is zero; where, so far as is known (see 13, p. 167) the process under anaerobic conditions is totally irreversible, all of the tension energy being converted into heat, rather than some being used to condense lactic acid back into a hexose, or into glycogen.

The anaerobic reconversion of lactic acid into glycogen is partially reversible, generally twice as much energy being consumed as required under ideal conditions, i.e., the second law efficiency is only about 50%. That is to say, when lactate is added to muscle in Ringer's solution, four to six molecules of lactate are reconverted per molecule of lactate burned to carbon dioxide, whereas according to the free energies involved about ten reconverted molecules are possible under perfectly reversible conditions.

The maximum second law free energy efficiency of aerobic muscular contraction (mechanical work done)/(chemical free energy consumed) is only about 15 to 25% (13), and according to the latest data of Hartree and Hill (25) the second law efficiency of anaerobic human arm muscle contraction reaches a maximum of about only fifty per cent, in the case of frog sartorius muscle contraction, thirty per cent. In the cases of the partially reversible reactions mentioned in this section, the machine efficiencies are practically as large as the second law efficiencies owing to the fact that the resting metabolism of the muscle is very small compared to the coupled reactions it carries out. This will also be true of other coupled reactions carried out by multicellular organisms, because the ordinary metabolic chemical energy liberated is much more organized and disciplined to subserve function. Brown (24) has shown, for example, that the "maintenance" metabolism of man is some 100 times as small as that of yeast per units of weight and time.

If the latest conclusion of Hartree and Hill (26) be accepted that the isometric relaxation heat represents the maximum mechanical work capable

of being performed by a twitched frog sartorius muscle under anaerobic conditions, then the second law efficiency (mechanical work)/(mechanical work + relaxation heat when work is done) = (mechanical work)/(isometric relaxation heat) may apparently reach the high value of 71% (26, Table II). Even under tetanic conditions (i.e., where the stimulus is continued for some time, .2 to .4 of a second), the corresponding second law efficiency attains values approximating 50% (26, Table IV, (d)/(d+f)).

The main thermodynamic work which microorganisms perform is that of growth.* Brown (24) has shown that when yeast is maintained at a concentration sufficient to prevent reproduction, the heat given off per gram of maltose fermented is 125 cal., whereas when growth is allowed to take place only 8.5% less heat is given off, 114.4 cal. It is likely that relatively little of this 114.4 cal. is necessary for true maintenance energy, since similar yeast juice containing no intact cells would give about the same value. Brown's findings confirm the view that the breakdown of carbohydrates, etc., by unicellular microorganisms is often if not usually conditioned chiefly by the concentration and activity of the cell enzymes necessary therefor and the concentration of carbohydrate, independently of whether the organisms are able to take advantage of the energy liberated. Wasted heat, as illustrated in the work of Brown, is chiefly the result of uncontrolled enzymes acting on an appropriate substrate, the organisms possessing no mechanism, as do multicellular organisms, for closely regulating the amount of substrate in contact with cell enzymes, and correlating most of the energy liberated with some vital function requiring free energy. The free energy efficiency of growth obtained by Brown (about 8.5%), it may be mentioned, is somewhat less than maximum values usually reported for yeasts, fungi, bacteria, etc., where, as has already been pointed out in discussing the amount of sugar required to produce a given weight of dry matter, the maximum efficiencies vary from about 15 to 30%.

In all these partially reversible reactions just discussed the same kind of difficulties in the way of proving the second law with regard to the processes involving the energy not appearing as work in the primary process obtains as in the case of nitrate reduction—too many assumptions become involved in the absence of all the necessary experimental data, which, it may be added, is often difficult or impossible to obtain. There is generally at least one unknown too many. We see how every much more difficult it is to prove the

* Angerer (22) and Ludwig (23) have shown that an inconsequential fraction of the metabolic energy of motile microorganisms is accounted for by motility, in the neighborhood of 0.1 per cent. Considering the relative amounts of energy involved in motility and Brownian movement by a single microorganism one might doubt that, although some organisms may be able to disobey the second law by in some manner converting the heat energy of Brownian movement into work, the amount of work so accomplished and gained would be significantly appreciable.

second law in heterotrophic rather than in the less complicated autotrophic coupled reactions.*

b. Highly Reversible Reactions.

There are a number of reactions occurring in biological systems which are highly reversible: chemical equilibria such as reactions between (1) haemoglobin and oxygen, (2) haemoglobin and methaemoglobin, (3) the respiration enzyme and oxygen, (4) the respiration enzyme and carbon monoxide, (5) hermidin and cyanohermidin, (6) reduced and oxidized echinochrome, (7) ordinary and active glucose (21), (8) hydrogen ion buffer systems, (9) nitrogen gas and an initially fixed form (18), and (10) succinic acid and methylene blue to give fumaric acid and leuco-methylene blue. Most of these reactions take place under approximately equilibrium conditions** and their free energy changes are consequently practically zero. It is also true that a number (i.e., (1), (2), etc.) are not coupled reactions in the sense used in this paper, since they do not involve a free energy storing process but only a heat change; in the case of hydrogen oxidation, for example, if hydrogen reacts with carbon dioxide, free energy is stored as carbohydrate (etc.) produced, and the reaction is coupled, whereas if hydrogen reacts directly with oxygen and the energy is given off as heat, no free energy is stored, and the reaction is not considered as coupled. Chemical free energy is considered as "stored" when the chemical substance or substances formed are still out of practical equilibrium with the environment (in the bacterial case, oxygen, i.e., carbohydrate would be out of equilibrium with oxygen, water, however, practically in equilibrium with oxygen).

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* If one were to set out to look for cases where the second law might not be obeyed in biological systems the most likely field, *a priori*, would lie in reactions involving small amounts of free energy, i.e., carbohydrate and protein hydrolytic equilibria, etc. A small shift in position of the equilibrium point would require little energy but could result in a large chemical change relatively easily detected. The difficulty of excluding extraneous free energy reactions would be greater, of course. Donnan's statement quoted previously was made with reference to systems of dimensions of the order of 10^{-14} ccm., or less; so that in order to consider a series of such systems amounting to macroscopic dimensions, it requires one additional logical step to suppose that the infra-microscopic systems might all fluctuate together simultaneously in such a manner that the second law would no longer be applicable to the macroscopic system as a whole. This logical step would, indeed, be the real issue awaiting test, since, beyond question, if the size of any one system is made small enough the second law as classically stated by Clausius could not apply. The utilization of fluctuations in the organized, non-random, and extensive manner indicated is to be classed as true perpetual motion of the second kind, whereas the occasional fixation of random fluctuations of the type indicated by Donnan would not necessarily involve such an implication, since compensation would in the long run probably take place.

** Although one can conclude from the fact that when equilibrium conditions exist the reversibility is very high or practically perfect, it does not follow, or course, that the second law is necessarily operating, since the biological machine (i.e., the organisms) may have shifted the equilibrium point without corresponding expenditure of energy upon its part. So far as the writer knows, there are no cases as yet where it has been shown that the equilibrium point is the same both in and out of the biological system, at least with any desirable degree of accuracy.

The second law efficiency of the photosynthetic process in plants whereby CO_2 is reduced to sugar may attain fairly high values. Thus in the simplest case as studied by Warburg and his co-workers, where all the incident light energy is absorbed by the photosynthesizing machine (Chlorella) a maximum efficiency of about 60% is obtainable. An accounting for the remaining unutilized 40% of the energy as heat (or possibly, in part, as other chemical energy) has not been made and it is conceivable (so far as present experiments may decide), although not probable, that the second law is not observed in some other reaction occurring simultaneously with sugar formation and that heat is being absorbed from the environment in addition to the radiation absorbed and that required by the second law. If the photosynthesizing process be considered from the standpoint of mechanism to form glucose and hydrogen peroxide, first, and then later glucose and oxygen, the second law efficiency of this first reaction considered as an isolated step, may approximate 100%. The final physiologically necessary change of hydrogen peroxide to oxygen and water would account for the subsequent loss of efficiency in the overall process.

Thus we see that in biochemical reactions there is a continuous range of reversibility between practically 100 and 0 per cents. In no case is perpetual motion of the second kind indicated.

Discussion

It has been shown that the numerous existing published efficiency data on certain autotrophic and other coupled processes often fail both (1) to test the applicability of the second law of thermodynamics to such processes, except in the crudest manner, and (2) to measure the reversibility of each of the processes *per se* apart from accompanying but extraneous, unrelated, normal metabolic processes of the microorganisms. It might be argued, in connection with the latter objection, that since these extraneous processes have always accompanied the coupled reactions, calculations correcting the machine efficiencies (i.e., the second law efficiencies as defined by the writer) are without point. However, this circumstance may not be true in the future. Indeed, attempts are being made to isolate important coupled reactions, so that if success should attend these efforts, then the extracellular efficiency will be the second law efficiency, and the machine efficiency will then, in turn, be without point. The problem is very real, and the determination of the second law rather than the machine efficiencies very necessary, therefore, regarding what would be the efficiency of a coupled process if it were isolated from the cells and carried on independently, and accordingly the title of this paper has been made to read "coupled reactions in biological systems" rather than "coupled biological reactions." In the case of nitrogen fixation, for example, the machine efficiency is only about one per cent, whereas the second law

efficiency is fifty to one hundred times this value (18), and there is good reason to believe that the process of fixation *per se* might be isolated and carried on independently of the organisms. No implication is intended, of course, that isolated coupled reactions will necessarily give exactly the same second law efficiency as when unisolated.

Summary

1. It has been the task of this paper to indicate the extent to which the applicability of the second law of thermodynamics to life processes has so far received direct *experimental* support. It is pointed out that, in general, critical data do not obtain.

2. The applicability of the law to autotrophic reduction of carbon dioxide by hydrogen has been shown to obtain very accurately to within an order of about one per cent, in the case of *Bacillus pycnoticus* Ruhland.

3. The reversibility of autotrophic reduction of carbon dioxide by hydrogen is practically perfect, $100 \pm 1.2\%$, when the extraneous energy consumed in the metabolic processes of the organisms is corrected for.

4. The reversibilities of the more important known coupled biological reactions have been described and summarized. Few, if any, attain 100% as in the carbon dioxide-hydrogen case.

5. It is shown that with respect to the possible thermodynamic free energy efficiencies of coupled reactions occurring in biological systems two fundamentally different types obtain: those in which the work done in any given reaction is compared to the total free energy dissipated by that reaction, and those in which the work done in any given reaction is compared to the total free energy dissipated by the organisms in carrying out all their life processes. The former has been termed the second law free energy efficiency and the latter the machine free energy efficiency.

6. The hydrogen bacteria constitute one of the few cases, if not the only case, where, with respect to the entire life processes of an organism, it has been possible experimentally to account for all the free energy consumed, with an order of one per cent, i.e., where it has been possible to draw a complete free energy balance sheet between the total free energy shown to have been utilized or dissipated by the organism and that known to have been consumed by the organism.

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June 28, 1930.

References

[1] Thomson: Proc. Roy. Soc. Edin., March 17 (1851).
[2] Grove: "The Correlation and Conservation of Forces," by E. L. Youmans: 82 (1865).
[3] Wand: Karl's Repertorium der Exp. Physik, 4, 390-400 (1868).
[4] Helmholtz: Sitzungsber. Akad. Wiss. Berlin, 1882, 34.
[5] Parker: Proc. Phil. Soc. Camb., 1892, Oct., 6.
[6] Parker: "Thermodynamics", 123 (1894).
[7] A. V. Hill: J. Physiol., 46, 469 (1913); Nature, 113, 859, 1924.
[8] Lewis and Randall: "Thermodynamics", Chap. 10 and 11 (1923).
[9] Guye: "Physico-Chemical Evolution" (1925).
[10] Lewis: "The Anatomy of Science", Chap. 6.
[11] Baas-Becking and Parks: Physiol. Rev., 7, 85 (1927).
[11a] Buchanan and Fulmer: "The Physiology and Biochemistry of Bacteria", 3, 185, lines 1-4 (1930).
[12] Donnan: J. Gen. Physiol., 8, 688 (1927).
[13] Burk: Proc. Roy. Soc., 104 B, 153 (1929).
[13a] Watson: Science 72, 220 (1930).
[14] Thomson: Trans. Roy. Soc. Edin., 16, 541 (1849).
[15] Helmholtz: "Ueber die Wechselwirkung der Naturkräfte", 25 (1854).
[16] Tait: "Sketch of Thermodynamics", 56-59 (1877).
[16a] Clausius: Pogg. Ann., 120, 426 (1863).
[17] Ruhland: Jahrbuch. wiss. Bot., 63, 321 (1924).
[17a] Söhngen: Centr. Bakt., (2) 15, 513 (1906).
[18] Burk and Lineweaver: To be published.
[19] Warburg and Negelein: Bio. Z., 110, 66 (1920).
[20] Meyerhof: "Chemical Dynamics of Life Phenomena" (1924).
[21] Clifton and Ort: J. Phys. Chem., 34, 855 (1930).
[22] Angerer: Arch. Hyg., 88, 139 (1919).
[23] Ludwig: Arch. Protistenkunde, 62, 13 (1928).
[24] H. T. Brown: Ann. Bot., 28, 197 (1914).
[25] Hartree and Hill: Proc. Roy. Soc., 103 B, 243, 249 (1928).
[26] Hartree and Hill: Proc. Roy. Soc., 104 B, 1 (1928).

STUDIES ON ELECTROKINETIC POTENTIALS. VII
The Temperature Coefficient of the ζ-Potential*

BY HENRY B. BULL AND ROSS AIKEN GORTNER

Historical

Burton[1] determined the velocity of migration of silver particles in water at 11.0° and 21.0° C. He found that the velocities of the particles were 19.6×10^{-5} cm./sec. and 25.2×10^{-5} cm./sec., respectively, at these two temperatures, indicating a decided temperature coefficient. However, when these values were multiplied by the corresponding viscosities for these temperatures, he obtained 0.251 and 0.250 respectively.

Cruse[2] studied the electro-osmosis of distilled water through diaphragms of clay between 10° and 60°. He found a marked maximum for the rate of flow of water at about 38.0°. He did not correct for the change of conductivity, the viscosity, or the dielectric constant with the temperature, which as has been pointed out by Smoluchowski[3] must be taken into consideration.

Gee and Harrison[4] found with the streaming potential a decided maximum for H/P around 40° for wool, cotton, and silk against distilled water. Their experiments cover a range from 16° to 84°. They made no efforts to correct for the change of the conductance, the dielectric constant, or the viscosity, but they do point out that the factor $\eta\kappa/D$, where η is the viscosity, κ the specific conductance of water, and D the dielectric constant is approximately a constant from 15° to 70°. These results would indicate that the observed changes in H/P are accompanied by a corresponding change in the ζ-potential. It may be pointed out, in criticism of Gee and Harrison's work, that for the specific conductivity they used the specific conductance of distilled water and took no account of the surface conductance which may entirely invalidate their conclusions.

Briggs, Bennett, and Pierson[5] found no suggestion of a maximum for the rate of flow of water through a diaphragm of cellulose with electrical osmosis between 22° and 67°, but found rather a steady increase with the temperature. When the rate of water flow was multiplied by the corresponding viscosities at the different temperatures, a steady decrease was obtained. No account was taken of the change in conductivity.

Experimental

The apparatus and technic used were identical with those of our previous paper[6] and involved only slight modifications from those used by Martin and Gortner[7], which in turn were a modification of Briggs'[8] methods

In order to measure the temperature coefficient of the streaming potential, a constant temperature air bath was installed. It was 150 cm. in length, 60 cm. wide, and 60 cm. deep. The air was circulated over a series of heating

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coils by means of an electric driven Sirocco fan. It was possible to regulate the temperature to ±0.1° The streaming potential cell was placed inside the air bath and shielded wires brought out to the electric measuring apparatus. Before making a determination, the bath was brought to the desired temperature with the cell in place and allowed to remain at this temperature for one hour before a measurement was attempted.

Some difficulty was expected from the change of the cell constant of the diaphragm with temperature. It was thought that the cellulose might become more hydrated with increasing temperature, with a result that the fibers would swell and change the cell constant of the diaphragm. This was found not to be the case, as is adequately demonstrated by the data in Table I.

The ethyl alcohol used was freshly distilled over metallic sodium. The alcohol was found to be extremely hygroscopic, and considerable care was exercised in order to protect it from the moisture of the air. Both the inlet and the outlet of the streaming cell were connected to absorption towers of barium perchlorate, so the alcohol in the cell was at all times protected from the moisture of the air. The cellulose was allowed to remain for two weeks in contact with absolute ethyl alcohol before the determination was attempted

The Cell Constants of the Cellulose Diaphragm in Relation to Temperature

TABLE I

Temperature °C	Cell Constant of Diaphragm	Temperature °C	Cell Constant of Diaphragm
Diaphragm No. 1		Diaphragm No. 2	
24.8	1.318	24.8	0.891
25.0	1.311	25.0	0.905
30.4	1.296	31.5	0.913
31.5	1.321	37.2	0.904
37.2	1.288	44.0	0.900
44.0	1.320	50.4	0.897
50.4	1.288		

The resistance of the diaphragm could not be measured with any degree of precision with the usual conductivity apparatus because the resistance was too high. A Leeds and Northrup alternating-current galvanometer was accordingly employed in place of the usual head phones. An accuracy with less than 1% error was possible.

The data for the change of the specific conductance, the ratio of the observed electromotive force to the pressure, the factor $H\kappa_s/P$, the viscosity, the dielectric constant and the ζ-potential are given for ethyl alcohol-cellulose, distilled water-cellulose and an aqueous solution of 0.1 = 10^{-3} N NaCl with various temperatures. Certain of these results are graphed. The values of the coefficient of viscosity were obtained from the International Critical Tables. The dielectric constant for water at the various temperatures was calculated from Drude's[9] formula. The dielectric constant for 0.1 × 10^{-3} N NaCl was assumed to be equal to that of water. The dielectric constant and its change with temperature for ethyl alcohol was obtained from the International Critical Tables.

The data for ethyl alcohol-cellulose interface are shown in Table II and summarized in Table III and Figs. 1, 2, 3, and 4.

The data for the water-cellulose interface are given in Table IV and summarized in Table V and Figs. 5, 6, 7, and 8.

The data for the 0.1×10^{-3} N NaCl solution against cellulose are shown in Table VI and summarized in Table VII and Figs. 9, 10, 11, and 12.

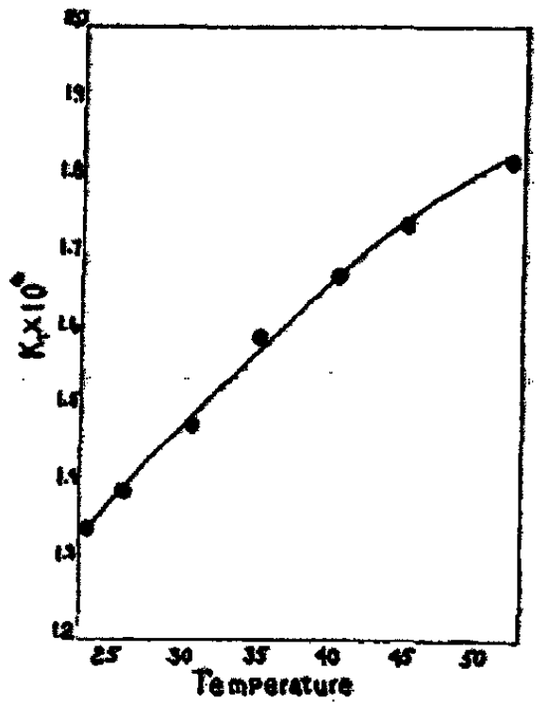


FIG. 1

Showing the relation between the specific conductivity of ethyl alcohol in the diaphragm and the temperature.

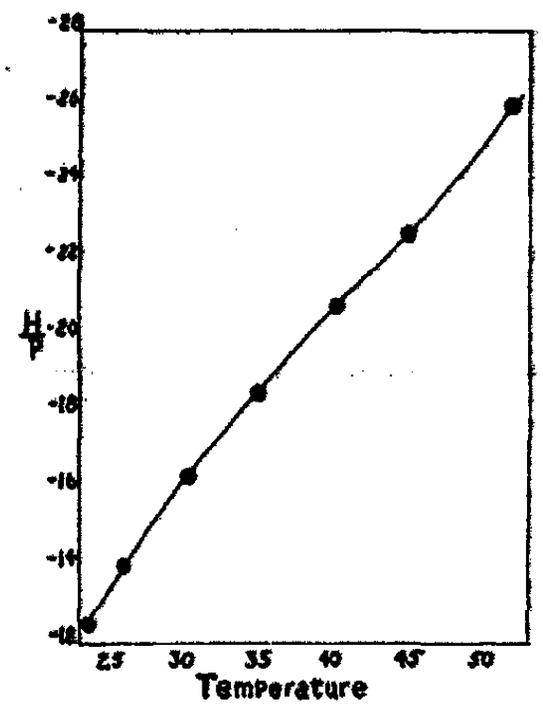


FIG. 2

Showing the relation between $\frac{H}{P}$ and the temperature for an ethyl alcohol-cellulose interface.

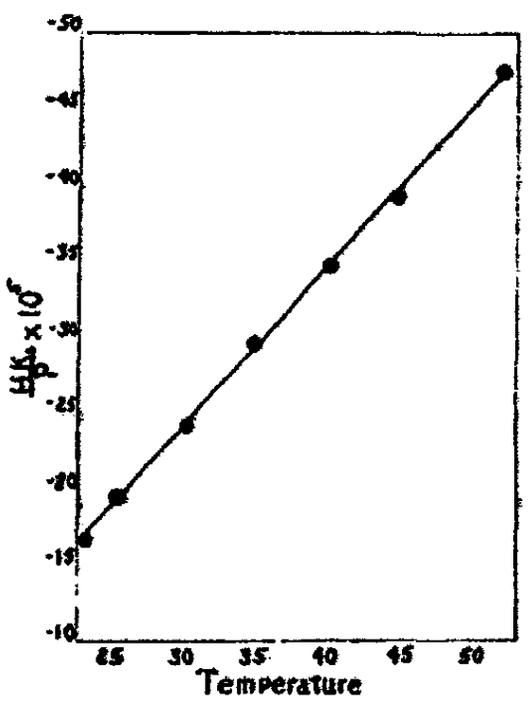


FIG. 3

Showing the relation between $\frac{H_{KS}}{P}$ and the temperature for an ethyl alcohol-cellulose interface.

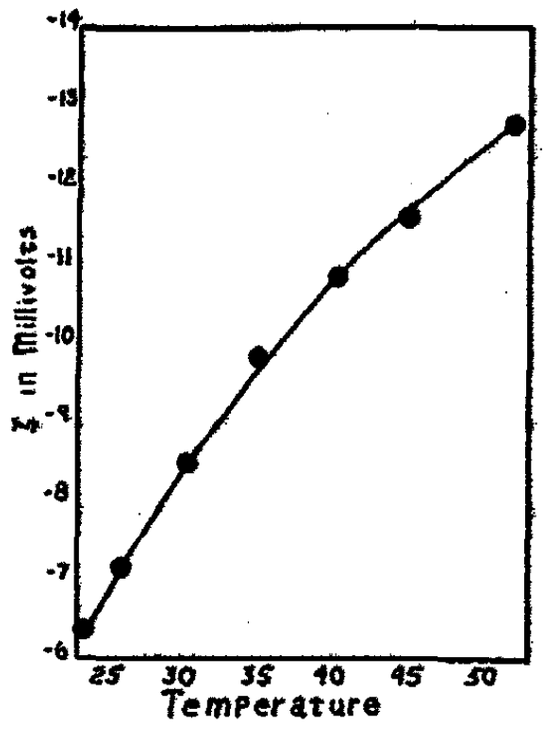


FIG. 4

Showing the relation between ζ-potential of an ethyl alcohol-cellulose interface and temperature.

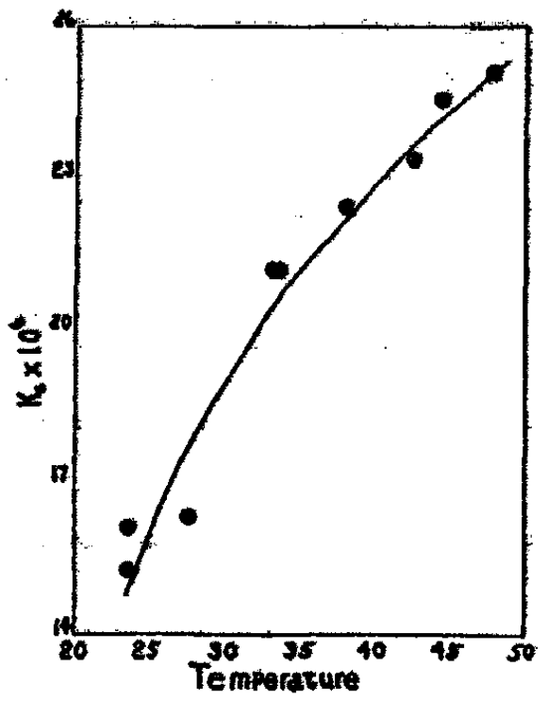


FIG. 5

Showing the relation between the specific conductivity of water in the diaphragm and the temperature.

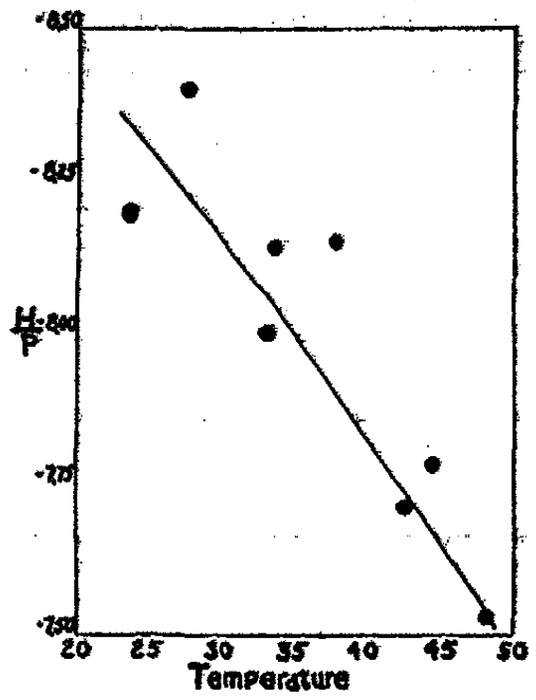


FIG. 6

Showing the relation between $\frac{H}{P}$ and the temperature for a water-cellulose interface.

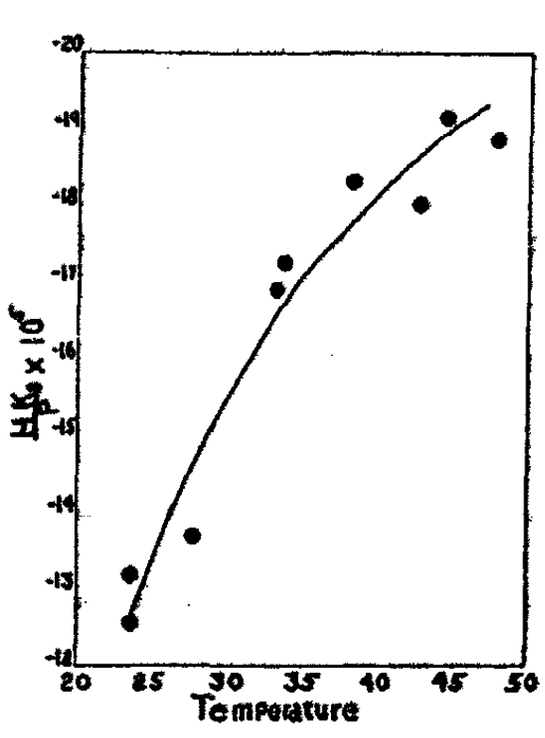


FIG. 7

Showing the relation between $\frac{H_{ES}}{P}$ and the temperature for a water-cellulose interface.

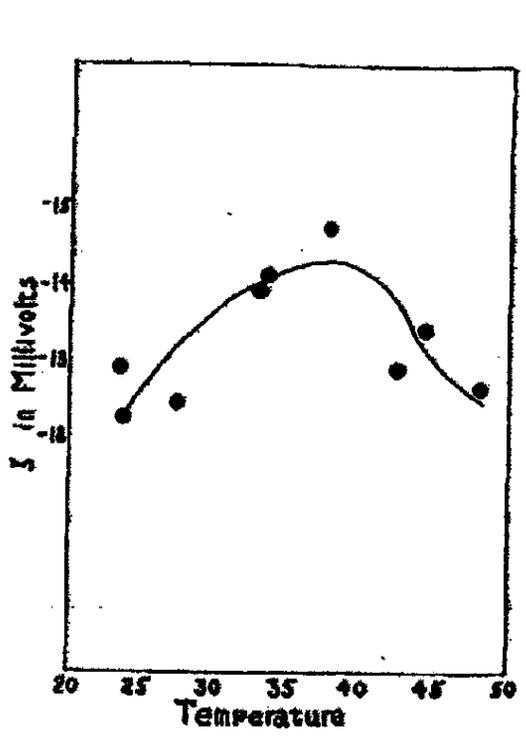


FIG. 8

Showing the relation between the ζ-potential and the temperature at a water-cellulose interface.

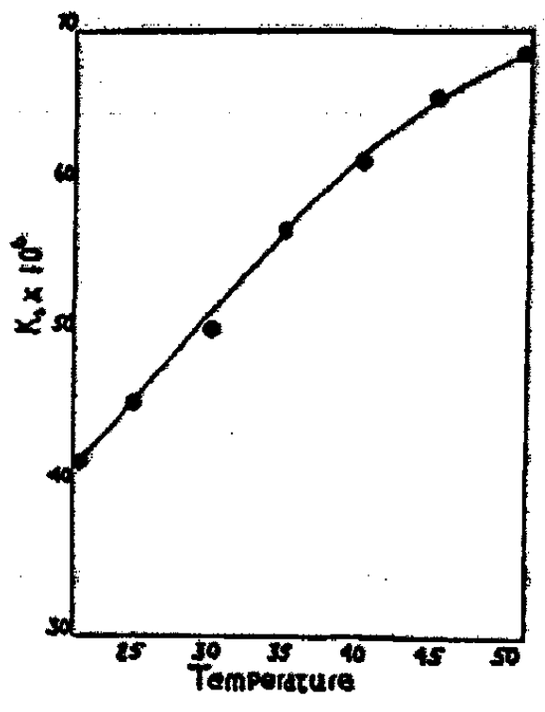


FIG. 9

Showing the relation between the specific conductivity of 0.1×10^{-3} N solution of NaCl in the diaphragm and the temperature.

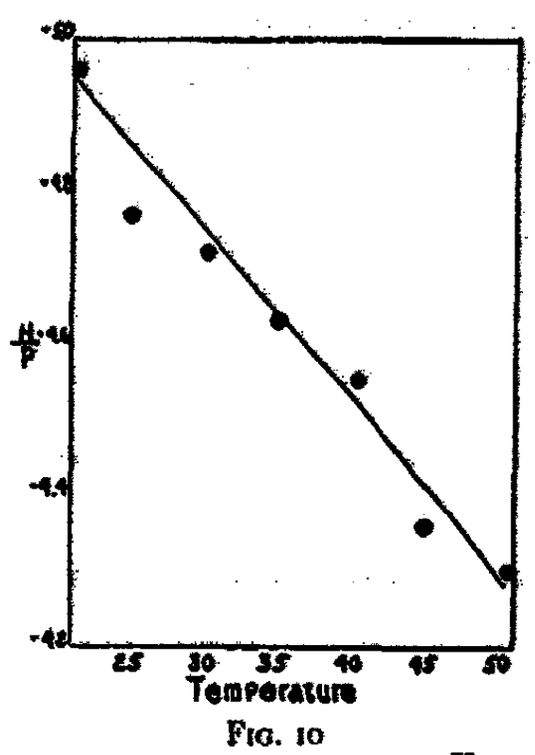


FIG. 10

Showing the relation between $\frac{H}{P}$ and the temperature for a 0.1×10^{-3} N NaCl-cellulose interface.

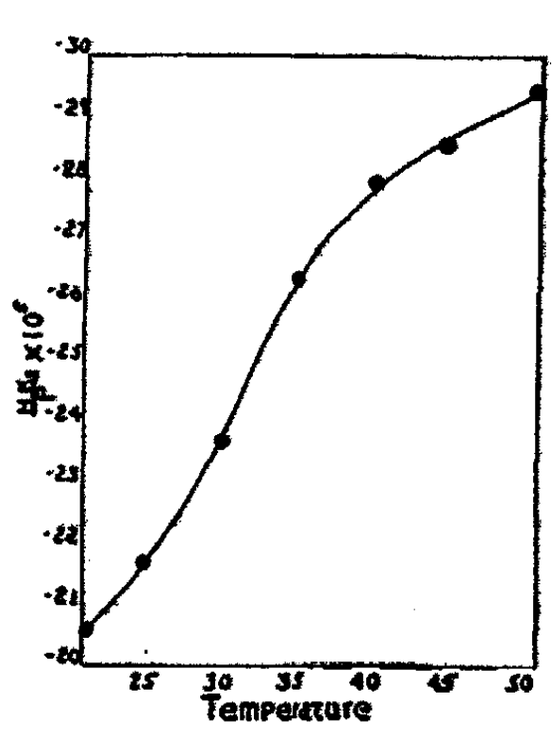


FIG. 11

Showing the relation between $\frac{H_{KS}}{P}$ and the temperature for a 0.1×10^{-3} N NaCl-cellulose interface.

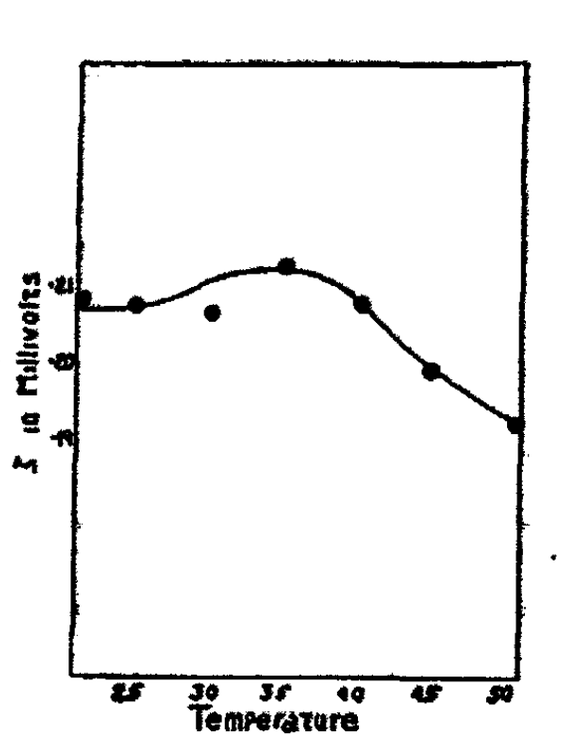


FIG. 12

Showing the relation between the ζ-potential and the temperature at a 0.1×10^{-3} N NaCl-cellulose interface.

Discussion

It is clear from the results that we have a marked positive temperature coefficient for the ζ-potential at an ethyl alcohol-cellulose interface. The cause of this change of ζ with temperature is not known.

TABLE II

Data for Ethyl Alcohol-Cellulose Interface

Temperature 0°C.	Pressure cm.Hg	H/P	Pressure cm. Hg	H/P
23.5	29.7	−12.51	29.7	−12.63
	33.7	−12.53	33.6	−12.42
	37.9	−12.36	37.7	−12.45
		Average H/P = −12.483		
26.0	34.4	−14.04	20.5	−13.58
	37.9	−13.97	25.1	−13.78
	41.1	−14.03	30.7	−13.77
		Average H/P = −14.011		
30.4	28.0	−16.66	31.5	−16.47
	32.4	−16.38	35.9	−16.42
	34.9	−15.84	39.1	−16.54
		Average H/P = −16.385		
35.0	18.2	−18.43	27.5	−19.07
	23.7	−18.65	30.6	−18.59
	29.4	−18.62	37.7	−18.09
		Average H/P = −18.58		
40.5	23.7	−21.29	23.0	−20.52
	29.9	−21.17	28.5	−20.75
	33.8	−20.53	35.3	−20.62
		Average H/P = −20.81		
44.9	20.9	−23.09	21.3	−23.10
	26.9	−22.81	27.1	−22.54
	33.8	−22.25	32.0	−21.97
		Average H/P = −22.62		
52.1	29.8	−25.72	24.9	−26.67
	21.5	−26.39	30.0	−26.06
	26.5	−26.13	33.0	−25.47
		Average H/P = −26.07		

TABLE III
Summary of Data for Ethyl Alcohol

Temperature °C.	$\kappa_s \times 10^6$ mhos	H/P	$\frac{H\kappa_s}{P} \times 10^6$	η poise	D	ζ mv.
23.5	1.345	−12.483	−16.78	0.01125	25.12	−6.370
26.0	1.393	−14.011	−19.51	0.01073	24.72	−7.178
30.4	1.480	−16.385	−24.24	0.00995	24.05	−8.501
35.0	1.596	−18.58	−29.65	0.00915	23.40	−9.8275
40.5	1.673	−20.81	−34.82	0.00830	22.65	−10.816
44.9	1.738	−22.62	−39.32	0.00768	22.06	−11.603
52.1	1.826	−26.07	−47.50	0.00670	21.10	−12.785

TABLE IV
Data for Water-Cellulose Interface

Temperature °C.	Pressure cm. Hg	H/P	Temperature °C.	Pressure cm. Hg	H/P
23.7	69.5	−8.316	27.6	74.4	−8.474
	73.1	−8.194		79.7	−8.393
	81.9	−8.113		84.1	−8.359
Average H/P =		−8.207	Average H/P =		−8.408
33.6	76.1	−8.258	38.0	70.8	−8.114
	80.5	−8.136		77.1	−8.035
	85.5	−8.023		82.6	−8.293
Average H/P =		−8.139	Average H/P =		−8.147
42.6	77.7	−7.786	48.0	70.9	−7.637
	81.9	−7.710		79.2	−7.525
	85.1	−7.655		84.6	−7.432
Average H/P =		−7.717	Average H/P =		−7.534

TABLE V
Summary of Data for Water-Cellulose Interface

Temperature °C.	$\kappa_s \times 10^6$ mhos	H/P	$\frac{H\kappa_s}{P} \times 10^6$	η poise	D	ζ mv.
*23.6	16.09	−8.199	−13.19	0.00924	79.30	−13.02
23.7	15.30	−8.207	−12.55	0.0092	79.30	−12.34
27.6	16.29	−8.408	−13.69	0.00843	77.90	−12.55
*33.1	21.149	−7.993	−16.90	0.00746	75.98	−14.06
33.6	21.20	−8.139	−17.25	0.0074	75.85	−14.26
38.0	22.44	−8.147	−18.28	0.00679	74.36	−14.12
42.6	23.35	−7.717	−18.02	0.00622	72.88	−13.03
*44.5	24.61	−7.785	−19.15	0.00602	72.25	−13.52
48.0	25.07	−7.534	−18.88	0.00567	71.20	−12.75

* These determinations were made several months after the other data recorded in the table.

TABLE VI

Data for 0.1×10^{-3} N NaCl

Temperature °C.	Pressure cm. Hg	H/P	Pressure cm. Hg	H/P
21.35	71.2	−4.985	81.3	−4.913
	77.7	−5.019	85.4	−4.894
	82.9	−5.012	73.0	−4.952
		Average H/P = −4.962		
25.05	78.0	−4.839	77.7	−4.738
	82.0	−4.823	82.5	−4.715
	85.8	−4.841	85.7	−4.708
		Average H/P = −4.777		
30.15	78.2	−4.642	66.3	−4.849
	82.4	−4.624	76.1	−4.803
	85.7	−4.626	81.7	−4.779
		Average H/P = −4.720		
35.15	81.7	−4.645	79.4	−4.622
	84.5	−4.633	82.9	−4.620
	74.1	−4.662	85.4	−4.637
		Average H/P = −4.636		
40.3	80.1	−4.544	81.6	−4.589
	82.5	−4.527	83.8	−4.600
	85.5	−4.519	86.5	−4.595
		Average H/P = −4.561		
45.0	79.2	−4.362		
	82.1	−4.354		
	85.7	−4.378		
	Average H/P = −4.364			
50.6	80.8	−4.288		
	83.7	−4.289		
	85.9	−4.324		
	Average H/P = −4.300			

TABLE VII

Summary of Data for 0.1×10^{-3} N NaCl

Temperature °C.	$\kappa_s \times 10^6$ mhos	H/P	$\frac{H\kappa_s}{P} \times 10^6$	η poise	D	ζ mv.
21.35	41.4	−4.96	−20.57	0.00976	81.25	−20.94
25.0	45.4	−4.77	−21.70	0.00894	78.8	−20.87
30.1	50.27	−4.72	−23.73	0.00793	76.95	−20.73
35.1	56.89	−4.63	−26.37	0.00718	75.26	−21.35
40.4	61.20	−4.56	−27.91	0.00649	73.62	−20.86
45.0	65.54	−4.36	−28.60	0.00597	72.12	−20.07
50.6	68.55	−4.30	−29.47	0.00544	70.42	−19.30

If we treat the Helmholtz double layer as a condenser, we have the relation

$$\zeta = \frac{4 \pi q d}{D}$$

where:

q is the charge per unit area on the plates of the condenser,

d is the thickness of the double layer, *i.e.*, the distance between the plates of the condenser,

D is the dielectric constant.

Substituting the values for ζ and D at the various temperatures, we have the values for $4 \pi q d$ shown in Table VIII.

These results show that as we increase the temperature, we increase either the charge or the thickness of the Helmholtz double layer, or perhaps both the charge and the thickness increase with increasing temperature.

The temperature coefficient of the ethyl alcohol-cellulose system is of sufficient magnitude to require consideration in precise work.

As is shown in Figs. 8 and 12 the ζ-potential for both pure water-cellulose and 0.1×10^{-3} N NaCl cellulose interface exhibit a maximum around 38°C.

Again employing the relation

$$\zeta = \frac{4 \pi q d}{D}$$

we have, upon substituting the known values for ζ and D at the various temperatures, results for $4 \pi q d$ shown in Table IX.

Both water-cellulose and 0.1×10^{-3} N NaCl interfaces show a slight maximum for the function $4 \pi q d$ around 40°, although the values show less variation with temperature than does the ζ-potential.

It is clear from these results that the temperature coefficient of the ζ-potential is much different from that for the electrode potential or Freundlich's so-called thermodynamic potential, which is an additional argument in favor of the view of their independence of each other.

TABLE VIII

The Effect of Temperature on the Electrical Forces acting at a Cellulose-Ethyl Alcohol Interface

Temperature °C.	$4\pi qd$	Temperature °C.	$4\pi qd$
23.5	160.0	40.5	244.9
26.0	177.4	44.9	255.9
30.4	204.4	52.1	269.7
35.0	229.9		

TABLE IX

The Effect of Temperatures on the Electrical Forces acting at Cellulose-Water and Cellulose-Salt Solution Interfaces

Pure Water		0.1×10^{-3} N NaCl	
Temperature °C.	$4\pi qd$	Temperature °C.	$4\pi qd$
23.7	97.8	21.3	170.1
27.6	97.7	25.0	164.4
33.6	108.1	30.1	159.5
38.0	110.4	35.1	160.6
42.6	94.9	40.4	153.5
48.0	90.7	45.0	144.7
		50.6	135.9

It is suggestive that the maximum for the ζ-potential for the pure water and for the 0.1×10^{-3} N NaCl comes at about 40° which is also the point for the minimum specific heat of water.

Summary

1. The temperature coefficients of the ζ-potential for the interfaces, water-cellulose, 0.1×10^{-3} N NaCl-cellulose, and ethyl alcohol-cellulose, have been investigated between 20° and 51°.

2. A marked positive temperature coefficient is exhibited by the ζ-potential at an ethyl alcohol-cellulose interface. The relationship, however, is not strictly linear, the temperature coefficient varying from approximately 0.31 mv. per degree in the range from 23.5° to 30.4° to 0.16 mv. in the range 44.9° to 52.1°.

3. The aqueous systems investigated show a much lower temperature coefficient than the ethyl alcohol-cellulose system. A maximum at about 40° was found for the temperature coefficient for the ζ-potential at both a water-cellulose and a 0.1×10^{-3} N NaCl-cellulose interface. For all practical purposes the temperature coefficient of aqueous systems can be ignored in streaming potential measurements made under ordinary laboratory conditions, since in small temperature ranges the temperature effect is much smaller than is the experimental error of the determination.

Literature Cited

[1] E. F. Burton: On the Properties of Electrically Prepared Colloidal Solutions, Phil. Mag., (6) 11, 425-447 (1906.)

[2] A. Cruse: Über die elektrische Kataphorese des destillierten Wasser durch poröse Tondiaphragmen (Pukallmasse), insbesondere ihre Abhängigkeit von Temperatur und Stromdichte, Physik. Z., 6, 201-204 (1905).

[3] M. von Smoluchowski: Zur Theorie der elektrischen Kataphorese und der Oberflächenleitung, Physik. Z., 6, 529-530 (1905).

[4] W. W. H. Gee and Wm. Harrison: The Electrical Theory of Dyeing, Trans. Faraday Soc., 6, 42-70 (1910).

[5] T. R. Briggs, H. S. Bennett and H. L. Pierson: Electrical Endosmose II, J. Phys. Chem., 22, 256-272 (1918).

[6] H. B. Bull and R. A. Gortner: Studies on Electrokinetic Potentials. VI. Electrical Phenomena at Interfaces, Eighth Colloid Symposium Annual, J. Phys. Chem., 35, 307 (1931).

[7] W. McK. Martin and R. A. Gortner: Studies on Electrokinetic Potentials. V. Interfacial Energy and the Molecular Structure of Organic Compounds. 1. Electrokinetic Potentials at Cellulose-Organic Liquid Interfaces, J. Phys. Chem., 34, 1509-1539 (1930).

[8] D. R. Briggs: The Determination of the ζ-Potential on Cellulose—A Method, J. Phys. Chem., 32, 641-675 (1928).

[9] P. Drude: Der elektrische Brechungsexponent von Wasser und wässerigen Lösungen, Ann. Physik Chem., 59, 17-62 (1896).

WALL STRUCTURE AND MINERALIZATION IN CORALLINE ALGAE*

L. G. M. BAAS-BECKING AND E. WAYNE GALLIHER

1. Introduction

In the last few decades an intensive study has been made of plant and animal membranes; particularly of their optical properties. This study was really, in a way, a revival of the older polariscopic methods of von Ebner,[5] Valentin,[24] and Naegeli,[18] reinforced by the modern X-ray methods.

It seems that, especially in the German school, the evidence obtained is applied to explain the phenomena in the light of Naegeli's micellar theory, according to which the building blocks of the membranes should be elongated, anisotropic and "crystalline" bodies.

The results of polariscopic work of Ambronn,[1] and also of Frey,[6,7] and their school are invariably explained by the existence of micellae and Frey goes so far as to say, in his paper on the structure of plant membranes, "die Theorie von Naegeli, die als Bausteine der Membranen längliche, optisch-anisotrope kristalline Mizelle forderte, darf daher in allen ihren Teilen als bewiesen gelten."

Now neither the polariscopic investigations of Heringa and Minnaert[10] on the animal tendon nor the X-ray evidence obtained by Sponsler[23] on plant fibers seems to suggest the presence of supra-molecular discrete and discontinuous units. It seemed desirable to apply the methods of the German school to other membranes because, in the first place, their work represents a decidedly new departure, inspiring, stimulating, and apparently almost unknown in this country (see, however, McNally and Sheppard).[14] In the second place, it seemed worth while to see in how far the presence of micellae is suggested by the experimental data and to what extent the phenomena could be explained without them.

For investigation of this question the coralline algae offered an interesting possibility because their cell walls are non-cellulosic (Oltmanns,[19] III, p. 2) and, under certain conditions, incrustated with carbonates of calcium and magnesium. The polariscopic study of these cell walls in their mineralized as well as in their decalcified state might lead not only to suggestions about the structure of the organic wall but also to the way in which the carbonate crystals are deposited.

Furthermore, especially in the mineralized material, the X-ray analyses would give an ultimate test as to the reliability of the polariscopic findings.

2. The Material and Its Properties

In our work we have used almost exclusively *Corallina officinalis Lamarck* and *Amphiroa dorbigniana Decaisne*. Preliminary work showed that the mineralized membranes of *Melobesia*, *Lithothamnion*, *Lithophyllum* and

*Jacques Loeb Laboratory of Stanford University, California.

Lithothrix have similar optical characteristics. *Corallina* and *Amphiroa* are both very common near the marine station. They have the additional advantage that they possess unmineralized internodes or genicula. The nodes or articula consist of thick-walled cells, particularly suited for polariscopic work. These cells originate either from embryonic cells in which rapid dehydration causes formation of a heavy wall or from calcified cells from which the minerals are removed secondarily. The mature geniculum represents a group of dead cells (analogy with mechanical tissues in higher plants) which gives flexibility to the alga which would otherwise be unable to withstand the continuous beating of the surf.

FIG. 1

Corallina officinalis L., decalcified longitudinal section, stained with ruthenium oxychloride. Leitz 3 mm. oil, ocular 20×. A, genicular fibres; B, articular fibers; C, cortical tissue.

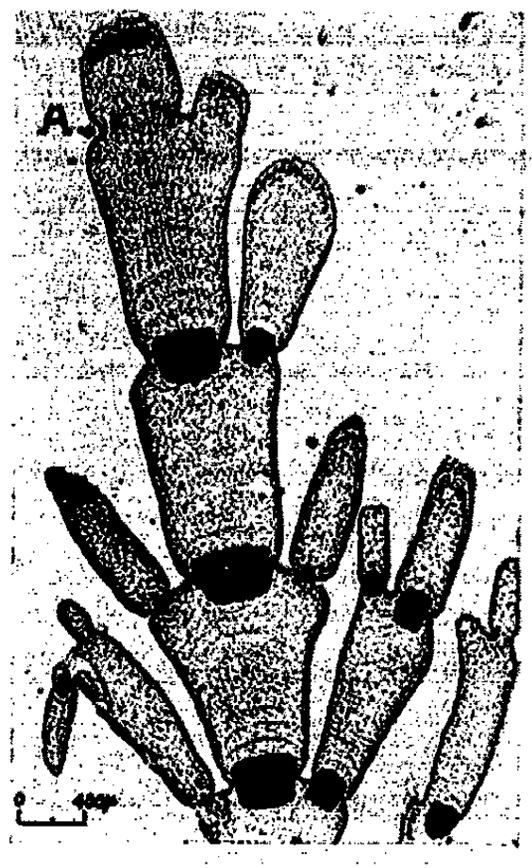


FIG. 2

Corallina officinalis L., decalcified longitudinal stained with ruthenium oxychloride. The young genicula (at A) are still thin-walled. Obj. 6, Zeiss; ocular 10×.

In Fig. 1, A marks the genicular tissue, B the particular central fibers, while the plastids are plainly visible in the cortex C. The pitting of the central fibers is indicated at D.

We are indebted to Lois Wilbur Hopper for the preparation of the microtome sections used in this research.

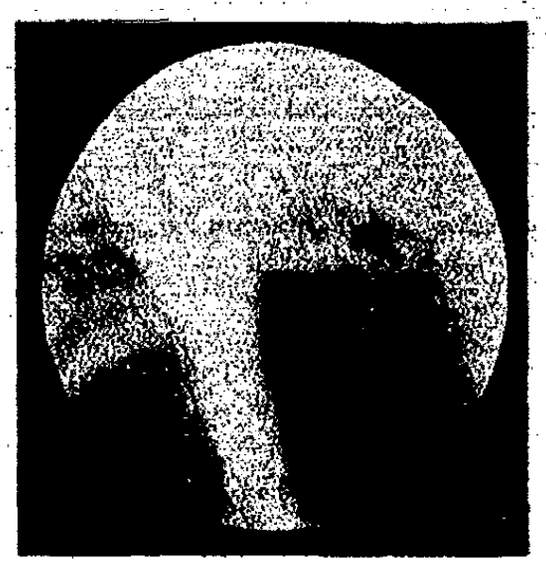
3. Chemical Nature of the Wall Substance

Oltmanns[19] (III, p. 2) states that a great variety of substances seem to collaborate in the formation of the algal cell-walls. It is, however, difficult to translate names like "callose," "pectin" into definite chemical pictures. The cell walls of the Corallines have the following properties:

They are:	1) Insoluble in ammoniacal copper	Interpretation: 1) Non-cellulosic
	2) Soluble in alkali	2) Non-cellulosic
	3) Stain with ruthenium-oxychloride	3) "Mangin reaction" on pectins
	4) Stain with anilin blue	4) Callose; pectin?
	5) Yield CH_3I on distillation with HI	5) Methoxy group present; pectin?
	6) Opaque to ultra violet light	6) Non-cellulosic

From this it follows that the walls are non-cellulosic and contain appreciable amounts of pectin-like substances.

Fig. 2 shows a longitudinal, decalcified section of *Corallina* which has been stained with ruthenium oxychloride. The genicular walls seem to stain better than the articular walls. This is primarily due to their greater thickness. At A, where the walls in the young geniculum are still thin, the intensity of the stain is approximately equal to that of the articular fibers.



0 400μ

FIG. 3

Amphiroa dorbigniana Decaisne, decalcified longitudinal section, unstained. Photographed in ultra-violet light. Filter Corning "violet ultra"; obj. Zeiss quartz, 2.5 mm.; glycerol immersion; ocular Zeiss quartz 5×.

Frey, in his paper on the structure of cell-walls in higher plants has made use of the fact that cellulose is transparent to ultraviolet light. A photograph of a plant section, therefore, will show the non-cellulosic material as dark structures, the cellulose remaining transparent. Photograms of the genicula of *Amphiroa* confirmed our opinion that the material is non-cellulosic (see Fig. 3). In our experiments we used Zeiss quartz optics, obj. 2.5 mm., ocular × 5 natural quartz throughout, quartz slide and cover slip and glycerol immersion. As a source of light we used the Hashimoto[9] quartz mercury lamp which is a simple and inexpensive source of ultraviolet light and which showed itself to be particularly adapted to microphotography. We are indebted to Mr. T. Hashimoto, research chemist of the Hopkins Marine Station, Jacques Loeb Laboratory, for collaboration in these experiments. The light was filtered through a Corning "Violet Ultra" screen 9.45 mm. filter. Even in reflected light, about 20 centimeters removed, we found that a 5-10 second exposure was fully sufficient.

4. Optical Properties of the Membrane

The genicular fibers as well as the decalcified articular fibers show a strong positive birefringence under crossed nicols in longitudinal sections (see Fig. 4). The walls of the fibers seem totally dark in cross section (see Fig. 6). As this

phenomenon had nothing whatsoever to do with mineral deposition we were led to consider its various possible causes. Pectin, according to Molisch[17] and Frey[7] is isotropic. Are the phenomena observed in the Corallines compatible with this view, or should we conclude that the fiber does not consist of pectin?

The refractive index of the fiber proved, according to Becke's method, to be 1.534 ± .002. If the properties of the hypothetical crystallites were different, it did not appear from these tests. The index is higher than that of chitin, lower than that of cellulose, and about equal to that of fibrous aluminum hydroxide.

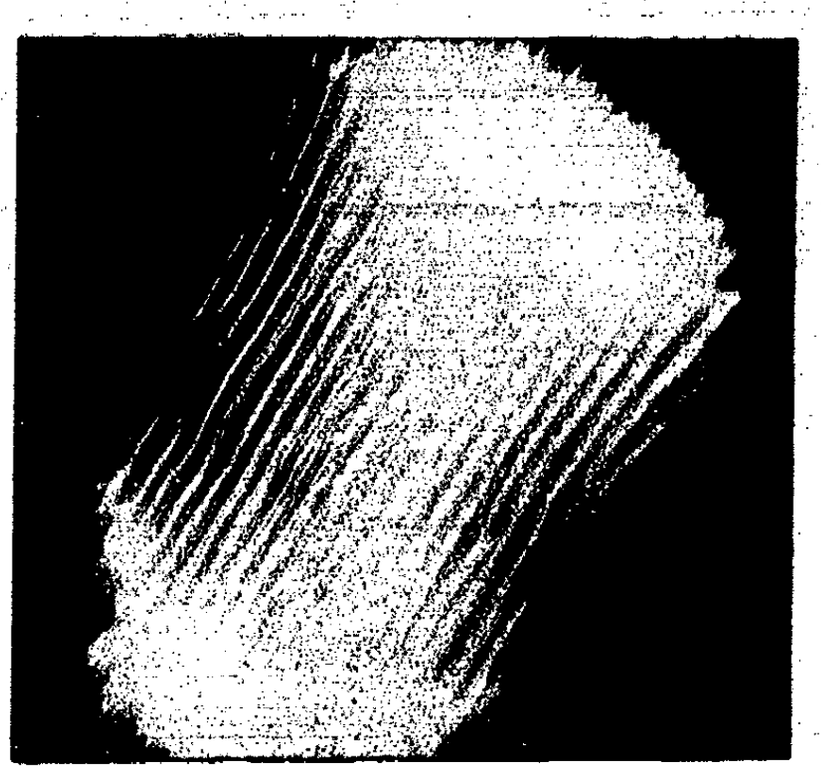


FIG. 4
Geniculum of *Corallina* observed in diagonal position under crossed nicols. Obj. 3 mm. oil; ocular 20×.

There are a great many causes for anisotropy apart from crystallinity. It would fall outside of the scope of this paper to discuss all of them. It may be said, however, that not only factors or forces influencing "directedness," such as tensions and currents, but also the form itself of the constitutional units in the material might contribute to the causation of optical anisotropy. This factor of "Formdoppelbrechung" was clearly recognized by the older authors, but it is only since theoretical work of Wiener,[25] and its application by Moehring[16] for chitin, Frey[7] for cellulose and other plant membranes, and a multitude of other authors, that we are able to interpret birefringence due to position of submicroscopic elements.

For a full discussion of these matters we refer to the original papers. It will suffice here to state the principle upon which the analysis is based. If, in a material system, ("Mischkörper" of Wiener) a mixed body, the disperse phase consists of parallel circular cylinders, the diameter of which is small in

relation to the wave length of light, and if these cylinders have a refractive index of n_1 and the continuous phase (imbedding medium) n_2, the system will be birefringent and will behave as an optically uniaxial body. The strength of the birefringence is a function of n_2^2 and n_1^2 and, of course, of the wave length of the light used and the thickness of the preparation. Should the disperse phase be arranged as parallel vertical lamellae (comp. Fig. 7) instead of parallel cylinders the same consideration holds except that the optical character is reversed.

In both cases we may plot $\Gamma\lambda/d$ (in which Γ is retardation in $m\mu$, λ wavelength in $m\mu$), against the n_2 of the imbedding medium. If the curve approaches zero for a certain value of n_2 we might say that in this case $n_2 = n_1$ and the disperse elements were optically isotropic. If, however, the curve either finds its minimum below or above the abscissa, we have evidence of true micellary birefringence, in the former case optically negative, in the latter of a positive nature.

It should be noted that, in Wiener's theory, the refractive index as such is not mentioned, but the dielectric constant which is assumed to be equal to the square of the refractive index, is used. In Wiener's general equation there appear the following components:

ϵ_m, the dielectric constant of the mixed body;

ϵ_1 and ϵ_2 respectively the dielectric constants of the first and second component element;

δ_1 and δ_2 respectively the fractional volume of the first and second component element; and

μ, which is called the form-coefficient and which is definite and different for any configuration.

For spheres in a continuum we have $\mu = 2\epsilon_2$, but for anisodiametric particles (cylinders or rods), parallel to the optical axis $\mu = \infty$, perpendicular to the optical axis $\mu = \epsilon_2$; for lamellae these values are $\mu = 0$ parallel and $\mu = \infty$ perpendicular to the optical axis.

By means of these values for μ, substituted in the general equation

$$\frac{\epsilon_m - \epsilon_2}{\epsilon_m + \mu} = \delta_1 \frac{\epsilon_1 - \epsilon_2}{\epsilon_1 + \mu}$$

we can get $\epsilon_m = \epsilon_p$ in one, and $\epsilon_m = \epsilon_s$ in another direction. In this fashion we get, for the configuration-birefringence of rods

$$\epsilon_p - \epsilon_s = + \frac{\delta_1 \delta_2 (\epsilon_1 - \epsilon_2)^2}{(\delta_1 + 1)\epsilon_2 + \delta_2 \epsilon_1}$$

and for the configuration-birefringence of lamellae

$$\epsilon_p - \epsilon_s = - \frac{\delta_1 \delta_2 (\epsilon_1 - \epsilon_2)^2}{\delta_1 \epsilon_2 + \delta_2 \epsilon_1}$$

The sign means that rods in general cause positive birefringence, lamellae negative birefringence. However, if rods are arranged in a fascicular fashion instead of in layers, the sign of the birefringence is inverted. It is better, therefore, to speak about "linear" and "stratified" configuration-birefringence than to talk about "bacillary" and "lamellary" birefringence.

As there is no way to determine $n_a - n_o$ from $n_a^2 - n_o^2$, both factors being variable, we might consider

$$(n_a - n_o)^2 < n_a^2 - n_o^2 < (n_a + n_o)^2 \text{ or}$$
$$n_a - n_o < \sqrt{n_a^2 - n_o^2} < n_a + n_o$$
$$n_a - n_o < \sqrt{(n_a - n_o)(n_a + n_o)} < n_a + n_o$$

or the harmonic mean between $n_a - n_o$ and $n_a + n_o$.

From our experimental data we may derive $n_a - n_o$ and dividing $n_a^2 - n_o^2$ (calculated from the equation) by this amount we should get $n_a + n_o$ and accordingly n_a and n_o may be determined. The values derived in this way are exceedingly improbable, showing that the theory of Wiener cannot be applied quantitatively to our data.

In Wiener's equation for bacillary birefringence $\epsilon_p - \epsilon_s > \sigma$. *In this case* Wiener claims that the birefringence $n_a - n_o$ is always positive. It goes without saying that if $n_a > n_o$, $n_a^2 > n_o^2$; but it is not quite clear how n_a^2 may be regarded as a measure of ϵ_p. For it has been repeatedly shown (cf. Pockels,[20] p. 69) that Maxwell's relation, giving the velocity of an electromagnetic disturbance in a certain substance,

$$g = \frac{c}{\sqrt{\epsilon\mu}}$$

(in which c is the velocity of light, μ the magnetic permeability, and ϵ the dielectric constant) only holds for a few cases and only in a very approximate way. The refractive index in general, if no anomalous dispersion influences the result, may be expressed by

$$A + \frac{B}{\lambda^2} + \frac{C}{\lambda^4} \ldots\ldots \text{ which limits to A for } \lambda = \infty.$$

A^2 should equal the dielectric constant. Neglecting the higher terms, and using the relation $A + B/\lambda^2$ Pockels calculates the agreement between n_α, n_β, and n_γ for sulphur and the dielectric constants determined by Boltzmann. In this case, in which correction was made for the λ, the discrepancies between the calculated and observed values amounted to 3-6 per cent.

Wiener states specifically (p. 600) "die vorliegende Theorie bezieht sich auf ruhenden Körper von ganz bestimmter unveränderlichen Dielectrizitätsconstanten."

From the foregoing it follows that, in general, Wiener's equation is useful as long as we remember that we can not apply it quantitatively in the majority of cases. It may give us a clue however as to the configuration of certain colloids and other substances that may be impregnated with liquids of different refractive indices.

In the following experiments we have followed closely the directions of Ambronn and Frey,[2] whose beautiful book has been a constant source of inspiration to us. We have imbedded, in various media of known refractive index, longitudinal sections of the genicular fibres of *Corallina* and *Amphiroa*. The thickness of the section was ascertained and the retardation in the various media determined by means of a Berek compensator for white light, and for

red, yellow, and blue light of wavelengths 656, 589, and 486 mμ ± 5 mμ respectively. The small Leitz monochromator was used to advantage in this work. Care was taken to assure complete imbedding, as incomplete penetration is the greatest source of error in this method. The following media were used:

Medium	n_D	Medium	n_D
Air	1.00	Oil cedar	1.51
Ether vapor	1.09	Oil cassia	1.60
Water	1.33	Carbon bisulphide	1.63
Oil paraffin	1.46	Monobromnaphthalene	1.65
Xylene	1.50		

While one may obtain a great many liquids with a refractive index from water (1.33) upward, there are, as yet, no media available with indices situated between air and water. However, it was found that vapors, when applied with some caution, make excellent "imbedding media" within the desired range. We have made use of ethyl ether. The procedure was as follows: a nickel chamber was prepared with two outlets and a glass bottom. A circular hole in the top allowed the mounting of a coverslip with the preparation. The coverslip was sealed onto the chamber by means of water glass. One outlet of the chamber was connected with a vacuum pump; the other with a bottle containing ethyl ether. After the ether was brought to boil and most of it evaporated the chamber was isolated and the optical retardation of the fibers in the preparation determined in the usual way.

Using the values of Lorenz from Landolt-Börnstein for ethyl ether, $n_D = 1.158$ at 0°C and 760 mm pressure, and those of Ramsay (from the same tables) for the vapor-pressure of ethyl ether at 20°C = 438 mm pressure, the refractive index of ether vapor in our experiment appeared to be

$$n_D = \frac{(n_{0\text{-}760} - 1).438}{(1 + \alpha t)\ .760} + 1 \text{ or } n_D = 1.085$$

The retardations determined in this medium in no way disturbed the continuity of our curve. We therefore believe that the procedure, while not yet entirely capable of giving absolute results, is worthy of future consideration.

The use of water may be, under certain conditions, objectionable. Whenever the fiber absorbs water, it may swell and even if the individual solid elements are not affected, the relation between the volume elements of the phases would be materially changed.

Comparatively small differences in δ_1 would give rise to large discontinuities in the curve (as may be calculated from Wiener's equation). The effect of swelling, which, moreover could not be determined microscopically, may contribute but little.

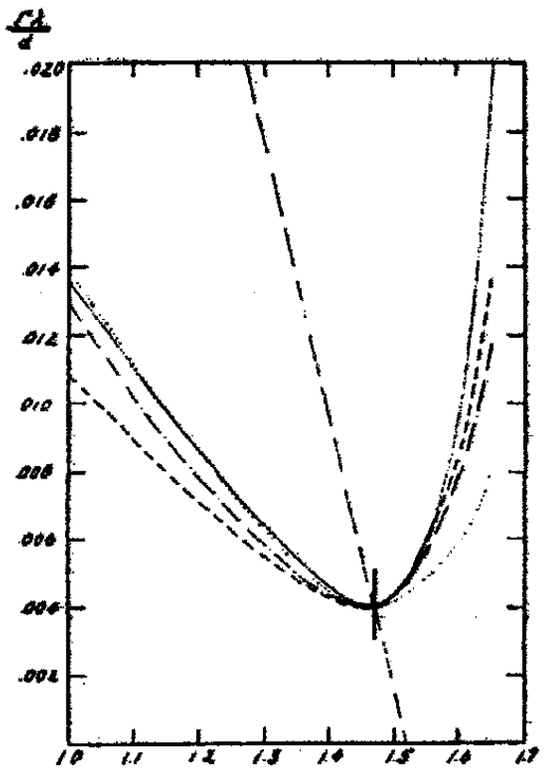
The accuracy of the method remains to be discussed. As in all subjective methods it is liable to the maximum number of errors, as the personal equation itself is a sum of disturbing factors. M. Berek[3] (p. 430) has shown that his

compensator is able to record retardations of the order of magnitude of 3 mμ. The limit of birefringence actually observable with fibres of about 5000 mμ thickness would be 0.0008. Actually readings below Γλ/d = 0.002 are difficult to perform. The genicular fibers, because of their greater thickness, are therefore better adapted for quantitative work on retardation, as Γλ increases linear with an increase in *d*.

It might be useful to illustrate the accuracy of the Berek method by a laboratory protocol:

Γλ/d for different fibers in air

	656mμ	589mμ	486mμ
Fiber No. 1	.0137	.0132	.0106
2	.0138	.0112	.0114
3	.0130	.0125	.0110
4	.0143	.0138	.0108
Average	.0137 ±0.0007	.0127 ±0.0015	.0110 ±0.0004



n_D of Imbedding Medium

FIG. 5

Retardation of genicular fibers of *Amphiroa dorbigniana* Decaisne, plotted against the index of imbedding medium. Inclined axis dashed; heavy line indicates limit of accuracy of determinations

White Light ————
656 mμ .....
589 mμ — · — · —
486 mμ — — — —

Hence the average accuracy amounted to about 0.001. Fig. 5 shows the experimental results. The curves are hyperbolic, the symmetry axis is inclined to the left. The minimum birefringence occurs at a lower index of refraction than that found by the Becke method. There is a residual birefringence of about 0.004 (comparable to that of tridymite, dahllite, etc.). In relation to Wiener's theory we may say that, 1) there is a positive birefringence due to configuration (form) and, 2) there is a small residual birefringence.

Positive birefringence due to configuration of elements may be due to rod-shaped elements or to lamellae, both arranged parallel to the longitudinal axis of the fiber. In the first instance the birefringence $n_a - n_o$ is related to the indices of the rods and imbedding medium as follows:

$$n_a^2 - n_o^2 = \frac{\delta_1 \delta_2 (n_1^2 - n_2^2)^2}{(\delta_1 + 1) n_2^2 + \delta_2 n_1^2}$$

in which δ_1 and δ_2 are the volume elements of the rod and embedding medium ($\delta_1 + \delta_2 = 1$). The curve is asymetric in relation to n_2 and n_1. If we plot the value of $n_a^2 - n_o^2$ for various values of δ_1 and n_2, assuming $n_1 = 1.53$ we

obtain a series of hyperbolae, in which the symmetry axis is always inclined to the right. Obviously our curve does not correspond to a system possessing bacillary birefringence.

The lamellary birefringence follows the relation

$$n_a^2 - n_o^2 = \frac{\delta_1 \delta_2 (n_1^2 - n_2^2)^2}{\delta_1 n_2^2 + \delta_2 n_1^2}$$

The relation is symmetrical in n_1 and n_2; moreover, for small values of δ_1 we find that the curve may be represented by a hyperbola the axis of which is inclined towards the left, as in our experimental curve. Because the expression is symmetrical in n_1 and n_2 it is immaterial whether the solid lamellae preponderate or whether the imbibition medium occupies most of the space in the cell wall. As soon as δ_1 is less than 0.1 the curve approaches in *shape* to our experimentally obtained one. Now it may be observed that in any mounting medium, the fibers remain dark between crossed nicols in transverse section. (comp. Fig. 6)

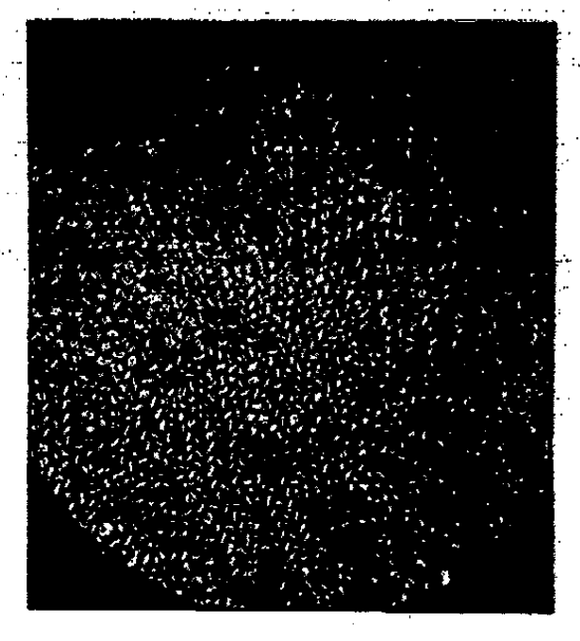


FIG. 6
Cross-section of genicular fibers of *Amphiroa dorbigniana* Decaisne photographed under crossed nicols. ×600.

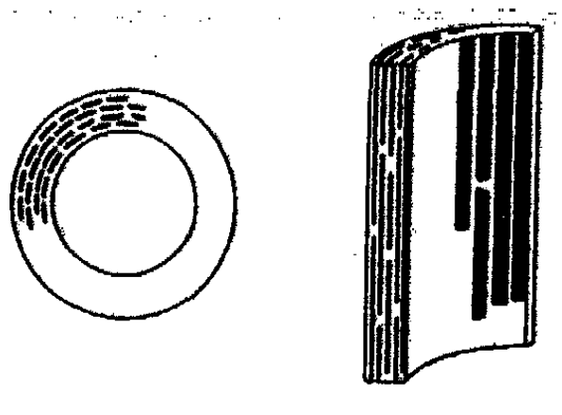


FIG. 7
Diagrammatic sketch of structure of a fiber. Not to scale.

If we suppose the lamellae to be arranged in tangential fashion parallel to length of fiber (Fig. 7), we would expect, when viewing the preparation in longitudinal section, to obtain birefringence in the wall, and a plotting of such should follow the equation for "Plättchendoppelbrechung" given by Ambronn-Frey,[2] page 119*; $n\gamma$ should likewise be oriented parallel to the length of the lamellae. Viewed in cross-section, however, we expect to find a condition of isotropy, inasmuch as an entirely closed system (that is, a completely circular system) would produce no birefringence as depicted by Ambronn-Frey, page 122. It seems, then, that lamellae in tangential arrangement will fit the observed facts, and this arrangement is shown diagrammatically in the accompanying figure (Fig. 7). A critical examination of the other possible arrangements shows that the observed conditions could not possibly be fulfilled.

*There is a typographical error here, as the equation should read

$$n_a^2 - n_o^2 = -\frac{\delta_1\delta_2 (n_1^2 - n_2^2)^2}{\delta_1 n_2^2 + \delta_2 n_1^2}$$

In view of the water content of the fiber, which is difficult to determine experimentally, but in any case smaller than 90 per cent, we are inclined to believe that the fiber is built up of tangentially arranged elongate lamellae of pectin-like material, interspersed with concentric interstices. The pectin phase and the interstices are both small in relation to the wavelength of light, but the interstices occupy roughly less than one tenth the volume of the fiber.

The minimum in our curve at 0.004 may be interpreted in two ways. Krausse,[13] in his study on the structure of fibrous alumina obtained a curve of the same general shape as ours and with a minimum retardation of low value. He mentions the two possibilities, which we may apply to our case (page 288): "die Tonerdefasern sind aus länglichen Teilchen aufgebaut, deren Grösse und Entfernung von einander klein sind gegen die Wellenlänge des Lichtes. Diese Teilchen sind entweder isotrop oder positiv doppelbrechend in bezug auf ihre Längsrichtung."

X-ray photograms of powdered fibrous alumina as well as of our algal material seemed to indicate amorphic material.

The non-coincidence of the calculated and observed minima in our curve, as well as the curious retardations observed in various wavelengths may be explained by anomalous dispersion. It is well known that even small differences in light absorption for various wavelengths may cause a great difference in the refractive index. While the spectroscope revealed no such absorption bands in the coralline material, the cells, on visual inspection, are faintly but unmistakably yellowish.

As yet we have no conclusive evidence showing that the individual elements are, in themselves, birefringent. It would be rather like stressing the point to call these elements micellae. For they might as well run the whole length of the fiber. We meet here with the same difficulty that follows from Sponsler's[23] work on the fine structure of cellulose. Any division of the molecular chains is arbitrary. We cannot say, therefore, that our findings point to a micellar structure. (See, however, McNally & Sheppard,[14]) An elementary application of analytical geometry will convince us that the curve, experimentally obtained, actually represents a case of lamellary birefringence.

The expressions

$$Y = -\frac{\delta_1 \delta_2 (c - x)^2}{\delta_1 x + \delta_2 c} \qquad (1)$$

and

$$Y = +\frac{\delta_1 \delta_2 (c - x)^2}{(\delta_1 + 1) x + \delta_2 c} \qquad (2)$$

represent hyperbolae of the general form

$$Y = a + b x + \frac{c}{x + d} \qquad (3)$$

the Y^2 term being absent. In this expression, the asymptotes are represented by $Y = a x + b$ and by $x = d$ respectively. The latter asymptote is therefore parallel to the ordinate axis.

The simple hyperbola $\frac{Y^2}{b^2} - \frac{a^2}{x^2} = 1$ transforms by rotation and translation of its axis into a hyperbola with one asymptote parallel to the ordinate if we rotate over $\alpha = \pm \text{ arc tg } \frac{b}{a.}$ The general translation being $y = q$, $x = p$.

For a counterclockwise rotation $(-\alpha)$ we obtain

$$Y = -\frac{1 + tg^2\alpha}{2tg\alpha} x + \frac{1 + tg^2\alpha}{2tg\alpha} p + q - \frac{ab}{2} \frac{1 + tg^2\alpha}{1 - tg^2\alpha} \frac{1}{x - p} \quad (4)$$

and for a clockwise rotation $(+\alpha)$

$$Y = \frac{tg^2\alpha - 1}{2\,tg\alpha} x - \frac{tg^2\alpha - 1}{2\,tg\alpha} p + q + \frac{ab}{2} \frac{1}{x - p} \quad (5)$$

When we bring expressions (1) and (2) in the generalized form (3) we get; For lamellary birefringence

$$Y = -\delta_2 x + \frac{1 - \delta_1^2}{\delta_1} c - \frac{1 - \delta_1}{\delta_1^2} c^2 \frac{1}{x + \frac{1 - \delta_1}{\delta_1} c} \quad (6)$$

For bacillary birefringence

$$Y = \frac{\delta_1 \delta_2}{\delta_1 + 1} x - \frac{\frac{\delta_1 \delta_2^2}{2\delta_1 \delta_2 \delta_1 + 1}}{\delta_1 + 1} + \frac{\delta_1 (1 - \delta_1) 2 - \delta_1) (3 + \delta_1)}{(\delta_1 + 1)^3} \frac{1}{x + \frac{\delta_2}{\delta_1 + 1} c} \quad (7)$$

Equations (1), (4) and (6) correspond to the general expression

$$Y = -ax \pm b \pm \frac{c}{x \pm d} \text{ asymptote } Y = -ax \pm b$$

In this case the axis of the hyperbola is inclined to the left.
(lamellary birefringence)
Equations (2), (5) and (7) correspond to the general expression

$$Y = +ax \pm b \pm \frac{c}{x \pm d} \text{ asymptote } Y = +ax \pm b$$

The axis of the hyperbola is inclined to the right (bacillary birefringence). The curve obtained in this investigation may be interpreted as an expression of lamellary birefringence.

5. The Nature of the Mineral Deposition

Examination of thin sections of undecalcified Corallines show strong birefringence. In these sections we have been able to observe very small crystals oriented with n_α perpendicular to the cell wall. Their size was just about at the limit of the resolving power at aperture of 1.4. This would bring their length to a few tenths of a micron. Several attempts were made to ascertain the mineralogical nature of the crystals. We found that Meigen's

reaction and the ferrous sulphate reaction were in conflict (compare also Johnston, Merwin, and Williamson.[12] These reactions have been shown to be unreliable. Direct inspection of the individual elements was impossible because of their size. Separations by specific gravity failed because of the small size of the crystals as well as their tendency to adhere to cellular fragments. Prolonged grinding in an agate mortar and grinding for forty eight hours in a ball mill failed to separate the individual crystals. n_ϵ and n_ω could not be determined, but inasmuch as no index of the calcareous material exceeded 1.633, it is reasonable to assume that the carbonate material is calcite. (Highest index of aragonite 1.685, dolomite 1.698, magnesite 1.700). This was already claimed by Meigen[15] who found no aragonite but only calcite in the Corallines, while the incrustated *Chlorophyceae* possessed aragonite. As his evidence was based upon color reactions of doubtful value, not much stress can be laid upon his confirmation. However, Dr. O. L. Sponsler had the kindness to prepare X-ray powder diagrams from both decalcified and natural *Amphiroa*. In measuring out his film Dr. Sponsler obtained identical results with Gibson, Wyckoff and Merwin[8] who worked with pure calcite. In the following table the first column represents the double angle from Gibson, Wyckoff and Merwin, Fig. 2, calcite; the second column represents Sponsler's results with powdered *Amphiroa;* the third column represents the quotients of the corresponding numbers in column B and A:

A Arc 2θ (G.W.M)	B Arc 2θ (O.L.S.)	$\frac{B}{A}$
12.3	28.0	2.28
16.0	35.7	2.23
19.5	43.5	2.23
21.3	47.5	2.23
23.4	52.0	2.23
25.5	56.7	2.21
26.2	57.5	2.20
30.1	67.5	2.24
32.3	71.5	2.21
34.5	76.0	2.20

The last column is constant within the experimental error. The incrusting material is, therefore, calcite with the c-axis oriented perpendicular to the cell wall. It may be said that the magnesium which is present in the deposit (Clarke and Wheeler[4]) might obscure the results. Our chemical analyses show that the magnesium content not only varies individually but that within the same organism it may fluctuate and may be zero in a great many cases. This is especially true in the younger parts of the plants which were sent to Dr. Sponsler for examination. Clarke and Wheeler[4] have repeatedly stressed the variability in the magnesium content of the Corallines. It is our belief that a comparative study of such forms as *Halimeda*, *Acetabularia*, which contain only small quantities of magnesium, and of the Corallines might lead to interesting results.

Summary and Conclusions

1. The cell-walls of the coralline algae are made of a non-cellulosic material; probably pectin or pectin-like substance.

2. The walls are birefringent in longitudinal- and isotropic in cross section.

3. The fibers are probably built up of tangentially arranged, elongate lamellae interspersed with concentrically arranged interstices, both of which are small in relation to the wavelength of light.

4. The only mineral that is deposited by the living Coralline is calcite. The individual calcite crystals are at most a few tenths of a micron long and are arranged with the c-axis perpendicular to the longitudinal axis of the fiber.

5. The deposition of magnesium in the corallines is a secondary phenomenon.

6. Our findings, while capable of being interpreted in accordance with the micellary hypothesis do not require this theory. The units in the cell wall are discrete, but not, within the cell, discontinuous.

Literature cited

[1] H. Ambronn: (1919) cited in Ambronn 1926.
[2] H. Ambronn and A. Frey: "Das Polarisationsmikroskop" (1926).
[3] M. Berek: Centralbl. Mineral. usw., 1913, 388, 427, 464, 580.
[4] F. E. Clarke and W. C. Wheeler: The Inorganic Constituents of Marine Evertebrates. U. S. Geol. Survey, Prof. Paper, 124 (1922).
[5] V. v. Ebner: "Ueber die Ursachen der Anisotropie der organisierten Substanzen" (1882).
[6] A. Frey: Doppelbrechung der Dispersoide. Kolloidchem. Beihefte, 20, 299 (1924).
[7] A. Frey: Die submikroskopische Struktur der Zellmembranen. Jahrb. Wiss. Bot., 65, 195 (1926).
[8] R. E. Gibson, R. W. Wyckoff, and H. E. Merwin: Vaterite and Mu-Calcium Carbonate. Am. J. Sci., 10, 325 (1925).
[9] T. Hashimoto and C. C. Wu: A simple laboratory quartz mercury lamp. Science, N. S. 65, 187 (1927).
[10] G. C. Heringa and C. M. Minnaert: Concerning an Optic Phenomenon in Tendons. Proc. Roy. Acad. Amsterdam, 30, 1 (1927).
[11] L. Irving and L. B. Becking: Observations on the Metabolism of the Corallines. Proc. Soc. Exp. Biol. and Med., 22, 162 (1924).
[12] J. Johnston, H. E. Merwin, and E. D. Williamson: The several forms of calcium carbonate. Am. J. Sci., 41, 473 (1916).
[13] W. Krausse: Zur Kenntnis des optischen Verhaltens der Tonerdefasern. Kolloidchem. Beihefte, 21, 282 (1925).
[14] J. G. McNally and S. E. Sheppard: Double refraction in cellulose-acetate and nitrate films. J. Phys. Chem., 34, 165 (1930).
[15] W. Meigen: Beitr. zur Kenntnis des kohlensauren Kalkes. Thesis. Freiburg (1902).
[16] A. Moehring: (1922) cited from Ambronn (2).
[17] H. Molisch: "Mikrochemie der Pflanzen" (1923).
[18] C. v. Naegeli: Beitr. zur wiss. Botanik, 1863, Heft 3.
[19] C. Oltmanns: Morphologie und Biologie der Algen (1904).
[20] F. Pockels: "Lehrbuch der Kristalloptik", (1906). See, for more modern treatment of analogous matters: J. Errera: "Polarisation Diélectrique" (1928).
[21] W. J. Schmidt: "Die Bausteine des Tierkörpers in polarisiertem Lichte" (1924).
[22] Graf zu Solms-Laubach: "Die Corallinenalgen des Golfes von Neapel" (1881).
[23] O. L. Sponsler and W. H. Dore: The Structure of Ramie Cellulose as derived from X-ray Data. Colloid Symposium Monograph, 4, 174 (1926).
[24] G. Valentin: Die Untersuchung der Pflanzen und der Tiergewebe in polarisiertem Lichte" (1861).
[25] O. Wiener: Die Theorie des Mischkörpers f. das Feld d. stationaren Strömung. Abh. Math. Phys. Kl. Sächs. Ges. der Wiss., 32, 507 (1909).
[26] K. Yendo: Study of the genicula of Corallinae. J. Imp. Coll. Sci. Tokyo, 19, (1904).

THE DISSOCIATION OF STRONG ELECTROLYTES. III*

Complete Dissociation and Optical Properties

BY MORRIS B. JACOBS AND CECIL V. KING

The supposed additivity of color or light absorption, of refraction and of dispersion by the ions in solutions of strong electrolytes has in recent years been cited in favor of complete dissociation, just as thirty years ago similar data were used to support the Arrhenius dissociation theory. The Arrhenius theory indicates that some properties of strong electrolytes should be found which can be assigned to the undissociated molecule; and the difficulty of specifically assigning any properties to such a portion of the electrolyte has recently been interpreted in favor of its complete absence.

Color and Absorption.—As far back as 1892 Ostwald[1] called attention to the fact that a solution of any electrolyte should show at least three absorption spectra—one for each ion and one for the undissociated molecule; if complexes were formed, the absorption spectrum would be even more complicated. Ostwald showed that thirteen different metal permanganates, at a dilution of one equivalent in 500 liters, had absorption bands in identical positions in the spectrum. Ten salts of fluorescein showed the edge of their absorption band in the same place, and eosin and anilin violet salts were similar in this respect. Ostwald took this, of course, to mean that these salts were highly dissociated in these dilute solutions, and that the metal ions and anions were highly independent; for the changing or substitution of atoms or radicals in non-conducting organic molecules is usually attended by pronounced color changes. Ostwald did not attempt to show evidence of absorption by the undissociated molecules of these salts.

Also in 1892 Magnanini showed that two solutions of copper sulfate of the same concentration, one containing considerable sulfuric acid, had exactly the same light absorption. He interpreted this as evidence against ionization, but Ostwald replied that undissociated $CuSO_4$ might well have the same absorption, in solution, as copper ion. Magnanini then (1893) proceeded to show that the addition of KNO_3 to potassium violurate did not change the absorption; he was under the impression that violuric acid and the violurate ion (if it existed) were not colored and that undissociated potassium violurate was the only colored substance present. Donnan[2] describes the above experiments and shows that Magnanini's work was marred by the impurity of his materials. Donnan himself shows that, assuming that the color is due to the violurate ion only, one can calculate the percentage ionization and the dissocia-

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* Contribution from the Department of Chemistry, Washington Square College, New York University.

[1] Ostwald: Z. physik. Chem., 9, 579 (1892).

[2] Donnan: Z. physik. Chem., 19, 465 (1896).

tion constant of violuric acid from the color at various dilutions, and obtain results identical with those from conductivity measurements. This is pointed out by Halban[1] who shows that $\mu/\mu_\infty = \epsilon/\epsilon_\infty = \alpha$ for this acid. (μ=equivalent conductivity, ϵ = extinction coefficient).

Bjerrum[2] found that the color, in solution, of certain chromium salts was practically constant on dilution, i.e., the molecular extinction coefficient did not change with the concentration; he interpreted this to indicate the absence of undissociated molecules. In 1918 Bjerrum[3] summarizes the evidence for complete dissociation and points to his earlier conclusion from the color of these chromium salts. He points out that α and i-1 (from conductivity and from colligative properties) do not agree and remarks that if these are abandoned as a measure of the degree of dissociation the "anomaly of strong electrolytes" disappears. He emphasizes that his conclusions from the color of salts apply *only when no complexes are formed.*

Noyes[4] on the basis of similar observations concluded that since the optical activity, color, etc. were independent of the concentration (when referred to equivalent quantities), these properties were additive with respect to the ions even at concentrations where much of the salt was un-ionized. At that time, in other words, Noyes interpreted constancy of color or absorption to mean that *ionization is an optically indifferent process*, and that the color is the same whether the ions are "bound" or "free", a view which has been held for many years by Hantzsch.[5] Hantzsch, like Bjerrum, found that many strong electrolytes show practically no change in molecular extinction coefficient on dilution. This was true for the Sr, Li, Na, Cs, Tl salts of acetyloxindon, for some copper salts and copper complexes in water, aqueous ammonia and other solvents, for permanganates, chloroplatinates, potassium diamminetetranitrocobalt, and for K and Ba salts of trichloroacetic acid (in ultra-violet light). Further, he showed that trichloroacetic acid has exactly the same absorption in *petroleum ether* as in water, and that HBr is optically identical in water, alcohol and ether; also that many salts show the same constancy of molecular absorption in alcohol solution as in water. Recently, with more exact experimental work, he shows that the ultraviolet absorption by various halides is not strictly additive, and ascribes the discrepancies to minor chemical changes such as hydration. Remembering that substitution in un-ionized organic compounds has often a pronounced effect on the color, and that ionization should be less in some of these non-aqueous solvents than in water, Hantzsch concludes that ionization is an optically indifferent process.

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[1] Halban: Z. Elektrochemie, 34, 489 (1928).

[2] Bjerrum: Det Kgl. Dansk. Vid. Sel. Skr., (7) 4, 26 (1906); Z. anorg. Chem., 63, 140 (1909).

[3] Bjerrum: Z. Elektrochemie, 24, 321 (1918).

[4] Noyes: Science, 20, 577 (1904).

[5] Hantzsch and co-workers: Ber., 41, 1216, 4328 (1908); 58, 612 (1925); 59, 1096 (1926); Z. physik. Chem., 63, 367 (1908); 72, 362 (1910); 84, 321 (1913); 86, 624 (1913); Z. Elektrochemie, 29, 221, 434 (1923); 30, 194 (1924); 31, 167 (1925).

Hantzsch in this matter disagrees with Halban,[1] who has also done much experimental work on absorption by strong and weak electrolytes.

Halban at first agreed with Bjerrum's view, and not Hantzsch's; since Beer's law is obeyed by strong electrolytes and not by weak ones, ionization cannot be an optically indifferent process. He even showed, as has been mentioned, that the percent ionization of a weak electrolyte might be calculated from the extinction coefficients. Later, however, Halban came to the conclusion that Beer's law is by no means generally valid even for strong electrolytes; he points out that the salts cited by these workers were mostly rather complex salts, while the relation is not obeyed by some of the simplest salts. For instance, while for the complex chromium salts ϵ is practically constant with concentration while μ is not, for the absorption in the ultraviolet by lithium nitrate ϵ follows much the same type of curve as μ. Also, while according to Bjerrum's idea addition of another salt should have no effect on the absorption by the first, actually enormous effects may be observed.

Halban, while assuming practically complete dissociation in such cases, explains the invalidity of Beer's law according to the electron-shell deformation theory of Fajans.[2]

Halban and Ebert, in a careful piece of experimental work, show with exact measurements that Beer's law is not strictly valid for several strong electrolytes and that the absorption of various salts is influenced greatly by the addition of non-absorbing salts.

Halban and Fajans both admit the possibility of hydration or of equilibria which may include undissociated electrolyte or groups of ions of both signs in equivalent or non-equivalent amounts. Fajans[3] admits the necessity of this since neither the molecular absorption or refraction is strictly additive for many strong electrolytes. Part of the discrepancy, he decides, is due to ion deformation; but this does not account for all the variations and the presence of molecules, ion groups or complex ions is indicated.

In many cases color changes are apparently connected with changes in the degree of hydration of the salt. The molecular absorption of cobalt chloride in water and various alcohols[4] was found not to be constant with changing concentration, but to increase, decrease, or pass through a minimum as the dilution progresses. The gradual change in color in passing from a dilute to saturated aqueous solution and then to alcoholic solutions is perhaps best explained by a change in the degree of hydration of the salt.

E. F. George[5] found the absorption of light by certain electrolytes to change with concentration, to be presumably a function of their state of dissociation, and to be influenced by the addition of salts having a common ion.

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[1] Halban: Z. Elektrochemie, 29, 434 (1923); 30, 601 (1924); 34, 489 (1928); Halban and Ebert: Z. physik. Chem., 112, 321 (1924).

[2] Fajans: Naturwissenschaften, 11, 165 (1923). Also other papers by Fajans and coworkers.

[3] Z. physik. Chem., A 137, 361 (1928).

[4] Hulbert, Hutchinson and Jones: J. Phys. Chem., 21, 150 (1917).

[5] George: Dissertation, Ohio State (1920).

Hüttig and Keller[1] found that exact measurements showed the molecular absorption in the ultraviolet of all the halides of lithium to change with concentration.

Houstoun and his coworkers[2] studied the absorption of many salts in aqueous and non-aqueous solutions; mostly salts which show extensive hydrate and complex ion formation, as ferric, nickel, cobalt, and copper halides. With these salts no constancy of extinction coefficient with concentration is found; no additivity of absorption for anion and cation. Houstoun reaches the conclusion that solvation plays an important role in the color of ions; and that in dilute solutions where additivity is to be expected, the spectrophotometric methods in use at that time were inadequate to prove constancy of molecular absorption.

Very often the factor of complex ion formation and its effect on color have been neglected. Bjerrum repeatedly emphasizes that absorption may be additive for the ions and one can expect this to mean complete dissociation *only when no complexes are formed*. Considerable work has also been done to show a parallelism between color change and complex formation in certain cases.[3]

From the above can be seen the difficulties involved in using color or light absorption in support of the theory of complete dissociation. The possibility of complex ion formation even in dilute solution limits the application of this theory considerably.[4] For color and absorption data to be entirely satisfactory evidence of complete dissociation, Beer's law should hold unqualifiedly for strong electrolytes, and color and absorption should be strictly additive for anion and cation; but these conditions are met only with good approximation in some cases and not at all in others. Hence one can adopt any of several views:

(1) The older view of Noyes: that undissociated molecules of strong electrolytes are potentially ionized and dissociation of these ions is an optically indifferent process;

(2) The view of Hantzsch: that ionization itself is an optically indifferent process, and change in color is connected, rather, with a change in chemical constitution;

(3) The view of Bjerrum: that ionization is not an optically indifferent process and that validity of Beer's law indicates complete dissociation (minor divergences being explained by Bjerrum's ion-association theory or other factors);

(4) The view of Halban and Fajans: that ionization is not an optically indifferent process, that even large departures from additivity or from Beer's

[1] Hüttig and Keller: Z. Elektrochemie, 31, 390 (1925).

[2] Physik. Z., 14, 424 (1913); Proc. Roy. Soc. Edinburgh, 33, 35, 44, 137, 147, 156 (1913).

[3] For example—Denham: Z. physik. Chem., 65, 641 (1909); Mecke and Ley: 111, 385 (1924); Ley and Heidbrink: Z. anorg. allgem. Chem., 173, 287 (1928); Getman: J. Phys. Chem., 26, 377 (1922).

[4] See also McBain and Ryselberge: J. Am. Chem. Soc., 50, 3009 (1928); 52, 2336 (1930). See, however, Freed and Kasper: J. Am. Chem. Soc., 52, 2632 (1930).

law can be explained by the ion-shell deformation theory, and that some small percent of the electrolyte may be in the form of groups of ions or even neutral molecules;

or (5) The view that we wish to emphasize here, namely that the percent dissociation can no more be calculated with certainty from color or absorption data than from α $(=\mu/\mu_\infty)$ or i-1.

Refractive Index.—The above statements apply almost verbatim to the supposed additivity of refraction by the ions. The smallness of change in molecular refractivity with concentration has often been cited in support of complete dissociation. Thus Bjerrum[1] commented on the work of Fajans. Fajans answered that if such small changes are real, they must be significant. When the Arrhenius theory was first presented, the approximate additivity of refractive index was used as a support for the theory; now it is used as evidence of complete dissociation, and the discrepancies are explained by ion association, deformation, hydration, complex formation, etc. It will be seen that almost every experimenter has his own explanation for the small or great divergences from true additivity.

Additivity of refractive index has been cited as evidence of complete dissociation by Lewis[2] in his famous address "The Use and Abuse of the Ionic Theory"; by Lewis and Randall[3]; by Lange,[4] who says the existence of appreciable numbers of molecules in solutions of strong electrolytes has not yet been provided by optical (or other) means; by Harned[5] who says "The additivity of the refractive indices, rotatory powers . . . is well known"; etc.

With refractivity we have the same difficulty in explaining the experimental data as with optical rotation and light absorption. Actually the molecular refraction is usually not additive for the solid electrolyte and the solvent; and sometimes the calculated molar refraction of the solute remains nearly constant with change of concentration, sometimes it does not. If it does remain nearly constant, we can interpret this fact in two ways: (1) the electrolyte is completely dissociated at all concentrations; or (2) the electrolyte has very nearly the same refractive power whether ionized or not. If the refraction does not remain constant, we can interpret this fact in two ways: (1) the electrolyte is completely dissociated, and the change in refraction is caused by ion association, ion deformation, or some other factor; or (2) the ions and the molecules have widely different refractive powers.

Walden[6] measured the molar refractivity of tetramethylammonium iodide, tetrapropylammonium iodide, and phenylethyldimethylammonium iodide in water and in a series of other solvents of high and low dielectric constants. He found only 1 or 2 percent change over a wide concentration range in most

[1] Trans. Faraday Soc., 23, 376 (1927).

[2] G. N. Lewis: Z. physik. Chem., 70, 212 (1909).

[3] Lewis and Randall: J. Am. Chem. Soc., 43, 1112 (1921); "Thermodynamics", 318, 319 (1923).

[4] Lange: Physik. Z., 29, 760 (1928).

[5] Taylor's "Treatise of Physical Chemistry", 2, 790 (1925).

[6] Walden: Z. physik. Chem., 59, 385 (1907).

of the solvents; also a rather small difference in solvents of high and low dielectric constants. It is hard to see how these results can be interpreted in favor of complete dissociation in aqueous solution; if the salts are really unionized in the non-aqueous solvents of low dielectric constant, then the molecular form has nearly the same refractive power as the ionized form.

H. C. Jones and his coworkers[1] carried out many experimental studies on the refractive index of salt solutions. They found that, in general, the refractivity of the electrolyte was proportional to its concentration. In many cases the refractivity of the pure electrolyte could be predicted from the study of its solutions; they concluded that when this could not be done, the electrolyte formed hydrates in solution.

Rimbach and Wintgen[2] used the refractive index to determine the formation of complexes in solution. They found the refraction to be additive for pairs of salts which form no complexes, as NaCl-KCl, $AgNO_3$-$LiNO_3$ etc. Likewise the refraction was additive for the components of mixtures which deposit double salts, as alums, which led to the conclusion that these double salts are completely dissociated in dilute solution. Mixtures of salts which are known to form complexes, as $CdCl_2$-KCN, $AgNO_3$-KCN, gave entirely different results, the refraction being not at all additive. Thus, they say, measurements of refractive index can be used to give qualitative knowledge of complex formation; but the change in refractive index is too small for quantitative work (usually not over 1% even for concentrated solutions).

Schwers[3] shows that the ratio of change of density to change of refraction with change in concentration, for sulfuric acid, increases with the dilution. From a study of this coefficient he concludes that in many cases—HCl, HBr, HI, H_2SO_4—the refractive index change, for the same specific volume change, is less in dilute than in concentrated solution; or in other words, that ionization (assuming the Arrhenius theory) lowers the refractive index (at constant density). Schwers points out that LeBlanc came to the opposite conclusion, i.e., that the ions have a greater refractive power than the molecules. Other authors reached the conclusion that the ions and molecules have the same refractive power; in other words, that ionization is an optically indifferent process.

Chéveneau[4] made careful determinations of the refractive indices of solutions of KCl, NH_4NO_3 and $Mg(NO_3)_2$. He found practical constancy of specific refraction of the electrolyte over a considerable concentration range, but in very dilute solutions there was a pronounced increase or decrease. In 1910 he indicated the possibility that this was due to lack of adequate temperature control; but in 1921 the experiments were repeated with all precautions for keeping the temperature constant and the previous results were completely verified. Chéveneau interpreted these results to indicate that

[1] Many papers in Am. Chem. J.; Z. Elektrochemie; Z. physik. Chem.; Carnegie Institution Publications; etc.

[2] Z. physik. Chem., 74, 233 (1910).

[3] Z. physik. Chem., 75, 621 (1911).

[4] Compt. rendu, 150, 866 (1910); 172, 1408 (1921).

ionization has no appreciable influence on the specific refractive power in solutions of concentration over ½ gram per liter; the changes at higher dilution he attempts to explain on the basis of a change in vibration frequency of the constituents of the electrolyte, and compares the dissolved substance in dilute solution with an attenuated gas.

It can be seen that the earlier work on refraction by electrolytes in solution by no means gave the conclusive proof of additivity that the exponents of complete dissociation would have one believe. The difficulty of exact enough measurements, the uncertainty of calculation of the molar refractive power of the dissolved electrolyte, the lack of knowledge concerning formation of hydrates and complex ions all contributed to the uncertainty regarding the interpretation of refractive index data. The most accurate experimental work done prior to 1920 could scarcely distinguish between complete or 95% ionization, even if other complicating factors were absent. This was the status of the problem until the work of Debye and Hückel stimulated further research.

Fajans and his coworkers[1] have done much experimental work on refractive index with the express intention of learning the condition of strong electrolytes in aqueous solution. They point out that very few of the older measurements are sufficiently accurate to test rigorously additivity of refractive power of the ions; and show the difficulty of calculating the true refractivity of the solute in those cases where the refractivity of solvent and solute are not additive. The molar refractivity of sulfuric acid, Fajans says, is constant up to a concentration of 30%; this is, however, by no means true for HCl and many salts. For many salts the refraction extrapolated to infinite dilution is additive for the ions, but this is not true at finite dilution. The equivalent refraction of most salts shows a linear relationship with the concentration. Fajans concludes from refractometric and other optical data and from vapor pressures, that in solutions of strong electrolytes ion deformation plays an important role but that there are undoubtedly some neutral molecules or at least pairs of ions and complexes perhaps of the type H_2Cl^+. He points out emphatically that we have every gradation from the strongest to the weakest electrolytes. Strong electrolytes differ from weak electrolytes only in degree; the essential modification of the classical theory lies in taking account of the inter-ionic forces in any quantitative treatment of the subject.

The refractive index of the halides of lithium was measured by Hüttig and Keller:[2] it was found that the refractivity of the salts and the water was not additive, and the value for the salts varies with the dilution. Fajans remarked that the refraction of the solution was in all cases greater than the sum of that of the salt and the water, indicating greater ion deformation, the closer the salt atoms. Hüttig ascribed the effect to hydration, whether in conjunction with ion deformation or not.

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[1] Z. Physik, 23, 1 (1924); Ber., 59, 249 (1926); Trans. Faraday Soc., 23, 357, 375, 408 (1927); Z. physik. Chem., 130, 724 (1927); A 137, 361; B 1, 427 (1928); Z. Elektrochemie, 34, 1 (1928).

[2] Z. Elektrochemie, 31, 390 (1925).

Conclusions.—We can only conclude from the above that the "additivity of optical properties" is a myth; true in some accidental cases, nearly enough true in others so that the discrepancies were not noticeable in the older measurements or could be overlooked. Closer examination shows that from the very nature of the properties under consideration, since the experimental variations are so small, the older, less exact work could be interpreted in favor of the Arrhenius theory as well as the complete dissociation theory. In either case the most exact recent work shows that there are discrepancies to be explained by some other means than the degree of ionization. The observations considered here, in connection with the other experimental evidence, undoubtedly indicate that the conductivity ratio gives values too small for the degree of ionization; but there is mounting evidence of the existence of some small percent of undissociated molecules, or ion-pairs or groups, *in even the best examples of highly dissociated electrolytes.* Too many workers forget that the inter-ionic attraction theory does not require complete ionization. And it must be remembered that at the high dilutions where there seems to be fair agreement with the Debye-Hückel equations, even the Arrhenius theory postulates nearly complete dissociation.

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THE CHEMISTRY OF TURKEY-RED DYEING

BY LYTLE RAYMOND PARKS

Introduction

Knecht, Rawson and Loewenthal[1] discuss "Turkey-red" in general as follows: "The art of producing a fiery and permanent red on cotton with the aid of madder roots, fatty oils (buffalo's milk or sheep's milk), and aluminium salts was known in the East Indies centuries ago, from whence it spread westward through Persia, Armenia, and Syria to Turkey and Greece. Since the middle of the eighteenth century the art of dyeing this brilliant red was brought by the Greek dyers to Rouen, Lyons, and Languedoc in France, where several "Turkey-red" dye works were founded. In 1765 a pamphlet, written by d'Apligny, was published by the French government, in which full instructions are given for producing Turkey-red. As a result of this publication the process became widely known and employed in Western Europe. The first Turkey-red dye works in Great Britain were probably founded in Glasgow in the year 1790, in which district (Vale of Leven) the Turkey-red dyeing industry of that country is still chiefly located; Turkey-red is dyed also in large quantities in the vicinity of Mulhouse (Alsatia), Elberfeld-Barmen (Prussia), and elsewhere. In Western Europe Turkey-red was at first exclusively dyed on cotton yarn; but in 1810 Koechlin of Mulhouse introduced it as a dye for woven fabrics.

"The process as it came from the East was very lengthy, requiring as much as four months; but the time was much shortened prior to the discovery of Alizarin, some 125 years later; and now Turkey-red can be produced in three days which is as fast to light as the colour obtained by the long process. No difference exists between the fastness of the red dyed with madder or with Alizarin. But the colour obtained by the long process is more resistant to chlorine, and slightly clearer than the red produced quickly with the aid of Turkey-red oil, probably on account of the incidental bleaching of the fiber by the sun during the prolonged and frequent exposure in fields after the repeated oiling operations; and there are dyers in various parts of the world who still use the old method and obtain for the products correspondingly higher prices; but those form a very small part of the Turkey-red produced.

"During the last quarter of the nineteenth century a revolution in Turkey-red dyeing has been caused by the substitution of Alizarin for madder, and by the introduction of new methods of oiling. Dyers willingly accepted the artificial dyestuff, since it was well adapted for application by the long established dyeing process; but weavers at first complained that the yarns were too greasy and could not be sized well. Dyers, however, soon recognised the fact that the artificial dyestuff did not require such severe cleaning with

[1] Knecht: "A Manual of Dyeing" 2, 579 (1910).

soap and soda as the natural products, and that the amount of oil in the preparation of the yarns could be diminished; thus this drawback was rapidly overcome, and as early as 1873 Alizarin had completely displaced madder in some of the principal dye-works of Switzerland, notwithstanding the high price at which Alizarin was then sold. This was principally due to the brighter shades that could be obtained and the shortening of the process of oiling and brightening.

"In the old process lukewarm rancid olive oil is used. Under the name of "Steiner's process" a much shorter method of oiling the goods with very hot olive oil came into use. But olive oil has been replaced in most dye-houses altogether by new preparations of castor oil (or of olive oil), the so-called Turkey-red oils, with the aid of which products the oiling operations could be reduced in number and in time without too great a loss in fastness. Thus fine shades of New Turkey-red are obtained at relatively low prices and in a short time, which are exceedingly fast to light and soap, although inferior to the red obtained by the emulsion process. Finally, we may mention various processes of dyeing a red on cotton with the aid of Alizarin and aluminium mordant without any previous oiling of the goods, although an oiling follows the dyeing. These shades are not considered to be Turkey-reds; they are called Alizarin reds and are inferior in fastness and brilliancy to Turkey-red; still they belong to the fastest colours produced and are dyed in very great quantities, especially on cotton goods.

"Turkey-red, as produced on the fibre, is a very complicated compound, the basis of which probably is the calcium aluminium lake $(C_{14}H_6O_4)_3Al_2$, CaO,H_2O, described by Liechti and Suida. The following series of operations serves for the production of Turkey-red:—

(1) Oiling with a fatty oil (olive oil, castor oil, or Turkey-red oil).
(2) Sumaching.
(3) Mordanting or Aluming.
(4) Dyeing.
(5) Clearing.

"A considerable number of washings is absolutely necessary between these processes in order to obtain anything like a good red colour; but the formation of the colour itself is independent of these.

"(1a) Oiling with Olive Oil.—Oils of vegetable origin are exclusively used, olive oil being superior to all others. (In the East Indies the crushed castor oil seeds are used). The best kind of olive oil for this purpose is the rancid Gallipoli oil or emulsion oil (French, huile tournante) which has become rancid by the nitrogenous and extractive matter which it contains. It contains, owing to partial decomposition, more or less free fatty acids (oleic acid and others) as also free glycerin. This oil forms a milky emulsion with sodium carbonate, which emulsion may be partly a solution, and partly a mixture of the finely divided undecomposed oil with the soap (formed by the free acid and sodium carbonate), free acid and possibly glycerin. This emulsified oil is absorbed by the fibre with special facility. The process of oiling

consists in steeping the cotton material (yarn or piece goods) in the emulsion, and subsequently exposing the fibre with the oil to the action of the open air (ageing), or (in Steiner's process) to an elevated temperature in ageing rooms. To increase the quantity of oil thus deposited and transformed in the fibre the oiling and exposing process is repeated several times.

"By the exposure the oil is rendered insoluble so as to adhere permanently to the fibre. The chemical reaction effecting this change probably consists in a further decomposition of the olive oil into free acids and glycerin and in an oxidation and polymerisation of the liberated oleic acid under the influence of air, light, heat, moisture, and sodium carbonate. This has not been well established, but it is well known that oleic acid is very oxidisable and disposed to polymerise; according to Camille Koechlin, 1 part of oleic acid absorbs 300 to 400 parts (by volume) of oxygen under the influence of light. The fact that when recently oiled goods are piled up in heaps without being aired by turning, the temperature rises considerably, and may even reach spontaneous ignition, appears to favor the view that an oxidation takes place.

"From the fibre which has been prepared and well washed, a substance can be extracted by solvents which does not contain glycerin, part of which gives a soap with barium hydroxide, while another part is neutral and cannot be saponified. These compounds are probably the products of oxidation and polymerisation of oleic acid and possibly of the other components and admixtures of olive oil. The fibres which have been deprived of these substances do not yield a serviceable red with Alizarin, but a fair colour is obtained when cotton is impregnated with the extract and subsequently mordanted with alumina and dyed with Alizarin.

"The oil as fixed in the fibres has probably a double effect:

(i.) It combines with and helps to fix the metallic mordant, as in the case of Turkey-red with aluminium and calcium, and in the very similar case of violet with iron and calcium;

(ii.) It forms a colorless transparent varnish around the colour lake which protects the same from the influence of light, air, and chemical agencies, and, at the same time, increases the lustre and fastness of the shade. It may be assumed that in the more rapid processes of preparing the cotton sufficient time is not given for the formation of this varnish like substance; this would account for the inferior fastness of such kinds of Turkey-red.

"(1b) Oiling with Turkey-red Oil.—The use of an olive oil which had been treated with sulphuric acid, as is now the case in the manufacture of Turkey-red oil, was recommended as early as 1834 by Runge in his work, Farbenchemie (Chemistry of Colours). During the seventies of last century Fritz Storck and Dr. Wuth discovered, almost at the same time, the preparation of Turkey-red oil from castor oil, and by its use greatly simplified the process of Turkey-red dyeing.

"The nature of Turkey-red oil has been discussed in Part V, and it has been stated that it contains compounds of certain organic acids with the radical of sulphuric acid, which represent either a sulphate (ester) or a sulphonic acid of ricinoleic acid. These compounds are rapidly decomposed

under the influence of ageing and steaming, the sulphuric acid being separated from the organic acids and the latter being transformed into substances similar to those produced by the preparation of cotton with emulsive oil. The advantage of the Turkey-red oil over the emulsive oil is that it can be fixed in a short time by ageing, thereby allowing the laborious and lengthy exposure to the air to be dispensed with.

"The cotton which has been prepared with oil (by either method) is now treated with warm water and then with caustic soda (steeping). By this operation the fibre is purified, while the oil which has been fixed on the material is not affected.

"(2) Sumaching.—The cotton is usually saturated with a decoction of sumach after it has been impregnated with the oil. The object of this process is to introduce tannic acid into the fibre so as to render it capable of fixing, during the subsequent "aluming" operation, a larger quantity of alumina and of ultimately acquiring a fuller colour. It is uncertain whether the tannic acid enters into the ultimate colour lake or whether it forms a separate lake with the alizarate of aluminium and calcium. The sumaching operation is not absolutely necessary, since there is no decrease of fastness or of brilliancy of colour and no alteration of the shade if it is dispensed with. The sumaching, however, is considered by some dyers to give the colour a greater resistance towards the action of chlorine.

"(3) Aluming.—By the process of mordanting with aluminium salts, one of the metallic mordants which is required for the formation of the red colour lake—namely, aluminium—is incorporated with the material. It is permanently fixed by the subsequent operation of ageing, washing, and chalking, while the acid of the aluminium salt is removed. Calcium, the other metallic mordant, need not be introduced into the fibre before dyeing.

"Sometimes a small amount of stannous chloride or, better, stannous acetate is added to the mordanting bath to produce a more fiery shade; but what part the tin has in the formation of the colour lake is unknown. Some add the tin salt to the dye bath or to the second clearing bath; but nothing definite can be said as to its mode of action.

"(4) Dyeing.—The mordanted material is dyed in a bath which has been prepared with the required amount of Alizarin, and which must also contain a certain amount of lime salt to form the colour lake. If the water has great temporary hardness, it contains the required amount of lime salt in the form of calcium bicarbonate; but if it is very soft, some chalk or calcium acetate must be added. It has been shown by Liechti and Suida that Alizarin and aluminium do not combine in the absence of calcium compounds; but the addition of a calcium salt causes the rapid formation of a lake, which is probably constituted according to the formula $(C_{14}H_6O_4)_3\ Al_2.CaO.H_2O$. Sometimes a stannous salt is added to the dye-bath, which may have the double effect of producing an Alizarin-tin lake and of reducing ferric oxide, thereby preventing the latter from forming part of the colour lake; the ferric oxide, which is easily introduced into the dye-liquor as an impurity, has a very dulling effect on Alizarin-red shades.

"Alizarin and calcium are taken up by the fibre from the dye-bath; but the lake is not completely formed until the temperature is raised above 70°; if the goods have been dyed at a lower temperature, as is the case in the sulphated oil process, they possess a reddish-orange colour when they are taken from the bath, and the red is developed by steaming only, which process completes the long chain of operations required for the formation of the colour-lake, provided that in the second clearing bath no further change is effected.

"(5) Clearing.—The dyed goods are treated twice with hot solutions of soap. The first soaping merely removes a great amount of impurities which become attached to the fibre during the lengthy operations of oiling, mordanting, and dyeing. The utility of the addition of stannous chloride to the second soap bath is disputed. This salt makes the soap solution more neutral, sodium chloride and stannous soap being formed. Possibly the stannous salt exerts a reducing action on the ferric compounds which may have been taken up during the process and which would dull the shade, while the stannic oxide thereby formed enters the colour lake and renders the shade brighter and more fiery. It is contended, however, that stannous chloride cannot act in this way when added to the clearing bath, as the colour lake has already been formed, and that it should therefore be added to the mordanting liquor or to the dye-bath. According to another view, which is supported by Liechti's researches, a tin oleate is produced by the action of stannous chloride in the clearing bath, and is spread as a varnish over the fiber without entering into combination with the colour lake itself. Liechti has shown that 60 percent of the fatty acid of the soap employed may disappear and become fixed to the fibre."

The above-described process is so involved that we marvel at the results obtained, and especially at the ingenuity displayed in devising the original method and the modifications which followed. However by considering Turkey-red dyeing from the standpoint of Bancroft's Theory of Dyeing[1] and Mordants[2] the mystery disappears and the process stands out as comparatively simple.

According to the above-mentioned theory, dyeing consists in imparting a moderately fast color to a substance as the result of immersing it in a suitable, true or colloidal, solution called a dye-bath. Such a solution usually contains a colored substance dissolved or peptized but may contain a substance which can be converted into a colored material. Thus the indigo vat is not blue. The vat is yellow and contains reduced indigo (indigo white), the blue color appearing after the indigo white is oxidized on the cloth. In most cases the coloring matter is adsorbed by the substance dyed and does not form a chemical compound with it.

A mordant is considered as a substance which is strongly adsorbed by the fibre and which itself adsorbs the dye strongly.

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[1] Bancroft: J. Phys. Chem., 19, 50, 145 (1915).
[2] Bancroft: J. Phys. Chem., 26, 447, 501 (1922).

A study of the problem from the standpoint of the above-mentioned theory involves the consideration of five different things.

1. The relation of the metallic mordant to the fibre.
2. The relation of the fixing agent to the fibre.
3. The relation of the fixing agent to the metallic mordant.
4. The relation of the dye to the mordant.
5. The brightening of the color.

Procedure and Experimental Results

For these experiments unbleached muslin was converted into standard cellulose according to the method suggested by Leighton.[1] The cotton was heated for 18 hours on a water bath with a one percent solution of sodium hydroxide. It was washed with distilled water, then with dilute HCl and again with water until the wash was neutral to litmus, after which it was dried in an oven at 115° for six hours.

Taking up of Alumina by the Fiber.—A solution of aluminium acetate was prepared from aluminium sulfate and lead acetate in order to obtain the amount, if any, of alumina which was taken up by the cotton. 25 c.c. portions of this solution were precipitated by ammonium hydroxide, filtered, ignited, and weighed as Al_2O_3. The value found was 0.00466 grams Al_2O_3 per c.c. of solution. Two solutions were made up from this standard of known alumina content and a known weight of cotton placed in each and allowed to stand for 24 hours. 50 c.c. portions were then drawn off by means of a pipette and the alumina content determined as above described. The difference in the concentration before and after treatment with the cotton indicated the amount adsorbed. The following data show this to be very small.

TABLE I

Adsorption of Alumina by Cotton

g. cotton	g. Al_2O_3 used	g. Al_2O_3 found	g. Al_2O_3 adsorbed	total per 1 g. cotton
2.4444	0.1398	0.1385	0.0013	0.00053
2.1954	0.1864	0.1856	0.0008	0.00036

Adsorption of Sulphonated Oil by the Fiber.—Strips of wet cotton cloth were allowed to dry in the air, and then dried in an oven at 50°C for twenty-four hours. The strips were then placed in glass-stoppered weighing bottles and weighed. After weighing they were placed in solutions of Turkey-red oil of different concentrations and shaken for 18 hours at room temperature. The cloth was then removed from the solution and hung up to dry at room temperature without previously pressing out the oil. However the surplus oil could drain from the sample. After air-drying the samples were placed in an oven at 50°C for twenty-four hours and again weighed. The gain in weight

[1] Leighton: J. Phys. Chem., 20, 32 (1916).

represents the amount of oil adsorbed. While this method does not give absolute adsorption values, the results show relative adsorption. The experimental data is given in Table II and shown in graphic form in Fig. 1.

An examination of Fig. 1; where C equals the grams of oil in the filtrate at equilibrium and x/m the grams of oil adsorbed by one gram of adsorbent; shows that a smooth curve is obtained, free from breaks, indicating the adsorption of Turkey-red oil by the cotton.

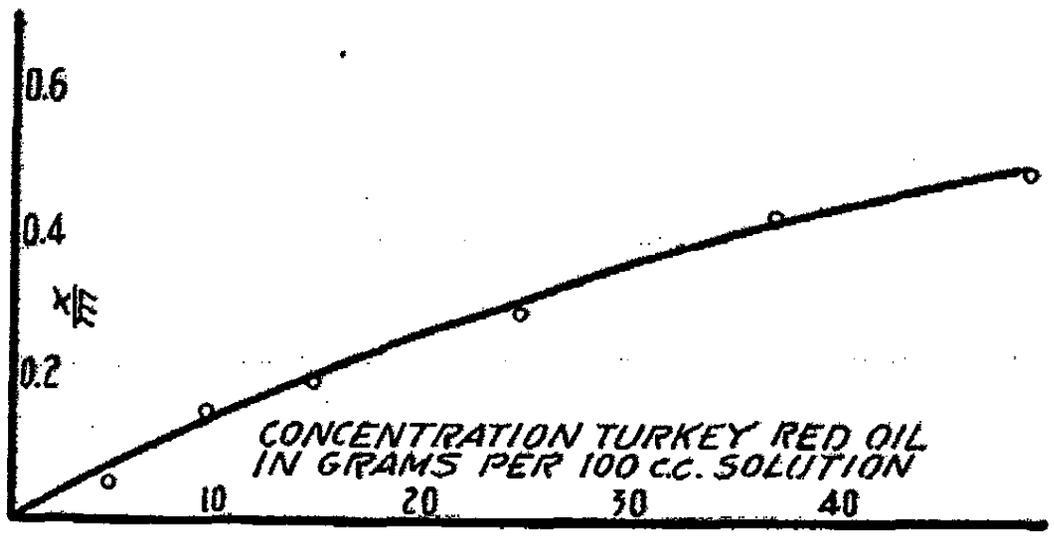

FIG. 1
Adsorption of Turkey Red Oil by Cotton

TABLE II
Adsorption of Sulphonated Oil by the Fiber

No.	Gm. of cloth	Gm. of oil used	Gm. of oil adsorbed	C	x/m
1a	2.0245	5.0	0.0931	4.9069	0.0459
1b	2.1111	5.0	0.1090	4.8910	0.0517
2a	2.0801	10.0	0.2619	9.7381	0.1259
2b	2.1416	10.0	0.3584	9.6416	0.1673
3a	2.0800	15.0	0.3640	14.6360	0.1750
3b	2.0950	15.0	0.4315	14.5685	0.2060
4a	2.0600	25.0	0.5581	24.4419	0.2709
4b	2.0675	25.0	0.6254	24.3746	0.3024
5a	2.0901	37.5	0.8499	36.6501	0.4067
5b	1.7508	37.5	0.7481	36.7519	0.4276
6a	2.0700	50.0	0.9668	49.0332	0.4671
6b	1.7410	50.0	0.8553	49.1447	0.4901

Average of a and b

No.	C	x/m
1	4.8990	0.0488
2	9.6899	0.1466
3	14.6023	0.1905
4	24.4083	0.2868
5	36.7010	0.4177
6	49.0890	0.4786

Colloidal Alumina with Turkey-red Oil or with Soap.—5 c.c. of Turkey-red oil were used in each experiment, but the concentration of aluminium acetate was varied. It was found that through a narrow range a precipitate formed which settled leaving a supernatant liquid which could be filtered. However this filtrate was slightly opalescent. On either side of the precipitating region a white homogeneous solution was formed which passed through filter paper unchanged.

According to Knecht[1] vegetable oils are used exclusively for the mordanting of cloth, olive oil being superior to all others. The oil must be rancid which means it contains more or less fatty acids (oleic acid and others). This oil forms a milky emulsion with sodium carbonate which is readily adsorbed by the fiber. In other words it is a soap solution containing emulsified oil, glycerin and other impurities. It seemed, then, that the soap is essential for fixing the alumina on the fiber.

A tenth-normal solution of sodium oleate was prepared from Kahlbaum's neutral dry sodium oleate, 25 c.c. of this soap solution were used for each experiment, the concentration of aluminum acetate was varied as in the case of Turkey-red oil. Again a narrow range was found where the precipitate settled leaving a slightly opalescent filtrate. On either side a homogeneous colloidal solution was formed which could not be filtered. A number of large extraction thimbles were coated with collodion and placed in tight-stoppered glass jars. The solutions of various concentrations of aluminium acetate and soap were placed in these collodion-coated tubes and allowed to filter for three weeks. At the end of that time about one half of the solution had filtered through perfectly clear, thus showing that in every case the colloid had been removed. Furthermore if a solution of colloidal aluminium soap be held at 85°C for a few hours it precipitates completely, or precipitates immediately at the boiling point.

Adsorption of the Dye by Alumina.—A suspension of alumina was prepared by precipitating Baker's aluminium chloride with ammonium hydroxide. The precipitate was washed twice by decantation and then filtered and washed on the filter paper. This wet precipitate was then washed into a bottle and shaken with distilled water to obtain uniform distribution of the particles. 50 c.c. were evaporated to dryness ignited and weighed. 0.8087 grams Al_2O_3 were found. 2.88 grams of alizarin were dissolved in the theoretical amount of sodium hydroxide to give sodium alizarate and the solution made up to one liter. 50 c.c. portions of the alumina suspension were pipetted into erlenmeyer flasks, varying amounts of dye were added to each and enough distilled water to make a total volume of 200 c.c. These were allowed to stand for twenty-four hours. The supernatant liquid was decanted onto an ashless filter and the amount of alizarin determined in an aliquot part. From this value the total alizarin in 200 c.c. was calculated. All the filtrates were neutral to litmus.

[1] Knecht: "A Manual of Dyeing," 2, 581 (1910).

Analysis of Alizarin.—Knecht's method[1] for the determination of alizarin by titration with titanous chloride was found to be unsatisfactory. The method adopted was based on the colorimetric estimation of colloidal alizarin in an acid solution. So long as the concentration of alizarin is not too great the finely divided alizarin remains in suspension for days. An excess of acid does not affect the results. The following procedure was found to be very satisfactory.

A standard dye solution was prepared by dissolving 0.36 grams of alizarin in sodium hydroxide and diluting to one liter. 20 c.c. of this stock solution was then diluted to one liter. One c.c. contained 0.0000072 grams of alizarin.

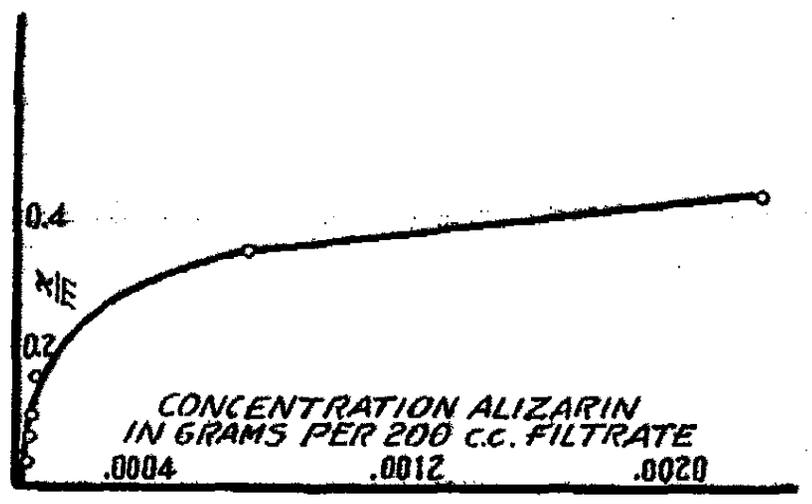

FIG. 2
Adsorption of Alizarin by Alumina

The standards were used in 100 c.c. Nessler tubes. Twelve standards were prepared by employing one c.c. of standard alizarin for number one and increasing the concentration of each succeeding tube by one c.c. After the addition of about 50 c.c. of water and 1 c.c. of sulphuric acid (1:2) the volume was made up to the mark. If the unknown solution for comparison was too concentrated, it was suitably diluted. By following this method it was possible to estimate the total amount of alizarin in 1 c.c. sample to 0.000000036 grams.

The data for the adsorption of the dye by hydrous alumina are shown in Table III and graphically in Fig. 2.

TABLE III
Adsorption of Dye by Hydrous Alumina

No.	Gm. dye used	Gm. dye in filtrate	x/m
1a,b.	0.0288	0.0000288	0.03558
2a,b.	0.0576	0.0000360	0.07119
3a,b.	0.0864	0.0000432	0.10680
4a,b.	0.1440	0.0000576	0.17810
5a,b.	0.2880	0.0007200	0.35523
6a,b.	0.4320	0.0023040	0.53142

[1] Knecht and Hibbert: Chem. Abs., 10, 823 (1916).

Fig. 2 is a typical adsorption isotherm showing that alizarin is adsorbed by the hydrous alumina in the absence of calcium.

Stripping of the Dye by Sodium Chloride and Sodium Sulphate.—50 c.c. portions (0.7900 g Al_2O_3) of a suspension of hydrous alumina were pipetted into erlenmeyer flasks, 25 cc of sodium alizarate (1.2 g. alizarin per liter) were added and the flasks allowed to stand over night. The supernatant liquid appeared free from dye. Various amounts of salt solutions (2.4166 N) were added together with enough distilled water to make a total volume of 125 c.c. Two samples were made up without salt solutions as a check on the amount of alizarin adsorbed under the same conditions in the absence of added salt. The flasks were then allowed to stand for four days after which the solutions were filtered and analyzed for alizarin as described above. The data are summarized in Table IV and shown in graphic form in Fig. 3.

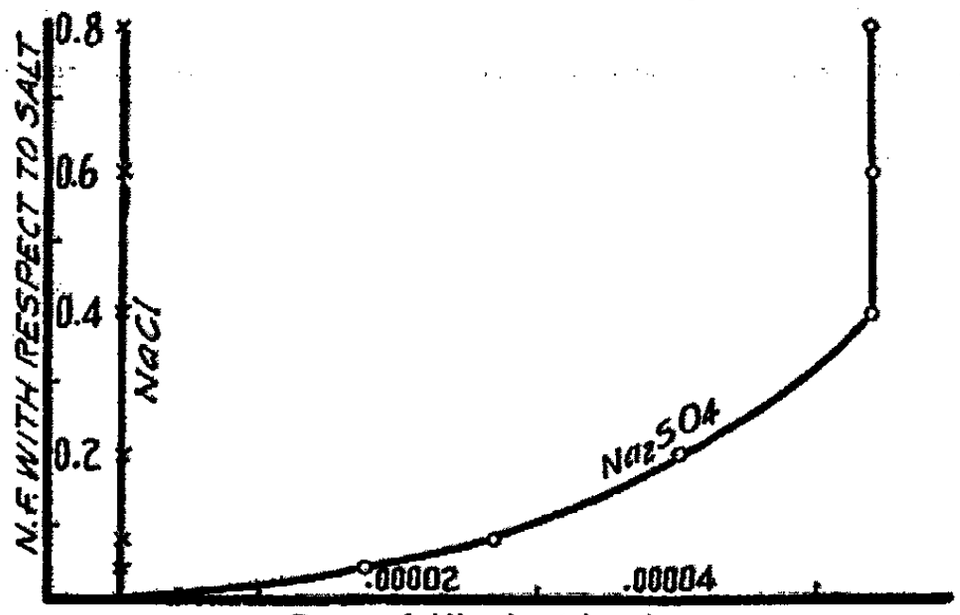

FIG. 3
Stripping of Dye by Salts

TABLE IV
Stripping of Dye by Sodium Chloride and Sulphate

No.	Salt	N.F. of Sol. with respect to salt	Gm. of alizarin in filtrate	stripped	% alizarin stripped
1a,b.	None	0.0	0.000027	—	—
2a,b.	NaCl	0.0403	0.000027	—	—
3a,b.	"	0.0806	0.000027	—	—
4a,b.	"	0.2014	0.000027	—	—
5a,b.	"	0.4028	0.000027	—	—
6a,b	"	0.6043	0.000027	—	—
7a,b.	"	0.8055	0.000027	—	—
8a,b.	Na_2SO_4	0.0403	0.0000450	0.0000180	0.060
9a,b.	"	0.0806	0.0000540	0.0000270	0.090
10a,b.	"	0.2014	0.0000675	0.0000405	0.135
11a,b.	"	0.4028	0.0000810	0.0000540	0.180
12a,b.	"	0.6043	0.0000810	0.0000540	0.180
13a,b.	"	0.8055	0.0000810	0.0000540	0.180

Fig. 3 shows the stripping action of sodium chloride and sodium sulphate on the adsorption complex formed by alumina and sodium alizarate. No stripping action is noticeable with sodium chloride, presumably because the impure alumina was already saturated with chloride ion; the alumina was prepared from aluminium chloride; and no more could be taken up at that concentration of sodium chloride, to cause a noticeable displacement of the strongly adsorbed alizarin anion. But with sodium sulphate there is an adsorption of sulphate ion which causes a partial displacement of alizarin from the alumina. The percentage of alizarin displaced was very small.

Calcium Alizarate.—A solution of calcium acetate 0.01 N was prepared and treated with sodium alizarate (1.2 grams alizarin per liter) according to the following scheme: 50 c.c. of the calcium acetate were measured into 14 erlenmeyer flasks, varying amounts of dye were added, and the total volume made up to 150 c.c. The flasks were allowed to stand for 24 hours, after

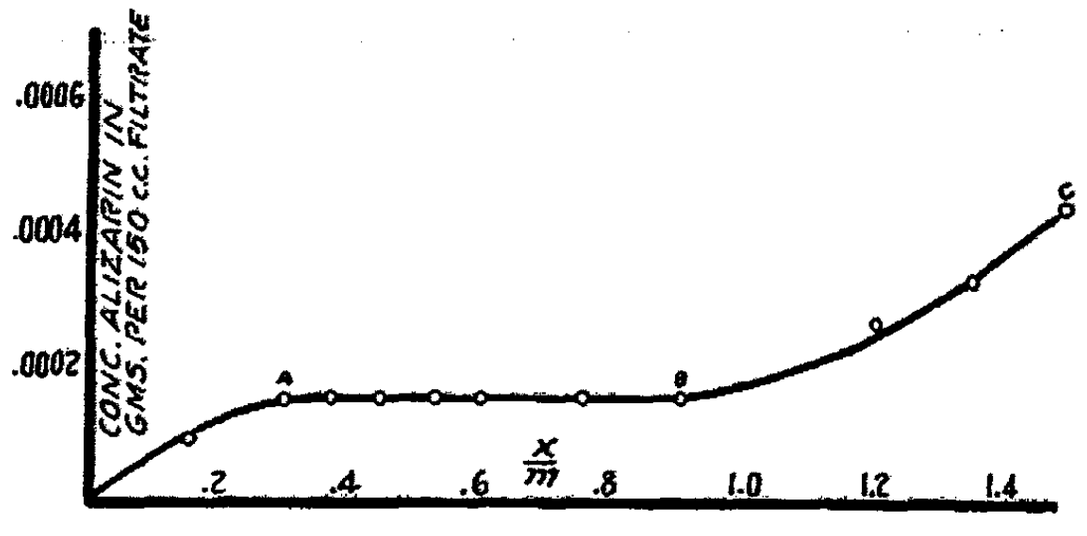

FIG. 4
Action of Sodium Alizarate on Calcium Acetate

which the solutions were filtered and the amount of alizarin determined in the filtrate. The first eleven flasks contained a precipitate, while the last three were completely free of solid matter. The precipitate had dissolved in an excess of sodium alizarate. The results are tabulated in Table V, and plotted in Fig. 4.

Fig. 4 is a most interesting diagram. O to A represents the salting out effect of calcium acetate. That is, the relatively high concentration of calcium ion decreases the solubility of the alizarate. From A to B the calcium alizarate is formed without undue influence of the calcium acetate. At B peptization of the salt by sodium alizarate begins to appear and from C on there is complete peptization.

The solubility of calcium alizarate, as calculated from this diagram, is 0.00012 grams per 100 c.c. of solution at room temperature.

Adsorption of Soap by Alumina.—50 c.c. of a tenth normal soap solution were shaken with about ten grams of ignited alumina and filtered. The alumina was prepared by precipitating aluminium chloride with ammonium hydroxide. The filtrate was neutral to phenolphthalein and methyl orange, and when acidified with hydrochloric acid no precipitate was formed. The

TABLE V

Formation and Peptization of Calcium Alizarate

No.	Gm. dye used 150 c.c.	Gm. dye in 150 c.c. filtrate	Gm. dye taken up per 1 gm. $Ca(Ac)_2$ (x/m)
1a,b.	0.0060	0.00009	0.1496
2a,b.	0.0120	0.000151	0.3000
3a,b.	0.0150	0.000151	0.3760
4a,b.	0.0180	0.000151	0.4519
5a,b.	0.0210	0.000151	0.5279
6a,b.	0.0240	0.000151	0.6038
7a,b.	0.0300	0.000151	0.7557
8a,b.	0.0360	0.000151	0.9069
9a,b.	0.0480	0.000259	1.2084
10a,b.	0.0540	0.000324	1.3590
11a,b.	0.0600	0.000430	1.5081
12a,b.	0.0720	—	—
13a,b.	0.0840	—	—
14a,b.	0.0960	—	—

alumina had removed the soap from solution as the original soap solution was strongly alkaline to the indicator and gave a precipitate of fatty acid with the mineral acids.

Discussion and Interpretation of Results

Bancroft[1] objects to the use of alum or aluminium sulphate baths for mordants because the sulphate coagulates the hydrolyzed salt so readily that large amounts of alumina or basic salt are precipitated in the bath or in the fiber in such a form that it readily rubs off. He suggests the use of aluminium salts of organic acids, which hydrolyze more easily than the sulphates and yet keep the colloidal alumina peptized in a finer state of subdivision.

Napier[2] states that aluminium acetate has several advantages over the sulphate in that acetic acid is not so harmful to the dye; it has less affinity for the alumina, and consequently yields the alumina during the drying process of freshly mordanted fibers.

From the above it is evident that if alumina is adsorbed by cotton a greater adsorption will be shown with aluminium acetate solutions than any other. A glance at the data of Table I shows that cotton has a very feeble adsorbing power for alumina.

Since it is the alumina which has the lake-forming properties, some substance must be found which has a great affinity for the alumina and also for the fiber. Turkey-red oil has been found to be such a substance. It runs about 50% fatty acid, but the general character of the graph will not be changed whatever the fatty acid content may be. An examination of Fig. 1 shows that a smooth curve is obtained, free from sudden breaks, indicating the adsorption of Turkey-red oil by the cotton.

[1] Bancroft: J. Phys. Chem., 26, 515 (1922).
[2] Napier: "A Manual of Dyeing," 121 (1875).

The experiments with Turkey-red oil and soap solutions show that whenever they come into contact with aluminium salts a colloid is formed. Therefore if sulphonated oil or any soluble soap be adsorbed by the fiber and this brought into a bath of aluminium acetate, a colloid is formed which is fixed to the fiber. And since experiment shows that alumina removes soap from solution, the above-mentioned colloid must be due to the adsorption of alumina from solution by the sulphonated oil or soap. In fact the fiber is mordanted with alumina fixed by the oil or soap. The same reasoning applies to mordants produced by sulphonated oils or soaps with iron, chromium, tin, etc.

Heat coagulates this colloid, which then has the property of adsorbing more sulphonated oil or soap, and this can adsorb more alumina. This is a property made use of by the dyers who repeat the oiling and metallic mordanting process several times in order to obtain a suitable amount of oxide on the fiber. The mordanted fiber is stoved before each new application of mordant.

Liechti and Suida[1] were of the opinion that alizarin is not taken up by alumina in the absence of calcium; but that in the presence of calcium a calcium aluminium alizarate lake is formed. Davison[2] found that hydrous alumina prepared from aluminium acetate, in the absence of calcium salts, takes up more alizarin than that prepared from the sulphate. When basic aluminium sulphate is used as mordant, the calcium eliminates the sulphate.

Williamson[3] investigated the aluminium lake of alizarin and came to the conclusion that the lakes are adsorption complexes of sodium alizarate and hydrous alumina, and that aluminium alizarate was not formed since the hydroxide equivalent to alizarate was not set free as would be the case if a double decomposition took place.

Weiser and Porter[4] object to the latter conclusion on the basis that whenever hydrous oxides are brought in contact with salts which yield a strongly adsorbed anion, it is the anion and not the molecule of salt which is adsorbed. They employed an alumina gel which was peptized by sodium alizarate and precipitated with an excess of the sodium alizarate. After this precipitate had settled, the supernatant liquid was nearly colorless, showing that the dye had been practically all removed. They analyzed this liquid and found almost as much sodium present as was originally combined with the alizarin.

Weiser and Porter report that the sodium was present in the clear supernatant liquid as sodium chloride. Therefore the chloride ion was originally present in the alumina gel as ammonium chloride. What Weiser and Porter proved was that adsorbed free alizarin is red. In acid solution one gets a red from the free alizarin which is apparently dissociated very completely. In alkaline solutions, one has sodium alizarate or calcium alizarate as the case

[1] Liechti and Suida: J. Soc. Chem. Ind., 5, 525 (1886).
[2] Davison: J. Phys. Chem., 17, 737 (1913).
[3] Williamson: J. Phys. Chem., 28, 891 (1924).
[4] Weiser and Porter: J. Phys. Chem., 31, 1824 (1927).

may be. The fact that calcium alizarate is so insoluble means that a red containing lime will be faster to washing than a red which is either sodium alizarate or free alizarin.

The goods after the dyeing operation possess a dull red color, which is transformed by the brightening process into the brilliant Turkey-red shade. The brightening of the color consists in washing out the excess oil and dirt collected from the various operations with soap. Some dyers recommend the addition of sodium carbonate. The addition of the latter is very detrimental, as the presence of the strongly adsorbed hydroxyl ions, formed by hydrolysis, tend to strip the dye from the fiber.

Kutschera and Utz[1] have shown that the high temperature produced when a piece of cloth mordanted with chromium and dyed with alizarin is steamed, makes the dye faster to washing. In order to account for the fastness to washing and the change in color one must postulate an increase of particle size. If the particles increase in size, their solubilities decrease. It has long been known that owing to difference in the variation of the absorption of light with varying thickness of the absorbing agent, a substance may be one color in films and another in thicker masses. Keane and Scheetz[2] have shown that yellow bricks are obtained by burning highly calcareous clay even though the iron content is higher than that which would give a red brick if the lime were not present. Bancroft[3] states that it is probable that the ferric oxide is present in such a fine state of subdivision that it is yellow and not red. This, then, is probably the case in Turkey-red dyeing. The particles of calcium alizarate are so finely divided that they appear dull yellowish red when the fabric is taken from the dye bath. The hot clearing bath or steam bath provides suitable conditions for the growing of larger particles at the expense of the smaller ones, just as the particles of barium sulphate grow larger on digestion. These larger particles appear bright red, and of course, are more insoluble than the smaller ones, thus increasing the brilliancy and the fastness to washing. It may be that there is some precipitation of an adsorption complex of lime and alizarin, just as there is with hydrous copper oxide and eosinic acid.[4] If so, the steaming would tend to convert it into calcium alizarate.

Mullin[5] discusses the brightening of colours by heat as follows: "Haller and Rupert report some interesting work upon the orientation of coloring matters within acetate silk and other fibers. When acetate silk is dyed at low temperatures with Para-Red, it has a yellowish shade, the dye being uniformly distributed within each fiber. After immersion in hot or boiling water, the shade becomes redder and the dye agglomerates into larger particles. Similar results are obtained, although with greater difficulty

[1] Kutschera and Utz: J. Soc. Chem. Ind., 5, 532 (1886).
[2] Keane: J. Phys. Chem., 20, 734 (1916): Scheetz: 21, 570 (1917).
[3] Bancroft: "Applied Colloid Chemistry" 242 (1926).
[4] Mullin: "Acetate Silk and its Dyes," 116 (1927).
[5] Gilbert: J. Phys. Chem., 18, 586 (1914).

(steaming under pressure is necessary), when Para-Red is obtained from naphthol AS instead of β-naphthol, or when aminoazobenzene is used instead of p-nitroaniline.

"Similar changes are observed in nitro silk dyed with the same dyes and also with Indigo, Thioindigo Red, and Indanthrene Blue. Nitro silk dyed cold with Naphthylamine Claret (α naphthylamine coupled on the fiber with β-naphthol) contains the dye evenly distributed. When heated in water under one atmosphere pressure the dye agglomerates slightly without change of shade, but when heated for a prolonged period in boiling water or subjected to a short steaming under six atmospheres pressure, agglomeration becomes complete, the dye migrates towards the surface of each fiber and is deposited there as well-defined crystals which may be removed by washing and pressing, the fibers being thereby decolorized. Thioindigo Red dyed on nitro silk behaves similarly. Chrome Yellow, from lead acetate and a dichromate, dyed on nitro silk, is at first evenly distributed, but after steaming under four atmospheres pressure, agglomerates, and becomes orange, even in the absence of alkali, although no migration of the pigment occurs.

"Similar changes are observed by steaming dyed cotton, except that the agglomerated dyes migrate to the boundaries of the lumen in each fiber as well as to the cuticle, the migration, change of shade, and condensation or crystallization of the particles of dye being favored by prolongation of the steaming or rise of temperature. Vat dyes, Indigo, and Thioindigo Red easily, and Indanthrene Red 5GK, Indanthrene Brilliant Violet RK, and Indanthrene Blue RS with greater and increasing difficulty, crystallize and migrate within cotton fibres to the lumen and cuticle when steamed, accompanied by a change in shade. Uncertain results are obtained by steaming cotton dyed with direct dyes.

"Alizarin Red dyed on cotton mordanted with aluminium acetate is evenly distributed within each fibre, but when steamed for an hour under a half atmosphere pressure the pigment agglomerates and migrates to the lumen and cuticle. That deposited near the cuticle is removed by washing with water, the fibre being left colorless. Under similar conditions the presence of Turkey-red oil considerably retards the agglomeration and migration, and the dye which migrates to the cuticle cannot be removed by washing. The decrease in fastness to rubbing produced by steaming cotton dyed with indigo is due to migration of the dye to the cuticle of each fibre.

"Haller reports work of a similar nature upon the color changes of the blue and violet benzidine dyes on cotton, wool, and acetate silk, especially on touching the dyed cotton with a hot iron. His experiments are stated to confirm the view that these dyes form colloidal solutions of different degrees of dispersion, the larger particles coloring the cotton fibre blue, the smaller corinth-red. Solutions of a low degree of dispersion are particularly sensitive to temperature changes or to variations in the medium employed. Thus, in hot dye baths, wool and cotton are dyed red by aqueous solutions; but on cooling, the color on the bottom becomes blue-violet. Alcoholic solutions hardly affect wool but dye cotton a permanent corinth-red.

"The effect of touching the dyed cotton with heated metal is to increase the degree of dispersion of the dye in the fabric, with a change of color from blue to red. The addition of hydrazine hydrate to aqueous Diamine Blue 3R solution causes a similar change, and the solution will then dye cotton corinth-red. The absorption of the dyes by fibrous alumina and barium sulfate indicates a fixed relationship between the degree of dispersion of the dyestuff and that of the absorbent. The surface of the absorbent plays a decisive part also when fibres are used, for swelling causes inner micellar surfaces to come into play, the difference in the sizes of these accounting for the different behavior of different absorbents.

"Wool and acetate silk, after swelling, have larger inner surfaces than cotton. Thus an alcoholic solution of Diamine Blue 3R causes swelling of acetate silk and dyes it corinth-red. After saponification with sodium hydroxide, washing the fiber, and acidifying, the color changes to blue, showing that during saponification the inner structural conditions are changed. The reddening of blue-dyed cotton is also produced by desiccation over sulfuric acid, but to a less extent than by heating. The observed color changes on heating, and drying may thus be connected with dehydration and simultaneous increase in the degree of disperison of the dyestuff within the fiber."

The addition of tin crystals to the dye bath or the clearing bath cannot correct for the iron present, because ferrous and ferric iron both give a violet color with alizarin on an alumina mordant. If a tin-alumina-alizarin complex was formed, the final product would be more yellow in color since alizarin dyed on an alumina mordant in the presence of tin salts is yellow to orange. Consequently the only purpose of the tin salt in the clearing bath is to form a tin soap colloid which is adsorbed on the color lake. This acts as a varnish which cuts down the scattering of light from the surface of the pigment, and at the same time forms a protective coating.

A Short Process for Turkey-Red Dyeing

It has been shown that in Turkey-red dyeing as practised today there are really four things to consider; namely, the relation of the fixing agent to the fiber, the relation of the metallic mordant to the fixing agent, the relation of the dye to the metallic mordant, and the brightening operation. Furthermore one sees that the fixing of the metallic mordant on the fiber is the most clumsy, unscientific, and lengthy process of all. Therefore in order to shorten the actual time required for dyeing this color, the greatest opportunity for improvement is offered in the application of the latter.

Since alumina adsorbs soap from soap solutions, and soap adsorbs alumina from aluminium salt solutions, the problem resolves itself into the preparation of a colloidal solution of alumina and soap, then fixing such a colloid on the fiber; provided it is adsorbed by the fiber.

Experimental

Preparation of the Mordant.—A colloidal solution was prepared from N/10 sodium oleate and 0.2N aluminium acetate solutions. Sodium oleate was selected because of its great solubility; and aluminium acetate because the

salts of the weakly dissociated organic acids do not have the coagulating properties possessed by the salts of stronger acids. Consequently colloidal solutions of a greater alumina content can be prepared. Aluminium acetate of much greater concentration than 0.2N show considerable coagulating effects and greater care must be exercised in the preparation of the mordant.

A series of mordant baths was prepared, each bath containing 25 c.c. of the soap solution, but increasing amounts of aluminium acetate from 5 c.c. to 200 c.c. Strips of wet standard cotton were dipped into each and then well washed in cold distilled water. The strips were cut into two pieces. The colloid was fixed on one piece by heating in boiling water; on the other piece by stoveing at 50 C for 18 hours. The samples were then all placed into one dye bath of alizarin and dyed in the usual manner. The samples which were heated in boiling water for a few minutes appeared to take the dye as well if not better than those which had been stoved. Concentrations above 25 c.c. of aluminium acetate take the dye best. The mordant composed of 25 c.c. soap solution and 100 c.c. of aluminium acetate was chosen for all the following experiments. Boiling water was used as the fixing agent.

Amount of Colloid fixed on the Fiber.—Strips of wet cotton were dried in a drying oven at 105° for two hours. The strips were then placed in glass-stoppered weighing bottles, allowed to cool and weighed. The strips of cloth were thoroughly wetted in boiling distilled water and placed in cold water before the mordant was applied. They were immersed in the mordant bath for 15 seconds. The cloth was next washed in distilled water at room temperature, and then placed in boiling water for 30 seconds. This process was repeated, with sample number two, three times; and nine times with sample number three. After the mordant had been applied the samples were dried at 105 C and weighed. The data of Table VI shows that the grams of mordant fixed per gram of cotton is practically a linear function of the number of times the mordanting process was repeated. Sample number three was ignited and the residue dissolved in nitric acid. A heavy precipitate of aluminium hydroxide was thrown out with ammonium hydroxide.

TABLE VI

Amount of Colloid fixed on the Fiber

Gm. Cotton	Times mordanted	Gm. mordant per gram cotton
1.3549	1	.0021
1.3907	3	.0045
1.3389	9	.0152

Adsorption of the Mordant by Cotton.—500 c.c. of the mordant was prepared from 400 c.c. of .2N aluminium acetate and 100 c.c. of N/10 sodium oleate solutions. Varying proportions of this stock solution were measured into erlenmeyer flasks and sufficient water added to make a total volume of 150 c.c. The total solids are equal to the number of grams of dry normal aluminium acetate and sodium oleate. Thus the total solids in 1 c.c. of stock solution are equal to 0.017 grams.

Strips of cotton were dried and weighed as described above. They were then thoroughly wetted with water, and placed in the flasks containing the mordant of varying concentrations. After standing for 24 hours the cloth was well washed in distilled water, dried and weighed. The gain in weight represents the amount adsorbed. The experimental data are given in Table VII and shown in graphic form in Fig. 5.

Examination of Fig. 5 shows that the mordant is adsorbed by the cotton fiber.

Dyeing.—Pure alizarin on an aluminium mordant in the presence of calcium salts produces a dark pink color and not the fiery Turkey-red. Accord-

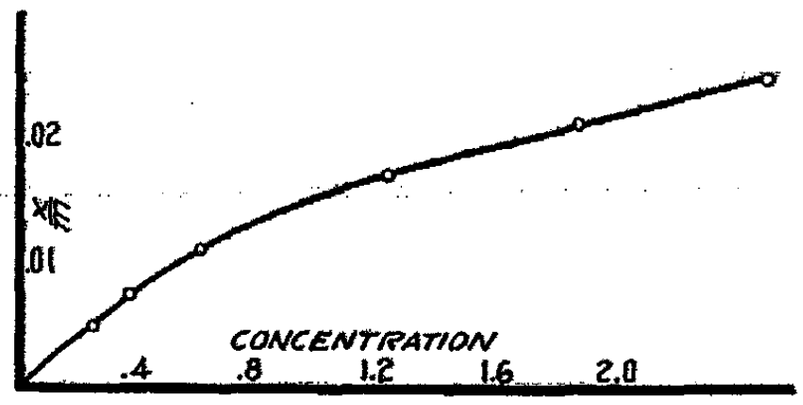

FIG. 5
Adsorption of Alumina Soap Colloid by Cotton

TABLE VII
Adsorption of the Mordant by Cotton

No.	Gm. Cloth	Total solids used	Gm. mordant adsorbed	C	x/m
1a.	1.2939	0.2550	0.0060	0.2490	0.0046
1b.	1.3622	0.2550	0.0067	0.2483	0.0049
2a.	1.3205	0.3825	0.0099	0.3726	0.0075
2b.	1.3526	0.3825	0.0091	0.3734	0.0067
3a.	1.2327	0.6375	0.0132	0.6243	0.0107
3b.	1.3098	0.6375	0.0144	0.6231	0.0110
4a.	1.2978	1.2750	0.0221	1.2529	0.0170
4b.	1.3034	1.2750	0.0223	1.2527	0.0171
5a.	1.3427	1.9125	0.0289	1.8836	0.0215
5b.	1.2663	1.9125	0.0267	1.8858	0.0211
6a.	1.2077	2.5500	0.0299	2.5201	0.0248
6b.	1.2695	2.5500	0.0323	2.5177	0.0253

No.	Average C	x/m
1.	0.2486	0.0048
2.	0.3730	0.0071
3.	0.6237	0.0109
4.	1.2528	0.0171
5.	1.8847	0.0213
6.	2.5189	0.0251

ing to Knecht[1] alizarin "G", which is mainly a mixture of Iso- and Flavo-purpurin containing some alizarin, is used for the dyeing of reds. A sample of alizarin "G" was kindly supplied by the "General Dyestuff Corporation" of New York City to whom I wish to express my appreciation. Standard cotton cloth was mordanted five times as described under the heading of "Amount of Colloid fixed on the Fiber". Without drying, the mordanted cloth was placed in a flask prepared with from eight to ten per cent of alizarin paste, containing twenty percent of alizarin. To this was added one to one and a half percent of solid calcium acetate. The cloth was treated in the dye-bath for about a quarter hour at ordinary temperature. After this the bath was gradually heated so that in about three quarters of an hour it began to boil and the boiling was continued for one and a half hours. The cloth was removed from the dye-bath and washed. It had a dull red color.

Brightening.—The cloth was placed in a large beaker filled with distilled water and kept at the boiling point for twelve hours. The color had changed to a deep red but was more or less without the brilliancy of Turkey-red. The cloth was next mordanted three times and boiled for three hours. After drying the color was a beautiful bright fiery red.

Fastness of the Color.—The fastness to light was tested by covering part of the sample with a thick card board, placing the entire specimen under glass and exposing it to the action of light from a northwest window of the laboratory. The exposed and unexposed parts were compared at the end of four weeks. The color apparently had not faded in the least.

Fastness to acids was tested by steeping a strip of the dyed material for one hour in a 5% solution of acetic acid. Another sample was boiled for 15 minutes in a solution containing 0.5 grams of sulphuric acid per liter. After the samples had dried they were compared with a piece of the original. The color remained practically unchanged.

Fastness to bleeding was tested by boiling a sample in distilled water for ten minutes. The water was allowed to cool and placed in a 100 c.c. Nessler tube and compared with distilled water. There was no noticeable difference in color between the two.

Discussion and Interpretation of Results

The data of Tables VI and VII show very clearly that cotton adsorbs the soap-alumina colloid which is easily and quickly fixed on the fiber by boiling water. By repeating the mordanting process any amount of mordant desired can be fixed on the fiber and in a very short time.

Soap is not essential in transforming the dull red produced in the dye-bath to the fiery red shade. However the brilliancy of the color is not brought out until the pigment is mordanted with some substance which has a higher index of refraction than air, which prevents the scattering of light at the pigment surface.

The experiments conducted in reference to fastness show that the color produced on the soap alumina mordant with alizarin "G" is exceedingly fast.

[1] Knecht, Rawson and Loewenthal: "A Manual of Dyeing," 578 (1910).

Conclusions

In the old process for Turkey-red dyeing the cloth was freed from the resinous substances by treatment with sodium carbonate, and then allowed to bleach in the sun. This treatment removed the greater amount of lignin from the fiber yielding a more or less pure white cellulose which easily took up the "green liquor".

The second operation consisted in saturating the cloth in a bath ("first green liquor") containing an emulsion prepared by mixing sodium carbonate, rancid olive oil, and sheep or cow dung with water. Edward Bancroft[1] states that oil of sesamum, hog's lard, fish oil, or in fact any animal or vegetable oil may be employed. However he was of the opinion that the drying oils as linseed oil produce a blackening due to oxidation. After the goods are thoroughly saturated they are piled in heaps and exposed to the air until dry. They are then placed in stoves and heated at 60° for about 12 hours. This process is repeated three times.

The next four operations consist of treating the oiled yarn with solutions of sodium carbonate. A different carbonate bath is used for each treatment. By this process most of the surplus oil is removed from the fiber forming an emulsion which imparts a white color to the bath, hence the name "white baths". It is claimed that this treatment avoids the formation of so-called "surface" colors which rub off and smear.

After removal from the last "white liquor bath" the goods are well steeped in water at 55 C for 24 hours and stoved at 60°.

The materials used in the "green liquor baths" and "white baths" are soap-forming in nature. The method of treatment is conducive to the formation of soap. So in reality the bleached fiber now contains adsorbed soap and practically no free oil.

The tenth operation is known as "sumaching or galling". The cloth while still warm is steeped for six hours in a solution of sumach at 50° and then hydro-extracted. The cloth has now in addition to the soap taken up a certain amount of tannic acid. This latter operation, many dyers claim, may be omitted without affecting the color.

The cloth is now ready for the alum mordant. Alum is dissolved in water and a solution of about one fourth its weight of soda crystals are added, together with 15 to 20 percent of aluminium acetate and 0.5 to 0.7 percent of stannous chloride. However it is claimed by experienced dyers that the aluminium acetate and tin crystals are not essential. The goods are placed in this solution at 40 to 50 C for twenty four hours, then thoroughly washed and hydro-extracted. After which they are ready for the dye-bath.

In brief, the goods which contain adsorbed soap and tannin are brought into a solution of alum in which the free acid of hydrolysis has been partially neutralized; the temperature is raised which is favorable to further hydrolysis, thus making it easier for the soap and tannin to adsorb alumina from the

[1] Edward Bancroft: "Experimental Researches concerning the Philosophy of Permanent Colours," 2, 199 (1814).

solution, without excessive coagulation. Coagulation would be detrimental to the formation of a smooth mordant which will not rub off. As has been pointed out before, aluminium acetate is preferable to the sulphate since it hydrolyzes easier and to a greater extent without coagulation. Also any stripping of the dye by sulphates is avoided.

The dye-bath is made up with hard water free from iron; or water to which has been added either ground chalk or calcium acetate; and ground madder or a 20 percent paste of alizarin "G". The goods are placed in the dye-bath and the temperature gradually raised to boiling during one hour and maintained at this point for about the same length of time. The goods are of a dull red color which is brightened by the clearing operations.

Calcium alizarate is a very insoluble salt which tends to make the dye more fast. Unless madder is used it is necessary to use so-called alizarin "G", which is a mixture of the purpurins with some alizarin, rather than pure alizarin. The latter produces pinks and not the fiery reds.

The thirteenth and fourteenth operations are called the "first clearing" and "second clearing" respectively. The "first clearing" consists in boiling the yarn in a soap solution and sodium carbonate. The "second clearing" bath is composed of a dilute soap solution to which has been added about 0.15 percent (of the weight of cotton) of stannous chloride.

The function of the "first clearing" is two fold. First, to remove all surplus oil and any dirt which may have accumulated during the various operations. Second, long heating at the boiling point is favorable for the growing of larger particles of calcium alizarate from the smaller ones, thus changing the color from the dull red to the fiery red. Soap as has been shown before is not essential for converting the dull red colored particles to the more brilliant form.

The "second clearing" bath likewise is favorable for the production of larger particles of calcium alizarate. In addition the stannous chloride and soap form a tin soap which is very strongly adsorbed on the surface of the dye pigment, acting as a varnish which prevents the scattering of light at the pigment surface. This varnish also acts as a protective coating, protecting the dye from rubbing and the action of chemicals.

In brief the process of dyeing Turkey-red as practiced may be summarized as follows:

1. The fiber is bleached.
2. Some soap-forming oil is adsorbed on the fiber.
3. The oil is saponified on the fiber.
4. The excess soap and oil is removed from the fiber.
5. The soap containing fiber adsorbs alumina.
6. The alumina adsorbs calcium alizarate.
7. The clearing operations remove the dirt, increase the size of the calcium alizarate particles, and varnish the dyed fiber with a very thin film of tin soap.

In the short process for dyeing Turkey-red, as proposed in this paper, an alumina-soap colloid is prepared from aluminium acetate and sodium oleate. The wet yarn when immersed in this mordant adsorbs the alumina soap colloid which is readily fixed on the fiber by boiling water. By repeating this process any amount of alumina can be fixed on the fiber.

The goods at this point are ready for the dye-bath without any further treatment; and possess an alumina mordant just as in the old process. As compared to the old method of dyeing this color, one has accomplished as much in one operation as with eleven of the original. Thus a great amount of time, labor and material is saved, as well as storage room, vats, heating stoves, fuel and so on.

The yarn is dyed as in the old process. The bath is composed of a mixture of 20 percent alizarin "G" paste, calcium acetate and water free of other metallic salts. The goods are immersed in the dye-bath and gradually brought to a boil and held at this point from an hour to an hour and a half. The yarn possesses a dull red or yellowish red color when it comes from the dye bath.

No strong clearing solution is needed for brightening this color, as there is no excess of oil to remove, and practically no way for the yarn to accumulate dirt during the two operations. Consequently the goods are steamed or boiled with water until the particles of calcium alizarate have increased to such a size as to produce a brighter red color. The yarn is again mordanted in the original mordant bath or in one prepared from stannous acetate and soap and again heated. The fibers are thus quickly varnished with an aluminium soap or tin soap which brings out the brilliant color desired.

The color as produced by the short process is probably just as bright, fast to light, washing, and so on, as any produced by the old time method.

Summary

1. Sulphonated oils are adsorbed by cotton.

2. Alumina is adsorbed feebly by cotton.

3. Turkey-red oil and soap solutions form colloidal solutions.

4. Alumina adsorbs soap from solution and soap adsorbs alumina from aluminium salt solutions.

5. Alizarin anion is adsorbed by alumina in the absence of calcium.

6. Sodium sulphate tends to strip alizarin anion from alumina.

7. Calcium acetate and sodium alizarate form a very insoluble chemical compound, calcium alizarate, which is peptized by an excess of sodium alizarate.

8. The function of the calcium ion when aluminium sulphate is used is to keep the sulphate from preventing the adsorption of alizarin by the alumina. Owing to its insolubility calcium alizarate gives a faster red than sodium alizarate.

9. Heating with steam or hot water after the dyeing operation is believed by Mullin to increase the size of the calcium alizarate particles in the lake,

thus changing the color from a dull yellowish red to the fiery red and increasing the fastness to washing. If there were any lime and alizarine adsorbed separately, the steaming would convert them into calcium alizarate.

10. The function of tin crystals in Turkey-red dyeing is to form a varnish about the pigment thereby increasing the brilliancy and fastness of the dye.

11. No calcium aluminium alizarate is formed.

12. A method has been proposed for the determination of small amounts of alizarin.

13. Cotton adsorbs a soap-alumina colloid.

14. The soap-alumina colloid is fixed on the fiber by boiling water.

15. Weiser's experiments indicate that small amounts of free alizarin adsorbed on an alumina mordant are completely dissociated giving the color of the alizarin anion.

16. Alizarin "G" produces the fiery reds.

17. The color can be brightened by boiling in water free from soap, but does not possess the brilliancy of Turkey-red.

18. The brilliancy can be produced by mordanting the dyed fiber with an alumina soap mordant and heating.

19. A quick method of mordanting with alumina has been proposed which is probably applicable to other metals, such as chromium, iron, and tin.

Acknowledgment

It is with great pleasure that I take this opportunity to express my sincere appreciation to Professor Wilder D. Bancroft at whose suggestion this investigation was undertaken. I feel greatly indebted to him for his kindly interest, helpful criticism, valuable suggestions, and encouragement throughout the progress of the work, and for the invaluable help in the prepatarion of this thesis. And especially do I wish to express my appreciation to my dear wife Mabel B. Parks, whose assistanee and encouragement were invaluable.

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THE CHEMISTRY OF DISINFECTION*

BY WILDER D. BANCROFT AND G. HOLMES RICHTER**

The development of the problem of disinfection and antisepsis has undergone the usual series of events that one finds in the evolution of many problems of biology and medicine. In the race to gain new knowledge of this subject the empirical data have become quite voluminous, while the theoretical interpretations are very meager. Few, if any, of the theories of disinfection attempt to cover all phases of the subject, and up to the present time, these attempts have not been in keeping with the development of other branches of knowledge that have a direct bearing on this problem.

After the discovery of Lister, that phenol is an antiseptic, countless numbers of organic compounds have been tested, by empirical methods, for this property and many good disinfectants and antiseptics have been discovered. Since the demands of the professional men have been satisfied by the provision of fairly good drugs and our patience has been taxed by the trial and error methods, the time is now ripe to turn our thoughts to the theory of the action of toxic agents.

At the outset we realize that bacteriology is a descriptive science and can offer no basis for a theoretical interpretation. In dealing with the effect of drugs on living tissue we must realize the colloid nature of all living material and express our results in terms of colloid chemistry rather than clinical symptoms. The most outstanding and universal physical property of protoplasm is its colloidal structure. Theoretically it is possible to alter colloidal systems by chemical or physical means, the result being: coagulation or alteration of surface conditions such as swelling or contraction, displacement of adsorbed material, formation of emulsions, the increasing or decreasing of the charge on the particles, or reversal of the sign of the charge, peptization, formation of a jelly, stabilizing the sol, etc. The normal state of the colloids of any tissue varies with the age and the individual. Some of the variations, mentioned above, of the cellular colloids will bring about rather startling reactions in the tissue. For example it was found that a reversible coagulation was responsible for the action of anesthetics or narcotics.[1] Substances with a narcotic action when placed in contact with living protoplasm either directly or indirectly caused the colloids to coagulate. Upon the removal of the narcotic the colloids again became peptized to the normal state. In many cases these changes are easily observed with the aid of the ultra-microscope.

The case is just this, a direct narcotic enters the cell and is adsorbed upon the colloids to which it is most attracted. The first effect is the displacement

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** National Research Fellow in Chemistry.

[1] Bancroft and Richter: J. Phys. Chem., 35, 215 (1930).

of material that was already adsorbed upon the surface. The displacement of this normal material increases its "effective concentration" in the water phase. This increase in concentration, in accordance with the mass law, will speed up the chemical reactions which the substance is undergoing. This is nothing more than the stimulating effects on the chemical reactions of a cell by narcotics and toxic agents that have been observed by all workers. The greatest stimulating effect will be on those reactions that show a small tendency to be reversible, such as oxidations.

The accumulation of the narcotic upon the colloids of the cell eventually reaches such a point that the combined effect of the narcotic and the electrolytes of the cell will result in the coagulation. The slowing down of the diffusion of the material in the cell from the high viscosity of the coagulated protoplasm, and the blocking of the surface of the enzymes by the narcotic will result in narcosis.

An indirect narcotic does practically the same thing but in a different manner. Here the coagulating action is due to the products that accumulate through the interference by the narcotic of some normal function. Thus a substance that interferes with the adsorption of oxygen by the respiratory enzymes can behave as an indirect narcotic; the incompletely oxidized products such as acids will cause the coagulation.

Upon removal of the agent that is responsible for the coagulation, the colloids may be peptized again. If this happens there is a return to normal without any symptoms of toxic action. However if the surfaces of the colloid micellae have become so drastically altered that peptization does not take place upon removal of the agents that caused the coagulation, or if the agent is irreversibly adsorbed, then clearly, this effect can cause considerable damage to the affected tissue or cell.

Now a moment's reflection will show that always two effects, narcosis and toxic action, and nearly always a third, stimulation, can be obtained from one and the same substance. It is probable that the initial stimulation is always present, but if the increase in the effective concentration by displacement is negligible the stimulation may be overlooked. These effects are controlled by the concentration of the drug or more properly by the degree of adsorption. There is nothing astounding in this conclusion, it has been known from empirical data for a long time. Some prefer to regard it as a law and have named it the "Schulz-Arndt law". The only new thing about it is the correct explanation.

The organisms that are most frequently exposed, or are involved in man's attempt to expose them, to toxic agents are the pathogenic bacteria and protozoa. The three stages or effect mentioned above are frequently observed.[1] Very low concentrations sometimes stimulate the organisms which we wish to kill, by increasing the concentration of the drug we can inhibit the growth, but not produce death until still higher concentrations are used. The in-

[1] Archiv Hyg., 91, 231 (1922).

hibition of the organism by the drug is due to narcosis and the toxic effect of high concentrations is undoubtedly due to an irreversible coagulation. A closer analysis of this last phase of drug action is the object of this paper.

The first important question is whether the effects of drugs on an organism are physical or chemical. Colloid chemists for a number of years have been submitting evidence that dyes, electrolytes, drugs, and most organic compounds are only adsorbed upon bio-colloids. The work of Traube has been of great value because he has clearly emphasized the role of adsorption in drug action.[1]

Bechhold[2] also has presented a vast amount of data supporting this view. The quantitative experiments of Herzog und Betzel[3] show clearly that in the average case we are dealing with an adsorption of the drug upon the colloids of the organism. An application of the phase rule to such a system as organism-disinfectant showed that there was no definite chemical compound formed with a number of the common disinfectants. Thus the amount of disinfectant taken up by the organism is proportional to the concentration if the temperature is constant; and there is no possibility of a chemical reaction because there is no stoichiometrical relation between the two substances. The disinfectants that behaved in this manner were: silver nitrate, mercuric chloride, chloroform, and phenol. The only compound that showed evidence of a chemical reaction was formaldehyde, that is, the amount taken up was independent of the concentration of the formaldehyde. One can readily understand why it is active over a wide range of dilutions whereas other substances like phenol become inactive on dilution.

Perhaps the easiest approach to the problem is by first examining the effect of toxic electrolytes on lower forms of life. Wolfgang Ostwald[4] in his study of the toxic effect of electrolytes on living tissue recognized clearly that adsorption of the ion or molecule was necessary before any effect was produced and furthermore that the toxic effect was proportional to the adsorption.

What happens after the adsorption of the toxic ion takes place? Either one of two things can take place, there will be a tendency to increase or decrease the degree of dispersion, that is, peptize or coagulate the colloids of the cell. The colloid theory of narcosis has already indicated that irreversible coagulation is the most probable.

Most workers prefer to regard disinfection as occurring in at least two stages, the first being the true adsorption of the agent by the bacteria and the second step being the further action of the agent on the protoplasm. The first condition, that adsorption occurs, is generally accepted; the nature of the action after adsorption is subject to great differences in opinion, in spite of the logical conclusion that it is either a peptization or coagulation. There is a natural reluctance on the part of some workers to believe that dilute

[1] Biochem. Z., 19, 197 (1919); 120, 90 (1921).
[2] "Die Kolloide in Biologie und Medizin" (1929).
[3] Z. physiol. Chem., 67, 309 (1910); 74, 221 (1911).
[4] Archiv. ges. Physiol., 120, 19 (1908).

solutions of disinfectants can coagulate the cell colloids. Nevertheless, the work of Heilbrunn gives undisputed evidence that this is the case.

Heilbrunn[1] in his study of the effect of mercuric chloride on the colloids of protoplasm gives us a clear picture of this coagulative effect. He says: "By actual viscosity tests it can be readily shown that low concentrations of mercuric chloride produce a coagulation, or at least a great increase in viscosity, in various types of protoplasm. *Arbacia* eggs treated with m/10000 $HgCl_2$ in sea-water very soon become altered so that the granules of the cell can no longer be moved by the centrifugal force. The same experiment can also be performed on protozoan cells. When the flagellate *Euglena* is centrifuged, it loses its spindle-shaped contour and becomes spherical, the granular inclusions massing at one end. But when a small quantity of mercuric chloride solution is added to the culture medium in which the *Euglena* lives, no shifting of the granules occurs when the protozoa are centrifuged. The protoplasm ceases to behave as a fluid and is a gel or coagulum. The coagulative action of mercuric chloride, at any rate in higher concentrations, apparently involves a precipitation of proteins from the hyaline ground-substance, that is to say the intergranular material, of the protoplasm. Not only is this a logical assumption, but there is also actual experimental evidence in its favor. When *Arbacia* are first centrifuged, and then treated with dilute solutions of mercuric chloride in sea-water, new granules can be seen to appear in the hyaline region previously free from granules.

"Dilute solutions of copper chloride which have little or no acidity may have a very pronounced action on protoplasm. Thus in one series of unpublished experiments, the following five solutions of copper chloride were prepared: m/1000, m/5000, m/10000, m/50000, and m/100,000. Even the m/5,000 was dilute enough so that there was practically no effect of the hydrogen ion concentration (the pH of this solution was 7.8). All the solutions produced a coagulative effect on sea-urchin eggs, as was clearly shown by centrifuge tests. This coagulation did not occur very rapidly. Thus a test of the eggs in the m/5000 solution showed no coagulation and no increase in viscosity after a 20 minute exposure, whereas a test after 54 minutes did show coagulation."

In these experiments the solutions are so dilute that there can be no question of an osmotic effect on the organisms, furthermore the pH of the solutions was normal so the effect can only be ascribed to the colloidal changes, that is, coagulation. Research workers in Naegeli's time were so completely mystified by this simple coagulation that they immediately named it "oligodynamic action".

Naturally, it is desirable to extend and confirm this work by using other disinfectants and testing for coagulation by a different method. Some experiments along this line have been carried out in this laboratory.

A direct observation of some of the colloids in the living cell of an organism is possible by using an ultra-microscope. If we work within the natural

[1] "The Colloid Chemistry of Protoplasm" (1928).

limitations of this instrument, then it is possible to satisfy our curiosity concerning coagulation by disinfectants and antiseptics. The yeast cell is an excellent object to start with and it is not too difficult to observe colloidal material within the cell. In addition, the work of Herzog and Betzel has already shown that yeast cells adsorb the disinfectants and that there was no chemical reaction except with formaldehyde. Thus these organisms are an ideal starting point.

Ordinary baker's yeast inoculated in Laurent's medium with 1.5% glucose was the stock culture. When fresh material from this culture was examined under the ultra-microscope one could see faintly some colloid material in Brownian movement. A photograph of the appearance of the normal cell

FIG. 1
Normal yeast cells

FIG. 2
Coagulated yeast cells

is given in Fig. 1, the cells appear optically empty due to the fact that the light from the micellae is too faint to make an impression on the plate.

The culture was then treated with a solution of mercuric chloride until the concentration was about 1-1000. The material was then allowed to act for a short time and then again examined under the ultra-microscope. The bichloride has produced a drastic change in the colloidal make-up of the cell, the material is completely coagulated. Fig. 2 shows the appearance of the cells in the ultra-microscope. One can readily understand why the organisms die.

As mentioned above the effect can be either of two kinds, a reversible coagulation or an irreversible coagulation. If a substance merely produces a reversible coagulation, then it could easily inhibit the growth and give all external appearances of behaving as an antiseptic, because if removed, the organisms will again develop and show no ill effects. Chloroform is an example, it is a much better antiseptic than a disinfectant. De la Croix[1] showed that, generally, concentrations of 1-100 would inhibit the growth of bacteria but did not kill them until much greater concentrations were used. Koch[2] showed that this inhibition did not kill certain bacteria even if it were maintained over long periods of time. Ballner's[3] study of this phenomenon led him to the view that it was closely related to narcosis.

[1] Archiv. exp. Path. Pharmakol., 13, 175 (1881).
[2] Mitt. Kaiserl. Gesundsheitamt, 1, 234 (1881).
[3] Z. Bakt., (2) 19, 572 (1907).

This effect, a narcosis or aseptic state can also be demonstrated. Fig. 3 is a reproduction of a photograph of the same culture treated with a small amount of chloroform. There is a striking difference between this and the effect of the mercuric chloride. It is quite easy to reverse this coagulation, by merely washing the organisms with fresh media. The relation between these two types of action is that of the reversibility of the coagulation. In most cases in which irreversible coagulation is the ultimate result there is a preliminary stage in which reversibility is possible. On the other hand, substances that generally produce a reversible coagulation also produce an irreversible coagulation if allowed to act in higher concentrations. Thus it is difficult to draw a sharp distinction between a disinfectant and an antiseptic. It is also for this same reason that there is no sharp boundary between drugs classed as narcotic and toxic. Some theories are so confused on this point that they paradoxically explain narcosis and toxic action on the same basis! Thus the distribution coefficients of narcotics and toxic agents show no characteristic difference, the same is true of their surface tensions. *The distinction is not a physical property of the drug, it is the colloidal property of the protoplasm which determines whether the effect is narcotic or toxic.* Hence we can readily understand why the studies of Meyer and Overton, and Traube can never lead to a definite conclusion concerning the nature of narcosis or toxic action.

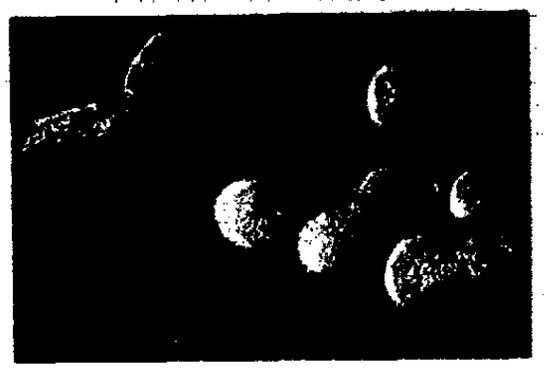

FIG. 3
Narcotized yeast cells

The effect of phenol on yeast was studied in the same manner. Herzog and Betzel have shown that there is no chemical reaction between phenol and yeast. The yeast only takes up the phenol in the sense of a physical adsorption. Dilute solutions of phenol are toxic to yeast, Herzog and Betzel state that .7% solutions will kill the cells after exposures of 5 hours. Phenol solutions of twice this concentration were prepared and diluted with an equal volume of the culture, the material was then examined under the ultramicroscope. As to be expected, coagulation occurred. The coagulation is quite marked after five hours. However, phenol and other agents, to be described later, did not show the same density of coagulation that $HgCl_2$ produces; thus there is a greater tendency towards antiseptic action than disinfection, at least in solutions of this concentration.

Since phenol is so generally used as an antiseptic it would be of interest to examine this effect on some other form of organism than yeast, *i.e.*, bacteria. It must be kept in mind that rather concentrated solutions are required to kill many bacteria. Thus in order to kill the following organisms in 15 minutes the concentrations of phenol required are:[1]

[1] Biochem. J., 6, 362 (1912).

Pest and Typhus	7%
Diphtheria	5%
Coli	8%
Staphylococcus	10%

If weaker solutions are used a greater length of time is necessary before the organisms are killed; in still lower concentrations only inhibition is produced. The concentration of phenol in the two following experiments was 0.5%.

A pure strain of B. *Megatherium* was grown in the ordinary manner and a loop-full of the material was placed in 3cc of normal saline, an equal volume of 1% phenol was added; the concentration of phenol being 0.5 %. This material was then examined periodically in the ultra-microscope. At the end of two or three hours there was evidence of coagulation in a large number of the cells; another examination was made 48 hours later and the colloids of all the organisms were coagulated.

The same type of experiment was also tried on B. *Aerogenes*. In the same concentration of phenol as above there was no visible evidence of coagulation within the first two or three hours, at the end of 48 hours coagulation had taken place in all cells. In neither of the above experiments was the reversibility of the coagulation tested.

The observation of colloid material in these two bacterial cells is a little difficult, especially in B. *Aerogenes*. This is due to the smallness of the cells and also to their shape. The light reflected from B. *Aerogenes* when the substage mirror is at certain angles makes these organisms appear as coagulated diplococci. However, when all adjustments are carefully made there is no doubt that the effect of the phenol on these organisms is no different from that on yeast cells.

There are several different types of disinfectants and antiseptics: heavy metals such as mercury compounds, aliphatic compounds such as chloroform and carbon tetrachloride, aromatic phenols, oxidizing agents, and acid or basic dyes, or analogous substances. The evidence up to this point, based on the study of a representative member of the first three groups, shows that they all act in the same manner, *i.e.*, by coagulation. It is desirable to see if members of the other groups behave in this same manner. As a representative of the oxidizing class of compounds hydrogen peroxide was chosen, as it is a mild agent and no one would be inclined to believe that it was a coagulating agent. The experiment was performed on the same type of yeast culture as was used above. By means of a graduated pipette a given volume of the culture was treated with a three percent solution of hydrogen peroxide until a final concentration was 1%. This treated culture was permitted to stand for four hours and then examined in the ultra-microscope. The changes were quite marked, a very extensive coagulation had taken place.

The same type of experiment was next tried with Yatren,[1] an acidic substance. A solution whose concentration was 1-500 of the sodium salt of

[1] The authors are indebted to E. H. Volweiler of the Abbott Laboratories for the samples of Yatren and Acriflavine.

Yatren was prepared and diluted with an equal volume of the yeast culture. The treated culture was allowed to stand for four hours and then examined as above. The culture used in this experiment was not pure, it was contaminated with some unidentified bacteria. The examination revealed that all the organisms were affected in the same manner, the colloids within the cells were flocculated.

The effect of Acriflavine on the organisms was next investigated. The culture in this case also was contaminated with foreign bacteria. The Acriflavine was made up to a concentration of 1-500 and diluted with an equal volume of the culture. After standing three or four hours the material was examined in the usual manner. In this case the yeast cells were slightly coagulated while the other organisms were not so affected, thus showing a selective action. The coagulation of the yeast cells is not marked as in the other cases and is reversible at this stage. Since the culture is acidic and Acriflavine is most active in alkaline media this effect was to be expected.

Thus from this superficial survey of the action of representative members of various groups of antiseptics and disinfectants, we are drawn to the conclusion that they all affect the organisms in the same manner, *i.e.*, by coagulating the colloids of the cell. This coagulation may be of two types, reversible or irreversible bringing about the conditions known as antisepsis or disinfection.

The kinetics of the coagulation of biological colloids offers an interesting study. The fact that the popular belief that there is a "relation between chemical constitution and physiological action" is evidence enough that many think that the effect of drugs on living tissues is, in the ultimate analysis, chemical. The justification of this view is based upon the fact that such phenomena can be expressed by the equations that are used to represent the velocity of chemical reactions. The literature is filled with studies showing that disinfection is a "monomolecular reaction".

This is indeed unfortunate; these equations that express velocities of chemical reactions are empirical and consequently are not specific for chemical reactions. They can express the velocities of physical processes with equal readiness, thus if we have a beaker full of a solution of a dye and turn a stream of water into the solution, the rate of disappearance of the dye follows the monomolecular equation. Or if a given volume is filled with a certain gas and another gas is blown in, the rate of change in the concentration of the gases can be represented by these equations. The rate of the dissolving of a crystal or the velocity of the swelling of gelatin in water can be expressed by the monomolecular equation, etc.

The velocity of coagulation of many sols, in certain regions, can also be expressed by these equations. Taking the data of Westgren and Reitstötter on the coagulation of a gold sol, we can express the data by the "bimolecular equation".

Time in min.	Rel. No. particles per cc	"K"
0	5.22	—
1	4.35	.0380
2	3.63	.0419
3	3.38	.0347
5	2.75	.0344
7	2.31	.0344

In spite of this good agreement, there can be no question of a chemical reaction, the process is purely physical. It is not surprising that many coagutions resemble chemical reactions, in the one case the velocity depends upon the collision of particles and in the other, collision of molecules. It is this same type of confusion that leads many to believe that the coagulation of proteins is a chemical process, or that disinfection is chemical in nature.

There is a characteristic difference however, between chemical and physical changes. This difference is in the acceleration of the velocity when the temperature is increased, for an increase of 10° the acceleration of the velocity of chemical changes is from 1.8 to 4, the average for a great number of cases is approximately 2.[1]

Cooper[2] has studied the effect of temperature on disinfection and has obtained some interesting results. The temperature range of his experiments was 17° (from 20° to 37°) and if purely chemical changes were taking place one should expect the effect of the disinfectant to be about four times greater at the higher temperature. Hydroxylamine hydrochloride, pyrogallol, m-cresol, and p-bromophenol acting on B. *Coli* were just as effective at the lower as at the higher temperature, the acceleration being zero. Phenol, hydrogen peroxide, ethyl alcohol, acetone, and quinol acting on B. *Coli* had a coefficient of 2-3 over this range. Picric acid, benzoquinone, toluquinone, quinhydrone, 2,6-dichloroquinone, and potassium permanganate acting on the same organisms had coefficients ranging from 10 to 20.

The coefficient of 2-3 for the phenol group indicates that a chemical reaction might be responsible for the effect. However, if the same series of disinfectants are tried on other organisms the above classification no longer holds, the individual members jump from one group to another depending upon the organism. One gathers the impression then that the effect of disinfectants, in the general case, is physical rather than chemical, this physical change being coagulation of the cell colloids.

There are other difficulties with a purely chemical concept of toxic action. In a typical chemical reaction one can predict accurately from a knowledge of the mass law the effect of varying the amounts of the reacting materials. Thus in the case of the reaction:

$$\text{alcohol} + \text{acid} \rightleftharpoons \text{ester} + \text{water}$$

[1] Taylor, "Treatise on Physical Chemistry".
[2] J. Hyg., 28, 163 (1928).

an increase in the amount of the acid or alcohol will increase the velocity of the reaction toward the right side of the equation and increase the yield of ester and water. Or if either the ester or water is added, the reaction is displaced towards the left side of the equation with the corresponding increase in the amount of acid and alcohol.

Now assume a reaction between the bacteria and disinfectant:

$$\text{bacteria} + \text{disinfectant} \rightleftarrows \text{dead bacteria}$$

It is common knowledge that increasing the concentration of the disinfectant will increase the velocity of disinfection and the number of dead bacteria at the new equilibrium will be increased. An experiment of McClintic will illustrate this point.[1] With a constant amount of bacteria a dilution of disinfectant "B" 1-1600 had no effect on B. *Typhosus* in 15 minutes, a dilution of 1-1500 killed the entire culture in 10 minutes, a dilution of 1-1400 would do the same thing in 5 minutes, and a dilution of 1-1300 killed all the bacteria in 2½ minutes. This is in qualitative agreement with the mass action law.

The experiment can be carried out in yet another way. If dead bacteria be added to the disinfection experiment the effect of the disinfectant should be decreased, if the reaction is reversible. Lange[2] did this experiment and indeed the effect of the disinfectant was decreased. Up to this point there is an excellent qualitative agreement with the analogy of a chemical reaction. There is left only one other experiment to make the analogy complete, the investigation of the behavior of the reaction when the amount of *live* bacteria are varied. If larger amounts of live bacteria be used then on the analogy of a chemical reaction the velocity of disinfection should be much greater. Experiments with constant amounts of disinfectant and increasing amounts of bacteria reveal a hideous disagreement[3] with the idea of a chemical reaction. The increasing mass of the bacteria cut down the effect of the disinfectant to a marked degree. McClintic found that when the bacterial mass was increased five-fold the phenol coefficient of disinfectant "B" dropped from 15.6 to 11.6. In any experiment if the number of bacteria be made very great then there will be no effect produced by the disinfectant. The analogy therefore breaks down beyond repair and we are driven to the conclusion again that disinfection, as a general rule, does not depend upon chemical reactions for its basis.

Some workers prefer to abandon chemical concepts altogether and explain these results on a biological basis, with the aid of mathematics. This is not necessary, for the phenomena are colloidal and can be explained by colloid chemistry. It has already been shown that the biological effects are produced by coagulation. The coagulation in turn depends upon the adsorption of sufficient ions or particles of opposite charge to lower the stabilizing charge to the point of coagulation. The stabilizing charge of the cell colloids can

[1] Hygenic Lab. Bull., No. 82 (1912).

[2] Z. Hyg. Infektionskrankh., 96, 108 (1922).

[3] Lange gives a summary of the literature up to 1922 in Z. Hyg. Infektionskrankh., 96, 117 (1922).

also be lowered by the adsorption of organic non-electrolytes as Freundlich and Rona[1] have demonstrated and explained. In this case the coagulation is due to the combined effect of the organic compound and the electrolytes of the cell.

The colloids of the cell behave as the substrate upon which the disinfectant is adsorbed. The coagulation of these bio-colloids proceeds in the same manner as that of other colloids, there must be the adsorption of some minimal amount of the coagulating agent before flocculation begins. Increasing concentrations of the flocculating agent, within certain limits, will hasten the coagulation. Thus it is not surprising that increasing the concentration of disinfectant will hasten the process of disinfection. Suppose that dead cells are added to the experiment (cells killed by heat), these cells will also adsorb the disinfectant and lower its effective concentration and thus slow the process down. The addition of living cells does the same thing and they are not materially damaged if they are numerous enough because the amount of disinfectant per cell is less than that required to produce irreversible coagulation. The whole process is clearly colloidal in nature and depends upon adsorption and coagulation.

If this conclusion is correct then the methods employed in disinfection and antisepsis must all be methods of coagulating bio-colloids. The available data seem to indicate that this is indeed the case. One can further postulate that any method of producing narcosis in higher animals is likely to inhibit the growth and activity of the bacteria and if pushed far enough will behave as disinfectants.

Consider some of the less common methods of narcosis and see if the conditions outlined above are not fulfilled. A physical blow will cause narcosis. We are familiar with the effects of a sharp blow on the head or striking our "funny-bone". In the discussion of narcosis we have presented evidence that this is due to the mechanical coagulation of the cell colloids.[2] The effect of mechanical agitation on bacteria has been investigated by several workers and the data are very interesting. Two effects are at once apparent, at first there is increased growth and activity and later inhibition but not death.[3] The experiments are usually carried out by shaking bacterial suspensions in a shaking machine for several hours. The first effect on the cultures was to increase the growth activity above that of the unshaken controls. On shaking for longer periods of time it was found that the growth was greatly retarded, or completely inhibited. This is not due to any mechanical damage to the cells for the culture would grow in the normal way when removed from the shaker. Thus there is a true stimulation followed by narcosis, the effect being due to mechanical coagulation.

Heilbrunn[4] discusses many cases of coagulation of cell colloids by mechanical means and has measured the viscosity changes produced by the coagu-

[1] Biochem. Z., **81**, 87 (1917).
[2] Bancroft and Richter: J. Phys. Chem., **35**, 215 (1931).
[3] Archiv. ges. Physiol., **17**, 125 (1878).
[4] "Colloid Chemistry of Protoplasm" (1928).

lation. The mechanical coagulation of other bio-colloids is by no means rare, the coagulation of blood fibrin, the inactivation of enzymes, and of immune serum by shaking are commonplace examples of this phenomenon.

The practical importance of the antisepsis produced by shaking is nil, although from the theoretical point of view it is valuable because it shows clearly that the process of disinfection is colloidal in nature.

It has been known for quite a time that the injection of distilled water around a nerve will cause narcosis. The effect is explained by the coagulation produced. Let us see if this type of coagulation plays any role in disinfection. The effects of distilled water on bacteria are very interesting. Fisher[1] would have us believe that the deleterious action of distilled water on bacteria was due to "plasmopsis" of the cell *i.e.*, a bursting of the cell due to the high internal osmotic pressure. He was able to observe the degeneration of the exposed organisms. Leuch[2] carefully repeated these observations and found that the degenerated fragments could be seen even if the bacteria were originally absent; or if the glass slides were well cleaned there was no plasmolysis. One gathers the impression then that the osmotic effects are of only secondary importance and that the distilled water exerts its effect by some other means.

Concerning the colloidal mechanism of this action it is not unlikely that the bio-colloids of the cell are peptized by the electrolytes of the medium. There must be a minimum concentration below which the adsorption of the ions is not sufficient to peptize the material to the proper degree. When the addition of the distilled water has been sufficient to dilute the ions to this value the bio-colloids merely flocculate. The whole process is similar to the flocculation of sols that have been dialyzed too long, or the coagulation of globulins when they are diluted with distilled water. The flocculation, as in most cases, is more easily reversible in the earlier stages than at a later period. In keeping with this it is found that bacteria exposed to the action of distilled water for short periods of time are not damaged as much as when the exposure is longer. The practical importance of disinfection by this means is not worth mentioning. However, the theoretical value of this phenomenon must not be underestimated. It is a well-established phenomenon and is not dependent upon osmotic effects as Leuch has shown. Still no theory of disinfection except the colloid theory is able to account for the action on the same basis as other types of disinfection. There could be hardly a question concerning distribution coefficients, surface tension changes, or chemical reactions; yet there are prominent theories that rest upon these effects as a basis. This is just another example of the frequent deviation of fact from the theories that do not consider the colloidal nature of living matter.

The effect of heat on bio-colloids is well known and little persuasion is needed to convince one that it is coagulation. Disinfection by means of heat is quite common, the colloid aspects of this method are however, not often

[1] "Vorlesungen über Bakterien" (1903).

[2] Archiv. Hyg., 54, 396 (1905).

clearly recognized. Most workers agree that coagulation occurs. The disagreement arises in the different concepts of coagulation. Biological workers in general support the view that the process of coagulation by heat is chemical in nature. The principal basis of this view is that the velocity of coagulation can be expressed by an equation that is "characteristic" for the occurrence of a chemical reaction.[1] The mistake in this view lies in the assumption that the equation is specific for a chemical reaction. That such an assumption is wrong has already been illustrated in the case of the coagulation of a gold sol, which can also be fitted to the equation.

The temperature coefficients of heat disinfection are high and show no tendency to remain constant over equal ranges of temperature. This is exactly what one would suspect if the phenomenon were physical or colloidal and by no reasonable twist of the inagination could such evidence be used to support a chemical view. Bancroft and Rutzler[2] have investigated the effects of heat on protein bio-colloids and their conclusions are that the coagulation is colloidal throughout. Their paper should be consulted for the theory and many interesting details of the phenomena of heat coagulation.

Turning to a less well known method of coagulation, that produced by light, let us examine the role of light in disinfection. Concerning the coagulation of proteins by light of short wave-length, Mond[3] has clearly demonstrated that the colloidal condition of many bio-colloids can be altered. The investigations of Clark[4] support the theory that the action of ultraviolet light on organic substances consists in the emission of electrons from the material. In sols that had a negative charge, the loss of electrons by light action would leave neutral or positive particles, the mutual action of the positive and negative colloids would tend to coagulate the sol. On the other hand, a positive sol when exposed to ultraviolet light, loses electrons and becomes more positive, hence it peptized to a greater degree. Neutral sols become peptized through the positive charge gained by the loss of an electron. Clark was able to demonstrate these effects with egg albumin exposed to ultraviolet light.

The coagulation by light is also produced *in vivo*. Gibbs[5] exposed *Spirogyra* to the rays from a mercury vapor arc, and followed the colloidal changes by viscosity measurements. The variations of viscosity that are characteristic for coagulating protoplasm were found to take place. Addoms[6] was able to see the coagulation, by means of the ultramicroscope, in wheat seedlings root hairs exposed to ultraviolet light. Here, as in other types of coagulation, the process is easily reversible in the initial stages; the toxic effects are associated with the irreversible stage of coagulation.

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[1] T. B. Robertson: "Physical Chemistry of Proteins."
[2] J. Phys. Chem., 35, 144 (1931).
[3] Archiv ges. Physiol., 196, 540 (1922).
[4] Am. J. Physiol., 61, 72 (1922).
[5] Trans. Roy. Soc. Canada, 20, 419 (1926).
[6] Am. J. Botany, 14, 147 (1927).

Light of short wave-length has the same effect on bacteria. As early as 1877 Downes and Blunt[1] discovered the bactericidal action of light. The most effective region of the spectrum is the range from 297 mμ to 210 mμ, that is the same region that is most effective in coagulating proteins.[2] Furthermore the action is direct and does not involve the formation of bactericidal substances such as peroxides, etc., as the amount of these substances produced is far below that necessary to cause the large effects. Moreover, the action is evident only when the light is on; after the light is cut off there is very little action due to the effects of the small amount of peroxides formed during the illumination. We can conclude then, that the action is direct. When ultraviolet rays are passed through suspensions of bacteria only the rays that are adsorbed are effective in killing the organisms. As already mentioned, Henri showed that the region of the ultraviolet light possessing the strongest bactericidal power is that which is absorbed by bacterial proteins. Moreover, the degree of action is almost exactly proportional to the extinction coefficient of protoplasm for these rays. Hence, we can be drawn to only one reasonable conclusion, the toxic action of light is due to the coagulation of the protein colloids of the cell. This is in complete harmony with other types of disinfection and strengthens our belief that disinfection and irreversible coagulation, by whatever means, are intimately related.

Briefly recapitulating, we can observe by means of the ultramicroscope, that all types of chemical disinfectants bring about an irreversible coagulation of the bacterial colloids. Reversible coagulations of the colloids are associated with antisepsis. The corollary that coagulation, by whatever means, will result in antisepsis or disinfection is verified by the types of coagulation produced by distilled water, mechanical agitation, heat, and light. Furthermore, the coagulation is colloidal in nature and not chemical. The fact that disinfection data can be fitted to chemical reaction velocity equations is without significance. The colloid theory is the only theory that can adequately explain the types of disinfection produced by physical means. Thus, from every phase of disinfection we are drawn to the conclusion that the process is colloidal in nature and consists merely in the irreversible coagulation of the bio-colloids of the bacteria.

In the development of this thesis up to this point, it has been stated or otherwise assumed that the coagulation has been produced directly by the bactericidal agent. This is by no means necessary, for as we have already indicated there is a group of narcotics that act indirectly and the same possibility exists that such a thing may occur in disinfection. The experimental researches of C. Voegtlin have led him to conclude that the action of arsenic upon trypanosomes was indirect. In his own words: "A long series of experiments carried out in recent years at the U. S. Hygenic Laboratory in Washington has furnished evidence to the effect that arsenic enters into combination with a sulphur compound (glutathione) which is widely distributed in animal

[1] Proc. Roy. Soc., 26, 488 (1877).
[2] Compt. rend. soc. biol., 73, 323.

cells and even in such low forms of plants as yeast. This sulphur compound had recently been discovered by the English bio-chemist, Hopkins, who found it essential for the maintenance of normal cellular combustion. Now it is significant that certain sulphur compounds have a great affinity for arsenic, as every chemist knows. It was therefore very important to find that the toxic action of arsenic on the trypanosomes could be completely checked in the test tube as well as in the living animal by simply furnishing the cells with an extra supply of glutathione. The effect of the latter substance is quite specific, as it proved to be the only substance of a great number of others occurring in the body which offered protection. Without going into further details we may therefore assume that arsenic kills by interfering with the normal cellular combustion or oxidation mechanism, and the cells die of "internal asphyxia"."

We may question the conclusion that death is due to "internal asphyxia." This lowering of the oxidation process of the cell will allow the toxic (coagulative) substances that are normally destroyed by oxidation to accumulate to the point where they coagulate the cell colloids and cause narcosis or death, depending upon the reversibility of the coagulation. Hence, if the mechanism outlined above is true, arsenic behaves as an indirect disinfectant. Heffter has suggested, and supported by several experiments the theory that free sulphur acts upon the glutathione and forms complex sulfides which stop the cellular oxidation. This would explain the toxic action of sulphur. It may be that there are numerous examples of this indirect class in the reducing type of drugs, but actual knowledge is meager at present.

Since the death of the organisms is due to irreversible coagulation the question of reversibility and the conditions which favor it are important. Normally in testing disinfectants the organisms are exposed to the agent, then placed in some medium to observe whether growth takes place or not. Indeed, this is a convenient but not very accurate method, for the peptizing agents of different substrates are quite different. For example, Liesegang mentions a case where the bacteria of bird cholera were exposed to 1:1000 mercuric chloride solutions for seven minutes; these organisms were then unable to develop on ordinary media. One would ordinarily conclude that they were dead. However, this is not the case for if they are placed in their natural environment, birds, they begin to develop after three hours. The conditions favoring peptization are much better in the animal body than in the laboratory media. Süpfle[1] gives a striking example of peptization of *Anthrax* bio-colloids after treatment with mercuric chloride. The organisms after exposure are apparently dead when tested on ordinary media. Süpfle mixed these organisms with a good grade of blood charcoal and cooled the mixture, to aid the adsorption. In this case the sublimate is adsorbed much stronger on the charcoal than on the bacteria so the material leaves the *Anthrax* cells and is deposited on the charcoal. Upon removal of the charcoal,

[1] Archiv. Hyg., 89, 351 (1920); 93, 252 (1923).

the organisms are found to be again normal and grow well on the ordinary media. In this way it was found that reversibility could be effected in organisms exposed to:

5%	sublimate	after	11 days
3%	"	"	38 "
1%	"	"	40 "

One can understand why it is much more difficult to disinfect living tissues with their favorable peptizing conditions, than inert substrates such as glassware, clothes, instruments, etc. The favorable peptizing conditions in the former case are probably the colloids of the tissue behaving like the charcoal in Süpfle's experiments. In the light of colloid chemistry the testing of disinfectants should be studied from the point of view of the reversibility of the coagulation produced by the disinfectant rather than the determination of growth, on relatively inert media, after exposure.

Some workers regard disinfection in a totally different light, thus McClendon[1] discusses disinfection under the head of cytolysis. However, he clearly recognizes that cytolysis does not always accompany death. Many anesthetics and disinfectants do actualy favor the cytolysis; from our knowledge of the effects of these drugs on protoplasm we can construct a mechanism of cytolysis. For example if a tissue is cut off from the blood supply it will after a time digest itself (autolysis); this is accelerated or favored by the presence of ether,[2] etc. We know that shortly after the oxygen supply is cut off narcosis occurs or a reversible coagulation of the tissue is produced; in time this passes into an irreversible coagulation and death. Autolysis occurs after this stage of irreversible coagulation and is brought about by the enzymes present in the tissue. It is known that the enzymes are not as easily affected as protoplasm by anesthetics or mild disinfectants. For example, when toluene is added to digestion experiments, it affects the protoplasm of bacteria and kills them while it is almost harmless to the enzyme. On the other hand, if the coagulation is extensive enough to damage the enzymes then autolysis cannot take place. Heilbrunn has studied the viscosity of protoplasm that is undergoing cytolysis and the evidence is that coagulation precedes digestion:

"In spite of the fact that Loeb many times emphasized the importance of the so-called cytolysis of sea-urchin eggs, he made little effort to explain the mechanism of the process. In pages 188 to 190 of his book he expresses some vague general ideas regarding the possible nature of cytolysis. Saponin and benzine, he states, dissolve the chorion or jelly of mollusc and annelid eggs. He then cites von Knafft-Lenz's views to the effect that cytolysis is due primarily to the liquefaction of lipoids, and he makes the following quotation from von Knafft-Lenz, "The mechanism of cytolysis consists in the liquefaction of the lipoids, and thereupon the lipoid-free protein swells or is dissolved by taking up water."

[1] "Physical Chemistry of Vital Phenomena."

[2] Archiv. exp. Path. Pharmakol., 60, 256 (1909).

"Loeb thus apparently believes that cytolysis in sea-urchin eggs is primarily a liquefaction of the protoplasm. This it most certainly is not, for viscosity tests indicate beyond the question of a doubt that during cytolysis, the viscosity of the egg protoplasm increases enormously.

"Our general conclusion is that in all types of protoplasm there is a definite type of response to such agents as distilled water, fat solvents, the electric current, mechanical injury, etc. This response is typically characterized by the appearance of numerous small vacuoles within the protoplasm. Frequently, though not always, it is accompanied by an increase in the volume of the cell. When pigment is present in the cell, this always escapes."

The phenomena exhibited by the bacteriophage are also of this type although it is referred to as a lysis. To begin with it has been noted by several workers that small quantities of the bacteriophage stimulate the bacteria.[1] We have already indicated that in the coagulation of cellular bio-colloids the increasing instability of the system is associated with the phenomena of stimulation. This alone would indicate that displacement adsorption and coagulation are concerned in the action of the bacteriophage. The excellent researches of J. Bronfenbrenner present more direct evidence that the colloidal condition of the cell is changed before digestion and that the digestion is due to the normal endoferments. "When swollen bacteria are stained by the method of Gutstein, the cytoplasm may be differentiated from the ectoplasm. The latter always appears continuous, and even in extremely distended cells it shows no evidence of "holes" described by D'Herelle as resulting from the puncturing of the membrane by the entering parasites. The cytoplasm, on the contrary, shows marked changes during swelling. It takes the stain less intensely and less evenly as the swelling progresses, so that in many instances it appears segmented or beaded. In cells photographed at this stage unstained, by means of ultra-violet light illumination, the cytoplasm appears to be of uneven density, quite unlike that of normal bacteria."

"The lysis of bacteria in a synthetic medium, devoid of all protein, gave unmistakable evidence of hydrolysis of bacterial protein.

"In the light of these experiments, the clearing of bacterial cultures in the presence of bacteriophage seems to be due to the hydrolysis of the bacteria. The active agent (bacteriophage) plays no part in the actual solution. The solution is the result of intercellular digestion brought about by normal endoferments."

Bacteriologists do not know, at present, how these enzymes become activated. Colloid chemistry is able to suggest a mechanism; it is common knowledge that enzymes, as all catalysts, must adsorb or be adsorbed by the substrate before they can act. Colloidal studies have indicated that the adsorption capacity of coagulated proteins is frequently greater than that of the uncoagulated sol; this is probably due to the jelly structure of the coagulum. Consequently, we should expect that coagulated proteins should be

[1] "The Bacteriophage and Its Behavior", 76 (1926); J. Infectious Diseases, 37, 35 (1925); Schweiz. med. Wochenschr., 52, 761 (1922).

more easily and rapidly digested; this has been found to be the case.[1] In regard to the swelling of the protoplasm referred to above, bacteriologists explain this as due to the increase in osmotic pressure within the cells.[2] Another possible explanation is that the swelling is due to the change in the pH of the cell during digestion, the degree of imbibition of most bio-colloids being very sensitive to changes in the acidity of the medium. It is interesting to note that when bacteria are shaken with distilled water or treated with other coagulating agents the "bacteriophage is spontaneously generated."[3] The coagulating action of distilled water has already been discussed.

The phenomena of drug resistance are well known and are important in bacteriology and medicine. Briefly, it has been found that if organisms are exposed to small amounts of toxic compounds for long periods of time then subjected to a full dose of the toxic agent they are not killed. Every phenomenon from the probability of the survival of the fittest to the loss of the parabasal body in trypanosomes has been used to explain this condition.[4]

Findlay in discussing the problem at the beginning of 1930 says: "It is obvious that at present no satisfactory explanation of drug resistance can be given. It is however, inevitable that the drug resistance which can be required by trypanosomes, spirochaetes, and bacteria, either *in vitro* or *in vivo*, should be compared with the acquired tolerance towards drugs, such as alcohol, exhibited by man." The reason that this problem has been so difficult for the biologists is because the condition is not dependent on biological phenomena. The whole thing is essentially colloidal in nature and is easily explained, including drug tolerance in man. The toxic action of drugs as we have already indicated, depends upon the coagulation of the bio-colloids of the tissue or organ in question; drug tolerance is based upon the well-known phenomena of fractional coagulation.

It is known that in many cases as in hydrated ferric oxide[5] and albumin sols[6] much less of the coagulating agent is required when added all at once than when added in small amounts over a long period of time, particularly when the slow addition causes a partial coagulation of the sol. This fractional precipitate not only removes the coagulating agent by adsorption on the precipitate which in many cases is greater than that of the original sol, but also alters the stability of the sol by decreasing its concentration. Other conditions being equal, a dilute sol, in general, is more stable than a concentrated sol, because the chance that any two particles can come in contact is less. Thus in the treatment of an organism or tissue, with a coagulating drug it need not surprise us that after several small doses the normal toxic dose does not produce the same effect as in the untreated controls, indeed it is rather to be expected. Since there are many sols in a living cell it frequently

[1] Lloyd: "Chemistry of Proteins".
[2] J. Gen. Physiol., 4, 245 (1922).
[3] Deutsch. med. Wochenschr., 48, 383 (1922).
[4] Compt. rend., 153, 226 (1911); Z. Immunitäts., 43, 253 (1925).
[5] Z. physik. Chem., 44, 143 (1903).
[6] Beitr. Chem. Physiol. Path., 5, 436 (1904).

happens that with two drugs, that are adsorbed upon the same sol, the one drug will make the cell resistant to the other drug. This is due to the fact that the first drug starts the fractional coagulation. In other cases where the two drugs are adsorbed on different sols, the one drug will fail to make the cell resistant to the other drug because it cannot partially coagulate the other sol. The phenomena of drug tolerance which are so difficult to explain on other theories are quite simple when examined in the light of colloid chemistry; it is the natural outcome of the coagulation theory.

The colloid theory is based upon the groundwork of logical interpretation of existing data and experimental observation of the colloidal changes with the ultramicroscope. The interpretation of the data in the light of colloidal chemistry must in time become increasingly evident to biological workers that it is not only logical, but flexible enough to cover the great mass of data without any unusual assumptions. In the consideration of this problem nothing but the most elementary facts and assumptions of colloid chemistry have been employed, yet this theory is able to account for and unify the most diversified facts in disinfection and antisepsis.

Turning to the experimental observations with the ultramicroscope it behooves us to state the limitations of this instrument. No one instrument or method will illustrate all types of biological coagulations. The study of the changes in viscosity is, perhaps, the ideal method, but in this particular case there are great experimental difficulties. The ultramicroscope affords the easiest method of study, but unfortunately it is not universal in application. The colloid particles of protein sols are practically invisible due to the fact that the index of refraction of the particles and the surrounding medium are nearly the same, and colloid particles in the ultramicroscope are recognized by the reflected light. The coagulated sols are frequently easy to observe because their optical properties are much different, coagulated egg white being a familiar example. However, there are cases where the transformation of sol to gel is not accompanied by any marked or drastic change in optical properties, ie. in gelatine. Heilbrunn, in fact, regards this as of very frequent occurrence and if it were not for his classical studies of the variations in the viscosity we would still be in the dark concerning some of the most important problems of biology. Naturally such changes as these are quite difficult to observe.

The opposite extreme also exists, if the organisms are surrounded by a thick membrane that reflects a large amount of light we will not be able to see within the cell, although the outlines of the organism are plainly visible. Staphylococci apparently belong to this group; even when these organisms are exposed to saturated bichloride of mercury solutions, or steam, the coagulation is barely perceptible.

We do not wish to give the impression, that the ultramicroscope is not a valuable instrument for this type of work. If the ultramicroscope were used as much in biology and bacteriology as the ordinary microscope, most workers would not have failed to observe phenomena that was already familiar to the minds of bacteriologists and colloid chemists.

The conclusions of this study of disinfection in the light of colloid chemistry indicate that antisepsis is merely a state of narcosis, which depends upon the reversible coagulation of the cell colloids; disinfection is brought about by the irreversible coagulation of the cell colloids. The corollary, that coagulation by whatever means will bring about antisepsis or disinfection, also holds and is exemplified by the action of heat, light, distilled water, and mechanical agitation on bacteria.

Summary

(1) Antisepsis and disinfection in bacteria are similar to narcosis and toxic action in the higher organisms.

(2) The decreasing stability of the cell colloids in the initial stages of coagulation is associated with the phenomena of stimulation; the stage of coagulation that is reversible is responsible for the inhibition of the activity or the organism but does not kill them; the state of irreversible coagulation is responsible for the death of the bacteria.

(3) These colloidal changes were observed in living cells and bacteria by means of the ultramicroscope.

(4) Antiseptics and disinfectants, like narcotics, can act in either of two ways, by directly coagulating the cell colloids, or by interfering with some normal function of the cell to such an extent that the accumulated toxic products will cause the coagulation. Phenol is an example of the first case and arsenic derivatives seem to be of the second type.

(5) The mechanism of disinfection consists of two phases, first the adsorption of the drug and secondly, the coagulation of the cell colloids.

(6) Most workers have confused the nature of the second phase of action with that of a chemical reaction because the velocity of disinfection can be expressed by equations that are used to express the velocity of chemical reactions. This confusion is cleared away by showing that these equations are not "specific for chemical reactions" but can also be used, in certain regions, to express the velocity of coagulation and other physical actions.

(7) The difficulties of a chemical concept of disinfection are shown by the inapplicability of the mass action law, lack of stoichiometrical relations and the abnormal temperature coefficients.

(8) The disinfection by lytic agents is discussed and evidence produced to show that coagulation is the initial phase, the digestion follows the coagulation.

(9) The phenomenon of drug tolerance is explained upon the basis of fractional coagulation: the adsorption of the drug by the coagulum and the increased stability of the diluted sol. This does not preclude the possible formation of substances which counteract the action of the drug.

(10) The limitations of the ultramicroscope in the observations depends on the optical properties of the coagulum being such that it reflects the light and the absence of a thick reflecting membrane around the cells.

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VAPOR PRESSURES OF SOME HYDROCARBONS

BY ERNEST G. LINDER*

In making a series of vapor pressure measurements for use in an investigation of some electrical properties of hydrocarbons, serious disagreements were found with published data in standard tables, such as the International Critical Tables and the Landolt-Börnstein Tables. The purpose of this note is to give the new data obtained and to indicate the disagreements and likely reason there-for. Data also have been included on some hydrocarbons

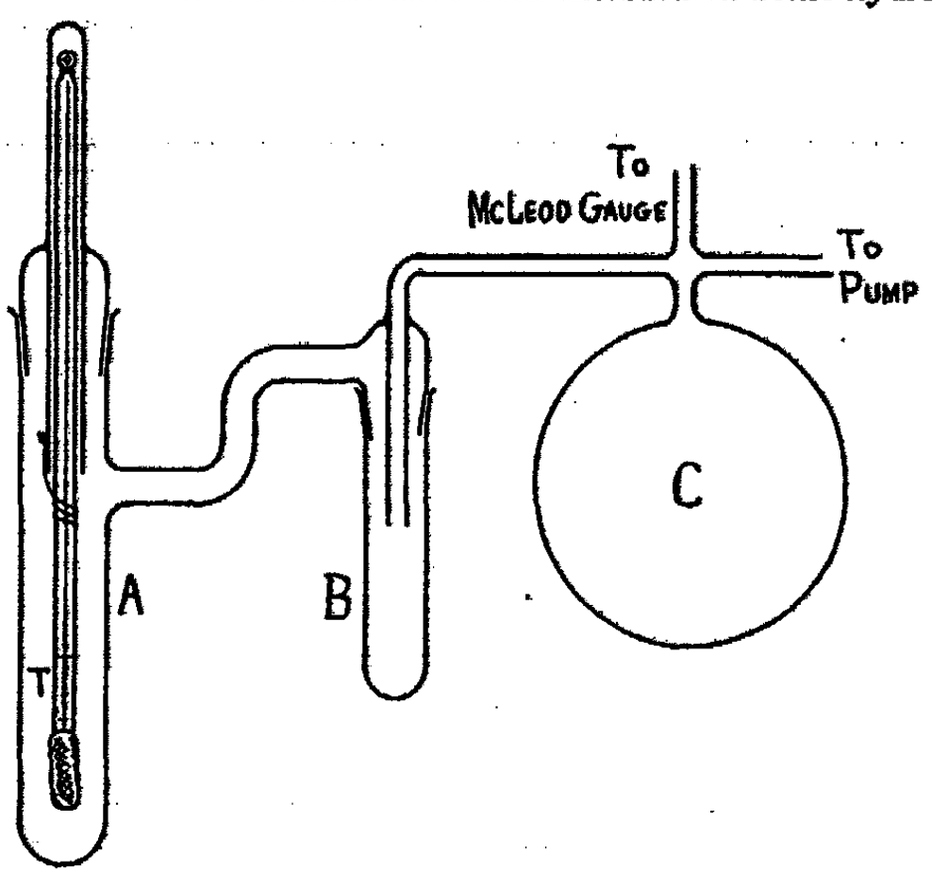

Fig. 1
Vapor Pressure Apparatus

on which no previous determinations of vapor pressure seem to have been made. The measurements extend over only a rather small temperature range, because it was desired merely to obtain sufficient data to determine the vapor pressure at 0°C.

The method used for these measurements was a slight modification of that due to Ramsay and Young.[1] The apparatus is shown in Fig. 1. The essential part is the glass chamber A, containing a thermometer T, with the bulb wrapped with two or three layers of cheesecloth saturated with the hydrocarbon whose vapor pressure is to be measured. B is a trap, cooled either by

* Research associate, Cornell University. This work is a part of an investigation of organic reactions in electrical discharge, being carried on with a fund maintained by the Detroit Edison Co.

[1] J. Chem. Soc., 47, 45 (1885).

TABLE I

Vapor Pressure of Hydrocarbons

t°C	V.P. mm Hg.	t°C	V.P. mm Hg.	t°C	V.P. mm Hg.
toluene		**mesitylene (E)**		**tert-butylbenzene**	
— 9.7	3.53	— 1.7	.34	— 2.0	.27
— 8.7	3.77	2.3	.50	2.3	.43
— 7.2	4.17	3.2	.53	10.8	.82
— 4.4	4.98			13.0	1.05?
— 4.35	5.00	**n-octane**		13.7	1.08
— 3.7	5.30	— 9.3	1.47		
— 3.5	5.36	— 3.0	2.32		
— 2.75	5.57	3.7	3.65	**p-diethylbenzene**	
tetrahydro-naphthalene		**durene**		— 6.7	.49
— 2.4	.015	— 1.7	.013	— 5.6	.54
— 1.2	.0235	— 1.3	.016	— 0.7	.83
25.0	.40	1.3	.033	6.2	1.35
65.0	.83	1.75	.033?[1]		
m-xylene		**n-tetradecane**		**m-diethylbenzene**	
— 8.4	.90	19	.007[-2]	— .8	.15
— 6.75	1.03			6.8	.30
— 2.8	1.37	**n-decane**		10.8	.43
dipentene		— 3.8	.165	15.7	.74
— 5.0	.10	.2	.21	**n-propylbenzene**	
.5	.25	.5	.23	— 6.8	.35
3.3	.31	8.5	.47	— .7	.58
11.75	.55	**n-butylbenzene**		3.6	.85
14.25	.75	— 4.7	.10	13.9	1.95
o-xylene		5.5	.25	**iso-propylbenzene**	
— 17.0	.20	12.2	.48	— 8.2	.43
— 10.7	.42	**sec-butylbenzene**		1.3	.93
.6	1.10	— 8.6	.10	13.7	2.25
p-xylene		— 3.0	.18	**octylene**	
— 9.5	.33	2.6	.32	— 9.0	1.57
— 2.5	.87	9.8	.53	— 2.0	2.70
.2	1.16			9.5	6.02
ethylbenzene				**di-iso-butylene**	
— 11.6	.56			— 9.5	5.12
— 1.2	1.38			— 8.3	5.75

TABLE I (Continued)

Vapor Pressure of Hydrocarbons

t°C	V.P. mm Hg.
2-2-4-trimethyl-pentane	
−30.5	1.08
−19.0	2.58
decane (di-iso-amyl)	
− 2.25	.43
.5	.52
5.5	.78
10.3	1.10
hexamethylethane	
−10.3	1.33
− 5.0	2.08?[1]
− .3	3.55
6.0	5.80?
p-menthane	
− 4.9	.32?
2.0	.54
11.8	1.17
p-cymene	
− 5.5	.14
− 5.3	.14
.0	.23
.8	.25
13.3	.68
phenylcyclohexane	
12.4	.017
styrene	
− 7.7	.65
− .5	1.13
8.2	2.16
1-methylcyclohexene	
− 6.5	3.15
− 1.5	5.25
methylcyclohexene	
−26.2	1.30
−17.0	3.19
− 9.6	6.50?
limonene	
− 5.3	.10
2.5	.23
12.2	.54
pinene	
− 6.00	.41
1.00	.72
13.25	1.78
dekahydronaphthalene	
− 4.2	.10
− 0.2	.14
9.5	.32
methylnaphthalene	
14.6	.031
cyclohexene	
−38	.80
diphenylmethane	
19.5	.02−[2]
mesitylene (Kb)	
− 2.75	.29
− 1.20	.33
1.5	.43
10.6	.91
mesitylene (E)	
− 4.2	.28
2.7	.50
10.2	.91
acenaphthene	
20.0	.02−
o-diphenylbenzene	
20.0	.02−

[1] A question mark indicates doubt regarding presence of equilibrium when reading was taken.

[2] A minus sign after a figure indicates that the vapor pressure is less than the given figure.

liquid air or a carbon dioxide-ether slush. Connections are made as shown to a McLeod gauge and vacuum pump. The three-liter flask C increases the volume of the apparatus so that the McLeod gauge can function properly.

In operating the apparatus, the entire system was first pumped down until the thermometer, cooled by the evaporating hydrocarbon, registered a temperature near o°C. The stopcock to the pump was then closed. After that, sufficient time was allowed for equilibrium to be reached, as indicated by a constant reading of the thermometer. Under equilibrium conditions the

part of the system to the left of trap B will be filled with hydrocarbon vapor, whereas nothing but air will be in the portion of the apparatus to the right of B. The air and vapor will be at the same pressure, hence the McLeod gauge will indicate the vapor pressure of the hydrocarbon at the temperature registered by the thermometer.

TABLE II

Vapor Pressures at 0C

Substance	from published Tables	Woringer	Linder
water	4.55[1]		4.50
toluene	6.97[1]		6.90
naphthalene	.006[1] .023 .022		.0175
octylene	4.00[3]		3.20
n-decane	.35[2]		.20
p-menthane	.40[2]		.43
dipentene	.30[2]		.25
di-iso-amyl	.70[2]		.50
o-xylene		4.0	1.06
p-xylene		8.29	.95
mesitylene		15.6	.375
ethylbenzene		5.9	1.57
n-propylbenzene		6.25	.60
n-octane	3.25[2]	4.00	2.95
iso-propylbenzene		6.45	.82

[1] Landolt-Börnstein Tables.
[2] Wilson: Ind. Eng. Chem., 20, 12, 1363 (1928).

This method is especially suited to the measurement of small vapor pressures, where considerable error is frequently committed due to gases absorbed in the liquid. This source of error is entirely absent in the method described here, since any gas given off by the hydrocarbon will be immediately swept over into the chamber C, and become merely a part of the gas contained there-in. Another advantage is that the vapor pressures of solids can be determined. To do this, it is only necessary to remove the cheesecloth wrapping from the thermometer bulb, and coat the bulb by dipping it in the molten hydrocarbon.

The complete data are given in Table I. For some substances, e.g., n-tetradecane, the pump was incapable of reducing the pressure in the system down to the vapor pressure of the substance, hence, for these substances, it can be stated only that the vapor pressure is less than the given figure.

Satisfactory checks of the accuracy of the method were made with water and toluene. These and some other comparisons are given in Table II. Wilson's data were taken from a nomographic chart, and the agreement with

the writer's data is very likely within the limits of accuracy of the chart in the region involved, especially since extrapolation on the chart was necessary in some cases.

The writer's data in the last column in the lower part of the table are in serious disagreement with Woringer's data quoted in the other column.[1] Woringer used a static method, i.e., one in which the vapor is contained within a closed space and the pressure measured directly for different fixed temperatures. With such a method small traces of absorbed gases will cause serious errors at low pressures. It seems likely that such an error was present in Woringer's measurements, especially since all his pressures, where there is a disagreement, are greater than the writer's.

In the case of mesitylene (which shows the greatest disagreement) three runs were made by the writer. The first two were made on mesitylene from the Eastman Kodak Company, one being made with carbon dioxide-ether cooling and the other with liquid-air cooling on the trap. Both these runs gave 0.39 mm. of mercury for the vapor pressure at 0° C. The third run was on Kahlbaum mesitylene. This gave 0.36 mm. of mercury. It seems that these figures must be fairly correct.

Summary

For thirty-nine hydrocarbons vapor pressure data in the neighborhood of 0°C. are presented. Some disagreements with published data in standard tables are pointed out and discussed.

The writer wishes to express his appreciation to the Detroit Edison Company for the financial support which has made this investigation possible, and for the permission to publish the data. Thanks are also due to the Physics Department of Cornell University for the laboratory facilities used.

Cornell University,
Ithaca, N. Y.
July, 1930.

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[1] Z. physik. Chem., 34, 257 (1900).

ACID ADSORPTION AND STABILITY OF NITROCELLULOSE

BY D. R. WIGGAM*

Introduction

It is well known that traces of acid adsorbed by nitrocellulose accelerate its thermal decomposition. The type of acid is unimportant, with the possible exception of the weakest organic acids. The stability is lowered in a degree proportional to the amount of acid adsorbed. The present work has been confined to strong acids, as it is these which are of principal importance to the manufacturer and user of nitrocellulose.

Experimental

The determination of acid adsorption is direct. Two grams of nitrocellulose, dried to constant weight at 70°C., were added to 50 cc. of N/100 acid and allowed to stand for 15-30 minutes with occasional stirring. Longer standing was not found necessary. An aliquot was withdrawn and titrated with standard base, using methyl orange as the indicator. The reading of the endpoint at these dilutions requires some practice but becomes quite precise after a few trials. Base consumption by the sample was carried out in an analogous manner. Adsorptions are reported as cubic centimeters of N/100 acid used up per gram of nitrocellulose.

Thermal decomposition was followed by the 134.5°C. methyl violet test. Two and five-tenths gram samples of oven-dry (70°C.) nitrocellulose are placed in special test tubes and tamped tightly. A methyl violet test paper is placed in the tube above the nitrocellulose and the mouth of the tube plugged with a perforated stopper. The tube is placed in a special constant temperature bath at 134.5°C. and heated until the paper has completely changed color to a salmon pink. The time required for this change in color is reported.

Two types of nitrocellulose were first studied, designated as 5119 with nitrogen content 13.09 per cent and 4200 with nitrogen content 13.47 per cent. These are smokeless powder types, and in the process of manufacture had been reduced to pulverulent condition. They were stabilized by usual methods of processing.

With sulfuric, nitric and hydrochloric acids, adsorption data are given in Table I.

Experiments 1, 2 and 3 indicate how closely the results of successive determinations checked. Sulfuric and nitric acids are adsorbed to the same degree; hydrochloric acid somewhat less.

The two nitrocelluloses were suspended in N/100 NaOH. Aliquots of the supernatant liquid were removed and titrated with acid. Three one-hundredths cc. N/100 NaOH were used up per gram of sample by 5119, and

*Hercules Powder Company.

TABLE I

A = cc. N/100 acid adsorbed per gm. N.C.

Exp. No.	N.C.	Acid	A	Exp. No.	N.C.	Acid	A
1	5119	H_2SO_4	0.44	5	5119	HCl	0.41
2	5119	"	0.46	6	4200	H_2SO_4	0.37
3	5119	"	0.45	7	4200	HNO_3	0.36
4	5119	HNO_3	0.46	8	4200	HCl	0.29

0.12 cc. N/100 NaOH were used up per gram by 4200. Faint traces of acid may be present on nitrocellulose from incomplete removal in its preparation or from incipient thermal decomposition on drying. At ordinary storage temperatures with moist material the latter reaction has almost zero rate.

If the residual adsorbed acid had been removed before suspending in acid, the adsorptions would have been as follows:

H_2SO_4	$-0.45 + 0.03 = 0.48$	cc./gm.	5119
HNO_3	$-0.46 + 0.03 = 0.49$	" "	"
HCl	$-0.41 + 0.03 = 0.44$	" "	"
H_2SO_4	$-0.37 + 0.12 = 0.49$	" "	4200
HNO_3	$-0.36 + 0.12 = 0.48$	" "	"
HCl	$-0.29 + 0.12 = 0.41$	" "	"

To verify the above results, samples of 5119 and 4200 were enclosed in semi-permeable nitrocellulose membranes and suspended for 30 days in distilled water, which was replaced continuously. No. 5119 then adsorbed 0.51 cc. N/100 sulfuric acid and 4200 adsorbed 0.50 cc. N/100 acid. The results agree within the limit of accuracy of the method.

Adsorptions were determined in the above manner on two further samples of nitrocellulose of different nitrogen contents. (Table II), No. 734 was long-fibre material of nitrogen 12.15 per cent, No. 4467 was pulverulent, with 12.86 per cent nitrogen.

TABLE II

A = cc. N/100 acid adsorbed per gm. N.C.

N.C.	Acid	A	N.C.	Acid	A
734	H_2SO_4	0.87	4467	H_2SO_4	0.36
734	HNO_3	0.88	4467	HNO_3	0.38
734	HCl	0.66	4467	HCl	0.34

The results follow, in general, the same trend as shown with the higher nitrogen samples. Base consumptions for the above samples showed that 0.58 cc. N/100 base were required per gram of 734 and 0.54 cc. for 4467. Had the samples been purified by dialysis the sulfuric acid adsorptions would have been,

734.....0.87 + 0.58 = 1.45 cc.
4467.....0.36 + 0.54 = 0.90 cc.

The total acid adsorption is thus dependent on the nitrogen content of the nitrocellulose. The total surface of the individual samples of nitrocellulose was not determined. The specific surface would vary from sample to sample, due to different degrees of pulping, but for any one sample would be substantially constant.

Known amounts of acids were deposited on nitrocelluloses 5119 and 4200, and the stabilities determined by the methyl violet test. After suspension in N/100 acid, the sample was filtered on a Buchner funnel and sucked as dry as possible. It was then stirred into 1000 cc. distilled water and agitated for several minutes, filtered and dried. Acid adsorptions were run with sulfuric, nitric and hydrochloric acids. Knowing the total adsorptive capacities from previous data, the retained acid could be calculated. Table IV gives this data, together with the methyl violet heat tests.

TABLE IV

N.C.	Kind of Acid	cc. N/100 Acid Ads. after Treatment	cc.N/100 Acid Ret'd.	Methyl Violet Test
5119	Original*	—	0.03	28 Min.
5119	H_2SO_4	0.20	0.29	26½ "
5119	H_2SO_4	0.32	0.16	27 "
5119	HNO_3	0.08	0.40	26½ "
5119	HCl	0.13	0.31	26½ "
4200	Original*	—	0.12	27½ "
4200	H_2SO_4	0.25	0.24	25 "

* This refers to untreated sample. Retained acid may be nitric or sulfuric or both.

Traces of free acid have a distinct effect in lowering the methyl violet test. In spite of their greater volatility at the temperature of the test, hydrochloric and nitric acid, when adsorbed, have approximately the same effect as sulfuric in lowering stability of nitrocellulose. None of the samples exploded in five hours in the bath.

Larger amounts of sulfuric acid were deposited on nitrocellulose by evaporation of dilute acid solutions in contact with 5119 at low temperature. After drying, the stabilities were determined by the methyl violet test. The results are given in Table V and Fig. 1.

TABLE V

Equivalent Vol. of N/100 Acid/Gm. N.C.	Mols Acid/Gm. N.C.	Methyl Violet Test	Explosion Time
4.793	0.00004793	5½ Min.	19 Min.
2.647	0.00002647	7 "	45 "
1.178	0.00001178	8½ "	5 + Hrs.
1.096	0.00001096	8¾ Min.	5 + Hrs.
0.649	0.00000649	10¼ "	5 + Hrs.
0.29 *	0.0000029	26½ "	5 + Hrs.

* From Table IV.

If the acid adsorbed is of the order of 3×10^{-6} mols. per gram of nitrocellulose or less, the effect on the resistance to decomposition (stability) is not serious. It should be noted that this figure applies only to high nitrogen content nitrocellulose for use in smokeless powder. For the lower nitrogen content nitrocelluloses, much larger amounts of acid would be required to have a proportionate effect.

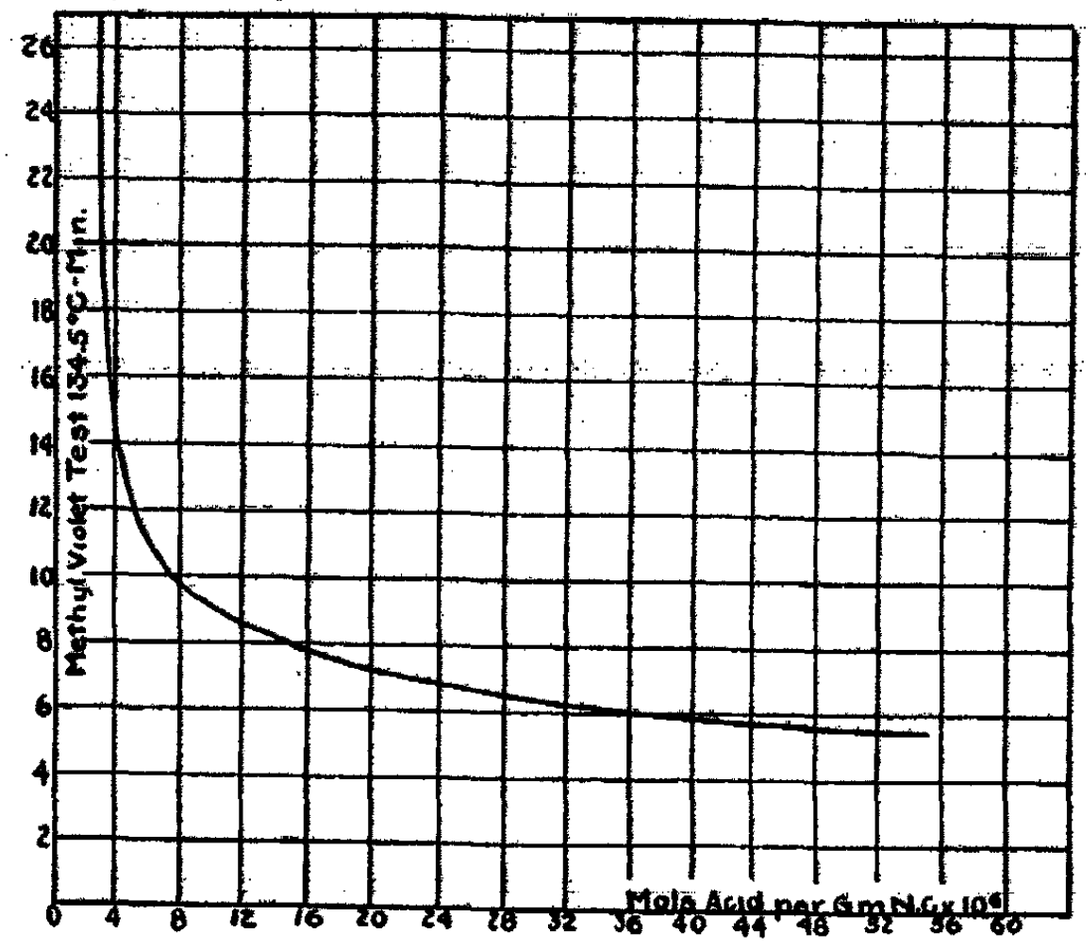

FIG. 1

Effect of adsorbed Acid on Stability

Summary

At the dilutions used in this work, nitric and sulfuric acids are adsorbed to approximately the same extent, while hydrochloric acid is adsorbed to a somewhat lesser degree. Base adsorption by nitrocellulose apparently does not take place. When nitrocellulose is dipped in dilute base, some of the latter is used up to neutralize the acid present on the fibre, accounting for an apparent adsorption. When this acid is removed by dialysis, the acid adsorption becomes equal to the acid plus base consumption of undialyzed fibre.

Acid retained by the fibre lowers the resistance to heating of nitrocellulose with a given sample. The effect of equal amounts of the three strong acids used lowered the heat resistance to approximately the same degree. A smooth curve is obtained by plotting the results of the methyl violet test (stability) against the acid adsorption.

NEPHELOMETRIC TITRATIONS. I. THE EQUAL-OPALESCENCE END-POINT*

BY CLYDE R. JOHNSON**

One of the outstanding procedures now in use in the determination of exact atomic weights is the so-called "nephelometric method" of titration. The general method consists in estimating the stoichiometrical ratio between a pure compound furnishing chloride or bromide ions, and pure silver, with the use of the nephelometer.

This method was first used by Richards and Wells[1] in 1905 to determine the NaCl:Ag ratio, from which the atomic weight of sodium may be calculated, by taking suitable values of the antecedent atomic weights of chlorine and silver. The method has subsequently been applied to the analysis of other chlorides and bromides, to determine the atomic weights of many elements. In these analyses, the procedure described by Richards and Wells has been used without essential modification, in determining the end-point of the nephelometric titrations (the equal-opalescence end-point).

At the present time the accepted values of a large number of atomic weights rest almost entirely upon ratios determined by the nephelometric method. This is in part due to the convenience and simplicity of the method; it has been preferred by investigators who have used modern methods to prepare pure compounds for atomic weight analysis. Furthermore, the "probable error" of atomic weights calculated from ratios determined nephelometrically is rather generally lower than the "probable error" of corresponding values calculated from ratios found by other chemical methods. In short, there has developed a tendency toward giving "nephelometric" values preference over the values obtained by other methods, which are regarded mainly for the confirmatory evidence which they furnish.

Curiously enough, in view of the wide application of the nephelometric method in atomic weight work, and the general reliance placed on "nephelometric" results, there have been few attempts to demonstrate the unqualified applicability of the method in the case of particular analyses. Richards and Wells, in a series of tests which showed the applicability of the method to the NaCl:Ag titration, established the essential soundness of the equal-opalescence end-point. Nevertheless, there are certain features of this end-point which make it seem desirable to extend the experiments of Richards and Wells, more particularly to titrations in which multivalent ions are present in the analytical solutions.

In the titrations under consideration, an acid solution containing the chloride or bromide ions from a weighed quantity of a pure compound is

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[1] Richards and Wells: J. Am. Chem. Soc., 27, 502 (1905).

precipitated with almost the theoretical amount of pure silver, weighed, and dissolved in nitric acid. The titration consists in adjusting to equality the silver and halide ions in the resulting supernatant solution, by the use of standard silver and halide solutions. In the equal-opalescence method, this adjustment is based on nephelometric tests which, presumably, show the *relative* amounts of silver and halide ions in the solution.

The end-point of each titration, and hence the calculated atomic weight, depends upon the comparison of two colloidal suspensions of silver chloride. These suspensions are formed in equal samples of the supernatant analytical solution, in two matched test-tubes, under conditions as nearly identical as possible. Silver nitrate is added in excess to one tube. An equivalent excess of a suitable alkali halide is added to the other tube, so that, according to the "solubility product" principle, one suspension represents practically all of the silver ions, the other practically all of the chloride ions present in the supernatant analytical liquid. At the stoichiometrical point, the numbers of silver and halide ions in the supernatant liquid are, supposedly, equal. If, from a solution at the stoichiometrical point, the above procedure results in the production of two suspensions possessing equal light-reflecting power during the time required for the nephelometric observations, the desired correspondence between the end-point and the stoichiometrical point is attained. In this case the opalescences in the two tubes are equal, and the two parts of the divided field seen through the nephelometer eyepiece are the same, when the ratio of the exposed lengths of the tubes is 1.00.

In every equal-opalescence titration, in spite of the attempt to compare the silver chloride suspensions under exactly similar conditions, there must be at least one very marked difference in the two sols. One, stabilized by the adsorption of excess Cl^- ions, is negative; the other, stabilized by the adsorption of excess Ag^+ ions, is positive[1]. Experiments may be cited to show that under certain special conditions this dissimilarity introduces no error into the nephelometric readings. For example, Richards and Wells[2] demonstrated that the "extra" ions present in the analytical solutions had no effect upon the end-point of the NaCl:Ag titration. Scott and Johnson[3] tested five saturated solutions of silver chloride containing varying amounts of nitric acid and found no deviation from equality of silver and chloride ions which would affect even the most accurate atomic weight analyses.

For the present purpose, it seems desirable to emphasize the fact that the ions involved in the above-mentioned tests were all univalent. In other atomic weight determinations, "extra" ions of the most widely varied character, di-, tri-, and tetravalent, derived from the compounds undergoing analysis, have been present in the test solutions examined in the nephelometer. The effect of the adsorption of these ions upon the quantity, state of division, structure, color, and stability of the sols (i.e., upon their light-reflecting power) cannot certainly be stated. However, it is known that the

[1] Lottermoser: J. prakt. Chem., (2) 72, 39 (1905); 73, 374 (1906).
[2] Richards and Wells: J. Am. Chem. Soc., 27, 503 (1905).
[3] Scott and Johnson: J. Phys. Chem., 33, 1981 (1929).

coagulating power of some ions is hundreds of times greater than that of other ions. Furthermore, any given ion is more likely to affect a sol of opposite charge than one having the same charge[1]. Only rarely, then, would one expect the action of any particular "extra" ion to be equal in the two nephelometer tubes,—in most cases its effect upon the properties of the two oppositely charged colloidal suspensions should be different.

The good general agreement between atomic weights determined nephelometrically and corresponding values determined by other methods insures that the effect under consideration must be small. Nevertheless, one would be unjustified in assuming that the effect is negligible. The nephelometer, as Richards and Wells[2] have often pointed out, is an extremely sensitive instrument. It seems very likely that the unbalanced action of certain ions (mainly multivalent ions) may cause differences in the light-reflecting power of the sols large enough to produce serious constant errors in the nephelometric observations.

There is nothing in the procedures described in reports of atomic weight titrations to assure one that the above-mentioned source of error has been avoided. The conditions (temperature, time after precipitation, etc.) under which the suspensions of silver chloride are compared in nephelometric titrations are really quite arbitrary, although they depend more or less upon the "solubility product" idea. In most cases it has been customary to compare the suspensions at the equilibrium condition which most facilitates the nephelometric observations. Since the equilibrium is influenced by factors which the "solubility product" rule does not take into account, the point of equal opalescence in any given titration may or may not correspond to the stoichiometrical point. Under the circumstances, one may reasonably question the unqualified general applicability of the equal-opalescence end-point to extremely accurate titrations. Only applications based on experiments such as those described by Richards and Wells would appear to be entirely trustworthy; the procedure should be tested for each analysis.

Some preliminary tests, made in this laboratory, indicate that a small effect exists, and emphasize the need for further experiments, which are to be undertaken at Princeton University, under a grant from the National Research Council.

Summary

A possible source of error in the equal-opalescence end-point used in nephelometric atomic weight titrations has been pointed out. The nature of the possible error suggests the advisability of testing some of the more general applications of the original procedure described by Richards and Wells.

The writer wishes to acknowledge his indebtedness to Dr. H. B. Weiser and to Dr. A. F. Scott for suggestions concerning this article.

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[1] Schulze: J. prakt. Chem., (2) 25, 431 (1882); 27, 320 (1883).

[2] Richards and Wells: Am. Chem. J., 31, 239, 241, 242 (1904); J. Am. Chem. Soc., 27, 486 (1905).

THE MECHANISM OF THE MUTUAL COAGULATION PROCESS

BY HARRY B. WEISER AND THOMAS S. CHAPMAN

When suitable amounts of two sols of opposite sign are mixed, complete mutual coagulation takes place.[1] This is ordinarily attributed to the mutual discharge of the electrically charged particles of opposite sign with subsequent agglomeration into clumps that settle out. The observations of Biltz are commonly cited to show that the action is determined only by the charge on the particles and not at all on their nature.[2] Thus a comparison of the precipitating action of a series of sols is said to disclose that while the optimum amount of positive sols required to precipitate negative sols varies, the order is always the same. Bancroft[3] pointed out that this deduction from Biltz's data is not justified. Wintgen and Löwenthal[4] state the generally accepted view in another way when they say that the mutual precipitation of oppositely charged sols is a maximum when the concentrations of the sols expressed in equivalent aggregates are the same, that is, when equal numbers of charges of opposite sign are mixed. This rule was likewise found not to hold when a highly dispersed sol of one sign is mixed with a coarser sol of opposite sign.

Lottermoser[5] observed that the most complete coagulation of positively charged AgI containing a slight excess of $AgNO_3$ and negatively charged AgI containing a slight excess of KI, was obtained when the excess of $AgNO_3$ in one sol is just equivalent to the excess of KI in the other. This suggests that interaction between the stabilizing ions is the cause of the mutual coagulation of oppositely charged sols. In line with this Freundlich and Nathansohn[6] found colloidal As_2S_3 sol and Odén's sulfur sol to be instable in the presence of each other. Since both sols are negatively charged, this instability cannot be due to mutual electrical neutralization but was found to result from interaction between the stabilizing electrolytes of the two sols, hydrogen sulfide and pentathionic acid. Following up the above observations, Thomas and Johnson[7] attribute mutual coagulation in other cases primarily to chemical interaction of the stabilizing electrolytes in the sols. Thus, the precipitation of Graham's colloidal ferric oxide, stabilized by hydrogen ion, and colloidal silica, stabilized by hydroxyl ion, was attributed to chemical neu-

[1] Graham: J. Chem. Soc., 15, 246 (1862); Linder and Picton: 71, 586 (1897); Henri: Compt. rend. Soc. biol., 55, 1666 (1903); Bechhold: Z. physik. Chem., 48, 385 (1904); Neisser and Friedman: Münch. Med. Wochenchr., 51, 465, 827 (1904); Biltz: Ber., 37, 1095 (1904); Billitzer: Z. physik. Chem., 51, 148 (1905); Teague and Buxton: 60, 489 (1907).

[2] Freundlich: "Kapillarchemie," 402 (1909); Thomas: Bogue's "Colloidal Behavior," 1, 325 (1924).

[3] J. Phys. Chem., 19, 362 (1915).

[4] Z. physik. Chem., 109, 391 (1924).

[5] Kolloid-Z., 6, 78 (1910).

[6] Kolloid-Z., 28, 258 (1920); 29, 16 (1921).

[7] J. Am. Chem. Soc., 45, 2532 (1923).

tralization. This view was supported by the observation that mutual precipitation was effected over a limited range of purity of sols, when the hydrochloric acid and sodium hydroxide concentration in the sols were approximately equivalent. The variation from equivalence was quite marked in case the sols were fairly pure. Thus a silica sol containing 16 SiO_2 to 1 NaOH was precipitated at various dilutions with a sol containing 13 Fe_2O_3 to 1 $FeCl_3$. At the highest dilution possible for obtaining accurate data, mutual precipitation was observed when an amount of colloidal silica was added corresponding to but 50 per cent of the hydrochloric acid. This variation was attributed to the metastability of pure sols, which causes them to precipitate with a subnormal disturbance. This does not seem quite convincing since, in the absence of contamination other than that mentioned, the purity of the sols would scarcely be great enough to make them abnormally sensitive. Erratic results were also obtained when the amount of peptizing agent was too large, say three times as much as in the case referred to above. Thus, to obtain data to support a purely chemical mechanism involving neutralization of the stabilizing agents, it seems necessary to choose the experimental conditions to fit the case. While everyone will agree that the peptizing agents of two sols may interact under certain conditions, thus affecting the stability of each, such a mechanism of the mutual precipitation process would not account for the repeated observation of mutual precipitation of sols where interaction between the peptizing agents is impossible or improbable.[1] In an attempt to throw some further light on the several factors which influence the mutual coagulation process, the experiments reported in this paper were carried out.

Preparation of Sols

Most of the sols used in this investigation were prepared by standard methods which in many cases have been modified by procedures already described in detail. To avoid repetition, the sols employed are listed in Table I together with references which give the details of the method of preparation used in each case. In general it may be said that special precautions were taken in the preparation of the sols. Chemicals of a high degree of purity were used and all operations were carried out in pyrex vessels. In every case with the exception of the night blue sol, the preparations were subjected to prolonged dialysis in Neidle[2] dialyzers using cellophane bags.

Two series of experiments were carried out with a six-month interval between. The sols were freshly prepared for each series. The concentrations in grams per liter of the sols used in getting quantitative mutual coagulation data are included in Table I. These values were obtained by evaporating a known volume of sol to dryness in a platinum dish, and weighing the residue after suitable ignition.

The zinc and copper ferrocyanide sols used in the first series of experiments were prepared by the interaction of hydroferrocyanic acid and copper salt

[1] Thomas questions whether any such cases exist: J. Chem. Education, 4, 418 (1927).
[2] J. Am. Chem. Soc., 38, 1270 (1916).

TABLE I

Sols used in Mutual Coagulation Experiments

Sol	Reference to Method of Preparation	Concentration g per l I	II
As_2S_3	Freundlich and Nathansohn: Kolloid-Z., 28, 258 (1928).	2.22	1.64
SnO_2	Weiser: J. Phys. Chem., 26, 682 (1922).	2.37	1.73
Congo red acid	Weiser and Radcliffe: J. Phys. Chem., 32, 1878 (1928).	1.95	0.61
$Cu_2Fe(CN)_6$	Weiser: J. Phys. Chem., 30, 1530 (1926).	3.28	3.23
$Zn_2Fe(CN)_6$	Same procedure as for $Cu_2Fe(CN)_6$ sol.	2.10	—
Sulfur	Weiser and Cunningham: Colloid Symposium Monograph, 6, 326 (1928).	—	0.30
Molybdenum blue	Biltz: Ber., 35, 4431 (1902).	—	0.18
Night blue	Addition to water	—	0.72
$Fe_2O_3(-)$	Hazel and Sorum: J. Am. Chem. Soc., 52, 1337 (1930).	—	0.30
$Fe_2O_3(+)$	Sorum: J. Am. Chem. Soc., 50, 1263 (1928).	2.59	1.72
Cr_2O_3	Neidle: J. Am. Chem. Soc., 39, 71 (1917).	2.17	0.82
CeO_2	Biltz: Ber., 35, 4431 (1902).	2.50	—
$BaSO_4$	Modification of Kato's method. See below.	14.79	5.60
$BaCO_3$	Buzagh: Kolloid-Z., 38, 222; 39, 218 (1926).		
Sb_2S_3	Biltz: Ber., 37, 1097 (1904).		
$Cu_3(FeC_6N_6)_2$	See below.		
AgI(−)	Lottermoser: J. prakt Chem., (2) 68, 340 (1903).		
TlI(+)	Ostwald: "Die wissenschaftlichen Grundlagen der analytischen Chemie," 209 (1904).		

while in the later experiments potassium ferricyanide was employed. The use of hydroferrocyanic acid to obtain the salt is advantageous since the precipitate is almost pure $Cu_2Fe(CN)_6$.[1]

Copper ferricyanide sol was prepared by mixing equivalent amounts of dilute solutions of potassium ferricyanide and copper sulfate, followed by washing the precipitated gel in the centrifuge until peptization was complete and dialyzing.

The colloidal barium sulfate used in the first series of experiments was prepared by the method of Kato[2] which consists in diluting a 1 molar solution of sulfuric acid with twice its volume of alcohol and adding to it an equivalent amount of a molar solution of barium acetate diluted with 5 times its volume of alcohol. The resulting gelatinous precipitate and milky sol were evaporated to dryness under reduced pressure below 40° and the precipitate was dispersed by shaking with water. Due to the difficulty of removing the acetic

[1] Cf. Weiser: J. Phys. Chem., 34, 343 (1930).
[2] Mem. Coll. Sci. Kyoto Imp. Univ., 2, 187 (1909-10).

TABLE II

Mutual Coagulation of Oppositely Charged Sols

Positive Sol	Stabilizing Ion	Negative Sol	Stabilizing ion Ion	Remarks
Fe_2O_3 (Sorum)	$H^{\cdot}$	$Zn_2Fe(CN)_6$	$Fe(CN)_6^{''''}$	$H_4Fe(CN)_6$ soluble and highly ionized
$BaCO_3$	$Ba^{\cdot\cdot}$	$Zn_2Fe(CN)_6$	$Fe(CN)_6^{''''}$	$Ba_2Fe(CN)_6$ quite soluble
$BaSO_4$	$Ba^{\cdot\cdot}$ and $H^{\cdot}$	$Cu_2Fe(CN)_6$	$Fe(CN)_6^{''''}$	$Ba_2Fe(CN)_6$ and $H_4Fe(CN)_6$ soluble
$BaCO_3$	$Ba^{\cdot\cdot}$	SnO_2	OH'	$Ba(OH)_2$ soluble
$BaCO_3$	$Ba^{\cdot\cdot}$	As_2S_3	HS'	BaHS soluble
Fe_2O_3 (Graham)	$H^{\cdot}$ and $Fe^{\cdot\cdot\cdot}$	$Cu_3(FeC_6N_6)_2$	$Fe(CN)_6'''$	$H_3Fe(CN)_6$ and $Fe(FeC_6N_6)$ soluble
Fe_2O_3 (Sorum)	$H^{\cdot}$	Congo red acid	Congo red anion	pH of Fe_2O_3 sol 6.8.
$BaSO_4$	$Ba^{\cdot\cdot}$ and $H^{\cdot}$	$Cu_3(FeC_6N_6)_2$	$Fe(CN)_6'''$	$Ba_3(FeC_6N_6)_2$ and $H_3Fe(CN)_6$ soluble
TlI	$Tl^{\cdot}$	SnO_2	OH'	TlOH soluble
$BaCO_3$	$Ba^{\cdot\cdot}$	AgI	I'	BaI_2 soluble

acid by this method, the sol used in the second series of experiments was prepared by mixing alcoholic sulfuric acid with a slight excess of alcoholic barium acetate, followed by dialysis. This procedure served to replace the alcohol with water and to remove the acetic acid giving a sol which has stood for two months without coagulating.

The Question of Interaction of Stabilizing Ions in Mutual Coagulation

If the stabilizing ions of two oppositely charged sols are capable of interacting to form an insoluble or a slightly dissociated compound it is altogether likely that such interaction will influence the mutual coagulation process. Thus, interaction between the stabilizing hydrogen and ferric ions in a Graham ferric oxide sol and the hydroxyl ions in a silicon dioxide sol will influence the mutual coagulation of the two sols as emphasized by Thomas and Johnson.[1] But mutual coagulation in general is not dependent on the removal of the respective stabilizing ions by such an interaction. This is illustrated by the results of some observations on the mutual coagulation of oppositely charged sols where there is no interaction between the stabilizing ions with the formation of an insoluble or slightly dissociated compound. In these experiments a 10 cc portion of one sol was taken and the other sol was added quite slowly until a point of complete mutual coagulation was found. A few combinations are recorded in Table II. The list may be extended by anyone who desires.

Quantitative Observations of Mutual Coagulation

First Series. The procedure employed in the first series of experiments was as follows: A suitable volume of one sol was taken and varying amounts of a second sol of opposite sign was added until the approximate range of complete mutual coagulation was located. The zone of complete coagulation was then determined more sharply by making a series of mixtures in the boundary region using a constant volume of one sol and slightly varying amounts of the second. The mixtures were allowed to stand 30 minutes after which they were centrifuged for 1 minute at 3000 r.p.m. in a No. 1 International-Equipment-Company centrifuge and examined for complete coagulation. When the presence of a small amount of colloid was not readily determined by visual observation as in the case of stannic oxide sol, a portion of the supernatant liquid after centrifuging was pipetted off and treated with an electrolyte containing a multivalent precipitating ion. The absence of a precipitate or floc on standing two hours was taken as an indication that no sol was present. The results are given in Tables III, IV, V, and VI.

The results recorded in Tables III to VI are represented in a diagram, Fig. 1. The right hand side of the diagram corresponds to 100 per cent by weight of Cr_2O_3, CeO_2, Fe_2O_3, and $BaSO_4$, respectively, and 0 per cent of As_2S_3, $Cu_2Fe(CN)_6$, Congo red acid, SnO_2, and $Zn_2Fe(CN)_6$; while the left hand side corresponds to 100 per cent of the latter compounds and zero per

[1] Loc. cit.

TABLE III

Mutual Coagulation of Fe_2O_3 Sol and Negative Sols

Sols mixed		Observations with mixtures								Range of mutual coagulation
		Excess positive sol		Complete mutual coagulation		Complete mutual coagulation		Excess negative sol		
+	−	cc +	cc −	cc +	cc −	cc +	cc −	cc +	cc −	% Fe_2O_3 by weight[1]
Fe_2O_3	SnO_2	10	1.6	10	1.8	10	2.0	10	2.2	86.0 to 84.5
Fe_2O_3	$Zn_2Fe(CN)_6$	10	1.2	10	1.4	10	4.0	10	4.2	90.0 to 75.5
Fe_2O_3	$Cu_2Fe(CN)_6$	5	1.0	5	1.25	5	2.0	5	2.25	76.0 to 66.5
Fe_2O_3	Congo red acid	5	1.5	5	1.75	5	4.75	5	5.0	79.0 to 58.0
Fe_2O_3	As_2S_3	5	5.0	5	4.25	5	6.0	5	6.25	57.5 to 49.0

[1] The concentrations of the several sols are given in Table I.

TABLE IV

Mutual Coagulation of Cr_2O_3 Sol and Negative Sols.

Sols mixed		Observations with mixtures								Range of mutual coagulation
		Excess positive sol		Complete mutual coagulation		Complete mutual coagulation		Excess negative sol		
+	−	cc +	cc −	cc +	cc −	cc +	cc −	cc +	cc −	% Cr_2O_3 by weight
Cr_2O_3	$Zn_2Fe(CN)_6$	5	6.0	2	2.5	2	6.5	2	6.75	45.5 to 24.0
Cr_2O_3	SnO_2	2	3.75	2	4.0	2	6.0	2	6.25	31.5 to 23.5
Cr_2O_3	Congo red acid	1	5.75	1	6.0	1	6.75	1	7.0	15.5 to 14.0
Cr_2O_3	$Cu_2Fe(CN)_6$	1	5.0	1	5.25	1	7.75	1	8.0	11.0 to 7.5
Cr_2O_3	As_2S_3	1	11.5	1	11.75	1	15.0	1	15.25	7.5 to 6.0

TABLE V

Mutual Coagulation of CeO_2 Sol and Negative Sols

Sols mixed		Observations with mixtures								Range of mutual coagulation
		Excess positive sol		Complete mutual coagulation		Complete mutual coagulation		Excess negative sol		
+	−	cc +	cc −	cc +	cc −	cc +	cc −	cc +	cc −	% CeO_2 by weight
CeO_2	$Zn_2Fe(CN)_6$	5	3.50	5	3.75	5	5.00	5	5.25	61.0 to 54.5
CeO_2	SnO_2	5	4.00	5	4.25	5	5.00	4.75	5.00	55.0 to 51.5
CeO_2	As_2S_3	3	1.50	3	1.75	3	11.00	3	12.00	66.0 to 23.5
CeO_2	Congo red acid	3	5.25	3	5.50	3	9.00	3	9.25	41.0 to 30.0
CeO_2	$Cu_2Fe(CN)_6$	3	4.25	3	4.50	3	6.75	3	7.00	39.0 to 25.0

TABLE VI

Mutual Coagulation of $BaSO_4$ Sol and Negative Sols

Sols mixed		Observations with mixtures								Range of mutual coagulation
		Excess positive sol		Complete mutual coagulation		Complete mutual coagulation		Excess negative sol		
+	−	cc +	cc −	cc +	cc −	cc +	cc −	cc +	cc −	% $BaSO_4$ by weight
$BaSO_4$	Congo red acid	5	1.50	5	1.75	5	6.00	5	6.25	95.5 to 86.5
$BaSO_4$	As_2S_3	5	3.00	5	3.25	5	4.25	5	4.5	91.0 to 89.0
$BaSO_4$	$Cu_2Fe(CN)_6$	5	1.25	5	1.50	5	3.75	5	4.0	94.0 to 86.0
$BaSO_4$	$Zn_2Fe(CN)_6$	5	4.00	5	4.25	5	6.00	5	6.25	89.0 to 85.5
$BaSO_4$	SnO_2	5	3.00	5	3.25	5	8.00	5	8.25	90.5 to 79.5

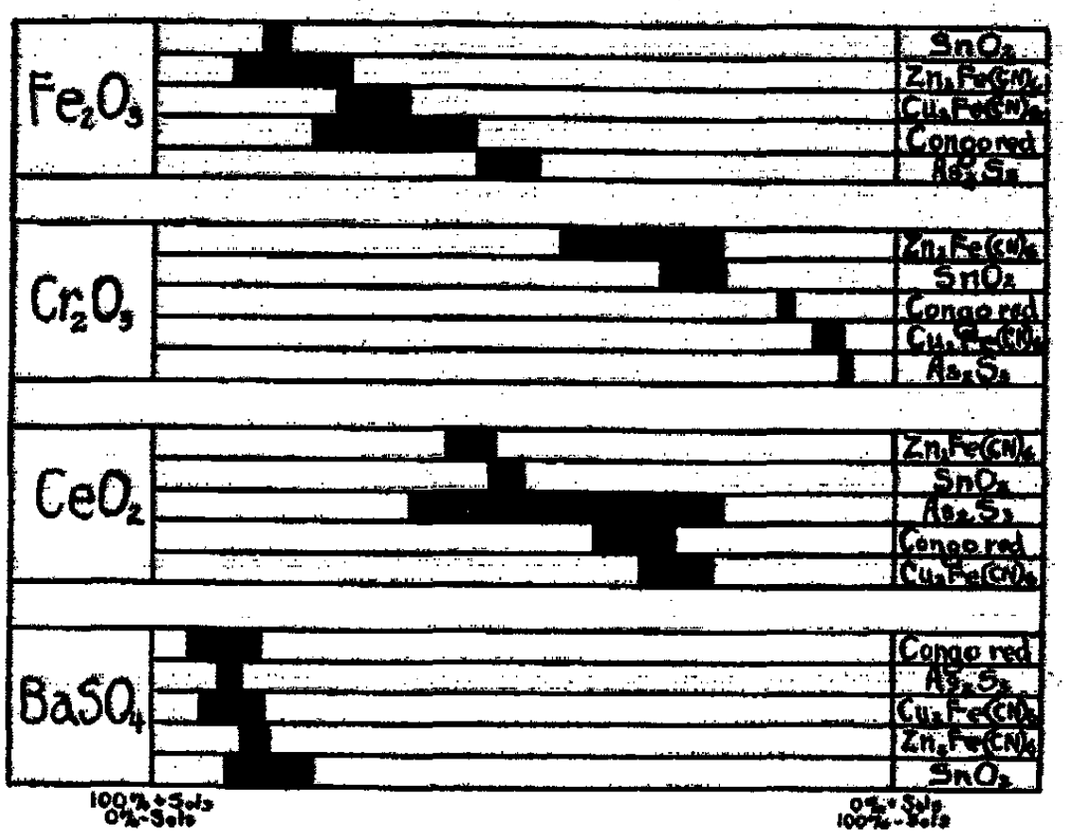

FIG. 1
Range of mutual coagulation of oppositely charged sols. Series I.

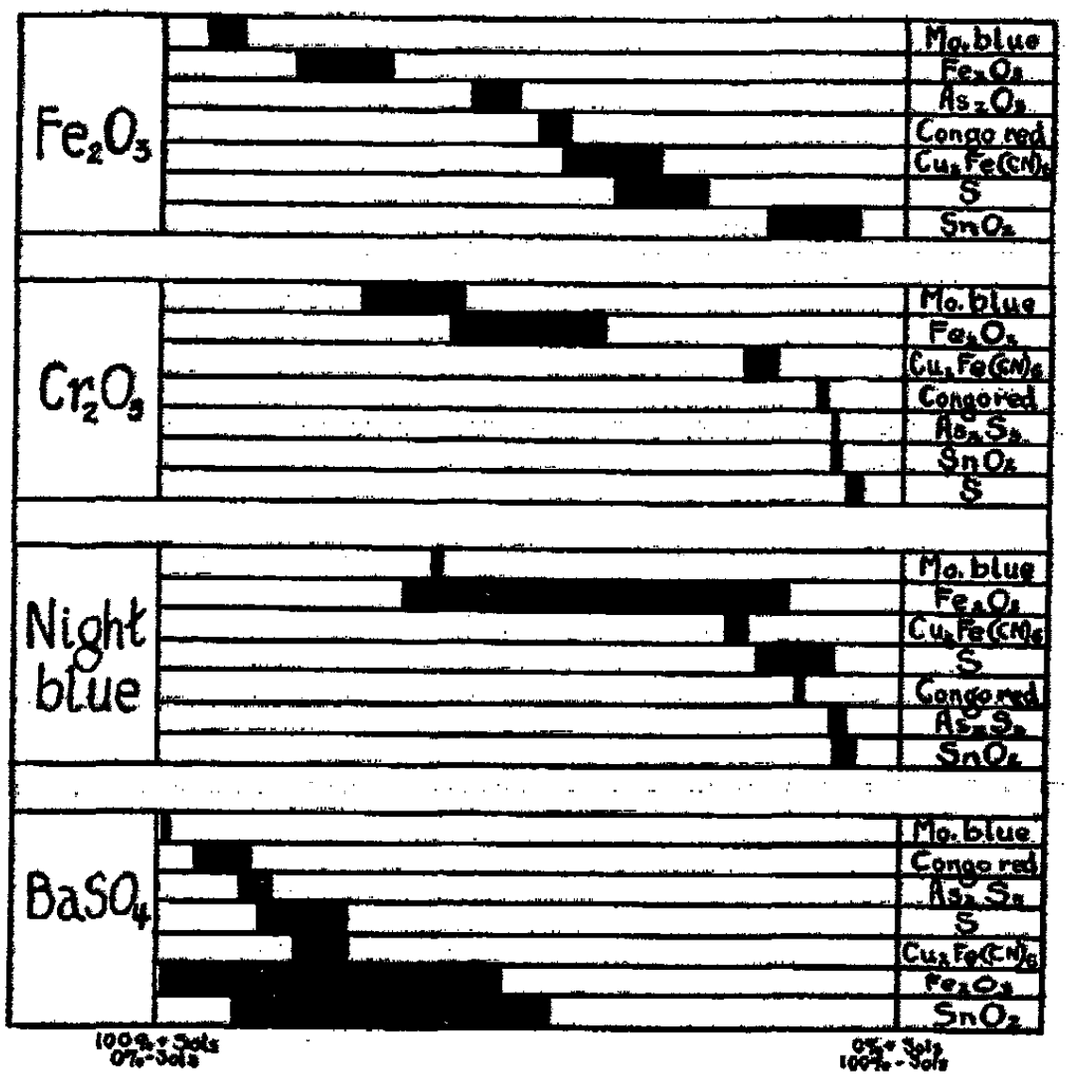

FIG. 2
Range of mutual coagulation of oppositely charged sols. Series 2.

TABLE VII

Mutual Coagulation of Fe_2O_3 Sol and Negative Sols

Sols mixed		Observations with mixtures								Range of mutual coagulation
		Excess positive sol		Complete mutual coagulation		Complete mutual coagulation		Excess negative sol		
+	−	cc +	cc −	cc +	cc −	cc +	cc −	cc +	cc −	% Fe_2O_3 by weight
Fe_2O_3	Molybdenum blue	4.8	5.2	4.9	5.1	6.3	3.7	6.4	3.6	94.2 to 90.2
Fe_2O_3	Fe_2O_3	2.8	7.2	2.9	7.1	4.5	5.5	4.6	5.4	82.5 to 70.0
Fe_2O_3	As_2S_3	5.1	4.9	5.2	4.8	5.8	4.2	5.9	4.1	59.1 to 53.2
Fe_2O_3	Congo red acid	2.2	7.8	2.3	7.7	2.6	7.4	2.7	7.3	49.8 to 45.8
Fe_2O_3	$Cu_2Fe(CN)_6$	4.7	5.3	4.8	5.2	6.2	3.8	6.3	3.7	46.5 to 32.9
Fe_2O_3	Sulfur	0.5	9.5	0.6	9.4	1.0	9.0	1.1	8.9	39.0 to 27.0
Fe_2O_3	SnO_2	0.5	9.5	0.6	9.4	1.8	8.2	1.9	8.1	18.0 to 6.0

TABLE VIII

Mutual Coagulation of Cr_2O_3 Sol and Negative Sols

Sols mixed		Observations with mixtures								Range of mutual coagulation
		Excess positive sol		Complete mutual coagulation		Complete mutual coagulation		Excess negative sol		
+	−	cc +	cc −	cc +	cc −	cc +	cc −	cc +	cc −	% Cr_2O_3 by weight
Cr_2O_3	Molybdenum blue	2.4	7.6	2.5	7.5	3.8	6.2	3.9	6.1	73.6 to 60.3
Cr_2O_3	Fe_2O_3	1.9	8.1	2.0	8.0	3.7	6.3	3.8	6.2	61.6 to 40.5
Cr_2O_3	$Cu_2Fe(CN)_6$	4.4	5.6	4.5	5.5	5.2	4.8	5.3	4.7	21.6 to 17.2
Cr_2O_3	Congo red acid	0.7	9.3	0.8	9.2	0.9	9.1	1.0	9.0	11.7 to 10.5
Cr_2O_3	As_2S_3	1.5	8.5	1.6	8.4	1.7	8.3	1.8	8.2	9.4 to 8.7
Cr_2O_3	SnO_2	1.5	8.5	1.6	8.4	1.8	8.2	1.9	8.1	9.4 to 8.2
Cr_2O_3	Sulfur	0.1	9.9	0.2	9.8	0.3	9.7	0.35	9.65	7.8 to 5.3

TABLE IX

Mutual Coagulation of Night Blue Sol and Negative Sols

Sols mixed		Observations with mixtures								Range of mutual coagulation
		Excess positive sol		Complete mutual coagulation		Complete mutual coagulation		Excess negative sol		
+	−	cc +	cc −	cc +	cc −	cc +	cc −	cc +	cc −	% Fe_2O_3 by weight
Night blue	Molybdenum blue	2.8	7.2	2.0	7.1	3.0	7.0	3.1	6.9	63.0 to 62.0
Night blue	Fe_2O_3	0.6	9.4	0.7	9.3	4.6	5.4	4.7	5.3	67.2 to 15.3
Night blue	$Cu_2Fe(CN)_6$	5.3	4.7	5.4	4.6	5.8	4.2	5.9	4.1	23.5 to 20.7
Night blue	Sulfur	0.3	9.7	0.4	9.6	0.9	9.1	1.0	9.0	19.2 to 9.1
Night blue	Congo red acid	1.0	9.0	1.1	8.9	1.2	8.8	1.3	8.7	13.8 to 12.7
Night blue	As_2S_3	1.4	8.6	1.5	8.5	1.8	8.2	1.9	8.1	8.8 to 7.2
Night blue	SnO_2	1.2	8.8	1.3	8.7	1.8	8.2	1.9	8.1	8.4 to 5.9

TABLE X

Mutual Coagulation of $BaSO_4$ Sol and Negative Sols

Sols mixed		Observations with mixtures								Range of mutual coagulation
		Excess positive sol		Complete mutual coagulation		Complete mutual coagulation		Excess negative sol		
+	−	cc +	cc −	cc +	cc −	cc +	cc −	cc +	cc −	% Fe_2O_3 by weight
$BaSO_4$	Molybdenum blue	6.3	3.7	6.4	3.6	7.8	2.2	7.9	2.1	99.1 to 98.2
$BaSO_4$	Congo red acid	4.3	5.7	4.4	5.6	6.6	3.4	6.7	3.3	94.8 to 87.8
$BaSO_4$	As_2S_3	6.2	3.8	6.3	3.7	7.1	2.9	7.2	2.8	89.3 to 85.3
$BaSO_4$	Sulfur	1.3	8.7	1.4	8.6	2.6	7.4	2.7	7.3	86.7 to 75.3
$BaSO_4$	$Cu_2Fe(CN)_6$	6.2	3.8	6.3	3.7	7.2	2.8	7.3	2.7	81.7 to 74.8
$BaSO_4$	Fe_2O_3	0.5	9.5	0.6	9.4	8.7	1.3	8.8	1.2	99.2 to 54.4
$BaSO_4$	SnO_2	2.1	7.9	2.2	7.8	7.3	2.7	7.4	2.6	89.6 to 47.6

cent of the former. The shaded portions of the diagram thus represents the composition of the coagulum in the range of mutual coagulation in weight per cent of the dry constituents.

The composition of the precipitates using each positive sol with the several negative sols is represented in the order of increasing amounts of the negatively charged constituent, assuming that the midpoint of the range of complete

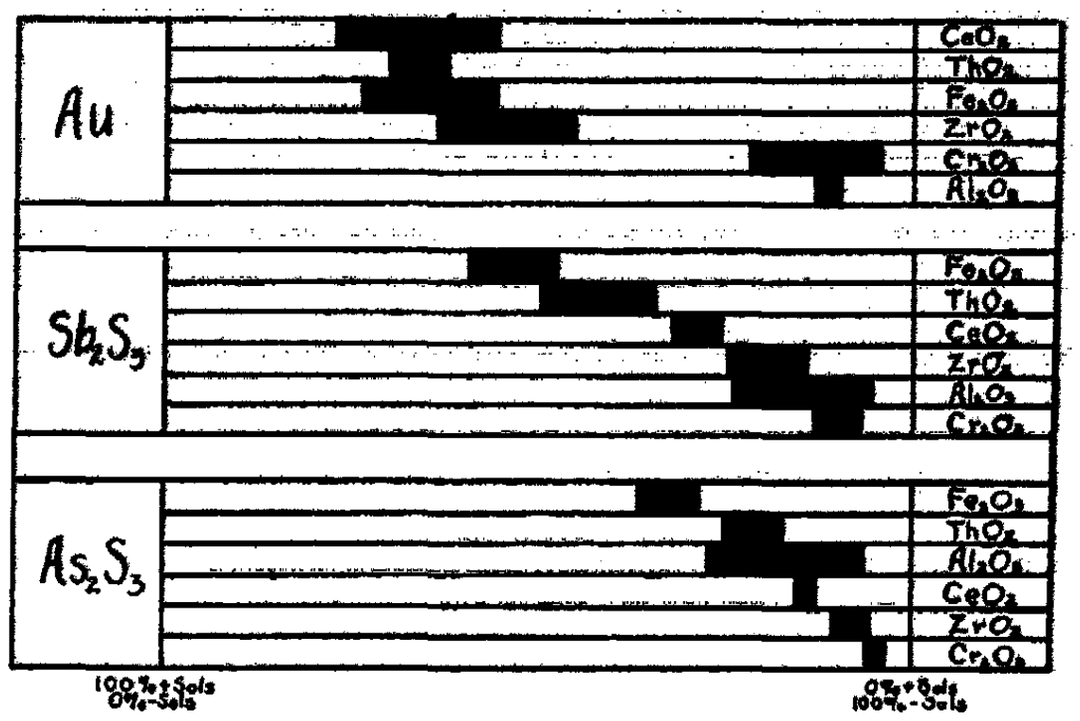

FIG. 3
Range of mutual coagulation of oppositely charged sols (Biltz).

mutual coagulation is the optimum point. It will be noted that the order in which the negative sols arrange themselves is not the same even for the hydrous oxide sols and is quire different with a different type of sol such as barium sulfate.

Second Series. The results recorded above were extended in a second series of experiments with different sols. The method of procedure in obtaining the zone of mutual coagulation was the same as that previously described except that the sols were mixed in such amounts that the total volume of the mixture was always 10 cc. The results are recorded in Tables VII to X and are shown in the diagram Fig. 2.

Observations of Biltz. From the mutual coagulation observations of Biltz,[1] the zone of complete mutual coagulation was estimated. These data are shown in Table XI and are plotted in Fig. 3. The hydrous oxides, which give positive sols, are arranged in order of decreasing amount in mixtures with Au, Sb_2S_3 and As_2S_3, respectively, assuming that the optimum point of mutual coagulation is the midpoint of the range. In this series of experiments also it will be seen that the order of oxides is by no means the same, as usually assumed.

[1] Ber., 37, 1104 (1904).

TABLE XI

Mutual Coagulation Data of Biltz

Milligrams of constituents in coagulam in the zone of mutual coagulation			Range of mutual coagulation Per cent by weight	
Au 1.4	CeO_2	4.8 to 1.8	CeO_2	77.5 to 56.0
Au 1.4	ThO_2	3.2 to 2.3	ThO_2	70.0 to 62.0
Au 1.4	Fe_2O_3	4.0 to 1.8	Fe_2O_3	74.0 to 56.0
Au 1.4	ZrO_2	2.2 to 1.2	ZrO_2	63.0 to 46.0
Au 1.4	Cr_2O_3	0.4 to 0.55	Cr_2O_3	22.0 to 4.0
Au 1.4	Al_2O_3	0.2 to 0.15	Al_2O_3	12.5 to 9.5
Sb_2S_3 5.6	Fe_2O_3	8.0 to 5.2	Fe_2O_3	50.0 to 48.0
Sb_2S_3 28.0	ThO_2	5.5 to 3.0	ThO_2	50.0 to 35.0
Sb_2S_3 28.0	CeO_2	13.5 to 9.6	CeO_2	32.5 to 25.5
Sb_2S_3 28.0	ZrO_2	9.1 to 4.5	ZrO_2	24.5 to 14.0
Sb_2S_3 28.0	Al_2O_3	9.0 to 1.5	Al_2O_3	24.0 to 5.0
Sb_2S_3 28.0	Cr_2O_3	4.0 to 2.0	Cr_2O_3	12.5 to 6.5
As_2S_3 12.0	Fe_2O_3	7.0 to 4.8	Fe_2O_3	37.0 to 28.5
As_2S_3 12.0	ThO_2	3.5 to 2.5	ThO_2	22.5 to 17.0
As_2S_3 24.0	Al_2O_3	9.0 to 1.5	Al_2O_3	27.0 to 6.0
As_2S_3 24.0	CeO_2	4.0 to 3.5	CeO_2	15.0 to 12.5
As_2S_3 24.0	ZrO_2	2.7 to 1.3	ZrO_2	10.0 to 5.0
As_2S_3 12.0	Cr_2O_3	2.7 to 0.4	Cr_2O_3	5.5 to 3.0

Discussion of Results

From the observations summarized in Figs. 1, 2, and 3 of the preceding section, the following facts in connection with the mutual coagulation process are brought out: First, the complete mutual coagulation of two sols of opposite charge may take place over a narrow range of concentrations or over quite a large range of concentrations. Second, when, for example, a given series of positive sols is arranged in order of the optimum concentration for mutual coagulation on mixing with negative sols, the order of the positive sols may vary widely with different negative sols.

These results indicate that the mutual coagulation process may be determined by a number of factors that are effective to different degrees with different sols. The more important of these will be considered in a general way in the following paragraphs.

1. *Mutual Electrical Neutralization.* Since coagulation takes place when the charge on the particles of a sol is reduced to a critical value below which the particles will agglomerate into aggregates sufficiently large to settle, it would seem to follow that, if no other factor comes in, mutual coagulation would result when amounts of sols bearing equal numbers of opposite charges are mixed. Moreover, if electrostatic neutralization were the only factor, one would expect the range of mutual coagulation to be relatively narrow and that

a given series of sols of one sign would always arrange themselves in the same order regardless of what sol of opposite sign is precipitated. From the experimental results it is obvious that the precipitating power of sols of one sign for sols of opposite sign is not determined exclusively by the charge on the colloidal particles. It may be, however, that this is the predominating factor when the range of coagulation is quite narrow.

Mutual Adsorption of Colloidal Particles. Since the mutual coagulation process is not independent of the nature of the colloidal particles, it is altogether probable that a specific adsorption between the two kinds of particles that is not determined by their electrical charge, will have an important effect in determining the range of mutual coagulation. Thus, if the mutual attraction is relatively great between two electrical neutral particles which yield sols of opposite sign, one would expect this force of attraction to supplement the electrostatic attraction between the oppositely charged colloidal particles and thereby extend the range of mutual coagulation. Fifteen years ago Bancroft[1] called attention to the importance of adsorption of the particles of one colloid by those of another in the mutual coagulation process, but his paper has been overlooked or has not been taken seriously by most people. Unfortunately, the magnitude of the effect on the mutual coagulation process, of mutual adsorption of particles which is independent of their charge, cannot be evaluated quantitatively until the magnitude of the mutual adsorption force is known.

Precipitating Ions in the Sols. The effect of the presence of unadsorbed multivalent ions in the sols as a factor in the mutual coagulation process has not been taken into account by anybody. For example, if the excess alkali ferricyanide used in the preparation of a negatively charged ferricyanide sol is not removed completely and this sol is employed to coagulate positive sols, the ferricyanide ion in the intermicellar solution will exert a precipitating action on the positive sol that is independent of the mutual coagulation of the oppositely charged particles. In such a case one would expect the range of coagulation to be relatively wide. In arranging the sols of one charge in order of their precipitating action toward sols of opposite charge it is not permissible to take the midpoint of the zone as the optimum mutual coagulation point, if a part of the coagulation is true electrolyte coagulation. In the experiments recorded above an attempt was made to avoid this complication by working with well dialyzed sols.

Interaction between Stabilizing Ions. Attention has been called to the observations of Lottermoser and of Thomas and Johnson, which show that interaction between stabilizing ions with the formation of an insoluble or slightly ionized compound, may sometimes play an important role in the mutual coagulation process. However, even in cases where such an interaction is possible, it is altogether unlikely that the effect is independent of the electrostatic attraction and the specific adsorption between the colloidal

[1] J. Phys. Chem., 19, 362 (1915).

particles. Certainly, one gets mutual coagulation where removal of stabilizing ions by chemical neutralization or precipitation is a remote possibility (Table I.)

In a subsequent paper special attention will be given to the effect on the width of the mutual coagulation zone of (1) mutual adsorption of the colloidal particles and (2) the presence of multivalent precipitating ions as impurities in the sols.

Summary

The results of this investigation are as follows:

1. The zone of complete mutual coagulation of two sols of opposite sign may be very narrow or quite broad.

2. When a given series of positive sols, for example, is arranged in order of the optimum concentration for mutual coagulation on mixing with negative sols, the order of the positive sols may vary widely with different negative sols.

3. The behavior noted in 1 and 2 is accounted for by the fact that the precipitating power of positive sols for negative sols is not determined exclusively by the charge on the colloidal particles. Other facts which influence the mutual coagulation process are (1) mutual adsorption of colloidal particles, that is independent of their charge (2) the presence of precipitating ions as impurities in the sols and (3) interaction between stabilizing ions.

4. Complete mutual coagulation is not due in general to interaction and consequent removal of the stabilizing electrolytes of oppositely charged sols; but this factor may be important in certain cases.

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A STUDY OF COLLOIDAL FERRIC OXIDE AND VARIOUS FACTORS WHICH INFLUENCE ITS ABILITY TO CATALYZE THE DECOMPOSITION OF HYDROGEN PEROXIDE*

I. The Temperature Coefficient, the Effect of Catalyst Concentration and the Effect of Electrolytes

BY RAYMOND J. KEPFER AND JAMES H. WALTON

Introduction

In spite of the fact that numerous investigations have been made on the decomposition of H_2O_2 by various colloidal systems only a few are mentioned in the literature concerning the decomposition of this substance by colloidal ferric oxide. The first of these was reported by Duclaux[1] in brief in 1907 and then in more detail in 1923. He found the reaction to be monomolecular with the velocity constants for any one reaction varying by as much as 10%. He also stated that the catalytic activity of the sol was determined by the amount of Fe_2Cl_6 in the colloidal particle and not by the amount of iron oxide. The addition of either K_2SO_4 or $K_4Fe(CN)_6$ inhibited the reaction. This inhibition he attributed to a true chemical reaction; for example

$$Fe_2Cl_6.nFe_2O_3 + 3\ K_2SO_4 \longrightarrow Fe_2(SO_4)_3 + 6\ KCl + nFe_2O_3.$$

He stated further that the sulphate had less effect than the ferrocyanide because the former gives a soluble product and thus an incomplete reaction while the latter forms an insoluble product and thus a complete reaction. More will be said concerning this work of Duclaux when the authors introduce some contradictory evidence. Shpitalskii, Petin and Burova[2] have also made an investigation in which they added various amounts of HCl or NaOH to dilute solutions of $Fe_2(SO_4)_3$ or $FeCl_3$ and then studied the effect of these hydrolyzing mixtures on the decomposition of H_2O_2.

Purpose

By means of a special high-temperature dialyzer Sorum[3] has succeeded in preparing a so-called "chloride-free" ferric oxide sol. Due to the fact that previous investigations of the decomposition of H_2O_2 by colloidal ferric oxide have been few in number, not so very extensive, and have made use

*Contribution from the Laboratory of General Chemistry of the University of Wisconsin. This communication is an abstract of a part of a thesis submitted to the Graduate School in partial fulfillment of the requirements for the degree of Doctor of Philosophy at the University of Wisconsin.

[1] Duclaux: Compt. rend., 145, 802 (1907); J. Chim. phys., 20, 18 (1923).

[2] Shpitalskii, Petin and Burova: J. Russ. Phys. Chem. Soc., 60, 1271, 1291, 1317 (1928).

[3] Sorum: J. Am. Chem. Soc., 50, 1263 (1928).

of ferric oxide sols containing much more electrolyte than that prepared by Sorum, a more extensive investigation of this decomposition using a sol prepared by the method developed by Sorum is desirable.

Experimental

Preparation of the Reagents.

The H_2O_2 used for this investigation was obtained by distilling Merck's 30% Superoxol in a Pyrex apparatus under reduced pressure and was stored in a quartz flask in the dark. The iron oxide sol was prepared by dropping a molar solution of $FeCl_3$ into vigorously boiling water in a Pyrex flask which had previously been steamed. The sol was dialyzed using the dialyzer and method developed by Sorum at a temperature of 85°-90° for three days after which it gave no test for chloride ion using $AgNO_3$. After dialysis the sol was stored in a large Pyrex flask which had likewise been previously steamed. Throughout the course of the investigation great care was taken to keep these stock reagents tightly stoppered as much of the time as possible. The iron oxide sol was withdrawn from the stock solution about 500 cc. at a time and stored in a small flask so as to open the stock solution container as seldom as possible. Each of these 500 cc. portions was titrated for iron content using the method reported by Knop.[1] Steamed Pyrex was used throughout the investigation since Ayres[2] found that iron oxide sols soon dissolved enough impurities from soft glass to change considerably such properties as flocculation values, etc.

Clayton,[3] Walton and Judd,[4] and likewise Lottermoser and Lehmann[5] have shown that in a decomposition of H_2O_2 the impurities in the water used are of utmost importance. For this reason all water used in this investigation for dilution purposes, making up solutions and the like was prepared in a conductivity-water still and kept in the usual manner.

The speed of the reaction was followed by titrating the undecomposed H_2O_2 with $KMnO_4$ in the presence of H_2SO_4. To make sure that colloidal iron oxide in the amounts used would not interfere with this titration, equal samples of H_2O_2 were withdrawn from a stock solution and titrated, some in the presence of colloidal iron oxide and some in its absence. It was found that checks could be obtained quite easily when the aqueous solution of H_2SO_4 used for rinsing out and diluting the samples contained enough $KMnO_4$ to give it a distinct violet color before using.

Experimental Detail.

After a series of preliminary experiments the following was adopted as a satisfactory method of experimentation. 20 to 25 cc. portions of reaction solution were made up in a 50 cc. beaker as follows. The required volume of

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[1] Knop: J. Am. Chem. Soc., **46**, 263 (1924).
[2] Ayres: Ph.D. Thesis. Univ. of Wisconsin (1930).
[3] Clayton: Trans. Faraday Soc., **11**, 164 (1915).
[4] Walton and Judd: Orig. Com. 8th. Intern. Congr. Appli. Chem. Appendix, **26**, 621 (1912).
[5] Lottermoser and Lehmann: Kolloid-Z., **29**, 250 (1921).

conductivity water was run in from a 50 cc. burette. Then the electrolyte solutions, if any were used, were added from 1, 2,5, or 10 cc. pipettes. Next the H_2O_2 was introduced by means of a 2 cc. pipette and finally the iron oxide sol in a similar manner. This order was followed throughout, since Lottermoser and Lehmann have shown that the order of addition of the constituents of the solution is an important factor.

This solution was then transferred to a 25 cc. burette and quickly run out into ordinary 5 inch Pyrex test tubes, 2 cc. into each test tube. These test tubes were covered with tin foil and black paint so as to exclude all light. The tubes were then corked and placed in a thermostat at 50°. At various intervals the content of one of these tubes of reaction solution was titrated with $KMnO_4$ to determine the amount of undecomposed H_2O_2. The first four runs made in this manner gave times of half life of 74, 77, 73 and 68 minutes which are satisfactory checks.

The following are some factors which affect the actual magnitude of the experimental results. The 2 cc. portions of reaction solution were measured so quickly that they probably lacked a small amount of being 2 cc. Also in spite of the fact that the tubes were corked there was some evaporation. Furthermore, H_2O_2 undergoes some decomposition at 50° when in contact with glass. However all of these sources of actual error are constant so their influence on the relative results of the following investigations can be neglected. Stark[1] has shown that ferric oxide sols are coagulated by oxygen bubbles. However a calculation made using his results and the amount of oxygen given off during one of the decompositions showed that since only about 0.065% of the sol would be coagulated during a run this effect could also be neglected.

However at times some factor did enter which caused considerable error. Although a majority of the runs could be checked within 5%, at times some run would fail to check a duplicate by as much as 30%. This, the writers feel, was due chiefly to the condition of the atmosphere in the room at the time the reaction solution was prepared. This belief is substantiated by the fact that if duplicate solutions were prepared at the same time much better checks could be obtained than when they were prepared at different times. Another reason for this belief is that, if there were enough fumes to give a distinct odor in the room at the time of preparation of a reaction solution, that run would invariably fail to check a run made at another time when no noticeable fumes were present. For this reason duplicate solutions were never prepared at the same time. Of course this would tend to give poorer checks than if the duplicate solutions were prepared at the same time but for a series of determinations from which one wishes to make comparisons more significant values can be obtained by preparing the reaction solutions at different times.

[1] Stark: J. Am. Chem. Soc., 52, 2730 (1930).

In the experiments that are to follow at least two determinations were made in each case. In all cases the tables give an average of the determinations made under similar conditions.

Method of calculating Results.

It was found that when these results were substituted in the equation for a monomolecular reaction and velocity constants calculated, exact constants were not obtained. This is shown by Table I which gives the average results of four similar runs taken at random from the experiments performed.

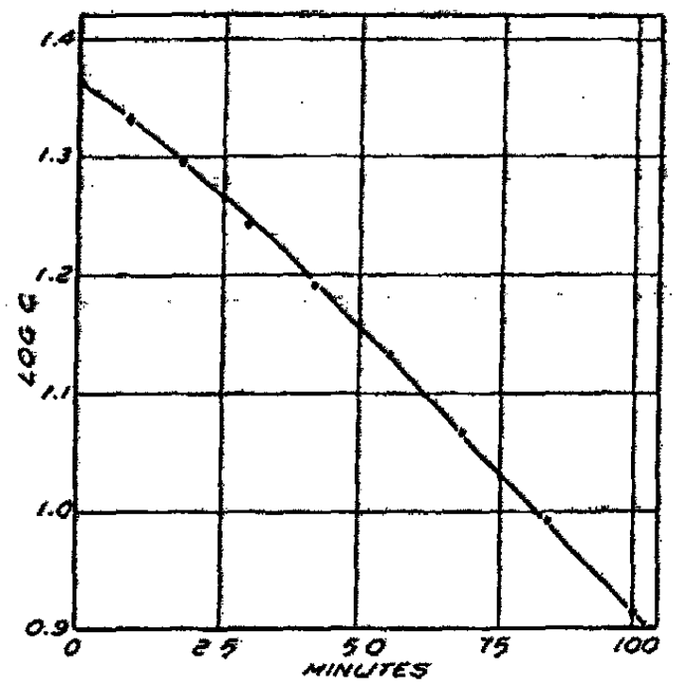

FIG. 1
H_2O_2 Decomposition catalyzed by Iron Oxide Sol.

TABLE I

Velocity Constants calculated for a Monomolecular Reaction

Temperature 50°

Concentration—1.166 grams Fe/l

Min.	cc. $KMnO_4$	Log C.	Log Diff.	k
0	23.08	1.3632	—	—
9	21.48	1.3320	0.0312	0.0080
19	19.72	1.2949	0.0371	0.0085
30	17.47	1.2423	0.0526	0.0110
42	15.56	1.1920	0.0503	0.0097
55	13.57	1.1326	0.0594	0.0105
69	11.55	1.0663	0.0663	0.0109
84	9.48	0.9930	0.0733	0.0113
100	8.21	0.91430.0787		0.0113

Although these constants certainly leave something to be desired in agreement they are as good as others that are reported in the literature for experiments of a similar nature.[1]

[1] Bredig and Collaborators: Z. physik. Chem., 31, 258 (1899); 37, 323 (1901); 37, 3 (1901); Tartar and Schaffer: J. Am. Chem. Soc., 50, 2604 (1928); Shpitalskii, Petin and Burova: J. Russ. Phys. Chem. Soc., 60, 1271, 1291, 1317 (1928).

The average k's were not calculated for most of the comparisons, but instead the average results of duplicate determinations were plotted, log of cc. of $KMnO_4$ against time in minutes, and then the time of half life was obtained from this curve. Such a curve is given for the data of Table I in Fig. 1.

Effect of Temperature.

For this study determinations were made at temperatures of 30°, 40°, 50° and 60°, other conditions being constant. Enough iron oxide sol was used to give a concentration of iron of 1.166 g. per liter. A summary of these results is given in Table II.

TABLE II

Summary of Effect of Temperature on the Reaction

Tem. A°	Min. of 1/2 life	Tem. Coef.	Recip. of Tem.	Log. of 1/2 life	k from 1/2 life	Critical Increment
303°	401	—	0.003300	2.603	0.00173	—
313°	157	2.14	0.003195	2.196	0.00442	17620 cal.
323°	69	2.27	0.003096	1.839	0.01006	16470 "
333°	32	2.58	0.003003	1.505	0.02170	16380 "

The average value of the temperature coefficient was about 2.33. In general when applied to heterogeneous reactions low temperature coefficients, for example 1.3, are associated with reactions in which diffusion is the determining factor while higher temperature coefficients are associated with true chemical reactions. Thus this average temperature coefficient of 2.33 seems to indicate that the decomposition of H_2O_2 is a true chemical reaction and is not dependent upon a process of diffusion so far as velocity is concerned.

However Taylor[1] points out that even though there are many contact catalytic reactions which give temperature coefficients of 1.3 there are many other examples especially with colloidal and enzyme catalysts which give the usual value of 2 or above. This may be due to the fact that the Brownian movement of the colloidal particles eliminates the necessity for diffusion as a determining factor, or it may be due to some surface phenomenon as proposed by Denham.[2] More will be said as to a possible mechanism later.

It has been shown that the relationship between temperature and rate of reaction can be expressed by the familiar equation proposed by van't Hoff and verified by Arrhenius: namely

$$\frac{d \ln k}{dt} = \frac{E}{RT^2}$$

in which k is the velocity constant, R the gas constant, T the absolute temperature and E the critical increment. That the data obtained for the effect of temperature on the reaction are in conformity with this equation is shown by the fact that a straight line (Fig. 2) is obtained when the reciprocals of the absolute temperature (column 4 of Table II) are plotted against the

[1] Taylor: "Treatise on Physical Chemistry", 2, 954 (1924).

[2] Denham: Z. physik. Chem., 72, 641 (1910).

logarithm of the time of half life (column 5 of Table II).

If the Arrhenius equation is integrated between two temperatures it takes the form

$$\log \frac{k_2}{k_1} = \frac{E(T_2 - T_1)}{2.303\, R\, T_2\, T_1}.$$

If this equation is used, taking R as 1.98, T_2 and T_1 as the two absolute temperatures, k_2 and k_1 as the corresponding velocity constants then E can

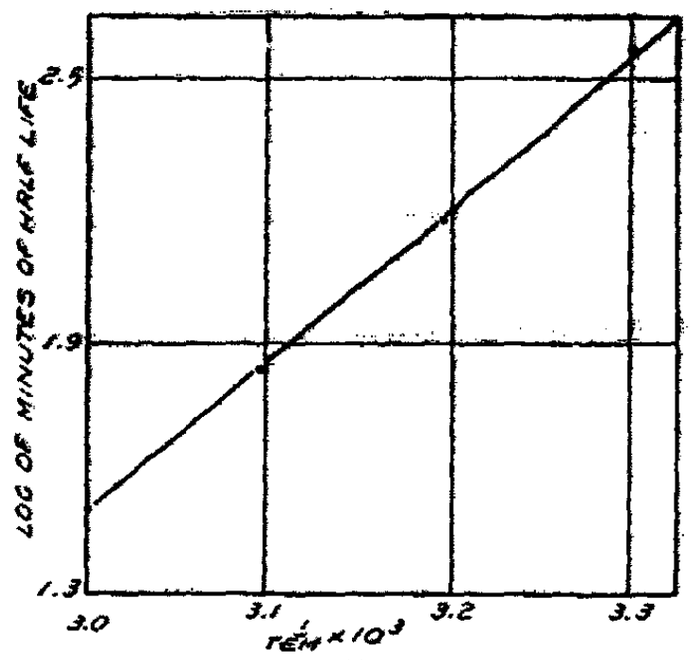

FIG. 2
Effect of Temperature on the Reaction.

be obtained. The k's (given in column 6 of Table II) to be used were obtained by substituting the times of half life (given in column 2 of Table II) into the equation for the velocity constant of a monomolecular reaction. When all these substitutions were made into the integrated equation the values given in column 7 of Table II, the average of which is 16820 calories per gram molecule, were obtained for the critical increment.

Effect of Catalyst Concentration.

In order to study the effect of catalyst concentration on the reaction several determinations, the results of which are given in Table III, were made using various concentrations of the colloidal iron oxide. Runs were

TABLE III

Summary of Effect of Catalyst Concentration on the Reaction
Temperature 50°C

Grams of Fe/l	Min. of half life	Recip. of half life
0.286	442	0.00226
0.563	168	0.00595
1.166	69	0.01449
1.708	45	0.02222
2.281	35	0.02857

not attempted at concentrations above 2.281 g. of iron per liter because at this concentration the iron oxide sol gave so much color to the solutions to be titrated that $KMnO_4$ end points were difficult to determine. As is shown by Fig. 3 a straight line is obtained when the reciprocal of the time of half life (given in column 3 of Table III) is plotted against the concentration of the catalyst, hence the speed of reaction is directly proportional to the amount of catalyst present between the limits used.

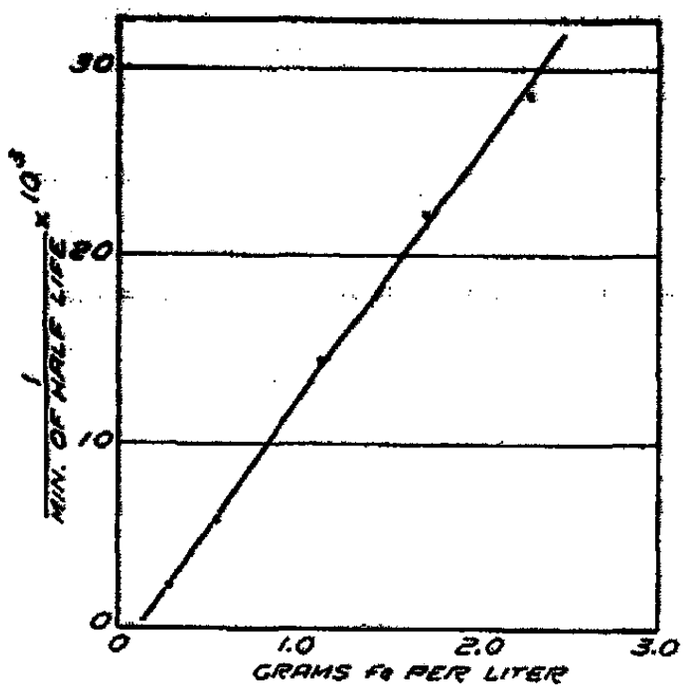

FIG. 3
Effect of Catalyst Concentration on the Reaction.

If now we read from this curve the reciprocal of the time of half life at concentrations of 0.5, 1, and 2 g. of iron per liter and divide one into another in turn we get 2.3 and 2.1 the average being 2.2. Hence on an average doubling the concentration of the colloidal catalyst multiplies the speed of reaction by 2.2. This is slightly lower but of the same order as other values given for reactions of a similar nature.[1]

Effect of Added Electrolytes

A great deal of work has been done on the effects of preservatives, inhibitors, negative catalysts or poisons upon the decomposition of H_2O_2 by colloids. As examples the investigations of Brossa,[2] Bredig and his collaborators, Loevenhart and Kastle,[3] Meyerhof,[4] Tartar and Schaffer, Iredale,[5] and Maxted[6] may be cited. Various reasons may be given for this inhibition. Electrolytes in general are probably adsorbed on the colloid, thus reducing the amount of exposed surface while some substances may exert a stabilizing influence on the H_2O_2.

[1] Bredig and von Berneck: Z. physik. Chem., 31, 258 (1899); Bredig and Reinders: 37, 323 (1901).
[2] Brossa: Z. physik. Chem., 66, 162 (1909).
[3] Loevenhart and Kastle: Am. Chem. J., 29, 397 (1903).
[4] Meyerhof: Arch. ges. Physiol., 157, 351 (1914).
[5] Iredale: J. Chem. Soc., 119, 109 (1921).
[6] Maxted: J. Chem. Soc., 121, 1760 (1922).

In spite of all this work on inhibition of catalytic reactions, little has been done with any inhibitors where catalysis of H_2O_2 decomposition by colloidal iron oxide is involved. Shpitalskii, Petin and Burova have studied the effects of NaOH and HCl on solutions of $FeCl_3$ and $Fe_2(SO_4)_3$ which were undergoing hydrolysis and at the same time catalyzing the decomposition of H_2O_2. As mentioned before Duclaux found that only very small additions of K_2SO_4 or $K_4Fe(CN)_6$ were necessary to double or even triple the time of half life of an H_2O_2 decomposition by his colloidal iron oxide catalyst.

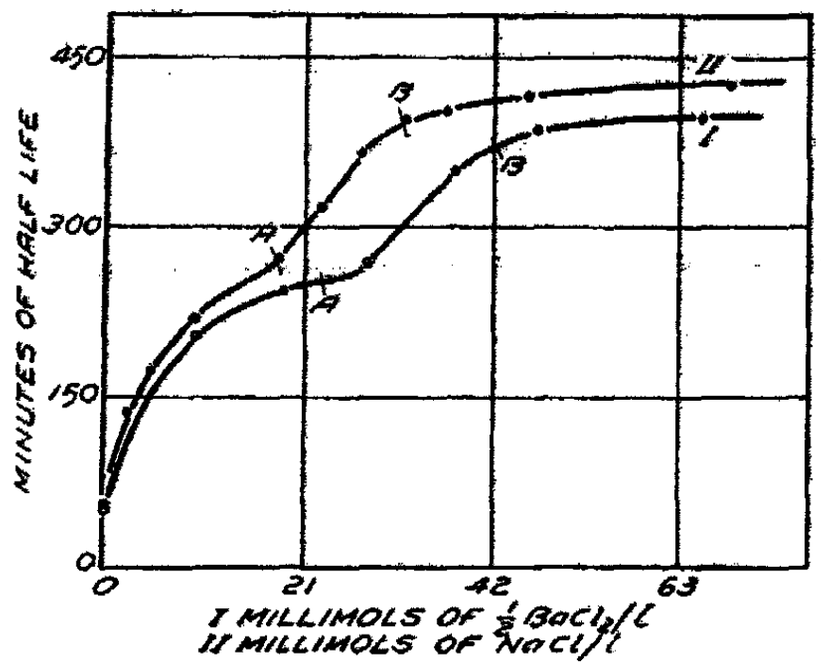

FIG. 4
Effect of NaCl and $BaCl_2$ on the Reaction.

Effect of NaCl.

In each case 21.66 cc. of reacting solution were prepared. Each of these solutions contained 0.465 g. of iron per liter and NaCl in amounts up to 68.85 millimols per liter. The results are given in Table IV and in Fig. 4, Curve II.

The curve so obtained might be divided into four parts; namely, (1) the first portion in which an addition of a small amount of salt causes a great decrease in the catalytic activity of the sol; (2) a gradual changing so that

TABLE IV

Summary of Effect of NaCl on the Reaction
Temperature 50°
0.465 g. Fe/l

Millimols NaCl/l	Min. of half life	Millimols NaCl/l	Min. of half life
0	56	27.54	364
2.30	136	32.13	397
4.59	173	36.72	403
9.18	221	45.90	415
18.36	270	68.85	426
22.95	317		

further additions of NaCl do not make so much difference in the catalytic activity of the sol; (3) another portion where small additions of NaCl greatly decrease the rate of reaction; (4) and finally a portion where the speed of decomposition is only slightly affected by addition of more NaCl.

The first two divisions are very similar in form to the adsorption isotherms first proposed and studied by Freundlich.[1] Since the colloidal iron oxide is acting as the catalyst for the H_2O_2 it must obviously be necessary for the molecules of H_2O_2 to come into contact with the particles of colloid for decomposition to take place. Then any change which takes place which would prevent the H_2O_2 molecules from coming into contact with the colloidal particles will slow down the reaction velocity. Accordingly, the conclusion that one may draw from these first two parts of curve II in Fig. 4 is that the rate of reaction is being slowed down by the adsorption of chloride ions on the particles of colloidal iron oxide catalyst. Thus the first two parts of this curve not only look similar to an adsorption curve but seemingly they correspond to one or may even be considered as being one. Evidently this method of studying the decomposition of H_2O_2 by colloidal iron oxide in the presence of various amounts of NaCl might be adapted to the study of the relative adsorption of chloride ions by colloidal iron oxide.

Although the change from the second to third portion of the curve is not an abrupt break, it is sudden enough to show that some distinct change has taken place. The same can also be said of the transition from the third to the fourth part of the curve. Bancroft[2] has pointed out that coagulation is always preceded by adsorption, hence if we attribute the first parts of the curve to adsorption effects then the next thing to expect would be flocculation of the sol and its effects on the reaction velocity. In order to reach some conclusion concerning this possibility, an investigation of the flocculation of the sol by NaCl in the presence of H_2O_2 was undertaken. For this study conditions throughout were maintained as nearly identical as possible with the conditions under which the decomposition studies were made. At the end of four hours observations were made as to the degree of flocculation.

On the basis of these flocculation studies two cross-marks A and B have been placed on the curve under discussion. A corresponds to the point at which the first signs of turbidity were observed, and B to the point at which complete precipitation took place. The third division (i.e. A B) of this curve then corresponds to the region of flocculation of the iron oxide sol. During this period the colloidal particles of iron oxide are probably uniting to form much larger particles, thus causing a great decrease in its specific surface. Such an action would doubtless slow down the decomposition velocity. Since the limits of this third part of the curve correspond to the limits of flocculation of the sol, this procedure might be employed to determine the flocculation value of an iron oxide sol by NaCl in the presence of H_2O_2. To be sure

[1] Freundlich: Z. physik. Chem., 44, 129 (1903); 57, 385 (1907).
[2] Bancroft: "Applied Colloid Chemistry" (1926).

it would be a slow method to employ for such a purpose, but evidently it will give results both for the point at which flocculation starts to take place and for the point at which it is complete.

After all of the iron oxide has been coagulated, further additions of NaCl can cause only slight changes in the physical make up of the coagulated oxide. However, Weiser[1] has shown that even the coagulated ferric oxide adsorbs more electrolyte. As before, this adsorption will cover up still more of the catalyst surface and thus further retard the rate of decomposition of the H_2O_2. The fourth part of the curve (i.e. from B to the right) in which further additions of NaCl cause only a slight decrease in the decomposition rate of H_2O_2, then is quite likely due to a further adsorption of NaCl by the coagulated ferric oxide.

Effect of $BaCl_2$.

$BaCl_2$ was chosen as the next substance to be used as a flocculating electrolyte. Since this electrolyte contains the same negative ion as NaCl this series of determinations should serve chiefly as a check on the preceding curve. For each run 21.44 cc. portions of reaction solution were prepared. This solution contained 0.465 g. of iron per liter, $BaCl_2$ in amounts up to 65.36 millimols of 1/2 $BaCl_2$ per liter and 2.53 cc. of stock solution of H_2O_2. The results are given in Table V.

These results were plotted in the same manner as before and curve I in Fig. 4 thus obtained. A flocculation value study was also made using $BaCl_2$ as the coagulating electrolyte. In the same manner as before the points

TABLE V

Summary of the Effect of $BaCl_2$ on the Reaction
Temperature 50°
0.465 g. Fe/l

Millimols 1/2 $BaCl_2$/l	Minutes of half life	Millimols 1/2 $BaCl_2$/l	Minutes of half life
0	51	37.35	350
9.34	205	46.69	384
18.67	244	65.36	396
28.01	265		

corresponding to first signs of turbidity and complete flocculation are indicated by cross lines A and B on curve I Fig. 4. As is quite evident this curve is very similar to that obtained when NaCl was employed as the flocculating agent. The writers have chosen to call these curves "flocculation curves" since they are so similar in form to those obtained in ordinary potentiometric titrations of acids against bases or of oxidizing agents against reducing agents. In somewhat the same manner as these latter curves show when neutralization or oxidation and reduction are complete so these flocculation curves show when flocculation is complete.

[1] Weiser: J. Phys. Chem., 25, 399 (1921).

Effect of K_2SO_4.

A flocculating ion having a valence of two was next used, K_2SO_4 being chosen as a representative electrolyte. 21.44 cc. portions of reaction solution were prepared. Each of these contained 0.465 g. of iron per liter, K_2SO_4 in amounts up to 0.560 millimol per liter and 2.47 cc. of stock H_2O_2 solution. A summary of the results is given in Table VI. The data contained in this table have been plotted in Fig. 5, curve II. The limits of the realm of flocculation are indicated by A and B. The curve so obtained is of the same general form as were the curves when NaCl and $BaCl_2$ were used.

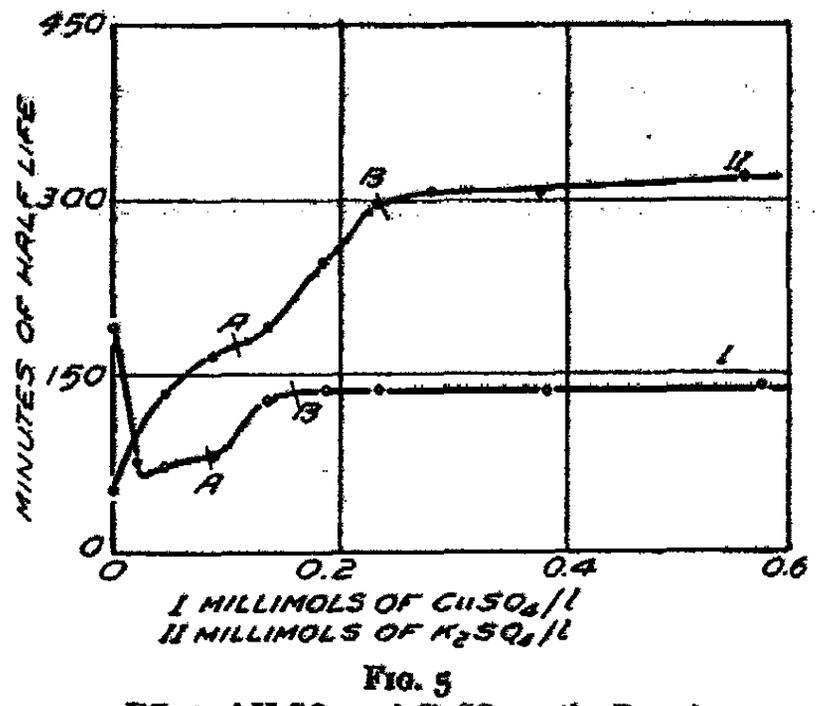

FIG. 5
Effect of K_2SO_4 and $CuSO_4$ on the Reaction.

TABLE VI
Summary of Effect of K_2SO_4 on the Reaction
Temperature 50°
0.465 g. Fe/l

Millimols K_2SO_4/l	Minutes of Half life	Millimols K_2SO_4/l	Minutes of Half life
0	51	0.233	296
0.047	139	0.280	306
0.093	164	0.373	306
0.140	191	0.560	320
0.187	246		

Effect of Na_2HPO_4.

Having studied the effects of a monovalent and a divalent ion on this decomposition the next logical substance to use would be a trivalent ion. Since acids and bases have a decided effect upon the stability of H_2O_2, it was desired to use some salt which would be as nearly neutral as possible. Na_2HPO_4, which is only slightly basic to phenolphthalein, was chosen as the electrolyte to be studied. The results are given in Table VII. The data

contained in this latter table have been plotted and curve I of Fig. 6 thus obtained. The limits of flocculation are indicated by cross lines A and B on the curve.

This curve is somewhat different from the others already mentioned. At the beginning where the other curves gave two parts which corresponded to

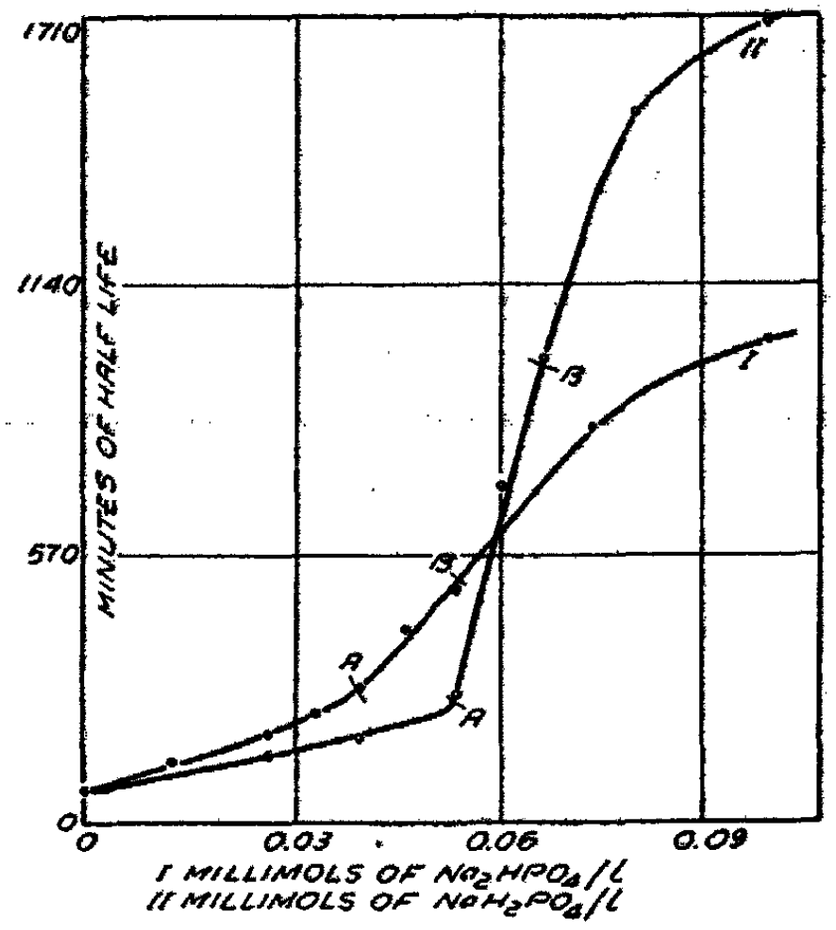

FIG. 6
Effect of Na_2HPO_4 and NaH_2PO_4 on the Reaction.

TABLE VII
Summary of Effect of Na_2HPO_4 on the Reaction
Temperature 50°
0.465 g. Fe/l

Millimols Na_2HPO_4/l	Minutes of half life	Millimols Na_2HPO_4/l	Minutes of half life
0	66	0.0467	409
0.0133	124	0.0534	495
0.0267	190	0.0734	832
0.0333	234	0.1000	1020
0.0400	291		

an adsorption isotherm, in this curve these two parts have flattened down into one part, that is, the first additions of phosphate ion do not have the relatively large effect of later additions of more phopsphate ion as was noticed in the case of the other flocculating ions. Secondly the break in the curve when flocculation begins is rather indefinite. Thirdly, there is no ap-

parent break in the curve at the point which corresponds to complete flocculation, and fourthly, after flocculation has taken place the rate of decomposition is much less than in the cases previously cited.

A majority of these differences can be explained by the stabilizing influence[1] of the phosphate ion on H_2O_2. For example, ortho phosphoric acid, although it is a weak acid, is a fairly good preservative for solutions of H_2O_2 and Quiesser[2] mentions the use of a mixture of salicylic acid and Na_2HPO_4 as a preservative for H_2O_2. Furthermore, Menzel and Gäbler[3] found that both Na_2HPO_4 and NaH_2PO_4 form addition compounds with H_2O_2 which are quite stable. This would account for the fact that the decomposition is greatly reduced after the iron oxide had been completely coagulated. The lack of a break in the curve at the point of complete flocculation would thus be accounted for, since no sudden change would take place if the addition of phosphate ion continues to decrease the rate of decomposition of the H_2O_2 after coagulation of the sol. The lack of a sudden break in the curve at the point which corresponds to the beginning of flocculation can be attributed at least in part to a similar cause. If one takes into account the fact that only very small concentrations of phosphate ion are required to have nearly a maximum stabilizing influence, it may be supposed that the slight break in the curve that finally does occur is due to the fact that the phosphate ion concentration is nearing the point where maximum stabilizing influence is reached.

There still remains an explanation of why the lower portion of the curve comes so close to being a straight line instead of taking the form of an ordinary adsorption isotherm. Several factors may exert some influence, among these being the following: the adsorption of phosphate ion by colloidal ferric oxide, the stabilizing effect of the phosphate ion on H_2O_2, and the effect of the slight basicity of the Na_2HPO_4. No one of these in itself seems sufficient to explain the course of the first part of the curve and just what the combined effect of all these together with other possible factors would be is difficult to foretell.

Effect of NaH_2PO_4.

As a check on the results obtained with Na_2HPO_4 similar studies were made with NaH_2PO_4. A summary of the results of these determinations is given in Table VIII. The data given in this table have been plotted to give curve II of Fig. 6. The limits of flocculation have been indicated on the curve in the usual manner.

As is evident from Fig. 6 the two curves are very similar. The following differences may be mentioned. In this second curve the point at which flocculation begins is indicated by a distinct break in the curve. It will also be noticed that the larger concentrations of NaH_2PO_4 slow down the reaction rate more than do equivalent concentrations of Na_2HPO_4. This can easily

[1] Fischer: Pharm. Zentr., 48, 57 (1907); Dohme and Engelhardt: Am. J. Pharm., 82, 69 (1910); Jensen: Chem. Drug., 93, 1036 (1920).

[2] Queisser: Ger. Pat., 321, 616, April 20 (1919).

[3] Menzel and Gäbler: Z. anorg. allgem. Chem., 177, 187 (1928).

TABLE VIII

Summary of Effect of NaH_2PO_4 on the Reaction
Temperature 50°
0.465 g. Fe/l

Millimols NaH_2PO_4/l	Minutes of half life	Millimols NaH_2PO_4/l	Minutes of half life
0	66	0.0600	715
0.0267	142	0.0667	980
0.0400	181	0.0800	1500
0.0534	272	0.1000	1700

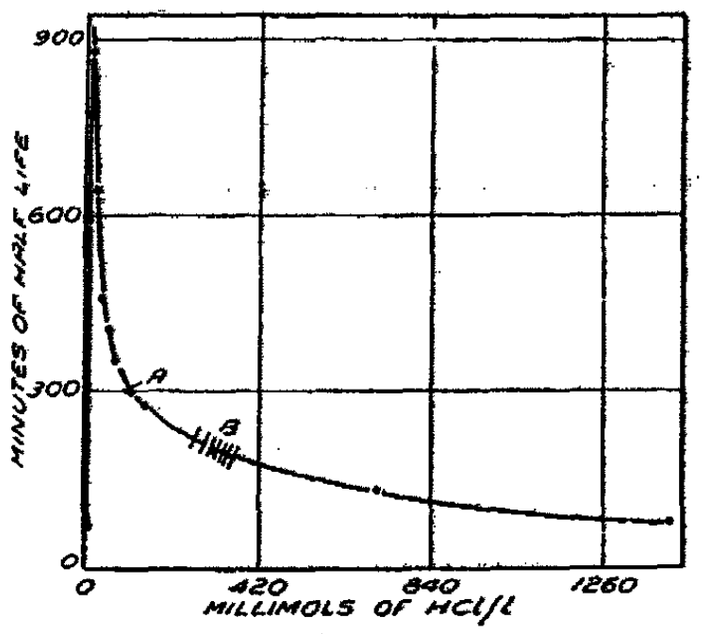

FIG. 7
Effect of HCl on the Reaction.

be accounted for when we recall that H_2O_2 is more stable in an acid solution than it is in a basic one. Freundlich found that the amounts of mono, di, and trivalent ions necessary to cause coagulation of a sol are in the ratio of about 500 to 7 to 1. Although the determinations in the present investigations were made in the presence of H_2O_2 the corresponding ratio was found to be of about the same order but of a somewhat different magnitude. Roughly the flocculation values obtained in this investigation using chloride, sulphate, and phosphate ions were in the ratio of 700 to 4 to 1.

Effect of HCl.

The effect of HCl was investigated next since it offered interesting possibilities. It is formed when the colloidal ferric oxide is prepared and there are some doubts as to whether or not it can be entirely removed by the process of dialysis. The results are given in Table IX. The data in this table are plotted in Fig. 7. On the basis of flocculation studies a cross line A has been placed on the curve to indicate the first appearance of turbidity and a series of broken lines B to indicate as nearly as possible the realm of complete precipitation. In this study, as was the case with Freundlich's work, no definite flocculation value could be obtained.

TABLE IX

Summary of Effect of HCl on the Reaction.
Temperature 50°.
0.496 g. Fe/l.

Millimols HCl/l	Minutes of half life	Millimols HCl/l	Minutes of half life
0	73	106.2	298
2.9	592	141.7	274
8.7	880	302.9	202
17.4	640	705	133
35.4	455	1420	78
52.8	400	2125	52
70.8	350	4250	15.5

The curve for the results of these determinations is decidedly different in form than any of the others thus far obtained. The activity of the catalyst is greatly decreased by the first additions of HCl due, perhaps, to the high adsorbability of the hydrogen ions. To this must also be added the adsorption of the chloride ions and also the fact that an acid stabilizes a solution of H_2O_2.

The rest of the curve can be explained in the following manner. Let it be assumed that after a small amount of HCl has been added it begins dissolving some of the iron oxide particles. This would give ferric ions which are fairly strong catalysts for the decomposition of H_2O_2, so that at that concentration of HCl at which enough ferric ions are formed to overcome the effects of further adsorption the reaction velocity will begin to increase as more HCl is added. From the curve it seems likely that at 50° this point is at a concentration of about 9 millimols of HCl per liter. As is shown by the curve further additions of HCl continue to increase the rate of decomposition at first rather rapidly, and then as there is less undissolved iron oxide remaining the rate of acceleration gradually decreases until finally further additions of HCl increase the speed of decomposition by only a very small amount. Since in the last determinations the iron oxide was all dissolved, the slight increase in speed of the decomposition is quite likely due chiefly to the rapidity with which the oxide dissolves and not to the amounts of it dissolved at the end of the run. As is further evidenced by the curve the catalytic effect of the ferric ions formed by the dissolving of the ferric oxide by the HCl is so great in proportion to the effect of the undissolved iron oxide, either colloidal or coagulated, that the curve extends right through the complete realm of flocculation without giving any indication that such an act has taken place.

Effect of NaOH.

The effect of sodium hydroxide was next investigated. A summary of these results is given in Table X. The significant results of the corresponding flocculation studies are given along with the curves in Fig. 8.

Curve I is for the addition of relatively small amounts of NaOH and has been plotted on a large scale (indicated at the bottom of Fig. 8). Curve II is for the whole series of determinations and is necessarily plotted on a much smaller scale (indicated at top of Fig. 8). The latter curve is still more complicated than any of the previous ones. An unusual curve was expected due to the

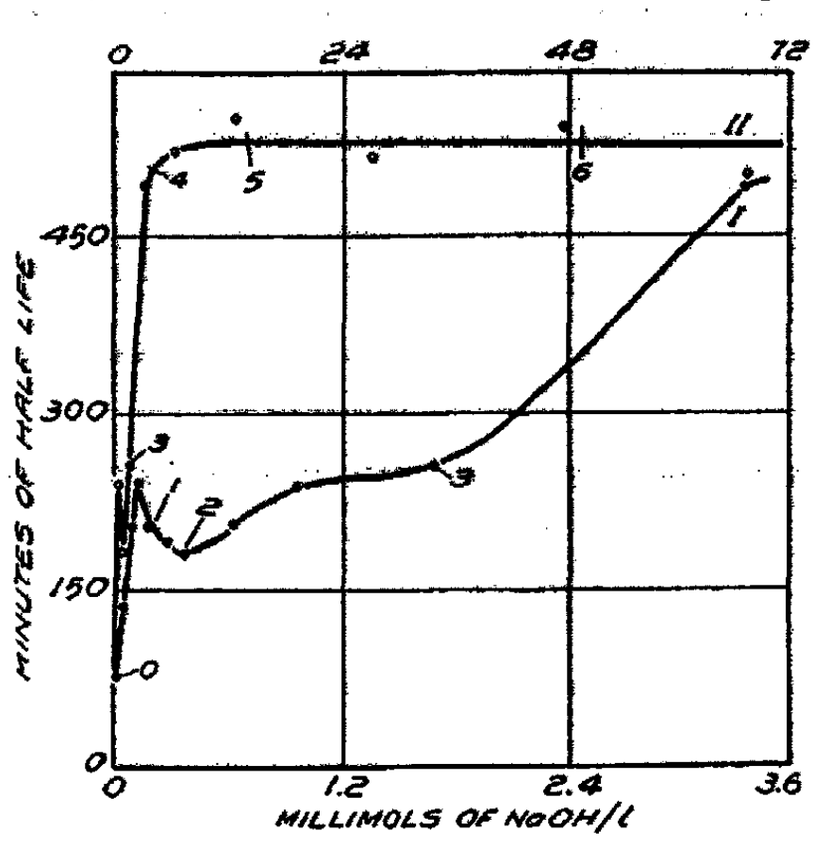

FIG. 8

Effect of NaOH on the Reaction
0-1. Stable positive sol.
1-2. Realm of precipitation of positive sol.
2-3. Complete precipitation of positive sol.
3-4. Restabilization of the sol.
4-5. Realm of stable negative sol.
5-6. Realm of precipitation of negative sol.
6- . Complete precipitation of negative sol.

TABLE X

Summary of Effect of NaOH on the Reaction.
Temperature 50°.
0.496 g. Fe/l.

Millimols NaOH/l	Minutes of half life	Millimols NaHO/l	Minutes of half life
0	73	0.933	239
0.015	90	1.675	256
0.046	134	3.35	490
0.093	205	6.70	515
0.139	241	12.14	546
0.186	205	26.81	514
0.279	194	47.12	540
0.372	183	67.15	500
0.597	210		

several factors that enter into the reaction. Among these are the following: (1) the increased rate of decomposition of H_2O_2 in the presence of a base, (2) the high adsorbability of the OH ion, (3) the fact that NaOH not only flocculates a positively charged ferric oxide sol, but in larger amounts causes the formation of a stable negatively charged sol, and, finally, in larger amounts causes the precipitation of this negatively charged sol.

As with most of the other curves the adsorption of the first amounts of electrolyte greatly decreases the activity of the catalyst. In most of the preceding examples the effects of adsorption became much less as more electrolyte was added. Such is probably the case here but when this happens the ability of NaOH to accelerate the decomposition of the H_2O_2 has a chance to make itself apparent, so that over a short range the rate of decomposition of H_2O_2 is increased by additions of NaOH. This continues until the sol has been precipitated and NaOH has been added in amounts up to where further additions do not have so much effect on the decomposition of H_2O_2. Then (point 2 on the curve) adsorption effects predominate again, and the ferric oxide continues to become less active as more NaOH is added. This evidently continues until the iron oxide has finally adsorbed all the NaOH that it can, and then (to the right of point 4 on the curve) the rate of decomposition of the H_2O_2 is not appreciably changed by further additions of NaOH. The surprising part of it is, that all of this latter change after the precipitation of the positively charged sol seems to be independent of the state of stability of the sol. If it is assumed that exposed surface is the chief deciding factor, then the amount of freely exposed surface of the iron oxide after first precipitation must depend almost entirely upon the amount of adsorbed NaOH and very little, if any at all, on the state of the iron oxide, that is, whether it is present as a precipitated positively charged sol, a stable negatively charged sol, or a precipitated negatively charged sol.

Effect of $CuSO_4$.

In their study of the decomposition of H_2O_2 by ferric salts Bohnson and Robertson[1] found that cupric ions acted as promoters. These contributions of Bohnson and Robertson suggested that a cupric salt be studied. The results of such a study are given in Table XI.

If Curve I Fig. 5 is divided into four parts as was done with the first curves in this investigation it will be noted that all the parts are very similar to the K_2SO_4 curve, except the first section. This first part of the curve is apparently due to the promoter effect studied by Bohnson and Robertson. Evidently this promoter effect of very small amounts of cupric ions is greater than the adsorption effects of small amounts of sulphate ion, so that the activity of the catalyst is increased by additions of very small amounts of cupric ion.

[1]Bohnson and Robertson: J. Am. Chem. Soc., 45, 2512 (1923); Robertson: 47, 1299 (1925).

TABLE XI

Summary of Effect of $CuSO_4$ on the Reaction
Temperature 50°.
0.227 g. Fe/l.

Millimols $CuSO_4$/l	Minutes of half life	Millimols $CuSO_4$/l	Minutes of half life
0	191	0.1907	136
0.0234	75	0.238	135
0.0469	73	0.381	133
0.0937	82	0.572	139
0.1406	129		

A flocculation curve has been plotted in Fig. 5 Curve I, and the results of the flocculation studies indicated as before. In this case two hours was chosen as the time of observation for that was more nearly the average time of half life of the various runs.

Mechanism of the Reaction

Earlier in this discussion reference was made to an investigation by Duclaux of the decomposition of H_2O_2 by colloidal ferric oxide. In this study Duclaux reached the conclusion that only the ferric ions which had not been removed from the colloidal iron oxide by dialysis acted as a catalyst and that the effects of various poisons on this reaction could be explained by their chemical reaction with these ferric ions. Bredig and von Berneck have also found evidence to indicate that colloidal ferric hydroxide has almost no effect on the decomposition of H_2O_2. Shpitalskii, Petin and Burova have stated that in an acid medium the ferric ions act as the catalyst while in an alkaline solution the actual catalyst is hydrated particles of Fe_2O_3. Spring[1] is also of the opinion that some of the catalytic effect is due to the colloidal particles in the solution.

From the results obtained in the present investigation the authors feel that almost beyond all doubt the colloidal iron oxide does act as the catalyst for the decomposition of H_2O_2. Practically all the data herein point towards that fact. The first portions of the flocculation curves obtained by the use of NaCl, $BaCl_2$, and K_2SO_4 are so similar in form to ordinary adsorption isotherms, that the most logical explanation is that these salts in being adsorbed by the colloid cover up some of its surface so that it can no longer act as a catalyst. Furthermore, the second part of the curve obtained by the use of $CuSO_4$ seems to correspond to the latter part of an adsorption isotherm. And moreover, the exceedingly large effect of the addition of very small amounts of HCl is most conveniently explained by its high adsorbability. Duclaux chooses to explain these poisoning effects by actual chemical reaction of the electrolyte with ferric ions that are present. Such can hardly be the case for this would make it difficult to explain the effects of chlorides on the decomposition. Furthermore, such an explanation would not show why

[1] Spring: Bull. Acad. roy. Belg., (3) 30, 32 (1895).

the addition of small amounts of HCl decreases the speed of the H_2O_2 decomposition so much more than does the addition of an equivalent amount of chloride ion in the form of NaCl or $BaCl_2$.

Moreover, Sorum has shown that iron oxide sols, prepared and tested as the sol used in the present investigation, do not contain more than 0.0001692 grams of chloride ion per liter calculated as HCl. Choosing the conditions and results of the first run in Table IV as a typical example of a determination in which no electrolyte was added the following calculation can be made. In that run 3.29 cc. of sol were used in 21.66 cc. of reaction solution. Thus the most $FeCl_3$ that could be present in this reacting solution would be

$$\frac{0.0001692 \times 35.46 \times 3.29}{3 \times 35.46 \times 21.66 \times 36.47} = 234.9 \times 10^{-9}$$ mols of $FeCl_3$ per liter.

Bohnson[1] has found that the time of half life of an H_2O_2 decomposition at 25° catalyzed by 0.002974 mols of $FeCl_3$ per liter is about 9 minutes. Now 234.9×10^{-9} would have to be doubled about 13 1/2 times in order to give a concentration of 0.002974 mols per liter. As has been determined earlier in this investigation doubling the concentration of the catalyst increases the velocity of decomposition about 2.2 times or divides the time of half life, which was 56 minutes for the particular run under discussion, by 2.2. Then if the concentration of the catalyst was doubled 13 1/2 times the time of half life would be divided by 2.2 thirteen and one half times. But this reaction was run at 50° and Bohnson's results are for 25°; hence the time of half life would have to be multiplied by the ten degree temperature coefficient about 2 1/2 times to make it apply at 25°. The temperature coefficient has already been determined to be about 2.3 which is roughly the same as 2.2 so that dividing by 2.2 thirteen and one half times and then multiplying by 2.3 two and one half times would be roughly the same as dividing by 2.2 eleven times. Dividing 56 by 2.2 eleven times gives 0.0096 minutes as the time of half life of H_2O_2 in a solution of catalyst containing not more than 0.002974 mols of $FeCl_3$ per liter. But this makes the solution of this catalyst containing not more than 0.002974 mols of $FeCl_3$ per liter about 1000 times as active as a solution containing 0.002974 mols of $FeCl_3$ per liter without any colloid being present so that most of the decomposition in this investigation must be attributed to particles of colloidal ferric oxide and not to the possible traces of ferric ions that may be present as $FeCl_3$.

The writers do not claim that, in cases such as those used by Duclaux and by Bredig and von Berneck where appreciable amounts of $FeCl_3$ still remain in the sol, some of the decomposition is not caused by ferric ions; but they do feel that the above investigators are mistaken when they say that colloidal particles of ferric oxide cause none or practically none of the reaction. Also it seems quite likely that the poisoning effects of K_2SO_4 and $K_4Fe(CN)_6$ noted by Duclaux are due mostly to the adsorption of these electrolytes on the colloidal iron oxide and not to their chemical reaction with the $FeCl_3$ that is present.

[1] Bohnson: J. Phys. Chem., 25, 19 (1921).

On the other hand, the writers do not maintain that the solid colloidal particles of ferric oxide are the actual catalyst. It seems entirely possible that some intermediate compound may be formed which serves as the catalyst. Bohnson regarded the decomposition of H_2O_2 by ferric ions as being due to the formation of ferric acid which served as the intermediate compound. In the light of his work a similar reaction mechanism could be advocated for the decomposition of H_2O_2 by colloidal particles of ferric oxide. In such a case the reaction could be represented by the following equations:

$$Fe_2O_3 + 3\ H_2O_2 \rightleftarrows 2\ H_2FeO_4 + H_2O$$

$$2\ H_2FeO_4 + 3\ H_2O_2 \longrightarrow Fe_2O_3 + 5\ H_2O + 3\ O_2.$$

No doubt the colloidal particles of iron oxide are somewhat hydrated so that more H_2O should be included in the above equations but this would not essentially change the mechanism.

No important objections to the above method of representing the reaction seem to present themselves. It is quite probable that the ferric acid formed remains adsorbed on the colloidal particles of iron oxide, so that when it is decomposed the surface of the micelles remains essentially unchanged. Such an action would preclude any objections which might maintain that if the colloidal ferric oxide is continually undergoing chemical reactions, such as those represented in the above equations, its physical constitution would soon be changed so much that a corresponding change in the decomposition velocity of the H_2O_2 should be noticed.

So far as the present work is concerned there are no indications that the intermediate compound formed is ferric acid. It could just as well be some higher oxide of iron such as those mentioned by Manchot[1]; namely FeO_2, Fe_2O_5, or FeO_3. The chief difference that this would introduce would be a difference in solubility of the intermediate compound or, in the case of FeO_3, just a difference in hydration. Other investigators have advocated the formation of intermediate oxide films in H_2O_2 decomposition. In fact it seems likely that oxide formation in many such reactions is an important factor. In general those metals which form more than one oxide, for example mercury, copper, gold and iron oxides, are more effective in decomposing H_2O_2 than are other metal oxides. Hence, the writers believe that some intermediate compound containing iron with a higher valence is formed in the present reaction. This work gives no indication as to whether this compound is ferric acid or a higher oxide of iron.

Summary

1. The subject of the catalytic decomposition of hydrogen peroxide by colloidal ferric oxide has been investigated at a temperature of 50° C. and in the dark.

2. The reaction has been found to be approximately an apparent monomolecular reaction.

[1] Manchot and Wilhelms: Ber., **34**, 2479 (1901); Manchot: Ann., **325** 105 (1902).

3. In general the velocity constants increased as the reaction progressed, especially so at the beginning of the reaction.

4. The average temperature coefficient for a ten degree rise of temperature has been found to be about 2.33 between 30° and 60° C. This temperature coefficient seems to indicate that the reaction velocity is governed by the speed of a chemical reaction rather than by a process of diffusion.

5. The rate of decomposition is multiplied by about 2.2 each time the catalyst concentration is doubled between the limits of 0.286 and 2.281 g. of iron per liter.

6. The effects of additions of NaCl, $BaCl_2$, K_2SO_4, NaH_2PO_4, Na_2HPO_4, HCl, NaOH, and $CuSO_4$ over a considerable range of concentration have been investigated. In the case of NaCl, $BaCl_2$ and K_2SO_4 typical "flocculation curves" have been obtained which show the effects of adsorption of the electrolyte by the colloidal iron oxide, the limits and effects of flocculation of the sol, and finally, the effects of adsorption of the electrolyte by precipitated iron oxide. In the case of the other electrolytes modifications of these flocculation curves were obtained which can be satisfactorily explained by the effects of these various substances on the stability of solutions of H_2O_2.

7. For electrolytes which have little effect on the stability of H_2O_2 this method of procedure can be used for a study of adsorption of the electrolyte by colloidal ferric oxide in the presence of H_2O_2 and for determining the flocculation value of the sol in the presence of H_2O_2.

8. Evidence has been found which indicates that particles of colloidal ferric oxide act as the catalyst and that the effects of addition of various electrolytes are due to their effect on these colloidal particles rather than to a reaction between these and the possible traces of $FeCl_3$ that may be present.

9. A possible mechanism for the reaction, involving the formation of ferric acid or some higher oxide of iron as an intermediate compound, has been proposed.

Madison, Wisconsin.

LIQUID AMMONIA AS A LYOPHILIC DISPERSION MEDIUM. II AMMONO-GELS OF CELLULOSE ACETATE

BY ROBERT TAFT AND JESSE E. STARECK

In previous papers[1] the senior author has called attention to the fact that liquid ammonia is an excellent dispersion medium for the cellulose esters. Further it was pointed out that in the case of cellulose acetate, gels were formed upon standing at room temperature. This paper deals with the extent of dispersion of cellulose acetate in liquid ammonia, the chemical action of the solvent upon this substance and lastly some of the properties of two types of gels formed by this system.

The cellulose acetate used in the investigation was that manufactured by the Eastman Kodak Co. which was air dried at 100°C before use. It is probably a mixture of acetates up to the triacetate. The product now marketed by this organization as cellulose triacetate is not so readily dispersable as is the product of lower acetylation.

The ammonia used was in some cases drawn directly from a cylinder of anhydrous liquid ammonia, the usual precautions being taken to prevent absorption of water. Later, when it became necessary to study the effect of water upon the gelatinization of these systems, the ammonia used was dried over sodium and distilled under slight excess pressure in a closed train into the tube containing the cellulose acetate, which was cooled by an external bath of the same liquid. In most cases observations were made with the samples under examination sealed in tubes of pyrex in order to continue the observations at higher temperatures than the boiling point of liquid ammonia (−33.5°C).

Dispersability

Apparently there is no limit to the dispersability of cellulose acetate in this liquid. Ammonosols ranging from very dilute ones up to 60 grams of cellulose acetate in 100 cc. of the dispersion medium have been prepared.[2] Higher concentrations can be obtained but the concentrations above this limit are difficult to estimate and the systems are so gummy and plastic that they are exceedingly difficult to work. In order to obtain these gels of higher concentration the following conditions must be observed: (a) low temperature must be maintained; it is necessary in order to secure dispersion, that the

[1] Taft: J. Phys. Chem., 34, 2792 (1930); Trans. Kansas Acad. Sci. 32, 58 (1929). Clancy, U. S. Patents 1,544,809 and 1,544,812 (1925), has covered the dispersability of cellulose nitrates and acetates with patents but no information is given upon the properties of such systems as herein described; Fenton and Berry (Proc. Camb. Phil. Soc., 20, 16 (1920)) were the first to point out that cellulose acetate disperses in liquid ammonia.

[2] In order to save words we have referred to our concentrations in terms of per cent. This is a misnomer but a 60% system means one containing 60 grams of cellulose acetate per 100 cc. of dispersion medium, etc.

temperature of the system be in the neighborhood of boiling ammonia (−33.5°C); (b) considerable mechanical agitation must be employed in order to secure the necessary circulation of the liquid and to secure as large a surface of contact as possible between the two phases. The latter was secured by stirring with a glass rod while the acetate was being added. In order to obtain the highest concentrations of the sol mentioned above it was necessary to evaporate a sol containing 30 grams of acetate per 100 cc. of solvent to one-half of its original volume.

Sols containing 1% or less of cellulose acetate were clear, colorless, mobile liquids. The viscosity was increased considerably over that of the pure dispersion medium and was a function of time, particularly at room temperature. When the sealed tubes were allowed to warm up to room temperature, the viscosity rapidly decreased at first but after a few hours began to increase again. This increase in viscosity, as will be shown, is due to a change in the composition of the dispersed phase. On the whole it may be said that the viscosities of these systems are affected by concentration, temperature, and age as is the case with many other lyophilic systems.

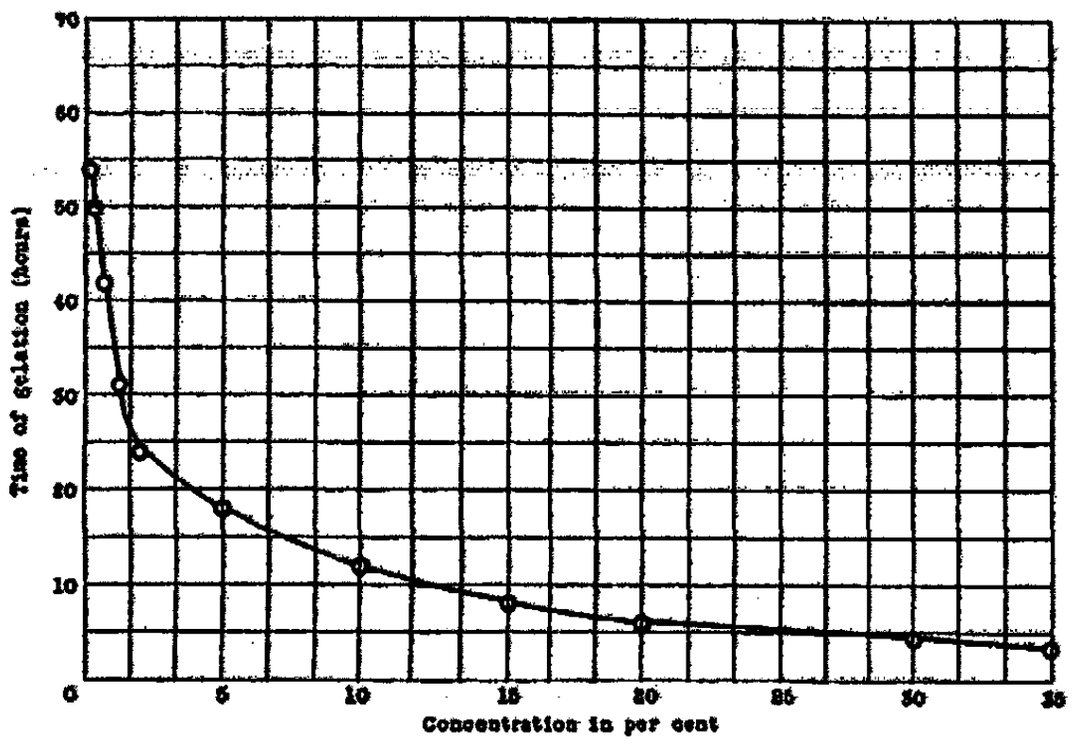

FIG. 1

Time of gelation as a function of concentration of cellulose acetate. Irreversible Gels.

Sols of higher concentration were very viscous, translucent, but of light brown color.

Heat Irreversible Gels

As was stated above, the ammonosols when allowed to warm to room temperature (ca 25°C) decreased in viscosity at first, but after several hours the viscosity increased, the system eventually setting to a gel. The gels thus formed were white opaque masses and did not redisperse when recooled to the temperature of boiling ammonia, i.e. they were heat irreversible. In one case the gel which had formed at room temperature was recooled in boiling

ammonia and kept at that temperature for several weeks without indication of melting of the gel. The time necessary for gelation was found to be a function of the concentration, the temperature, and the water content of the dispersion medium. Table I and Fig. 1 give the time of gelation as a function of the concentration of the cellulose acetate.

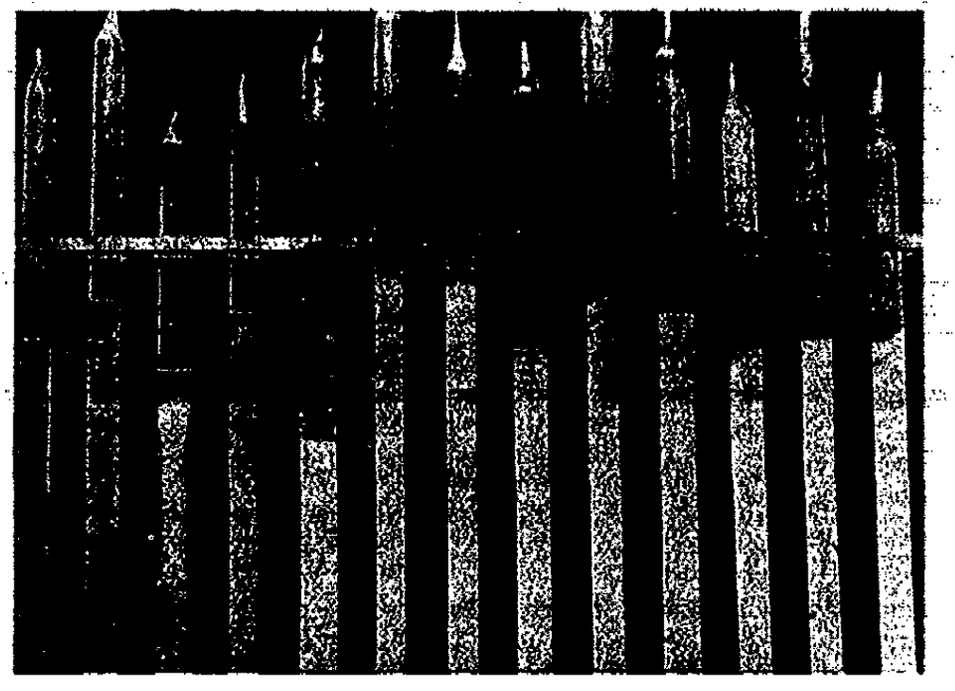

FIG. 2
Heat Irreversible Gels.
Tubes left to right have cellulose acetate content of:
0.0% 0.05% 0.1% 0.2% 0.3% 0.5%
1% 2% 5% 7.5% 10% 15% 20%

TABLE I

Conc. of cellulose acetate %	Time of Gelation Hours	Appearance of Gel
0.1	54	Soft clear gel; marked syneresis
0.2	46	Firm translucent
0.5	38	gel; marked syneresis
1.	31	Striated; some syneresis
2.	24	Vertical crack; some syneresis
5.	18	Opaque, rigid, white; "Sine
10.	12	curve" crack; syneresis apparent
15.	8	Striated; oblique cracks;
20.	6	marked syneresis of brown
30.	4-5	liquid; gel contracted.
35.	3-5	

The appearance of the gels is also recorded photographically in Fig. 2, the gels here depicted being approximately two weeks old. The time of gelation as a function of temperature is shown graphically in Fig. 3, the temperatures of observation being the boiling temperature of ammonia, the ice point and room temperature. In the case of the 5% gel the system was kept at $-33.5°C$ for two weeks, the sol becoming slightly cloudy in that time but gelation did not occur. On removing it from the bath and allowing it to warm to room temperature, gelation occurred in eight hours or about one-

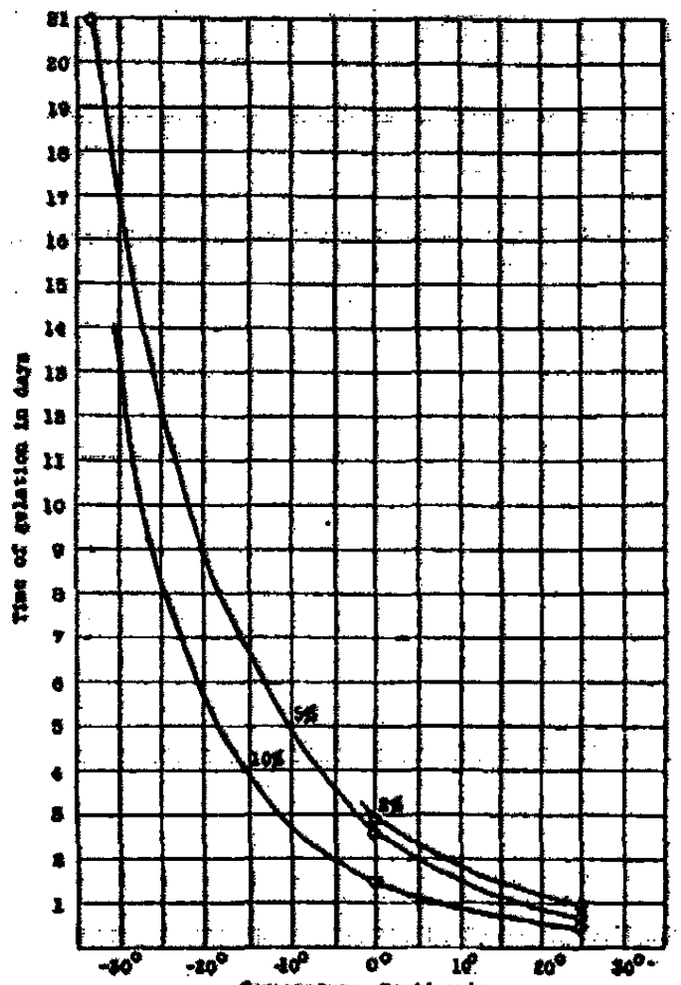

FIG. 3
Time of gelation as a function of temperature. Irreversible Gels.

third of the normal time. As will be shown, gel formation occurs as a result of chemical action, and consequently it was assumed that two-thirds of the reaction had taken place and it is upon this basis that we have plotted the point at $-33.5°C$. In the case of the 10% gel, a gel formed at the boiling point of ammonia within a few hours but this proved to be of the heat-reversible type described later. On warming, it melted and set to the irreversible type in about the usual time. This seems unusual for the more concentrated system would be expected to set more quickly, but apparently the reversible gel structure prevented the reaction between disperse phase and dispersion medium from proceeding so rapidly, i.e. the disperse phase is not in as intimate contact in the gel state as when in the sol form, for in the gel state most of the dispersion medium would be present in the gel pores.

In the more dilute gels considerable difficulty was at first experienced in obtaining concordant data on the time of setting for a gel of a given concentration. This was finally traced to the presence of small but variable quantities of water present in the dispersion medium. This led us to investigate the effect of water upon the dispersability of the acetate and upon the properties of the gels thus formed. Known quantities of water were added to ammonia distilled from sodium. Under these conditions results were obtained which were reproducible for dilute sols but for those more concentrated than 0.5% dispersion did not take place quickly enough to obtain a uniform system by simply shaking the tube containing the materials under examination. The data recorded in Table II and graphically in Fig. 4 shows the effect of varying quantities of water upon the structure of the gel and the time of gelation. Fig. 5 shows photographically the results at a concentration of 0.1% cellulose acetate.

The facts to be noted in connection with the effect of water are: (a) dispersion of small quantities of cellulose acetate can take place in the presence of large quantities of water;[3] (b) precipitation and not gel formation takes

TABLE II

Gels formed in the Presence of Water

Amount of H_2O	Time of Setting	Structure
	0.5% Cellulose Acetate	
None	38 hours	Coarse gel, gradually settling
1%	32	Slightly grainy gel
2%	27	Fine gel
5%	20	Fine opalescent gel
	0.2% Cellulose Acetate	
None	46 hours	Gelatinous precipitate
1%	36	Coarse, granular gel
2%	28	Fine gel
5%	22	Fine, opalescent gel
	0.1% Cellulose Acetate	
None	54 hours	Flocculent precipitate
1%	42	opalescent gel
2%	26	Precipitate
5%	21	Gelatinous precipitate
10%	15	Grainy, coarse gel
	0.05% Cellulose Acetate	
None	41 hours	Precipitate
0.5%	41	Precipitate
1%	35	Opalescent, soft gel
2%	25	Precipitate
5%	17	Precipitate
10%	9	Gelatinous precipitate
20%	3-6	Precipitate

[3] The range of dispersability is not great in the presence of large quantities of water, however. Thus a system containing 25% water and 0.1 gm. of the acetate to 100 cc. of dispersion medium showed no appreciable dispersion.

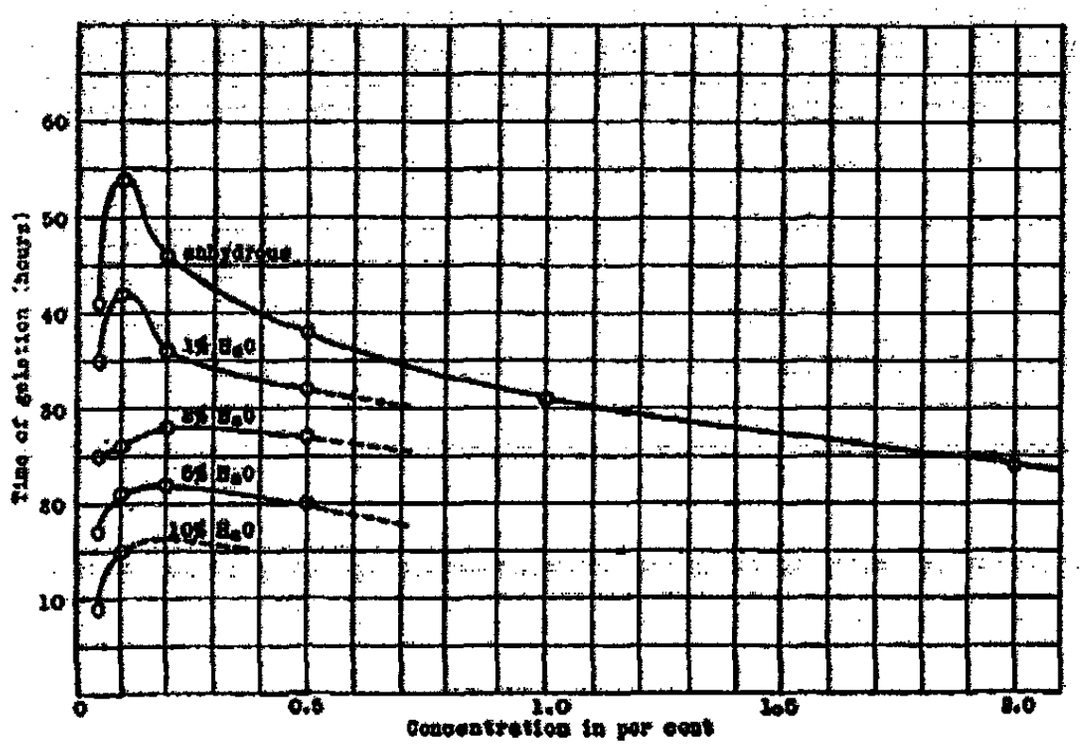

FIG. 4
Effect of Water on Time of Gelation. Irreversible Gels.

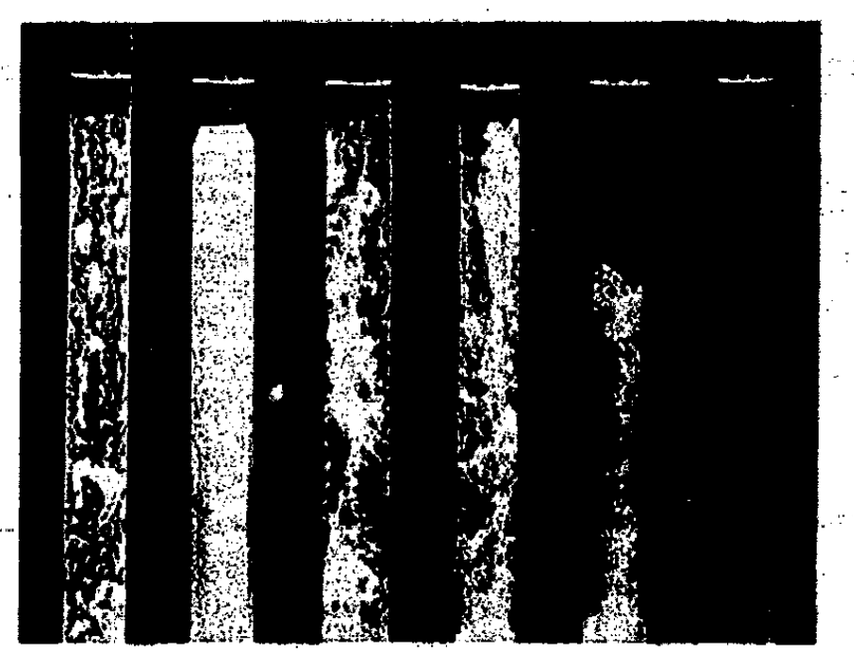

FIG. 5
Effect of Water Content on Gel Structure.
Cellulose acetate content 0.1%.
Tubes left to right have water content of:
0.0% 1% 2% 5% 10%
Tube on extreme right is pure ammonia.
The gels are not so opaque as these photographs would indicate.

place in the absence of water; (c) gels form more rapidly and are of firmer structure at an optimum value of water concentration; (d) very minute concentration of the acetate can produce gels. In connection with the last point it can be said that the lower limit of concentration of gel formation is at least as low as 0.05 per cent (rather 0.05 per 100 cc. of ammonia). This is probably the lowest concentration at which gelation has been recorded. Weiser[4] produced aqua-gels containing 0.09 per cent chromic oxide. Kruyt[5] states that an aqueous system containing 0.14% agar will gel at room temperature. As far as the writers are aware these are the lowest concentrations previously recorded for gel formation in other systems.

One striking peculiarity of these gels was observed, particularly in gels containing 7.5% of cellulose acetate. This was the development of cracks of very regular form, which we have termed "sine curve" breaks. These are shown photographically in Fig. 6; they were not restricted to gels of this particular concentration but characterized gels from 5 to 10%, appearing in from one to two days after gelation, depending upon the previous history of the sample. The "wave length" of these curves was found to be a function of the bore of the tube as shown in the illustration. These breaks are undoubtedly caused by the gel's contraction which begins shortly after gelation, but since the exterior surface of the gel adheres to the glass wall a strain within the gel is produced. As contraction proceeds, the stress produced finally becomes sufficient to rupture the structure. Since the structure is thinner near the walls of the tube it will tear there first as resistance to strain is proportional to cross sectional area, but also, as the membrane becomes thinner, it will stretch more for a given load, or stress; consequently the stress is relieved on this side before the break reaches the edge. But the stress on the other side must also be relieved since it is now greatest and a break is then produced in this region. The original production of strain is characterized by an absorption of all of the liquid of syneresis, giving the surface of the gel a dry appearance. After the completion of the break, however, syneresis takes place a second time.

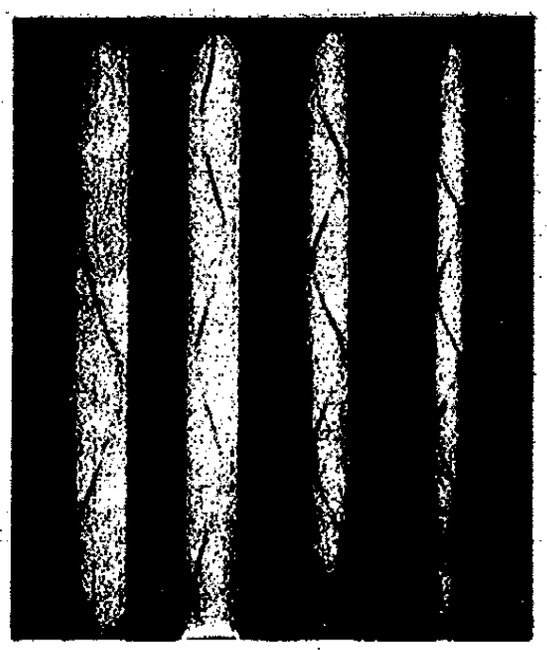

FIG. 6

We have observed the production of somewhat similar breaks in silica aqua-gels but never so regular as here shown. In fact we have noticed many points of similarity between these ammono-gels of cellulose and aqua-gels of silica. In external appearance they are very much alike; they are both heat

[4] J. Phys. Chem., 26, 431 (1922).
[5] "Colloids," 169 (1927).

irreversible; further the time of gelation is a somewhat similar function in both cases.[6] Freshly prepared gels of higher concentration vibrate also when struck, as do silica gels.

Evidence of Chemical Change in Heat-Irreversible Gels

A number of tubes containing gels were recooled in liquid ammonia, opened and the gels removed for examination. The 5 per cent gels were quite rigid and brittle, but shrank rapidly and increased in toughness as the ammonia evaporated. A gel four inches by one-half inch diminished in size to one inch by one-eighth inch, leaving a yellow transparent residue, which did not swell or disperse again when placed in liquid ammonia. Further this horn-like structure was not only inert toward ammonia but also to all liquids which disperse cellulose acetate. Hydrochloric acid had no effect upon it and concentrated sulfuric acid only softened it slightly in a few hours; the original cellulose acetate is rapidly attacked by these acids. These gel residues are dispersed, however, by Schweitzer's reagent. Apparently the material comprising the gel structure is cellulose, i.e. the dispersion medium reacts with the cellulose acetate converting it to cellulose. In the absence of any water in the dispersion medium, acetamide would likely be formed in addition to cellulose. In the presence of water ammonium acetate would be the most probable second material. To test this point out a gel was prepared and allowed to synerize. The tube was then cooled, opened and the synerized liquid removed. This liquid was then added to water (it produced no residue) and tested qualitatively by adding amyl and ethyl alcohols to separate tubes containing the above liquid in dilute sulfuric acid. The characteristic odors of banana oil and ethyl acetate were easily detected.

It will be recalled that for dilute concentrations of cellulose acetate, the best gels were formed in the presence of water. This would seem to indicate that traces of water are necessary for gel formation. That it is not solely a case of reaction is evident from a consideration of the data of Table II. If it be assumed that the reaction

$$[C_{12}H_{18}O_8(COOCH_3)_6]_x + 6H_2O = [C_{12}H_{24}O_{12}]_x + 6CH_3COOH$$

takes place, the mass of cellulose acetate is roughly five times that of the water involved. From Table II, 0.05 gram of cellulose acetate requires 1% of water to produce the best gel, whereas 0.5 gram of cellulose acetate requires 2 to 5% water to produce the best gel, i.e. relatively more water is required in the case of the dilute gels. It would appear that the gel structure is dependent upon *adsorbed* water to secure the firmest gel.

Diffusion Experiments

The ammono-gels thus described make suitable systems for diffusion experiments. We have not tried a great number of these but have carried out a few experiments with liquid ammonia solutions of sulfur in the hope that

[6] For example, Holmes (J. Phys. Chem., 22, 510 (1918)), showed that the time of setting of a silica aqua-gel was greatly increased at 0°C and decreased with rising temperature on curves similar in form to those shown in Fig. 3.

some information on the colloidity of these systems could be obtained. An inverted Y tube with the ends of the lateral branches sealed was made, so that the cellulose acetate sol could be placed in one branch and the sulfur solution in the other. The tube was then sealed, brought to room temperature and the gel allowed to set. The sulfur solution was then added to the top of the gel by tipping. Diffusion took place rapidly at the rate of about two inches in twenty-four hours. This rapid diffusion might indicate that a considerable proportion, if not all, of the sulfur was present in true solution. It was found necessary to carry these diffusion experiments out in the dark as the sulfur solutions were reversibly light sensitive, turning pale yellow in the light and deep blue in the dark. In fact the reversals on one specimen were carried out a number of times without any apparent effect on the sulfur.

Heat-Reversible Gels

As was stated previously, when the 10 per cent sol of cellulose acetate was placed in an ammonia bath for several days a gel structure appeared. This led to the investigation of the possibility of gel formation of a heat-reversible type upon cooling the ammonia below its boiling point. Reversible gels of cellulose acetate have been prepared in benzyl alcohol by Mardles[7] and Poole,[8] consequently one might expect an analogous system in liquid ammonia.

Samples of 5 and 10 per cent cellulose acetate were prepared and cooled in a bath of gasoline to which had been added solid carbon dioxide with the result that at $-45°$ C the 10 per cent sol changed to a beautiful opalescent gel which was quite rigid and brittle with an elasticity similar to that of gelatin gels. The color was also less intense for a given concentration than it was in the irreversible type. The 5 per cent sol remained fluid until a temperature of $-60°$C was reached, when a similar opalescent gel appeared. Thus it will be seen that the higher the concentration of the gel, the higher its temperature of gelation—a characteristic of heat-reversible gels such as agar or gelatin in water and cellulose acetate in benzyl alcohol.

On warming up the bath gradually, it was found that the gels would not melt at the same temperature at which they jelled, but a temperature of about ten degrees higher was necessary to bring about this change. This is similar to what Poole[8] found in studying cellulose acetate in benzyl alcohol and is generally characteristic of heat-reversible gels.

The above observations were made on samples sealed in pyrex tubes which were afterwards allowed to warm up to room temperature. The sols become more fluid at first but later set to the heat-irreversible type of gel previously described. The characteristic sine curve break already noted for gels of these concentrations formed in about twenty-four hours after gelation with the usual syneresis following.

[7] Trans. Faraday Soc., 18, 318 (1922).
[8] Trans. Faraday Soc., 22, 140 (1926).

Summary

1. Cellulose acetate will disperse in liquid ammonia apparently without limit. Sols as concentrated as 60 per cent have been obtained.

2. Ammono-sols of cellulose acetate present the unique case of forming two types of gels, one type being heat reversible; the second heat-irreversible.

3. The heat-irreversible gels, apparently consist of a structure of cellulose which has adsorbed water.

4. Heat-reversible gels may be obtained by cooling the ammono-sols to low temperatures. The setting points of these gels was found to be lower than their melting points, a phenomenon which is of common occurrence in reversible gels.

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THE POTENTIAL OF THE CADMIUM ELECTRODE

BY FREDERICK H. GETMAN

In a recent study of the copper electrode[1] it was pointed out that a single crystal of pure copper functions as a constant and reproducible electrode when immersed in solutions of copper sulphate. Shortly after the paper embodying the results of our experiments on the copper electrode was written, Anderson[2] published an account of his investigation of the electromotive behavior of single crystals of zinc. He measured air-free cells of the type

$$Zn,\ ZnCl_2(aq),\ Hg_2Cl_2,\ Hg,$$

and employed fifteen crystals prepared by three different methods. He shows conclusively that a single crystal of pure zinc behaves as a "reversible electrode capable of yielding potentials constant to a few hundredths of a millivolt and reproducible over dissimilarly prepared crystals to one or two-tenths of a millivolt." While Anderson's measurements were made with especial reference to the constancy and reproducibility of the potential of the primary cleavage, or (0001) face, of the zinc crystal, he also showed that "a cylindrical section of a crystal parallel to its major axis, containing along with the (0001) face, sharp edges and orientations other than the (0001) face, gives the same equilibrium potential as the isolated basal planes."

More recently, Straumanis[3] in a study of the electrochemical behavior of single crystals of zinc has found that the cleavage planes of a single crystal when immersed in a neutral solution of zinc sulphate always give rise to the same average difference of potential, and that the latter is in agreement with the difference of potential developed by immersing a polycrystalline electrode of pure zinc in the same solution.

In view of the foregoing results it seemed of interest to study in a somewhat similar manner the electromotive behavior of single crystals of cadmium.

The measurements of Horsch[4] on the cell

$$Cd(amalgam),\ CdCl_2(aq),\ AgCl(electrolytic),\ Ag,$$

undoubtedly afford the most accurate available data upon which to base calculations involving the potential of the cadmium electrode. Measurements of the cell

$$Cd,\ CdCl_2(aq),\ Hg_2Cl_2,\ Hg,$$

recently made by the writer,[5] while substantially in agreement with the data

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[1] Getman: J. Phys. Chem., 34, 1454 (1930).
[2] Anderson: J. Am. Chem. Soc., 52, 1000 (1930).
[3] Straumanis: Z. physik. Chem., 147, 161 (1930).
[4] Horsch: J. Am. Chem. Soc., 41, 1787 (1919).
[5] Getman: J. Phys. Chem., 32, 91 (1928).

of Horsch, are inadequate for the calculation of the electrode potential of cadmium because of the fact that the values of the electromotive force in the more dilute solutions were manifestly too low.

Experimental

Materials. Cadmium chloride of a high degree of purity was subjected to recrystallization before making up the mother solution.

All of the mercurous chloride used in the cells was prepared according to the electrolytic method of Hulett.[1]

Redistilled mercury was further purified by distillation in a current of air as recommended by Hulett.[2]

The single crystals of cadmium were prepared for the writer by Mr. J. H. Dillon of the University of Wisconsin according to the method recently developed by him for the preparation of single crystals of metals of low fusibility.[3] The purity of the metal from which these crystals were prepared is indicated by the following analysis: Cd 99.944%, As 0.001%, Fe 0.005%, Pb 0.050%. The polycrystalline electrodes were made either from cadmium especially purified for use in standard cells, or from so-called "spectroscopic" cadmium, kindly furnished us by Mr. H. M. Cyr of the Research Laboratory of the New Jersey Zinc Co. and guaranteed to contain not more than 0.001% of impurity.

The spark spectra of the cadmium from these three different sources when compared by means of a Hilger quartz spectrograph, failed to reveal the presence of more than a trace of foreign metals.

All of the water used in making up the solutions was prepared by redistilling ordinary distilled water with chromic acid and condensing in a block tin condenser. The water was stored in tightly stoppered bottles of Jena glass.

The nitrogen which was used to displace air from the electrolyte in the cells was obtained in cylinders and was purified before entering the cells by passing through aqueous solutions of potassium permanganate, alkaline pyrogallol, water and cadmium chloride of the same concentration as that in the cells.

Apparatus. The apparatus employed was the same as that used in our previous study of the copper electrode[4] and the same experimental procedure was followed both in setting up the cells and measuring their electromotive force.

Preparation of Electrolyte. A stock solution of cadmium chloride was prepared by dissolving a mass of the recrystallized salt in conductivity water sufficient to make a solution of approximately molal concentration. To this was added a small amount of pure cadmium hydroxide, after which the solution was shaken at frequent intervals over a period of several days. After standing until the excess of hydroxide had settled, the chlorine content of the

[1] Hulett: Phys. Rev., (2) 32, 32 (1900).
[2] Hulett: Phys. Rev., (2) 33, 307 (1901).
[3] Dillon: Rev. Sci. Inst., 1, 36 (1930).
[4] Loc. cit.

solution was determined gravimetrically as silver chloride. A simultaneous determination of the density of the solution with an Ostwald pyknometer supplied the necessary data for the calculation of its molality. This was found to be 0.99472 M. The solutions of smaller concentration were prepared by dilution in calibrated volumetric apparatus.

Electromotive Force Measurements

Immediately after setting up, the cells were immersed in the thermostat bath and their electromotive forces were measured, after allowing sufficient time for the establishment of thermal equilibrium. The measurements were continued at frequent intervals over a period of six hours. During this time the cells maintained a satisfactory constancy of electromotive force, except in the case of those in which the electrolyte was dilute. With the latter there was an increasing tendency toward a slight but steady drift in the electromotive force. The electrodes prepared from the highly purified "spectroscopic" cadmium were prone to exhibit erratic fluctuations of potential over a range of several tenths of a millivolt. The single crystal electrodes, however, did not show this tendency to fluctuation and proved to be almost as steady as cadmium amalgams. The experimental data given in Table II represent the mean of ten or more measurements of the electromotive force at each concentration. The electromotive force of six cells containing electrodes of either "spectroscopic" or "standard cell" cadmium is denoted by E_1 while that of two cells containing single crystals of cadmium as electrodes is denoted by E_2. In view of the statements of both Anderson and Straumanis, it was not deemed necessary to split the single crystals along their cleavage planes in order to expose only a single definite surface to the electrolyte. Because of the relative instability of cells in which the electrolyte is dilute, no attempt was made to measure electromotive forces in solutions having a concentration less than 0.01M.

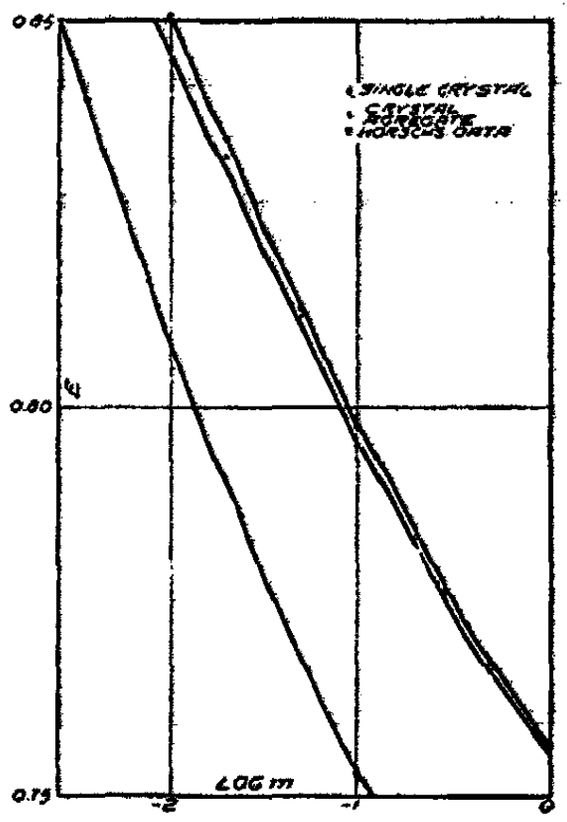

FIG. 1

It is apparent that the numerical value of the potential of the single crystal electrode is uniformly greater than that of the polycrystalline electrode. This result is similar to that obtained in our study of the copper electrode. The foregoing values, believed to be accurate to within 0.3 millivolt, are represented graphically in Fig. 1. By means of a large scale plot, similar to Fig. 1, the values of the electromotive force at even concentrations were read from the curves and tabulated in Table II.

TABLE I
Measurements of the E.M.F. of the Cell
$Cd, CdCl_2(m), Hg_2Cl_2, Hg$ at 25°

m mols $CdCl_2$/1000 g.H_2O	E_1	E_2
0.00966	0.84652	0.85021
0.04805	0.81165	0.81258
0.09986	0.79542	0.79758
0.20027	0.78208	0.78390
0.28766	0.77628	0.77641
0.49084	0.76625	0.76636
0.99472	0.75554	0.75646

TABLE II
Smoothed Values of the E.M.F. of the Cell
$Cd, CdCl_2(m), Hg_2Cl_2, Hg$ at 25°

m mols $CdCl_2$/1000 g. H_2O	E_1	E_2	ΔE
0.01	0.8435	0.8515	0.0080
0.02	0.8290	0.8340	0.0050
0.05	0.8097	0.8120	0.0023
0.1	0.7953	0.7973	0.0020
0.2	0.7820	0.7835	0.0015
0.5	0.7660	0.7675	0.0015
1.	0.7553	0.7563	0.0010

Calculation of Results

In order to calculate the normal electrode potential of cadmium, E_0, from the data of Table II, it is necessary to have recourse to the extremely accurate data obtained by Horsch with cells in which the electrolyte was very dilute. In his calculations, Horsch made use of the best available conductivity data and assumed that in extremely dilute solutions of cadmium chloride the values of the conductivity ratios are equal to the corresponding values of the activity coefficients. Quite recently, Randall[1] has developed a convenient method of extrapolation for the determination of normal electrode potentials from electromotive force data. Employing this method, we have recalculated the normal electrode potential of cadmium from Horsch's data. Having thus computed the value of E_0, the activity coefficients of cadmium chloride at different concentrations can readily be calculated and from these in turn, the potential, E_0, corresponding to the single cadmium crystal electrode can be evaluated.

The electromotive force of the cell

$$Cd, CdCl_2(m), AgCl, Ag,$$

studied by Horsch, can be computed by means of the equation

$$E = E_0' - \frac{RT}{nF} \ln (4\, m^3\, \gamma^3) \qquad (1)$$

[1] Randall: Trans. Faraday Soc., 23, 505 (1927).

In this equation E is the measured electromotive force of the cell, E_0' th normal potential of the cell, m the concentration in mols per 1000 grams o solvent and γ is the activity coefficient. The symbols R, T, n and F have their usual significance. Simplifying and transforming to common logarithms, equation (1) takes the form

$$E = E_0' - 0.08873 \log (1.588\, m\, \gamma). \quad (2)$$

Following the method of Randall, equation (2) may be transformed into

$$\log \gamma - E_0'/0.08873 = -(E/0.08873 + 0.2007 + \log m) \quad (3)$$

If the right-hand side of equation (3) be plotted against the square root of the ionic strength, μ, and the resulting curve be extrapolated to infinite dilution, the value of E_0' can readily be calculated by means of equation (3).

The experimental data of Horsch are reproduced in Table III and a partial graphic representation is given in Fig. 1.

TABLE III

Horsch's Measurements of the E.M.F. of the Cell $Cd, CdCl_2(m), AgCl, Ag$ at 25°

m	E	m	E
0.0001029	0.9594	0.0003659	0.9148
0.0001087	0.9557	0.000479	0.9050
0.0001137	0.9545	0.000924	0.8830
0.0001269	0.9512	0.002581	0.8491
0.0001527	0.9460	0.003519	0.8398
0.0002144	0.9337	0.0074	0.8165
0.0003363	0.9178	0.0995	0.7530

The data of Table III were plotted on a large-scale plot and the values of E corresponding to log m = $\bar{6}.0$, log m = $\bar{6}.1$, log m = $\bar{6}.2$, etc. up to log m = $\bar{7}.0$ were read from the curve and tabulated, together with the corresponding values of $\mu^{\frac{1}{2}}$ and (E/0.08873 + 0.2007 + log m) as shown in Table IV.

TABLE IV

Data derived from Horsch's Measurements

m	$\mu^{\frac{1}{2}}$	E	(E/0.08873 + 0.2007 + log m)
0.0001000	0.01732	0.9597	7.0107
0.0001259	0.01943	0.9523	7.0407
0.0001585	0.02181	0.9445	7.0407
0.0001995	0.02446	0.9365	7.0507
0.0002512	0.02745	0.9282	7.0607
0.0003162	0.0308	0.9199	7.0707
0.0003981	0.0346	0.9117	7.0807
0.0005012	0.0388	0.9035	7.0807
0.0006310	0.0435	0.8954	7.0907
0.0007943	0.0488	0.8876	7.1007
0.001	0.0548	0.8801	7.1197

On plotting the values of $(E/0.08873 + 0.2007 + \log m)$ versus $\mu^{\frac{1}{2}}$, as shown in Fig. 2, the averaged straight line through the points thus obtained intersects the zero ordinate at a point corresponding to 7.005. On substituting this value in equation (3), we find $E_0' = 0.6215$ volt, the normal potential of the cell.

In order to determine the normal electrode potential of cadmium, Horsch also measured the electromotive force of the cell

$$H_2\ (1\ atm.),\ HCl(0.01M),\ AgCl,\ Ag,$$

and found E = 0.4665 volt. Accepting 0.93 as the value of the activity coefficient of 0.01M HCl, we have

$$E_0 = 0.4665 + 0.05915 \log (0.01 \times 0.93)$$
$$= 0.2283 \text{ volt},$$

or $H_2,\ H^+\ (M),\ Cl^-\ (M),\ AgCl,\ Ag;\ E_0 = 0.2283$ volt.

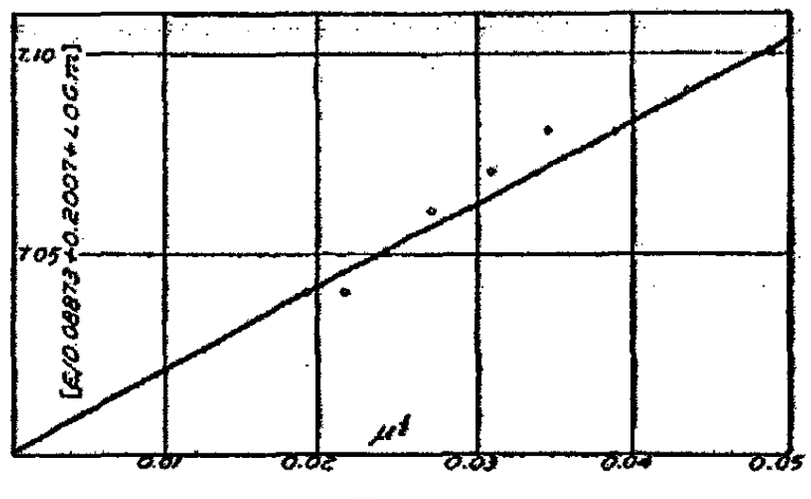

FIG. 2

Hence Horsch's value of the normal electrode potential of cadmium is

$$E_0 = 0.6215 - 0.2283,$$
$$= 0.3932 \text{ volt}.$$

Horsch actually obtained, as the result of his calculations based upon conductivity data, $E_0 = 0.3992$ volt.

Accepting 0.3932 volt as the value of E_0, we may now proceed to calculate the values of the activity coefficients of solutions of cadmium chloride by means of equation (2). The values of γ thus obtained together, with the corresponding conductivity ratios derived by Noyes and Falk[1], are given in Table V.

In Table V values of γ are slightly less than those calculated by Lewis and Randall[2] from the experimental data of Horsch. This lack of agreement is to be traced to the fact that Lewis and Randall apparently based their calculations on Horsch's observed values of the electromotive force of the cell

$$Cd(4.5\ amalg),\ CdCl_2(m),\ AgCl,\ Ag,$$

[1] Noyes and Falk: J. Am. Chem. Soc., 34, 475 (1912).

[2] Lewis and Randall: "Thermodynamics and the Free Energy of Chemical Substances", 362.

rather than on the calculated values of the electromotive force of the cell,

$$Cd, CdCl_2(m), AgCl, Ag.$$

The difference of 0.0534 volt between the electromotive forces of the two cells obviously represents the electromotive force of pure cadmium against the cadmium amalgam. When allowance is made for this difference, their values for γ are in close agreement with those given in Table V. A comparison of the values of γ and α shows that Horsch was not justified in assuming the equality of these two ratios, even in dilute solutions of cadmium chloride.

TABLE V

Activity Coefficients of Cadmium Chloride Solutions (25°)

m	E	γ	α
0.0001	0.9567	0.969	0.975
0.0002	0.9360	0.898	0.960
0.0005	0.9050	0.802	0.931
0.001	0.8810	0.748	0.891
0.002	0.8573	0.690	0.830
0.005	0.8280	0.592	0.735
0.01	0.8085	0.491	0.664
0.02	0.7910	0.389	0.580
0.05	0.7688	0.277	0.453
0.1	0.7535	0.205	0.375
0.2	0.7390	0.149	0.308
0.5	0.7209	0.096	—
1.0	0.7080	0.067	—

We are now in possession of the necessary data for the calculation of the normal electrode potential of the single crystal cadmium electrode. Thus, on substituting the values of γ given in Table V, and the corresponding values of E from Table II, in equation (2) the value of E'_0 can be calculated. The data resulting from this calculation are collected in Table VI.

TABLE VI

Values of E'_0 for the Cell

Cd(single cryst.), $CdCl_2$(m), Hg_2Cl_2, Hg

m	E		E'_0
0.01	0.8515	0.491	0.6645
0.02	0.8340	0.389	0.6648
0.05	0.8120	0.277	0.6649
01.	0.7973	0.205	0.6654
	Mean		0.6649

The mean value of E'_0 is thus found to be 0.6649 volt. Since, according to Gerke[1] the potential of the electrode

[1] Gerke: Chem. Rev., 1, 384 (1925).

$$Hg, Hg_2Cl_2\ (s), Cl^-,$$

is −0.2700 volt, it follows that

$$Cd(s), Cd^{++};\ E_0 = 0.3949 \text{ volt.}$$

This value for the normal electrode potential, it will be observed, is nearly 3 millivolts less than the value assigned by Gerke[1] to this constant, viz. 0.3976 volt. Presumably, however, Gerke accepted the results of the calculations of Lewis and Randall based upon Horsch's data.

If the values of E in Table II be substituted successively in equation (3) and the resulting values be plotted against the corresponding values of $\mu^{\frac{1}{2}}$, an approximate value of E'_0 can be obtained by graphic extrapolation. Employing this method, we found $E'_0 = 0.6645$ volt, or $E_0 = 0.3945$ volt.

Since single crystals of copper, zinc and cadmium have been found to function as constant and reversible electrodes, it seems reasonable to base our calculations of normal electrode potentials upon measurements of the electromotive force of suitable galvanic combinations in which single crystals of these metals are employed as electrodes. As the result of such calculations based upon the foregoing experimental data, we are led to accept, as the value of the normal electrode potential of cadmium, $E_0 = 0.395$ volt.

Summary

(1) Measurements have been made of the electromotive force of the cell

$$Cd,\ CdCl_2(m),\ Hg_2Cl_2,\ Hg,$$

in which the cadmium electrodes were either single crystals or massive crystalline aggregates of the pure metal.

(2) Single crystals of pure cadmium were found to function as constant and reproducible electrodes.

(3) The numerical value of the potential of the single crystal electrode was found to be uniformly greater than that of the polycrystalline form.

(4) The measured values of the electromotive force of cells with single crystal electrodes were employed to calculate the normal electrode potential of cadmium. The value of this constant has been found to be $E_0 = 0.395$ volt.

Hillside Laboratory,
Stamford, Conn.

[1] Gerke: Chem. Rev., 1, 381 (1925).

THE OPTIMUM CONDITIONS FOR THE FORMATION OF SILICA GEL FROM ALKALI SILICATE SOLUTIONS. II

BY R. C. RAY AND P. B. GANGULY

In a previous paper[1] the optimum conditions for the formation of silica gel by the action of hydrochloric acid on solutions of potassium metasilicate and solutions of sodium silicate in which the ratio of $Na_2O:SiO_2$ was as 1:2.25 were determined. It was found that hydrogen ion concentrations were an important factor in the process of gel formation; for each concentration of alkali silicate solution there is a limiting range of pH value in which gel formation takes place. In the present paper the experiments have been extended to the case of two other solutions of sodium silicate in which the ratios of $Na_2O:SiO_2$ are as 1:3.3 and 1:4.0 respectively.

Our knowledge of the alkali silicates is meagre. Two views are prevalent regarding their composition, namely, (1) definite complex silicate ions are produced with increase of the amount of silica in the molecule, and (2) one or two simple silicates are formed and the excess of silica in the molecule of the higher ratio silicates is present as a colloidal aggregate. Schwarz and Menner[2] have obtained definite crystalline compounds of the compositions corresponding to $Na_2O.SiO_2$; $Na_2O.2SiO_2$ and $Na_2O.3SiO_2$ by fusing pure quartz with sodium carbonate at 1150°C. They obtained the last two compounds as glasses which transformed into definite compounds by prolonged heating at 700°C. Morey,[3] by his hydrothermal quenching method, obtained $Na_2O.SiO_2$ and $Na_2O.2SiO_2$ but not $Na_2O.3SiO_2$. A small amount of disilicate also occurs naturally as rivaite[4]. The formation of complex silicic acids has also to be assumed in order to explain the composition of a large number of naturally occurring silicates. On the other hand, Herman, who has recently made a systematic investigation on the nature of alkali silicate solutions, has come to the conclusion that only one or two simple silicates are formed and the extra silica in the higher silicates is mainly present in a colloidal form. Herman's results have been published in this journal between 1925 and 1928 in a series of papers entitled "Aqueous solutions of sodium silicates." If a considerable amount of colloidal silicic acid be present in alkali silicate solutions in which the ratio SiO_2/Na_2O is high, the curves representing the limiting range of pH values between which gel formation takes place might be expected to be of an entirely different type. The present investigation was undertaken with a view to find out if this was actually the case.

The experimental procedure adopted was exactly the same as described in the previous paper. There is for each concentration of the silicate solution a

[1] J. Phys. Chem., 34, 352 (1930).
[2] Ber., 57B, 1477 (1924).
[3] J. Am. Chem. Soc., 39, 1174 (1917).
[4] Zambonini: Atti Accad. Sci. Napoli, 12, 16 (1912).

definite range for the pH values beyond which no gelation takes place. The pH values corresponding to the points where gel formation just stopped were accurately measured. The results obtained are given in Tables I and II. Definite volumes of sodium silicate solutions were also previously analysed, and the ratio $Na_2O:SiO_2$ was determined in each case.

TABLE I

Showing the region of gel formation for sodium silicate solutions of different concentrations

Ratio of $Na_2O:SiO_2 = 1:3.3$

Mols SiO_2 per litre	Limiting pH (Acid side)	Limiting pH (Alkali side)
0.618	2.18	11.18
0.517	2.30	10.96
0.309	2.86	10.20
0.206	3.46	9.74
0.103	4.01	9.07

TABLE II

Showing region of gel formation for sodium silicate solutions of different concentrations

Ratio of $Na_2O:SiO_2 = 1:4.0$

Mols SiO_2 per litre	Limiting pH (Acid side)	Limiting pH (Alkali side)
0.923	1.65	11.1
0.738	1.75	10.8
0.369	2.56	10.4
0.184	3.40	9.4
0.074	4.31	8.0

The ranges of gel formation for the two sodium silicate solutions, have been represented in Fig. 1, where the concentrations of the silicate solutions, expressed in terms of mols SiO_2 per litre, have been plotted against the limiting pH values. The curve for the sodium silicate solution in which the ratio of $Na_2O:SiO_2$ was as 1:2.25 has also been included for comparison.

The investigations of Herman[1] and the viscosity measurements of Main[2] seem to show that as the molecular proportion of SiO_2 in the sodium silicates increases, the amounts of silica present in a colloidal form also increases. It was therefore expected that by using sodium silicate solutions containing gradually increasing proportions of silica, the range of pH values within which silica gels are formed would change appreciably. From Fig. 1, however, it is seen that the curves for all the three sodium silicate solutions have the same shape and differ very little from one another. The ranges for the pH

[1] J. Phys. Chem., 31, 355 (1927).
[2] J. Phys. Chem., 30, 535 (1926).

values on the alkali sides of the curve are practically coincident, whereas on the acid side the range widens slightly, though quite uniformly, as the molecular proportion of silica in the silicates increases. It is evident, therefore, that the presence of a certain amount of silica in a colloidal form in the sodium silicate solutions does not appreciably alter the limiting ranges of hydrogen ion concentrations as determined in these experiments.

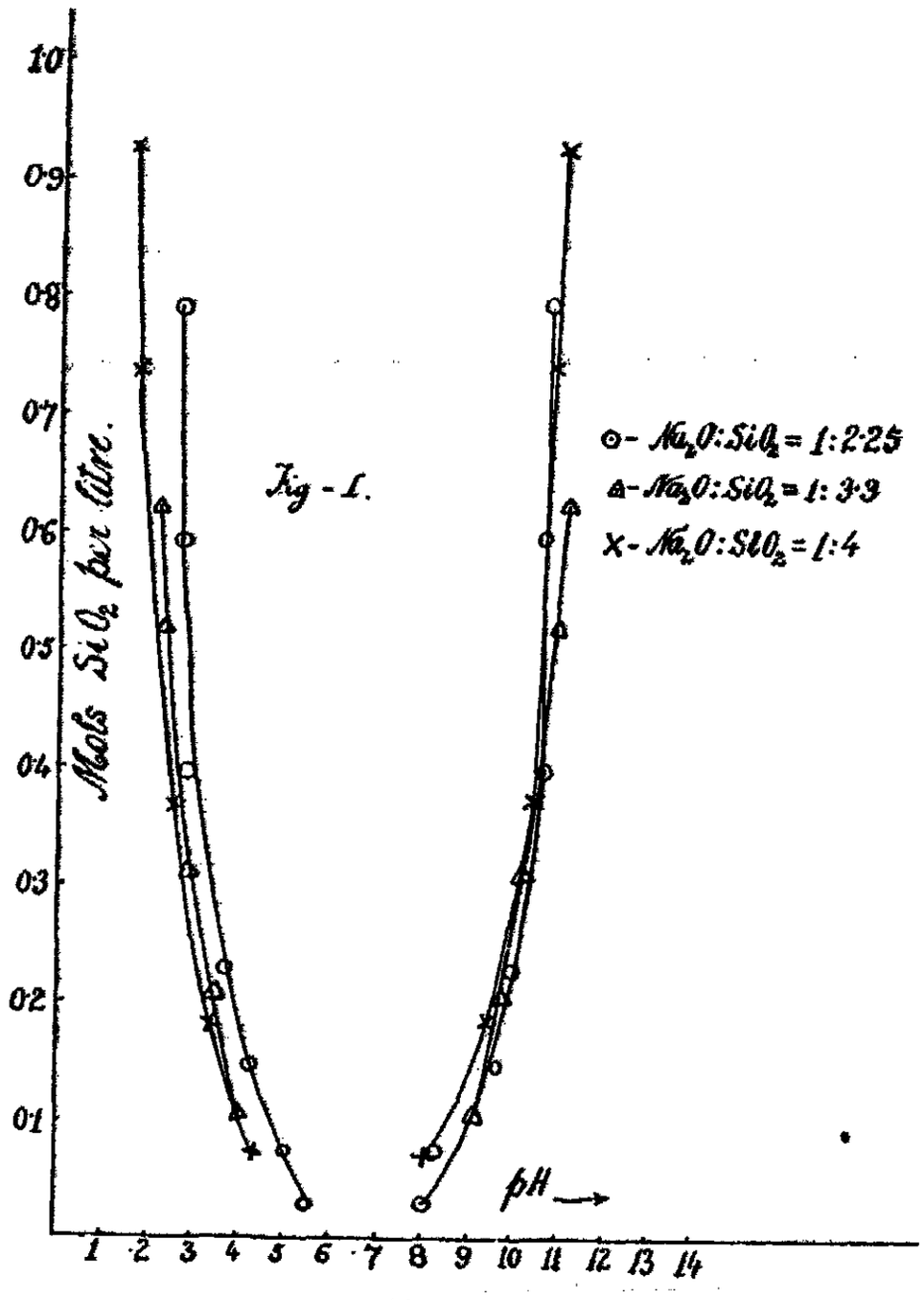

FIG. 1

In the previous paper, the formation of silica gels by the action of ferric chloride on sodium silicate solutions was also studied, and from the results of our experiments it was suggested that when ferric chloride was added to a sodium silicate solution ferric silicate was formed in the first instance. During the course of the present investigation, an attempt has been made to obtain further experimental support for the above view.

Solutions of the alkali silicates can be titrated quite consistently against ferric chloride solutions by using potassium ferrocyanide as the indicator.

The end point, which is indicated by the appearance of green colour, is quite sharp, and the titration values obtained are quite concordant. It is necessary, however, to carry out the titrations in sufficiently dilute solutions in order to avoid the formation of a gel. A solution of potassium metasilicate and solutions of sodium silicates, containing Na_2O and SiO_2 in the ratios of 1:2.25, 1:3.3 and 1:4 respectively, were made exactly equivalent with respect to a N/$_2$-solution of hydrochloric acid. They were then titrated against a standard ferric chloride solution and gave the following results:

TABLE III

	Gram-mols K_2O or Na_2O per litre	Gram-mols SiO_2 per litre	Ratio SiO_2 Na_2O or K_2O	Volume of M/5-ferric chloride per 10 c.c. of silicate sol
Potassium meta-silicate	0.415	0.415	1	15.15 c.c.
sodium silicate	0.415	0.934	2.25	14.65 c.c.
sodium silicate	0.415	1.37	3.30	14.0 c.c.
sodium silicate	0.415	1.66	4	13.65 c.c.

From the above values, it is clear that the volumes of a M/5-ferric chloride solution, required to react completely with 10 c.c. of sodium silicate solutions of different ratios but of equivalent alkali content, are all within 10 per cent. of one another. Evidently, therefore, the reaction depends mainly on the alkali content of the solution, rather than the amount of silica it may contain, suggesting that ferric hydroxide is formed in each case. As all the silicate solutions contained the same amounts of Na_2O (or K_2O), the amounts of ferric chloride required for titration should be the same if all the added ferric chloride were to be converted mainly into ferric hydroxide. On the other hand, the fact that the amounts of ferric chloride solution required for titration with the various silicate solutions, do not vary from one another by more than 10 per cent., does not in any way disprove the possibility of the formation of ferric silicate, because a greater silica content does not necessarily mean that a greater amount of silicate ions is present. If the excess of silica in the 1:3.3 and 1:4 ratio silicate solutions be present either in the form of complex silicate ions or as colloidal aggregates, the sodium silicate solutions might titrate with the same amounts of ferric chloride.

In order to elucidate the above point, a series of measurements of the amounts of heat developed during the reaction between a standard ferric chloride solution and the alkali silicate solutions have been carried out. The heat measurements were performed in a seamless silver calorimeter which was kept suspended in a long Dewar cylinder by means of fine silk threads. An arrangement was set up for stirring the solutions at a uniform rate, and the temperatures were read by means of a Beckmann thermometer. The heat capacities of the calorimeter together with its contents were carefully determined in each case separately after each heat measurement.

A series of dilute solutions of the alkali silicates equivalent in terms of Na_2O (or K_2O), were prepared and were titrated against a standard dilute ferric chloride solution. Measured volumes of the silicate solutions and the requisite amount of ferric chloride solution were allowed to react in the calorimeter with uniform stirring. The ferric chloride solution was also placed inside the Dewar vessel so that it attained the right temperature before it was mixed with the silicate solution. The amounts of heat developed when one gram mol of ferric chloride has been completely reacted upon by alkali silicate solutions are given below:

TABLE IV

Showing the amount of heat developed per gram mol of ferric chloride reacted upon

Silicate solution	Molar ratio Na_2O (or K_2O)/SiO_2	Amount of heat
Potassium meta-silicate	1:1	20036 calories
Sodium silicate	1:2.25	11051 "
Sodium silicate	1:3.3	8164 "
Sodium silicate	1:4	6629 "

From Table IV, it will be seen that as the ratio of SiO_2 in the silicate solutions increases, the amounts of heat, per gram mol of ferric chloride reacted, decreases very markedly. The amount of heat developed when one gram mol of ferric chloride is acted upon by sodium hydroxide is 25530 calories, which is distinctly greater than any of the amounts of heat developed during the present measurements. The amount of heat developed in the case of potassium metasilicate is 20036 calories, which, after allowance is made for the difference between the heats of formation of potassium chloride and sodium chloride, is about 25 per cent less than the amount of heat developed when one gram mol of ferric chloride is converted into ferric hydroxide. In the case of the other sodium silicate solutions the difference is still greater. Thus, so far as these experiments go, it seems unlikely that ferric hydroxide is the main product of the reaction between ferric chloride and the alkali silicates.

As a result of a series of investigations on the sodium silicate solutions, Herman[1] has come to the conclusion that only two compounds are indicated as stable in solution, namely, $Na_2O.SiO_2$ and $Na_2O.2SiO_2$; the 1:3 and 1:4 ratio silicate solutions are not definite salts but consist of complex aggregates or ionic micelle in concentrated solutions. From the heat measurements, it is found that the amounts of heat developed decrease in about the same proportion in which the molar ratio of SiO_2 in the silicates increases. If the above view of Herman be taken as a true representation of the constitution of the silicates, the simplest explanation for the values, obtained from the heat measurements, appears to be that as the molar ratio of SiO_2 in the silicate solutions increases in an arithmetic progression, the rate of formation of the complex aggregate or ionic micelle increases in a geometric progression.

[1] J. Phys. Chem., 31, 355, 511 (1927).

It may be pointed out, however, that as the ratio SiO_2/Na_2O (or K_2O) increases from 1 to 4, the heat of reaction with ferric chloride decreases regularly. If the reaction product was entirely ferric hydroxide in every case, the heats of reaction would have been more or less the same and fairly close to the heat of reaction between ferric chloride and sodium hydroxide. If, on the other hand, all the alkali silicate solutions contained only one or two simple silicates with aggregates of colloidal silica in the case of the higher ratio silicates, it might be expected that the heat of reaction would attain a constant value after a certain stage. The regular decrease in the heats of reaction, taken in conjunction with the titration results given in Table III, appears to point to the formation of complex silicate ions with increase of silica in the molecule. Herman[1] has determined the transport number of the silicate ion in aqueous alkali silicate solutions. In ratios 1:2, 1:3 and 1:4, the transport number of the silicate ion is high, and the silicate anion contains more than one SiO_2 per divalent charge; the average number of mols SiO_2 per divalent charge being equal to the ratio. In ratios 1:2, 1:3 and 1:4 the anion is not simple SiO_3 ion but may be definite complex silicate ion. Schwarz and Menner (loc. cit.) claim the existence of at least seven silicic acids or hydrates of SiO_2, although our knowledge of these is only very slight. Considering, however, the fact that the sodium silicate solutions, which are equivalent in terms of Na_2O, react with practically the same amounts of a ferric chloride solution, it would appear that there are more than one kind of ferric silicate, each having a different heat of formation. In the absence of further experimental data it is, however, not possible to come to any definite conclusion.

Summary

1. The optimum conditions for the formation of silica gel by the action of hydrochloric acid on sodium silicate solutions of 1:3.3 and 1:4 ratios have been studied; the limiting ranges of pH values, in which gel formation takes place, have been accurately determined.

2. The presence of a large amount of silica in the higher ratio sodium silicate solutions, either in the form of colloidal aggregates or as definite complex silicate ions, does not appreciably affect the conditions of gel formation.

3. Ferric chloride solutions can be titrated against sodium silicate solutions with the help of potassium ferrocyanide as an indicator.

4. The amounts of heat developed when one gram mol of ferric chloride is acted upon by sodium silicate solutions of different ratios have been determined.

5. The heat of reaction decreases in a regular manner with increase in the ratio SiO_2/Na_2O (or K_2O) from 1 to 2 to 3 to 4.

6. The heat measurements lend support to the view that the reaction between ferric chloride and the sodium silicate solution results mainly in the formation of ferric silicates.

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[1] J. Phys. Chem., 30, 359 (1926).

THE DETERMINATION OF THE HYDROGEN ION CONCENTRATION IN GOLD SOLS

BY T. R. BOLAM AND J. CROWE

Introduction

Despite the large amount of research which has been carried out on gold sols, considerable uncertainty exists regarding the use of the hydrogen electrode for the determination of the hydrogen ion concentration in these systems. Herstad,[1] who appears to have been the first to apply the method, states that by careful working reliable results could be obtained. Actually his pH values are uncertain by at least ±0.5 pH. The next reference to the subject is to be found in a paper by Kautzky and Pauli,[2] who reported that it was impossible to obtain a steady potential with red gold sols and that the latter were coagulated by the hydrogen. These conclusions were based on an investigation by Adolf and Pauli,[3] an account of which appeared in the following year. Dialysed sols, prepared by Zsigmondy's method, were the object of study and the hydrogen electrode was found to be extremely sensitive to either dissolved or colloidal gold. To quote from the paper itself, "Diese Veränderung der Elektrode tritt schon bei so geringen Goldspuren ein, dass sie unter Umständen jedem feinen analytischen Goldnachweis gleichkommen oder sogar überlegen sein kann". No difficulty was encountered in measuring the hydrogen ion concentration in ordinary solutions of potassium or barium chloride, or in the solution ("Flockungsfiltrat") obtained by coagulating a sol with a sufficiently large amount of these salts and removing the gold by filtration. In the latter case the hydrogen ion concentration was found to be about 1×10^{-5} N. The experience of Tartar and Lorah[4] was the same as that of Adolf and Pauli. These workers were investigating the influence of pH (over the range 2-9) on the protective action of gelatine on Zsigmondy sols and found that the hydrogen electrode gave erratic results unless the gold was carefully eliminated. The gelatine itself did not cause variations greater than 0.2 millivolt. Wo. Ostwald[5] also reports that he encountered the same difficulties as Pauli and Adolf.

Beaver and Müller in a paper[6] describing a very careful study of the action of ultraviolet light on various gold sols make the following statement. "Electrometric titrations of the chloroauric acid with 0.1 N potassium carbonate were therefore made at room temperature (22-25°). A curve was then plotted of c.c. of potassium carbonate against pH of the solution for the given gold content, and from this curve solutions of definite pH were made, heated to 65° and reduced." There is no mention of any difficulty with the hydrogen electrode due to the presence of gold in the solution. In one series of experiments the pH varied from 3-10 approximately. The latest work involving the use of the electrode in gold sols is that of Reinders and Bendien.[7] In this

case the sols were prepared by Bredig's method, and gelatine and casein were added to them. Here again there is no suggestion that the E.M.F. measurements were troublesome.

The following is an account of an investigation undertaken to ascertain whether it is possible to define conditions which permit of the accurate determination of the hydrogen ion concentration in gold sols by means of the hydrogen electrode.

Apparatus

Some difficulty was experienced in finding a suitable form of hydrogen cell. The apparatus shown in Fig. 1 was finally devised and found to be satis-

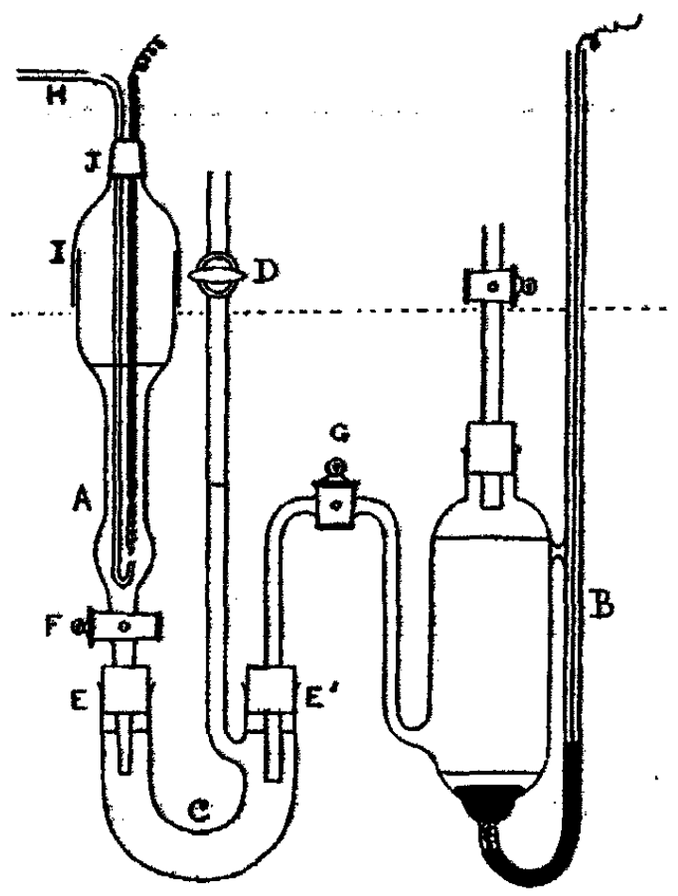

FIG. 1

factory. A is the hydrogen electrode, B is a saturated potassium chloride calomel half-cell, and C a bridge of saturated KCl. By opening the tap D the pressure is released when the rubber stoppers E and E′ are inserted in the U-tube. Taps F and G are opened only when a reading is actually being made, D being then closed. A spiral of platinised platinum or gold wire was found to give better results than a sheet of platinised platinum as the electrode itself. The hydrogen is introduced at the lower end of the spiral by means of a narrow turned-up glass tube H. A stream of fine bubbles is thus formed which fills the inside of the spiral and passes out between the coils. In this way rapid equilibrium is established between the electrode and the sol or solution to be investigated. I is a glass cap, and J a rubber ring holding the electrode in position. The advantages of this form of apparatus are:

(1) Only 3 or 4 c.c. of sol are necessary for a determination.

(2) The column of poorly conducting liquid between the electrode and the saturated KCl is very short. A high resistance is thus avoided and the null point can be accurately determined.

(3) The hydrogen electrode attains equilibrium rapidly.

(4) The simple form of the apparatus permits of quick and thorough cleansing.

(5) The cell can be immersed in a thermostat.

The hydrogen was generated from zinc and hydrochloric acid and purified by passing through (1) conc. KOH, (2) alkaline $KMnO_4$, (3) neutral $KMnO_4$, (4) distilled water, (5) sol (or solution). The E.M.F. values were obtained by the usual compensation method, the instruments employed being such that individual determinations were accurate to 0.1 millivolt. All experiments were carried out at 20° C, the cell being immersed in a glass-walled thermostat up to the level indicated in Fig. 1. Two saturated calomel electrodes (S.E.) were used as working electrodes and checked by comparison with two N/10 calomel electrodes (D.E.). All four were prepared from carefully purified mercury, electrolytic calomel, and Kahlbaum KCl. The E.M.F. of the combination, Hg, Hg_2Cl_2, satd. KCl, N/10 KCl, Hg_2Cl_2, Hg was found to be 0.0886 volt, with both sets of electrodes, so that taking 0.3379 volt as the standard electrode potential of the D.E.[8] at 20°C., that of the S.E. was equal to 0.2493 volt. Clark[8] gives 0.2492 volt. A test was made of the hydrogen electrode with three of Sörensen's standard phosphate mixtures (pH = 5.91, 6.47, 6.81 respectively).[3] The electrode rapidly attained equilibrium and gave very steady and reproducible potentials, the derived pH values differing from Sörensen's by not more than 0.01.

Zsigmondy and Nordenson Sols

Repeated trials showed that it was impossible to obtain a constant E.M.F. with a sol* prepared by Zsigmondy's method (reduction by formaldehyde of gold chloride made alkaline with potassium carbonate). There was a continuous increase in the E.M.F., which amounted to about 30 millivolts in the first two hours. In no case however could any sign of coagulation of the sol during an experiment, or even hours after, be detected. A pronounced drift in the same direction also took place with the liquid obtained by precipitating the gold with potassium chloride and removing the precipitate by filtration.

In contrast with the Zsigmondy sols, those prepared by Nordenson's method gave very satisfactory results. The principle of the method is the reduction of gold chloride by hydrogen peroxide under the influence of ultra-violet radiation. In the present instance a small quantity of potassium carbonate was added, which, while insufficient to give a neutral or alkaline sol,

*All the sols used in this investigation, whatever the method of preparation, were bright red in colour, showed no sign of opalescence, and proved to be very stable. Further details of preparation, etc., will appear in a subsequent communication.

was found to increase the degree of dispersion. Table I contains the data for the sol prepared from 2.0 c.c. of 0.6% $HAuCl_4, 4H_2O$ (Merck) in 125.0 c.c. conductivity water + 0.6 c.c. of 0.2 N K_2CO_3 (Kahlbaum) + 0.4 c.c. Perhydrol (Merck), which is quite representative. A separately prepared sample of the sol was used for each experiment.

TABLE I

Nordenson Sol

Preparation	Time (mins.)	E.M.F. (volts)	pH
1.	19	0.4772	3.92
	32	0.4774	3.92
	52	0.4793	3.96
	74	0.4799	3.97
	122	0.4802	"
2.	25	0.4777	3.93
	45	0.4777	"
	65	0.4779	"
	90	0.4766	3.91
3.	30	0.4779	3.93
	52	"	"
	171	"	"

It was thought that if the Zsigmondy sols were buffered by the addition of small quantities of suitable electrolytes it might be possible to get steady E.M.F. values. Accordingly 20 c.c. Zsigmondy sol (2.0 c.c. 0.6% gold chloride in 120 c.c. water + 3.0 c.c. 0.2 N K_2CO_3 + 3.0 c.c. 0.4% formaldehyde (specially prepared) were mixed with 1.0 c.c. M/15 Na_2HPO_4(A.R.) + 1.0 c.c. M/15 KH_2PO_4 (A.R.), and three portions of the mixture tried. The results are given in Table II.

TABLE II

Zsigmondy Sol + Phosphate Buffer

	Expt. I		Expt. II		Expt. III	
Time (mins.)	E.M.F. (volts)	pH	E.M.F. (volts)	pH	E.M.F (volts)	pH
10	0.6620	7.10	0.6637	7.12	0.6642	7.13
20	0.6630	7.11	0.6648	7.14	0.6652	7.15
30	0.6633	7.12	0.6650	7.15	"	"
60	"	"	"	"	"	"
84	"	"	"	"	"	"

It would appear that the change in E.M.F. observed with the original Zsigmondy sol was not due to any deleterious action of the gold upon the electrode but to the absence of equilibrium between the solution and the hydrogen, i.e. to change in the hydrogen ion concentration. There is every reason to believe that the relatively high concentration of potassium carbonate used in the preparation of these sols is the source of disturbance. In dilute unbuffered alkaline solutions (the above Zsigmondy sol had pH = 9 approx.) the participation of any CO_2 present in the acid-base equilibrium is of great importance.[8] We may therefore attribute the E.M.F. drift in Zsigmondy sols to the removal of CO_2 by the hydrogen stream.

Experiments with "Citrate" Gold Sols

If the above explanation is correct no difficulty should be experienced in obtaining a steady and reproducible potential in sols prepared by replacing potassium carbonate in the Zsigmondy procedure by tri-sodium citrate. Table III gives the results in the case of a "citrate" sol containing 0.31 millimols per litre of sodium citrate. Two quite separate preparations were examined.

TABLE III

"Citrate" Sol

Preparation	Time (mins.)	E.M.F. (volts)	pH
1. Sample (a)	15	0.5461	5.11
	30	"	"
	42	"	"
" (b)	12	0.5469	5.12
	25	"	"
	40	"	"
2.	12	0.5458	5.10
	23	0.5463	5.11
	33	0.5461	"

Variation of E.M.F. with Composition of Sol

Three series of sols were prepared by reduction with formaldehyde in the absence of potassium carbonate, the first containing increasing amounts of sodium citrate, the second, of disodium hydrogen phosphate, and the third, of sodium hydroxide (from the metal). In every case the reduction mixture contained 1.0 c.c. 0.6% gold chloride (diluted with sufficient water to give final volume of 128 c.c.) + 0.4 c.c. M sodium citrate 10/($C_6H_5O_7Na_3 . 5\frac{1}{2} H_2O$

TABLE IV

"Citrate" Sols

Final concn. of Sodium Citrate (millimols/litre)	Concn. of Na (milligrm.-equivs./litre)	E.M.F. (volts)	pH
0.31	0.93	0.5461	5.11
0.35	1.05	0.5553	5.27
0.57	1.71	0.5801	5.69
0.64	1.92	0.5857	5.79
0.71	2.13	0.5923	5.90
0.78	2.34	0.5982	5.95
0.85	2.55	0.5989	6.02
1.06	3.18	0.6063	6.14
1.42	4.26	0.6165	6.32
1.80	5.40	0.6236	6.44
2.13	6.39	0.6274	6.51

TABLE V

"Phosphate" Sols

Final concn. of Na_2HPO_4 (millimols/litre)	*Concn. of Na (milligrm.-equivs./litre)	E.M.F. (volts)	pH
0.08	1.09	0.5578	5.31
0.16	1.25	0.5722	5.56
0.31	1.55	0.5927	5.91
0.78	2.49	0.6295	6.54
1.17	3.27	0.6497	6.89
1.56	4.05	0.6623	6.11
2.34	7.28	0.6722	7.28
2.73	7.36	0.6767	7.36
3.52	7.42	0.6806	7.42

TABLE VI

"Hydroxide" Sols

Final concn. of NaOH (millimols/litre)	*Concn. of Na (milligrm.-equivs./litre)	E.M.F. (volt)	pH
0.0780	1.008	0.5611	5.37
0.156	1.086	0.5787	5.67
0.31	1.24	0.5961	5.97
0.47	1.40	0.6194	6.37
0.62	1.55	0.6428	6.78
1.56	2.49	†(0.777 ±)	(9.1 ±)
3.12	4.05	†(0.895 ±)	(1122 ±)

*0.31×10^{-3} M sodium citrate present in every case.

†In the case of these preparations there was a drift in the E.M.F. The initial values are, however included to indicate the order of magnitude of the pH.

by Kahlbaum). To this was added the appropriate quantity of citrate, phosphate, or hydroxide and then, after heating, 3.0 c.c. 0.4% formaldehyde. E.M.F. determinations were made on two separate portions of each sol and the mean values are given in Tables IV, V, and VI. With the exception of the last two preparations in Table VI, the E. M. F.'s were very constant and reproducible. Duplicates agreed generally to 0.1 millivolt, and were never farther apart than 0.5 millivolt.

If the curves showing the variation of the pH with concentration of sodium are drawn (Fig. 2.) it will be seen that they occupy positions to be expected from a consideration of the relative degrees of alkalinity of sodium

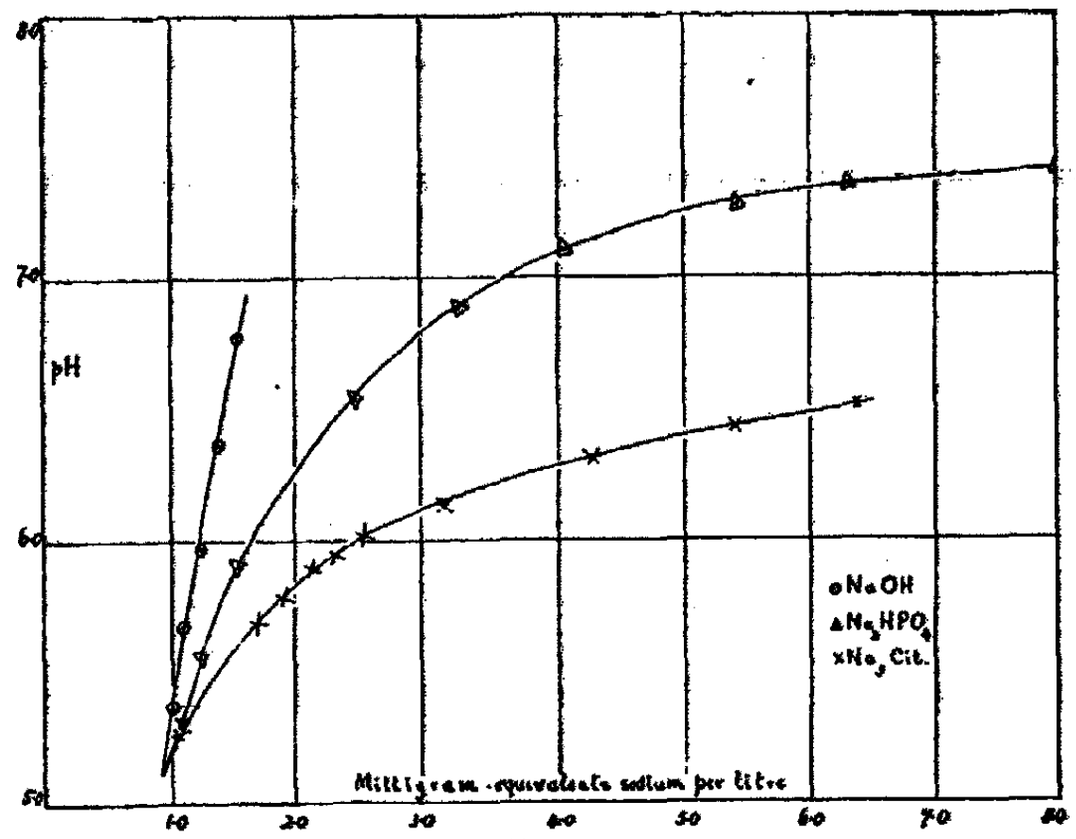

FIG. 2

hydroxide, phosphate and citrate. This affords strong evidence that the potential of the hydrogen electrode in these sols depends in the normal manner upon the activity of the hydrogen ion.

Morton[9] in the course of a very accurate electrometric titration of 0.01 M citric acid with 0.01 M sodium hydroxide found that when the ratio $\frac{\text{moles base}}{\text{moles acid}}$ was equal to 2.769, the pH was 6.405, the concentration of citrate in the mixture being 2.65×10^{-3} M. Extrapolating the data in Table IV to this concentration of citrate we find that the corresponding pH is about 6.60. In calculating the base/acid ratio for comparison with Morton's figure, account must be taken of the acid produced during the reduction of the gold chloride. Assuming that the reduction is complete and wholly due to the formaldehyde, then according to Vanino and Hartl[10] the liberation of 2 atoms of gold re-

quires 11 molecules of NaOH. In the present case this means that 0.626×10^{-3} moles per litre of base are neutralised by hydrochloric and formic acid. We therefore have for the citrate equilibrium, $\frac{\text{moles base}}{\text{moles acid}} = \frac{(3 \times 2.65) - 0.626}{2.65} =$ 2.764, i.e. almost identical with Morton's value. The difference of 0.20 between the pH values is probably connected with the fact that the citrate itself acts as a reducing agent, but the information necessary to make allowance for this is lacking at present.

It should be emphasised that in none of these experiments could there be detected the slightest tendency on the part of the gold to coagulate in the hydrogen cell. Moreover if an electrode was placed in a standard solution immediately after use in a gold sol it invariably acquired the correct potential within 20 minutes. If the gold exerted any ill effect upon the electrode it was certainly of a very transitory nature.

Conclusions

The results of this work establish beyond reasonable doubt that under circumstances the hydrogen electrode may be relied upon as a means of determining the hydrogen ion concentration in a gold sol. It has been shown that, as would be predicted from the behaviour of ordinary unbuffered solutions, the sol must be either sufficiently acid or suitably buffered in order to secure steady and reproducible potentials.

The unsatisfactory working of the electrode observed by Adolf and Pauli[3] and Tartar and Lorah[4] can hardly be due to the absence of the above conditions. The dialysed sols studied by Adolf and Pauli contained about 1×10^{-5} N hydrogen ion, and gelatine, which exerts a buffering action, was present in the sols of Tartar and Lorah. Moreover both pairs of workers report that, provided all the gold was removed, no difficulty arose in the use of the hydrogen electrode.

As far as the available information goes, the essential difference between the sols employed by these investigators and those examined in the experiments here described, appears to be that the former contained complex organic substances. Adolf and Pauli dialysed their sols by means of parchment paper membranes and the work of Wintgen[11] and of Thiessen and Heumann[12] has shown that appreciable quantities of some protective colloid passes into the sol from such membranes. Wintgen and his co-workers found that this substance could be present in the sol to the extent of 50% of the weight of the gold, and Thiessen that it was not eliminated by prolonged use and washing of the membranes. Gelatine of course was present in the sols of Tartar and Lorah. It may be tentatively suggested that the hydrogen electrode gave erratic results owing to some combined action of the gold and the foreign material. The sols investigated by Reinders and Bendien[7] also contained gelatine but unfortunately these workers give no description of their E.M.F. measurements.

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References

[1] Herstad: Kolloidchem. Beihefte, 8, 409 (1916).
[2] Kautzky and Pauli: Kolloidchem. Beihefte, 17 303 (1923).
[3] Adolf and Pauli: Kolloid-Z., 34, 30 (1924).
[4] Tartar and Lorah: J. Phys. Chem., 29, 794 (1925).
[5] Ostwald: Kolloid-Z., 40, 204 (1926).
[6] Beaver and Müller: J. Am. Chem. Soc., 50, 308 (1928).
[7] Reinders and Bendien: Rec. Trav. chim., 47, 978 (1928).
[8] Clark: "Determination of Hydrogen Ions", pp. 285, 456, 114, 267-9 (1923).
[9] Morton: Trans. Faraday Soc., 24, 14 (1928).
[10] Vanino and Hartl: Kolloid-Z., 1, 272 (1907).
[11] Wintgen: Kolloid-Z., 40, 301 (1926).
[12] Thiessen and Heumann: Z. anorg. Chem., 148, 387 (1925).

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ENTROPY, ELASTIC STRAIN, AND THE SECOND LAW OF THERMODYNAMICS; THE PRINCIPLES OF LEAST WORK AND OF MAXIMUM PROBABILITY

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The purpose of this paper is to point out a new mechanical aspect of entropy with special reference to simple fully excited gas. By relying on the geometrical expression for weight, $W = N^N (r_1 \ldots .r_N)$ and taking strains to include unit extensions in velocity and momentum space as well as ordinary space, a relation is established between entropy and the total strain: $S = kY$; $Y = \log W$, where S is the entropy, k is Boltzmann's constant, Y the total strain, and W is the a-priori probability. The Lagrange multiplier method is applied to statically indeterminate frames as well as gas theory, and both cases show that the Principle of Least Work, or Internal Energy is equivalent to the Principle of Maximum Entropy, Strain and a-priori probability. Furthermore the equations which by the Lagrange method determine the equilibrium state are shown to represent balance between true stress and strain both in gas theory and in the statics of indeterminate frames, revealing the operation in these two domains of the same identical principles (not an analogy). And the modulus of elasticity for these stresses and strains acting in momentum space is the ordinary bulk modulus p (the pressure) that also applies to volume expansions in ordinary space. Then the second law of thermodynamics and the automatic increases of entropy that it represents are explained as due to increased strain (in momentum space as well as ordinary space) under action of corresponding stresses, rather than as in statistics by the unsatisfactory ergodic hypothesis.

Altho these ideas are radical in that the statistical aspect is purposely put aside in favor of the geometrical and mechanical aspect, yet they have classical support from Boltzmann's H-theorem which shows by the method of collisions (and the forces involved) that the rate of change of entropy is positive. On the other hand Boltzmann's H-theorem implying the operation of *forces* to bring about the increase of entropy towards equilibrium, is in disagreement with any statistical theory that requires equilibrium to be reached *without* operation of forces, solely from probability considerations and the ergodic hypotheses.

It seems very possible that equilibrium between stresses and strains may accompany and account for various other phenomenon of gaseous equilibrium such as fluctuations and Brownian motion that usually are treated by the statistical method, and are not within the scope of the present article. Since the geometrical weight method has already been applied to the new quantum statistics,[1] it seems likely that the present mechanical stress-strain theory that comes from the geometrical weight method, can also be extended to include the new statistics.

[1] Chandrasekhar: Phil. Mag., 9, 621 (1930).

I. The Geometrical Expression for Weight and the Statistical Expression for Weight

The familiar expression for weight used in statistical mechanics is:

$$W = \frac{N!}{n_1!n_2!\ \ldots\ .n_k!}(\omega_1)^{n_1}(\omega_2)^{n_2}.\ \ldots\ .(\omega_k)^{n_k} \qquad (1)$$

where the ω's are small volumes in "μ-space" (of 6 to 12 dimensions according as we refer to molecules with three or six degrees of freedom). And their product (when each is raised to the indicated power) gives the elementary volume in so called γ-space, which is known as the geometrical part of the weight given by (1). The numerical coefficient involving the factorials of the n's is the statistical part and indicates the number of distinct arrangements in this γ-space.

This expression for weight (1) has been shown[1] to be equivalent to the geometrical expression for weight. To see this consider one dimension of velocity or momentum space, then each ω will refer to a velocity or momentum range including the corresponding n molecules, which we can refer to as s. If we use the approximation:

$$\log N! = N \log N - N \qquad (2)$$

then the statistical part of (1) is readily seen to be equivalent to $N^N / (n_1^{n_1}n_2^{n_2}\ \ldots\ .n_k^{n_k})$ so that (1) may be written:

$$W = \frac{N^N}{n_1^{n_1}n_2^{n_2}\ \ldots\ n_k^{n_k}}(s_1)^{n_1}(s_2)^{n_2}\ \ldots\ .\ (s_k)^{n_k} \qquad (3)$$

which refers to one dimension say of velocity space. Now it is noteworthy in connection with this theory that the ω's (and hence the s's) are arbitrary, (except that in the quantum theory they determine energy levels and are integral multiples of h) and it is in connection with this fact that the geometrical treatment differs from the statistical one, for the prevailing mode is to choose the ω's as all equal (or at least constant), and then one can readily employ the familiar method used by Boltzmann of maximizing W thru variation of the n's, keeping the total energy constant, and thereby derive the Maxwell Boltzmann distribution law. It is equally permissible, however, to keep the n's constant and let the ω's which are the geometrical part of (1) vary, instead of Boltzmann's method of keeping the ω's constant and varying the n's, i.e. the statistical part. And in particular we may take each n equal to unity, thereby removing the statistical aspect entirely and then if we refer to (3) instead of (1), the s's which correspond to the ω's will be the range[2] in velocity space corresponding to separate molecules:

$$r_i = \frac{1}{Nf(u_i)} = u_{i+1} - u_i \qquad (4)$$

[1] Kimball: J. Phys. Chem., 33, 1558 (1929).
[2] Kimball: loc. cit.

And these r's are the velocity differences between successive molecules in velocity space used in deriving the geometrical expression for weight:

$$W = N^N(r_1 r_2 \ldots . r_N) \tag{5}$$

Thus it is readily seen that (3) reduces to (5) when we take $s_1 = r_1$ and $n_1 = n_2 = n_3 \ldots . n_k = 1$. The expression (5) is geometrical because the variable, vital part is the geometrical velocity (or action) range that includes each particle. On the other hand, the variable, vital part of (1) and (3) is statistical being the n's, necessarily integers associated with arbitrary constant compartments of μ-space.

2. Entropy, Strain, Weight, A-Priori Probability and the Third Law of Thermodynamics

If we interpret the r's given by (4) as momentum ranges instead of velocity ranges, then the weight that measures the thermodynamic probability, taking account of ordinary space ranges as well as three dimensions in momentum space, is given by:

$$W = N^{3N}(r_1 r_2 \ldots . r_N)^3 V^N = (Nr)^{3N} V^N \tag{6}$$

where the right member gives the weight in the terms of the range r of a molecule in its mean energy state corresponding to the temperature in question. (See eqs. (32) and (39) of Entropy and Probability).[1] When (6) is substituted in Boltzmann's equation we have the known expression for entropy of monatomic gas,

$$S = k\log W + C = R\log V(2\pi emkT)^{3/2} + C = R\log VN^3 + 3k\Sigma\log r_i + C \tag{7}$$

and hence:

$$dS = R\frac{dV}{V} + 3k\Sigma\frac{dr_i}{r_i} = R\frac{dV}{V} + 3R\frac{dr}{r} \tag{8}$$

Equation (8) shows that the change in Entropy equals k times the sum of the corresponding strains for the separate molecules, both in ordinary space and in momentum space. Entropy thus appears as an extensive physical quantity, being k times the integral of the strains plus a constant, i.e., it is k times the total strain, and the constant of integration gives the lower boundary from which strain is to be measured. Thus if we let Y represent the total strain or yielding of the gas, we have:

$$S = kY;\ Y = \log W;\ W = e^Y \tag{9}$$

The concept weight is introduced into physics to avoid the indeterminate aspects of thermodynamic probability which should be a proper fraction, whereas the denominator to be used is unknown. Eq. (9) shows how this weight that measures the a-priori probability of a gaseous state is related to the strain. This gives additional physical significance to the idea of weight, heretofore known mainly as the volume in so called γ-space, and perhaps pushes thermodynamic probability further into the background. We show

[1] Kimball: Loc. cit.

below how the state of maximum probability corresponds to the equilibrium equations between stress and strain, and represents by (9) a state of maximum strain. It is like the statics of indeterminate frames (see below) where the equilibrium equations correspond to a state of maximum strain for given internal energy. That is to say, the gas yields as much as it can, subject to the boundary conditions on its volume and energy.

Altho these results are derived from considerations of monatomic gas obeying the gas law, they are readily seen to apply to complex gases having more than three degrees of freedom, since these gases also have their entropies expressible in terms of momentum and action range, according to Entropy and Probability,[1] equation (48), which form gives the dS like (8) as the sum of the strains. The present treatment suggests that perhaps any probability theory available to calculate entropy according to Boltzmann's equation (6) (or statistical theory resting on probability) has value by virtue of its relation to the forces and balancing strains, for mechanical strain appears to be the corner stone of *a-priori* probability wherever (9) can be applied to gases and other branches of physics.

It is to be emphasized that (9) refers *only* to *a-priori* probability. It is clear that there are other types of probability which are not based on the probability axioms and which are not related to entropy and mechanical strain according to (9). Thus the usual probability expression associated with the Maxwell distribution law, $dN/N = f(u)\,du$, is du times the reciprocal of the weight per molecule, $w = Nr = 1/f(u)$. It is this latter (Type A probability) which is based on the probability axioms and is related to entropy and strain according to (9). On the other hand f(u) du can not be used in (7) or (9) to give entropy and strain, and thus represents a type of probability (Type C) to which Boltzmann's equation does not apply. (See Entropy and Probability,[1] 4, eqs. (15) and (25)).

When entropy is clearly related to probability according to Boltzmann's relation, no case appears where it has been shown that these are not related to mechanical strain according to (9). The present paper shows how (9) applies in ordinary gas theory, and likewise it is planned to show how it applies to fluctuations in gas where equilibrium prevails. The applicability of (9) to electronics, the Schott effect and other cases remains to be proved or disproved.

If (9) holds true all the way down to absolute zero, the corresponding interpretation of the third law of thermodynamics is that the total strain of crystalline substances at the absolute zero is zero.

If entropy is proportional to strain, it suggests that the equilibrium state of maximum entropy and strain is brought about thru the action of stresses. To prove this we note how forces may act in velocity and momentum space, first, however taking note how the principle of maximum entropy, probability and strain is related to the principle of minimum internal energy.

[1] Kimball: Loc. cit.

3. The Principle of Maximum Entropy, Probability and Strain is Equivalent to the Principle of Least Work or Internal Energy

It is well known that equilibrium conditions in gas theory correspond to the state of maximum entropy and probability. If we restrict attention to one dimension of velocity space, the probability is given by (5) above.

The Maxwell distribution law of velocities is obtained by maximizing the probability (5) subject to the condition that the energy remain constant. Using the Lagrange method of multipliers we form the function:

$$F = W + \lambda U \tag{10}$$

where U the energy is a homogeneous quadratic function of the velocity coordinates, and take the partial derivatives of (10).

$$\frac{\partial F}{\partial u_i} = \frac{-Wd}{du_i}(\log f(u_i)) + \lambda m u_i = \frac{Wd}{du_i}(\log r_i) + \lambda m u_i = 0 \tag{11}$$

Equations (11) are of the same form as if W were kept constant and U were being minimized. Thus we see that these equations (11), and the Maxwell distribution law arising from them, represent the state of minimum internal energy for a given constant probability (or entropy) as well as the state of maximum probability for a given constant internal energy.

Altho (11) are merely conditions for the extremal values of W or U subject to the constancy of the other, it is readily shown by taking the second partials of U subject to the constant W condition that these partial derivatives are positive and satisfy the sufficiency condition to make U a minimum rather than a maximum.

The equivalence of these two principles also holds in the domain of elasticity theory as applied to engineering problems. Thus the problem used in Church's "Mechanics of Internal Work"[1] to illustrate Castigliano's Principle of Least Work, may be treated by the Lagrange method for conditional maxima and minima. The extension of a bar in the frame is given in terms of the tension by:

$$y = CT; \text{ and } C = L/EA \tag{12}$$

and L is the length, E the elastic modulus, and A the cross section of the ba and the internal energy is given by:

$$U = \tfrac{1}{2}(C_1T_1^2 + \ldots + C_6T_6^2) \tag{13}$$

Then if P is the load, we have from statics: (see figure 1)

$$P = T_1 + \frac{T_3}{\sqrt{2}} + \frac{T_6}{\sqrt{2}}; Q = T_3 - T_6 = 0; R = T_1 + \frac{T_4}{\sqrt{2}} + \frac{T_5}{\sqrt{2}} = 0; S = T_4 - T_5 = 0$$

$$\frac{P}{2} = T_1 - T_3. \tag{14}$$

where Q, R and S are convenient notations for the indicated zero value

[1] I. P. Church: "Mechanics of Internal Work."

constants of elementary statics. We take these as five conditions on the T's and form the function:

$$F = U + \lambda P + \mu Q + \nu R + \xi S + \rho \frac{P}{2} \tag{15}$$

where the Greek letters are undetermined constants. Now take the partial derivatives for the six independent variables:

$$\begin{aligned}
\frac{\partial F}{\partial T_1} &= C_1T_1 + \lambda + 0 + \nu + 0 + \rho = 0 \\
\frac{\partial F}{\partial T_2} &= C_2T_2 + 0 + 0 + 0 - \rho = 0 \\
\frac{\partial F}{\partial T_3} &= C_3T_3 + \frac{\lambda}{\sqrt{2}} + \mu + 0 + 0 + 0 = 0 \\
\frac{\partial F}{\partial T_4} &= C_4T_4 + 0 + 0 + \frac{\mu}{\sqrt{2}} + \xi + 0 = 0 \\
\frac{\partial F}{\partial T_5} &= C_5T_5 + 0 + 0 + \frac{\nu}{\sqrt{2}} - \xi + 0 = 0 \\
\frac{\partial F}{\partial T_6} &= C_6T_6 + \frac{\lambda}{\sqrt{2}} - \mu + 0 + 0 + 0 = 0
\end{aligned} \tag{16}$$

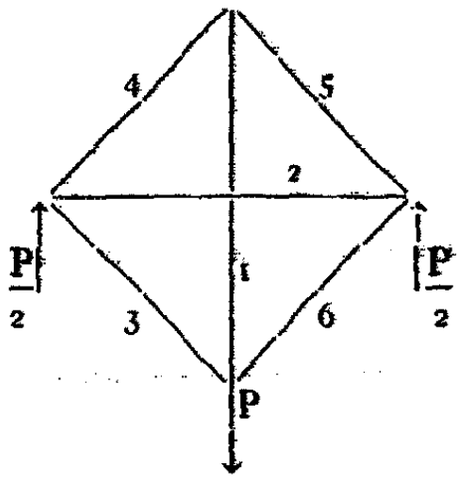

Fig. 1

These equations may be treated as homogeneous equations in the quantities $1, \lambda, \mu, \nu, \xi, \rho$ and the determinant of the coefficients set equal to zero. When the Greek symbols are eliminated and account taken of (14), we have: for T_1; (See Church)[1]

$$T_1 = P\frac{C_2 + C_3 + C_6}{2(C_1 + C_2) + C_3 + C_4 + C_5 + C_6} \tag{17}$$

and likewise for the other five T's.

Here again, as was the case with gas in the equilibrium state, the equations (16) that determine the minimum of U subject to a constant load P are identical with those determining a maximum P subject to a constant U. And hence the Principle of Least Work is the equivalent of a principle of maximum load for given internal energy. Altho exact proportionality between stress and strain holds in a very restricted domain, in general increased tension corresponds to increased strain according to some law or other. Likewise increased load corresponds to increased strain. Hence we see that equations (16) determine the state of maximum strain as well as the state of least work, and we conclude that in the domain of engineering statics as well as gas theory, the Principle of Maximum Strain is equivalent to the Principle of Least Work or Internal Energy.

4. Forces in Velocity and Momentum Space

Altho force is usually thought of as operating only in ordinary space, it is clear that a particle which takes on a change of momentum undergoes a change of position in momentum space and velocity space. Furthermore this change

[1] I. P. Church "Mechanics of Internal Work," Chapter III.

may take place by collisions without alteration of its position in ordinary space. Thus a molecule of gas in equilibrium or an atom of a solid may keep its position of equilibrium in ordinary space while changing its position in velocity space during an interval of time dt. Such a time rate of change of momentum involves, according to Newton's law, the operation of a force. This force which in the absence of displacements does no resultant work in ordinary space, may be thought of as doing work in velocity space or momentum space since the molecule on which it acts takes on a corresponding change of energy as the force acts to change its position in velocity or momentum space. Thus forces must (to the extent that Newton's laws apply to agitated molecules) be thought of as operating not only in ordinary space but in velocity and momentum space.

The corresponding energy equations take the form:

$$W - W_o = \int_{x_o}^{x} F_x dx. \tag{18}$$

$$\text{and} \quad W - W_o = \int_{mu_o}^{mu} mu\,du. \tag{19}$$

where the limits x and x_o refer to the *same* place in ordinary space at different times and to different places in momentum space where momenta are mu and mu_o respectively. This means that the interval $x\text{-}x_o$ over which the integrand is summed, amounts to zero when plus and minus signs are considered, altho physically it is ordinary space thru which the force acts (back and forth.

5. Theorem: The Equations that Determine the State of Maximum Entropy or Probability represent Equilibrium between Stresses and Strains in Velocity or Momentum Space

In this section we show that equations (11) or (16) which determine the state of maximum probability or least internal work, are to be interpreted as equilibrium equations between stress and strain. To do this, we replace λ, the undetermined constant, by its value $-W/kT$ which is determined from the distribution function in the usual way. Then if we transpose and multiply both sides of (11) by $kT\frac{du}{dx}$ and drop the subscripts, we obtain:

$$\frac{kT}{r}\frac{dr}{dx} = mu\frac{du}{dx} = m\frac{du}{dt} = F_x \tag{20}$$

We here view $dx = u\,dt$ as the absolute value of distance travelled (of plus or minus sign) in time dt, whose resultant is taken to be zero, and the du is the change in velocity magnitude, i.e. the change in agitation velocity according to the last section, so that the force referred to acts only in velocity

or momentum space. Where molecules are free to move it is always real and finite (zero when the above du is zero); and distinct from the force exerted by the molecules in ordinary space, (this latter will be zero when the plus and minus values of du/dt cancel each other). Equation (20) refers to the individual molecule in the Maxwell distribution where the velocity is u, and if the differential coefficients were known, the magnitude of (20) could be determined.

Since (20) is like (11) an equilibrium equation, and since the right member is the force corresponding to one molecule, the left member must be the reacting force per molecule, which is seen to include the corresponding strain multiplied by the elastic coefficient per molecule.

Thus dr/r is a true strain, i.e., a dimensionless physical quantity, a change in range per unit range. This range is the distance that separates successive molecules in velocity space, (or the excess distance in ordinary space acquired between them in unit time).

The way in which the foregoing fits into the theory of elasticity becomes more clear if we re-call that stress or internal force per unit area may be thought of as internal energy per unit volume. Thus in electrostatics where the field strength is F, the energy per unit volume is given by $F^2/2$ and this is also the expression for tension or ether stress along lines of force. Also for the Pascal case of hydrostatic equilibrium, the pressure p is the potential energy per unit volume, and also represents the three normal stresses. Consider also the isothermal bulk modulus of elasticity p, the ratio between pressure differences and the corresponding change in volume per unit volume:

$$E = \frac{-dp}{dV/V} = p = nkT \tag{21}$$

Here the dp is a force per unit area that refers not to the Pascal hydrostatic force equal in all directions, but to that stress which is balanced by the strain according to (21), being the *change* in potential energy per unit volume. For the Maxwell distribution of velocities we have from (20):

$$kT = \frac{mu_1du_1}{dr_{1/r_1}} = \frac{mu_2du_2}{dr_{2/r_2}} = \ldots = \frac{mu_Ndu_N}{dr_{N/r_N}} \tag{22}$$

which shows that for gas in equilibrium at temperature T, there is a constant ratio, i.e., an elastic coefficient per molecule, kT which is the ratio between energy difference and corresponding strain for the various positions of a molecule throughout velocity space. As the denominators of (22) are true strains, so it is clear that the numerators are pressure differences due to energy changes, which tend to change the positions in velocity space of molecules on which they act, being balanced by the corresponding strains.

Each position u_i in velocity space is (under equilibrium conditions) maintained by some molecule (or other) under action solely of pressure due to impacts, and this must be an unbalanced force as between molecules of different energy and position in velocity space. Thus the equations (11) which correspond to the Maxwell distribution are seen to be equilibrium

equations between the stress and strain in velocity and momentum space. Accordingly this distribution seems to be the result of forces acting in velocity space.

Likewise it will readily be understood that equations (16) can be shown to be the equilibrium equations between stress and strain. (Express the undetermined Greek constants in terms of the y's with the help of (12) and divide by the C's).

6. Magnitude of Stress and Strain acting in Velocity Space, where Thermal Equilibrium prevails, in Gas obeying the Gas Law

The proportion (22) still holds if we sum the numerators and sum the denominators for the n molecules in unit volume:

$$kT = \frac{\Sigma\, mu_i du_i}{\Sigma\, dr_i/r_i} = \frac{nmu\, du}{n\,\dfrac{dr}{r}} \tag{23}$$

or multiplying by n:

$$nkT = p = \frac{nmu\, du}{dr/r} = \frac{f_u}{dr/r} \tag{24}$$

where the numerator is seen to be the total force for all n molecules per c.c. due to energy differences of molecules that react against each other, and the modulus of elasticity p is the familiar isothermal bulk modulus for gas obeying the gas law according to (21). The numerator f_u is seen to be like the usual $p = \frac{1}{3}(nmv^2) = nmu^2$, except that $2mu$ of the latter, the change in momentum per impact in the x direction, is replaced by $2mdu$, the excess change of momentum that has to be balanced by strain in momentum space.

To calculate the magnitude of the stress f_u above, we note that the differentials in (23) and (24), which generally above have their usual interpretation as variables approaching zero, must be given a special interpretation if the numerators of these equations are to represent the actual stress or total unbalanced pressure due to energy differences. Thus if we take in the manner of elementary kinetic theory, $u_i/2$ as the number of impacts per second and $2mdu_i$ as the unbalanced change in momentum per impact for this component of this molecule, the product gives the excess change in momentum per second or unbalanced pressure as between two molecules at u_i in velocity space. But the r_i used throughout this paper is precisely the expression for velocity (or momentum) differences between successive molecules in velocity space, and it is only when such differences are used in (23) and (24) that the energy differences shown there represent unbalanced pressure of molecules that jostle each other in equilibrium. The same result is reached if no limit is imposed on the arbitrariness of the differentials which might be zero but then the number of molecules would increase indefinitely and still satisfy the distribution law. Thus for the stress or force per unit area in the x direction and acting only in velocity space:

$$f_u = nmu\,du = nmur = nu\frac{(2\pi emkT)^{\frac{1}{2}}}{n} = \sqrt{2\pi e}\,kT \qquad (25)$$

where the momentum range mr for the molecule in its mean energy state is introduced with the help of (4) and $mu^2 = kT$ for one component of the root mean square velocity. Also see the writer's Entropy and Probability[1], equation (38). And likewise the corresponding strain is:

$$\frac{dr}{r} = \frac{2u\,du}{\alpha^2} = \frac{2u(2\pi emkT)^{\frac{1}{2}}}{m\alpha^2 n} = \sqrt{2\pi e}/n \qquad (26)$$

It is noteworthy that no change of T occurs with the differentials of these equations because we are considering changes within gas where temperature equilibrium prevails, and also that the strain is a pure number depending only directly on the density and affected by temperature changes only indirectly according to the gas law.

It is to be emphasized that the stress (25) does not in general operate to change momentum in ordinary space except as applied to motions where the vector sum of the changes in ordinary space is zero, although they add up to increase agitation energy and absolute velocity, thus corresponding to a shift of position in velocity and momentum space. And yet f_u is a true stress in that it acts on unit area like hydrostatic pressure and is an energy difference for the n molecules per unit volume of ordinary space and would cause a time rate of change of momentum (in momentum space) unless balanced as per (24) and (11). Furthermore, it is an isothermal stress like the dp of (21) with the same modulus of elasticity $p = nkT$; and again if we divide both members of (21) by n and interpret dp/n as the pressure difference per molecule, then the elastic modulus per molecule will be kT for (21) as it is in (22).

If there were uniform molecular distribution in velocity space, i.e., if there were equal intervals between successive molecules in velocity space, then dr_i would be zero and there would be no reacting force (kT times the strain) to counterbalance the forces represented by the numerators of (22), (23) and (24). And those forces would operate by elementary mechanics to increase the energy of the slow molecules and reduce the energy of the fast moving ones, thus reducing the intervals r_i by bringing the molecules together in velocity space. But a smaller r_i makes an increased strain (other things being equal) and hence increased reacting force. The condition of equilibrium is thus a stress given by the numerators of (23) and (24) acting in velocity space through forces shown as numerators of (23) that tend to reduce the differences between agitation velocities (to reduce intervals in velocity space), which forces are balanced by the increased strains. Comparison of (21) and (24) shows that molecules "object" to all occupying the same position in velocity space with the same vigor (same modulus of elasticity) that they object to occupying it in ordinary space, and apparently for the same reason, i.e., more of them together in unit interval causes bigger reaction.

[1] Loc. cit.

7. The Second Law of Thermodynamics

According to this law automatic changes within a closed system always involve an increase of entropy till the equilibrium state of maximum entropy and probability is reached subject to the boundary conditions on the volume and energy of the system. No ergodic hypothesis is needed, according to the present treatment, to account for this fact that the rate of change of entropy is always positive:

$$\frac{dS}{dt} > 0 \tag{27}$$

For we have seen that the state of maximum entropy corresponds to the equilibrium equations between stress and strain in ordinary and momentum space. And likewise the unstable state corresponds to a failure to satisfy the equilibrium equations between stress and strain within the gas. That is to say the stresses within the gas are not completely balanced in the absence of the equilibrium condition of maximum entropy. And this refers to stresses acting in momentum and velocity space as well as ordinary space according to 4 and 5. Thus a gas at uniform temperature and pressure whose molecules were uniformly spaced, but wherein a Maxwellian distribution of velocities did not prevail, would involve stresses acting in velocity space which as pointed out in 6, would not be balanced by the strains corresponding to the equilibrium condition. Hence an immediate rearrangement in velocity space would take place involving a time rate of change of momentum of most of the molecules under the action of internal *forces*, i.e.: stresses would act in velocity and momentum space.

A simple illustration of the second law is found by considering equal quantities (N molecules) of the same type of gas at two *different* temperatures T_1 and T_2 but at the *same* pressure and separated by any conceivable barrier impervious to heat conduction. If we take $T_1 > T_2$ the first gas will occupy more volume than the second (i.e. $V_1 > V_2$) according to the gas law (since there are equal numbers of molecules). Hydrostatic equilibrium prevails since the pressure is taken to be uniform, and we assume that two gases are thermally insulated from the outside world by fixed walls impervious to heat tho separated from each other by a *removable* non conducting barrier. Now remove the imaginary barrier in such a way as not to disturb the two gases by the removal process, and note the operation of the second law of thermodynamics in this container where hydrostatic equilibrium prevails (but not thermodynamic). Molecules of the high temperature gas, having more kinetic energy, will as they impact with those of the cooler gas impart by elementary mechanics some of their kinetic energy to the latter until at length temperature equilibrium prevails at $T = (T_1+T_2)/2$, while the total agitation *energy* of the two gases together remains constant. This increase of energy of the cooler molecules involves time rate of change of momentum and the action of stresses (forces) within the gas to cause that rate of change. And the corresponding increased total strain parallels the known increase

of entropy according to (7), (8), and (9). And thruout this change no work is done in ordinary space wherein hydrostatic equilibrium is maintained.

Although no attempt is here made to extend this explanation to the multitudinous complicated cases to which the second law applies, yet it would seem that it would apply and account for the changes of states involved in the workings of the second law in all cases where the relation between entropy and strain is correctly given by (9).

8. Experimental Verification

We note that these relations between entropy, strain and a-priori probability are an immediate consequence of using in Boltzmann's equation the geometrical expression for weight (6) rather than the familiar statistical one. It was pointed out, however, in the writer's Entropy and Probability[1] that these expressions are mathematically equivalent and interchangeable. This makes the problem of distinguishing experimentally between the two points of view a difficult one. For if one starts with two equivalent expressions for entropy, one obtains equivalent theoretical results whenever equivalent mathematical lines of reasoning are applied to the two treatments. The Maxwell distribution of velocities viewed as the most probable distribution may be thought of as brought about spontaneously and explicable in statistics according to the ergodic hypothesis. The present theory indicates however, like *Boltzmann's H-theorem* that it comes about as a result of *forces*. The question arises, are the many so called "spontaneous" *deviations* from equilibrium which involve corresponding changes of entropy also explicable as due to the action of forces? The reasoning of the present paper indicates an affirmative answer for such probability deviations *provided* their probability is of the a-priori Type A and measured according to the probability axioms and related to entropy and strain according to (9) by Boltzmann's relation. There seems to be no case where it has been positively shown that there are no veiled forces to account for "spontaneous" changes in entropy like the veiled forces that the present treatment shows are involved in the Maxwell velocity distribution of maximum probability. The detailed application of this method to fluctuations within gas where a Maxwell distribution of velocities prevails, is planned in a subsequent paper. On the other hand the present theory has nothing to say about fluctuations and changes whose probability is not of Type A and hence not related to Entropy according to (9) by Boltzmann's relation. (See section two above).

The most outstanding verification of the present theory, however, seems to be the second law of thermodynamics itself. The ergodic hypothesis, as an explanation of why gas will go from an unstable, improbable state to the equilibrium state of maximum probability, does not appear satisfactory to most physicists and still presents, according to Tolman[2], "a baffling problem for further study". This marks a sore spot and partial failure in the statistical theory.

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[1] Kimball: loc. cit.

[2] Tolman: "Statistical Mechanics", 21, 39.

On the other hand, forces certainly do act in velocity and momentum space, and, as pointed out herein, may do work in these realms when no work is done in ordinary space, and cause strains there distinct from any strains in ordinary space. Thus, when entropy is viewed as k times the sum of the strains, it is readily suggested that it is the action of these forces that cause the state of maximum entropy and probability to be reached. This mechanical explanation of the second law is calculated to appeal to those who welcome the modern tendency to extend further the application of mechanical principles, as for example to the action of light photons.

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TEMPERATURE OF MAXIMUM DENSITY OF AQUEOUS SOLUTIONS. DEVIATIONS FROM THE LAW OF DESPRETZ

BY NORA GREGG-WILSON AND ROBERT WRIGHT

The generally accepted explanation of the phenomenon of the temperature of maximum density of water is derived from the fact that the density of water is greater than that of ice. In common with other liquids the density of water increases with fall of temperature, but as it approaches the freezing point ice molecules are supposed to form and their smaller density to counteract the increasing density of the water. At 4°, the temperature of maximum density (t.m.d.) of water, these two effects just balance, and between 4° and the freezing point the preponderance of ice molecules causes an increasing lowering of the total density.

The t.m.d. of aqueous solutions has been frequently investigated, and the most important generalisation put forward is that due to Despretz,[1] who found that the t.m.d. of water was lowered by the addition of a solute and that the lowering was directly proportional to the concentration of the dissolved substance.

The lowering of the t.m.d. by a solute does not depend, like the lowering of the freezing point, solely on the molecular concentration, but varies also with the nature of the dissolved substance. De Coppet[2] has measured the molecular lowering of the t.m.d., that is the lowering produced by a gram molecule of solute in a litre of solution, for a number of substances and found the result to vary greatly with the nature of the solute employed. In the solutions of simple binary electrolytes it would seem that each ion has its specific effect on the t.m.d., and that the molecular lowering of a salt solution can be calculated from the observed effects of other salts.[3]

All salt solutions which have been investigated, and the great majority of solutions of organic substances, obey the law of Despretz. The important exceptions are the dilute solutions of the lower alcohols;[4] of these ethyl alcohol is the most interesting. With dilute solutions this substance causes a rise of the t.m.d., but with greater concentrations a depression is produced. Solutions of ethyl ether also deviate from the law of Despretz[5] but they do not give an elevation of the t.m.d.

In considering the effect of a solute on the t.m.d. of water three factors should receive attention. The lowering of the temperature of production of ice molecules—i.e. of the freezing point, the temperature coefficient of expansion of the solution, and the density of the solution.

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[1] Ann. Chim. Phys., 70, 5, 49 (1839); 73, 296 (1840).
[2] Ann. Chim. Phys., 3, 246, 268 (1894); Compt. rend., 125, 533 (1897); 128, 1559 (1899); 131, 178; 132, 1218 (1900); 134, 1208 (1902).
[3] Wright: J. Chem. Soc., 115, 119 (1919).
[4] DeCoppet: Compt. rend., 115, 625 (1892); J. P. McHutcheson: J. Chem. Soc., 129, 1899 (1926).
[5] Nort: Landolt and Börnstein Tabellen.

Since the lowering of the freezing point depends only on the molecular concentration of the solute, it should be the same for all solutions of organic compounds of equal molecular concentration, though for salt solutions the effect will be greater owing to ionisation of the solute. In all cases the lowering of the freezing point will produce a corresponding lowering in the t.m.d. of the solution.

The coefficient of cubical expansion of any aqueous solution is greater than that of pure water. It therefore follows that the contraction caused by the fall of temperature, which has to be balanced by the formation of ice molecules before the t.m.d. is reached, is greater for a solution than for water, hence the increase in the coefficient of expansion will cause a lowering in the t.m.d.

The effect on the t.m.d. due to the density of the solution depends on whether that density is greater or less than that of water. If the solution has a density greater than that of water, then the separation of ice molecules in the neighbourhood of the t.m.d. will increase the concentration of the remaining solution and the resulting increase of density will have to be balanced by the further production of ice molecules before the t.m.d. is reached. That is, the t.m.d. will be lower on account of the solution being more dense than water. On the other hand if the density of the solution is less than that of water, then the removal of solvent by the formation of ice molecules will still further decrease the density of the remaining solution, and thus help the action of the ice molecules and tend to raise the t.m.d. of the solution.

We thus come to the conclusion that for solutions of greater density than water, all three contributary causes tend to lower the t.m.d.; whilst for other solutions, the lowering of the freezing point and the greater coefficient of expansion, will be to some extent balanced by the smaller density of the solution.

For dilute solutions all three factors, lowering of the freezing point, increase in the coefficient of expansion, and the density of the solution, will be proportional to the concentration of the solute, and therefore their combined effect will also be proportional to the solute concentration and hence the solution will obey the law of Despretz. As a rule with electrolytes all three contributary factors are relatively great, so that only dilute solutions, such as might be expected to obey the law of Despretz, have been investigated. With more concentrated solutions the t.m.d. is in general lower than the freezing point.

Solutions of hydrochloric acid and lithium chloride are however exceptions to the general class of electrolytes, since the molecular lowering of the t.m.d. (as calculated from dilute solutions) is in the neighbourhood of six degrees. These solutions were therefore examined up to a concentration of 2N with the result shown in the table:

N	Hydrochloric acid lowering of t. m. d.	N	Lithium chloride lowering of t. m. d.
0.5	2.9	0.5	2.7
1.0	6.9	1.0	5.9
2.0	16.4	2.0	12.5

It is at once obvious that at high concentrations the law of Despretz is not obeyed. This result is probably related to the well-known phenomenon of the excessive lowering of the freezing point which occurs with concentrated electrolyte solutions.[1]

With solutions of organic compounds the coefficient of expansion is generally less than that of salt solutions of a corresponding molecular concentration, and the depression of the freezing point owing to the absence of ionisation) will also be less. Further, if we confine our attention to those substances which give solutions of less density than that of water, we are dealing with a class of solution of which the molecular lowering of the t.m.d. will be the smallest possible. As a consequence we should be able to employ fairly concentrated solutions and have a good opportunity of observing deviations from the law of Despretz.

The number of organic compounds less dense than water, and at the same time sufficiently soluble, is considerably restricted. Apart from the alcohols, which have already been investigated, the most important group is that of the fatty amines. The values of the t.m.d. for a number of amines have been determined and the results are tabulated along with those obtained for a few other substances. It will be seen that in general there is a deviation from the law of Despretz for the stronger solutions, and that the deviation is in the direction of excessive lowering of the t.m.d.

The relative densities at 5° have also been tabulated and so have the coefficients of expansion between the temperatures 12.5° and 15°. The densities when plotted against the concentrations give approximately linear graphs, but the coefficients of expansion as a rule show excessive increases with increase of concentration. This abnormal increase in the coefficient of expansion is made clear by the table of "Molecular increase of coefficient of expansion", in which is given the values for $\frac{a_s - a_w}{N}$ where a_s is the coefficient of expansion of the solution, a_w that of pure water and N the concentration of the solute in gram molecules per litre. If the change in the coefficient of expansion was directly proportional to the concentration, then the value of $\frac{a_s - a_w}{N}$ should be constant. It will be seen however that for most solutions it tends to increase, and it is to this excessive increase in the coefficient of expansion with the more concentrated solutions that the excessive lowering of the t.m.d. is to be attributed.

Three substances among those investigated call for special mention. Ethyl alcohol, as already pointed out, first raises the t.m.d. and then lowers it. The coefficients of expansion of the alcoholic solutions are very near those for pure water in the case of solutions up to N/2 strength. So that for this substance the factor due to the small density of the solution outweighs the others in the case of dilute solutions, but at higher concentrations the increasing coefficient of expansion causes a lowering of the t.m.d. For aceto-nitrile, up

[1] Biltz: Z. physik. Chem., 40, 185 (1902); Jones: Carnegie Soc. Reprint 60 (1907.)

Lowering of Temperature of Maximum Density

	NH_3	CH_3NH_2	$(CH_3)_2NH$	$(CH_3)_3N$	$C_2H_5NH_2$	$(C_2H_5)_2NH$	CH_3CN	$(CH_3)_2CO$	C_2H_5OH	
N/8	0.2°	0.1°	0	0.1°	0.2°	0.1°	0.9°	0.4	−0.15	N/8
N/4	0.4°	0.2°	0	0.3°	0.4°	0.4°	1.6°	1.0	−0.20	N/4
N/2	1.1°	0.6°	0.5°	1.2°	1.2°	1.4°	3.5°	2.3	−0.20	N/2
N	2.4°	1.8°	2.6°	5.2°	3.2°	4.9°	7.3°	6.2	0.3	N
2N	5.4°	6.4°	10.2°	—	11.1°	14°	14°	—	3.8	2N

Relative Density at 5°C.

	NH_3	CH_3NH_2	$(CH_3)_2NH$	$(CH_3)_3N$	$(C_2H_5)_2NH$	CH_3CN	$(CH_3)_2CO$	$C_2H_5NH_2$	C_2H_5OH	
N/8	.9988	.9990	.9987	.9979	.9988	.9982	.9991	.9995	.9986	N/8
N/4	.9979	.9977	.9970	.9951	.9974	.9963	.9988	.9988	.9977	N/4
N/2	.9959	.9957	.9934	.9910	.9945	.9926	.9972	.9968	.9956	N/2
N	.9922	.9912	.9870	.9822	.9895	.9872	.9954	.9936	.9915	N
2N	.9851	.9826	.9765	——	.9805	.9759	.9908	——	.9856	2N

Coefficient of Expansion 12.5° and 15°C

	NH_3	CH_3NH_2	$(CH_3)_2NH$	$(CH_3)_3N$	$C_2H_5NH_2$	$(C_2H_5)_2NH$	CH_3CN	$(CH_3)_2CO$	C_2H_5OH	
N/8	.0001375	.0001360	.0001350	.0001375	.0001350	.0001350	.0001470	.0001363	.0001365	N/8
N/4	1415	1378	1360	1410	1350	1358	1550	1440	1380	N/4
N/2	1480	1432	1422	1574	1447	1565	1800	1670	1405	N/2
N	1610	1592	1690	2095	1725	2043	2220	1953	1495	N
2N	2310	2024	2450	——	2480	4037	3260	——	1900	2N

Molecular Increase of Coefficient of Expansion $\frac{\alpha_s - \alpha_w}{N}$

	NH_3	CH_3NH_2	$(CH_3)_2NH$	$(CH_3)_3N$	$C_2H_5NH_2$	$(C_2H_5)_2NH$	CH_3CN	$(CH_3)_2CO$	C_2H_5OH	
N/8	.0000200	.0000080	.0000000	.0000200	.0000000	.0000000	.0000960	.0000104	.0000120	N/8
N/4	260	112	40	240	000	32	800	360	120	N/4
N/2	260	164	150	448	294	430	900	640	110	N/2
N	260	242	340	645	375	693	870	600	145	N
2N	480	337	550	——	565	1343	905	——	275	2N

to 2N concentration, the coefficient of expansion is directly proportional to the concentration, and hence this substance obeys the law of Despretz. The same is true for ammonia but only up to N concentration.

The above results indicate clearly that the law of Despretz, like so many other generalisations, only holds in the case of dilute solutions and breaks down as soon as the solutions become concentrated.

Experimental. The determinations of the t.m.d. were carried out by means of a compensated dilatometer in the manner already described by one of us.[1] The coefficients of expansion were made with the same instrument, the stem being calibrated for the purpose. The choice of the temperature range 12.5° to 15° is an arbitrary one, but it was considered to be sufficiently removed from the t.m.d. to be free from the complication of the formation of ice molecules. The coefficient was calculated from the expression $a = \frac{V_{15} - V_{12.5}}{2.5 \times V_{12.5}}$ where V_{15} and $V_{12.5}$ are the volumes at 15 and 12.5 respectively.

In conclusion it should be recalled that the t.m.d. is not capable of exact determination and hence the above data are only approximate. Nevertheless there can be no doubt that the conclusion that the law of Despretz only holds for dilute solutions is correct.

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July 1, 1930.

[1] Wright: J. Chem. Soc., 115, 119 (1919).

INFLUENCE OF ELECTROLYTES ON THE SYNERESIS AND CLOTTING OF BLOOD

BY SATYA PRAKASH AND N. R. DHAR

In a previous communication,[1] we have advanced the view that clotting of blood and jelly formation are essentially similar processes. Blood may be regarded as an unstable colloidal system which remains fluid in the body partly due to its motion and partly to the capillary action of the blood vessels.

We[2] have investigated the influence of various electrolytes on the time of setting of jellies as well as on the extent of syneresis with numerous inorganic and some organic jellies. Moreover we have shown that a sol is stabilised by the adsorption of similarly charged ions and is sensitised by the oppositely charged ions, and under similar conditions, the uncharged particles are more hydrated than the charged ones. By the adsorption of similarly charged ions, the charge on the particles increases and the system becomes more stable, less viscous, and less hydrated.

Blood is regarded as a negatively charged fibrin sol, which exists in the liquid condition in some mysterious way. When it is collected in a glass vessel, it spontaneously forms a solid clot within a few minutes, but it is well-known that if it is received in solutions of sodium, or ammonium oxalate, fluoride or citrate, it can remain liquid indefinitely, and further if calcium chloride is added in excess to the oxalated or citrated blood, the clotting occurs normally. As normal blood also contains calcium, this behaviour was ascribed to the formation of insoluble or undissociated calcium salts of citrated and oxalated blood and thus to the removal of calcium ions. We have shown in the previous communication that blood has a great tendency to adsorb similarly charged ions from such electrolytes as sodium acetate, tartrate and citrates, and also potassium fluoride and oxalate, and the stabilising influence of the salt is due to this fact and not to the removal of calcium ions.

In the present communication, we have investigated the influence of the concentration of electrolytes on the extent of syneresis and have shown that blood is markedly stabilised by the addition of calcium chloride.

For these experiments on the syneresis of blood-clot, goat's blood was received in 250 c.c. glass bottles containing different amounts of electrolytes and made up to a definite volume. A blank experiment was always performed with the same blood, as the blood from different animals behaves slightly differently. After definite intervals, synerised serum was carefully collected in a graduated measuring cylinder and the volume was measured. The experiments were carried at the room temperature (27°-29°). The results are recorded in the following tables:

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[1] J. Phys. Chem., 33, 459 (1929).

[2] J. Indian. Chem. Soc., 6, 587 (1929); 7 (1930).

TABLE I

Influence of Dilution of Syneresis

Time	Amount of syneresis	
	250 c.c. blood	230 c.c. blood + 20 c.c. water
30 minutes	9 c.c.	28 c.c.
1 hour	30	58
1 hour 30 minutes	47	77
2 hours 30 minutes	67	99
3 hours 30 minutes	83	112
4 hours 30 minutes	93	118
5 hours 30 minutes	98	122
17 hours	127	151
22 hours	129	141

The serum when no water was mixed was straw-coloured, but in the presence of water, blood was hemolysed and the serum was dark red.

TABLE II

Influence of Potassium Chloride on Syneresis

5 c.c., 10 c.c. and 15 c.c. of 3N potassium chloride made up to 20 c.c. were taken into bottles in which 230 c.c. blood were received. In the blank bottle, 20 c.c. of water and 230 c.c. of blood were taken.

Time	Amount of syneresis			
KCl	0	5 c.c.	10 c.c.	15 c.c.
30 min.	10 c.c.	16 c.c.	2 c.c.	0.5 c.c.
1 hr.	38	30	5	1.0
1 hr. 30 min.	50	48	5	3
2 hr. 30 min.	67	63	7	4
3 hr. 30 min.	83	74	7.5	4.5
4 hr. 30 min.	93	81	8	5
5 hr. 30 min.	98	83	8	7
21 hr.	128	127	8	8

Hemolysis was checked in the presence of potassium chloride and the serum was straw coloured.

TABLE III

Influence of Calcium Chloride on Syneresis

Concentration of calcium chloride = 1.76 M

Blood = 230 c.c. Total volume = 250 c.c.

Time / $CaCl_2$	Amount of syneresis 0	5 c.c.	6 c.c.	7 c.c.	8 c.c.
30 min.	2 c.c.	0.2 c.c.	0	not set	not set
1 hr.	21	0.2	0	just set	not set
1 hr. 30 min.	51	0.2	0.1	0	not set
2 hr. 30 min.	73	0.2	0.1	0	not set
3 hr. 30 min.	86	0.2	0.1	0	not set
4 hr. 30 min.	92	0.7	0.1	0	not set
5 hr. 30 min.	92	1.0	0.1	0	not set
13 hr. 30 min.	108	2.0	1.0	0.5	—
21 hr. 30 min.	110	7.0	—	—	just set
48 hrs.	—	—	—	—	3 c.c.

TABLE IV

Influence of Ammonium Sulphate on Syneresis

Concentration of ammonium sulphate = 2M

Blood = 230 c.c. Total volume = 250 c.c.

Time / Am_2SO_4	Amount of syneresis 0	5 c.c.	8 c.c.	11 c.c.
30 min.	28 c.c.	29 c.c.	2 c.c.	not set
1 hr.	59	56	15	just set
1 hr. 30 min.	70	71	17	2
2 hr.	81	82	64	8
3 hr. 30 min.	102	103	84	27
4 hr. 30 min.	102	108	92	36
5 hr. 30 min.	108	113	94	41
13 hrs.	119	128	117	52
17 hrs.	122	128	118	55

TABLE V

Influence of Potassium Oxalate on Syneresis

Concentration of potassium oxalate = N

Blood = 230 c.c. Total volume = 250 c.c.

Time / Potassium oxalate	Amount of syneresis 0	2 c.c.	3 c.c.	4 c.c.
30 min.	10 c.c.	10 c.c.	not set	not set
1 hr.	57	57	2 c.c.	half set
1 hr. 30 min.	85	68	4	half set
2 hr.	96	70	5	just set
3 hr. 30 min.	115	75	8	2 c.c.
4 hr. 30 min.	118	78	12	4
5 hr. 30 min.	121	78.5	13	5

TABLE VI

Influence of Sodium Acetate on Syneresis

Concentration of sodium acetate = N

Blood = 230 c.c. Total volume = 250 c.c.

Time / Sodium acetate	0	Amount of syneresis 2 c.c.	4 c.c.	6 c.c.
30 min.	20 c.c.	30 c.c.	32 c.c.	39 c.c.
1 hr.	31	56	66	62
1 hr. 30 min.	66	75	84	78
3 hr. 30 min.	100	105	115	112
4 hr. 30 min.	108	108	118	117
5 hr. 30 min.	115	111	122	121
20 hrs.	130	111	135	135

TABLE VII

Influence of Sodium Tartrate on Syneresis

Concentration of sodium tartrate = N

Blood = 230 c.c. Total volume = 250 c.c.

Time / Sodium tartrate	0	Amount of syneresis 2 c.c.	4 c.c.	6 c.c.
30 min.	6 c.c.	34 c.c.	42 c.c.	32 c.c.
1 hr.	64	62	67	52
1 hr. 30 min.	77	77	80	66
2 hr.	82	84	86	74
2 hr. 30 min.	92	93	94	80
3 hr. 30 min.	106	102	107	91
4 hr. 30 min.	111	105	113	93
16 hrs.	120	120	125	113

TABLE VIII

Influence of Sodium Citrate on Syneresis

Concentration of sodium citrate = N

Blood = 230 c.c. Total volume = 250 c.c.

Time / Sodium citrate	0	Amount of syneresis 2 c.c	4 c.c.	6 c.c.
30 min.	26 c.c.	31 c.c.	half set	not set
1 hr.	61	62	half set	not set
1 hr. 30 min.	86	70	half set	not set
2 hr. 30 min.	109	94	half set	not set
3 hr. 30 min.	120	113	just set	not set
4 hr. 30 min.	121	116	0	not set
14 hrs.	—	—	10 c.c.	loose clot disturbed

TABLE IX

Influence of Potassium Fluoride on Syneresis
Concentration of potassium fluoride = 4.08 N
Blood = 230 c.c. Total volume = 250 c.c.

Time	Amount syneresis			
K_2F_2	0	1 c.c.	3 c.c.	5 c.c.
30 min.	21 c.c.	7 c.c.	not set	not set
1 hr.	56	14	setting begins	not set
1 hr. 30 min.	80	22	loose clot	not set
2 hr. 30 min.	97	30	0	not set
3 hr. 30 min.	104	39	0	not set
4 hr. 30 min.	111	44	0	setting begins
14 hrs.	122	50	7	0

TABLE X

Influence of Sodium Hydroxide on Syneresis
Concentration of sodium hydroxide = 2.47 N
Blood = 230 c.c. Total volume = 250 c.c.

Time	Amount of syneresis			
NaOH	0	2 c.c.	5 c.c.	8 c.c.
30 min.	19 c.c.	6 c.c.	not set	not set
1 hr.	53	17	not set	not set
1 hr. 30 min.	61	25	not set	not set
2 hr.	84	30	not set	not set
3 hr.	98	42	not set	not set
4 hr.	104	47	not set	not set
4 hr. 30 min.	—	—	setting begins	not set
5 hr.	110	54	sets	not set
17 hr.	122	65	firm clot, no syn. in 2 days	not set

Our results on the syneresis of blood recorded in the above tables show that as the concentration of electrolytes is increased, the amount of syneresis gradually decreases and in some cases the syneresis of blood clot is totally stopped. Even in two days, no marked syneresis is observed. In some cases, with the increase in the concentration of electrolytes, the blood becomes so stable that it either sets after a long time or it does not set at all.

In a previous communication,[1] we have investigated the influence of the concentration of electrolytes on the syneresis of various inorganic jellies. We have shown that as the concentration of the coagulating electrolytes, i.e., those electrolytes from which ions containing charge opposite to that of the sol are mostly adsorbed, is increased, the amount of syneresis is increased.

[1] J. Indian. Chem. Soc. (1930).

From our results we have also shown, that by increasing the concentration of coagulating electrolytes the time of setting of jellies is much decreased.

The behaviour of blood is quite contrary to that of the jelly-forming inorganic sols. It possesses a high tendency to adsorb similarly charged ions, i.e., anions; and does not appear to adsorb cations to a marked extent. For this reason, the addition of electrolytes invariably stabilises blood. The function of stabilising ions in the cases of jellies is to increase the original time of setting and decrease the extent of syneresis. Thus on increasing the concentration of the stabilising electrolytes, the following may happen:—

(i) Up to a certain limit—no marked influence on the extent of syneresis of the original clot.

(ii) Up to the second limit—gradual decrease in the amount of syneresis.

(iii) Within the next limited range—total inhibition of syneresis.

(iv) Above this limit—blood not clotting at all, but remaining fluid indefinitely.

Hence the function of stabilising electrolytes is just opposite to that of the coagulating electrolytes. From our observations, it will be seen that blood has a high tendency to adsorb chloride, sulphate, oxalate, citrate, fluoride and hydroxyl ions, and in presence of these, the amount of syneresis is markedly decreased. Acetate and tartrate ions do not possess much stabilising influence. In the following table, the comparative influence of acetate, tartrate, citrate and oxalate has been recorded.

TABLE XI

Concentration of salts = N

Blood = 230 c.c. Total volume = 250 c.c.

4 c.c. of N salts have been mixed with blood

Time	Amount of syneresis			
	Sodium acetate	Sodium tartrate	Sodium citrate	Potassium oxalate
30 min.	32 c.c.	42 c.c.	half set	not set
1 hr.	66	67	half set	half set
1 hr. 30 min.	84	80	half set	half set
3 hr. 30 min.	115	107	just set	2 c.c.
4 hr. 30 min.	118	113	set, no syn.	4 c.c.
5 hr. 30 min.	122	—	0	5

From this, it will be seen that the stabilising influence of these ions is in the following decreasing order:

citrate > oxalate > tartrate > acetate.

Our results on the influence of calcium chloride on the syneresis of blood clot show that even in presence of calcium, chloride ions are preferentially adsorbed, and the view that the stabilising influence of citrate, oxalate,

fluoride, and other anions is due to the removal of calcium ions appears to be incorrect. We have shown that by increasing the concentration of calcium chloride also, blood is much stabilised, and the amount of syneresis is markedly decreased, and at higher concentrations, blood does not set at all. This is due to the high tendency for the adsorption of chloride ions, as has been observed in the case of potassium chloride also.

In Table XII we are indicating the approximate concentrations of various salts necessary to stabilise the blood to such an extent that no marked syneresis may occur after formation of the clot within 12 hours.

TABLE XII

Electrolyte	Concentration to give clot undergoing no marked syneresis
Potassium chloride	0.12 N
Calcium chloride	0.0845 N
Ammonium sulphate	0.176 N
Potassium oxalate	0.016 N
Sodium citrate	0.016 N
Potassium fluoride	0.049 N
Sodium hydroxide	0.039 N

From the table it will be seen that the stabilising influence of these salts is in the following decreasing order:

$$Na_3Cit > K_2Oxalate > NaOH > K_2F_2 > CaCl_2 > KCl > Am_2SO_4$$

From this order it appears that the stabilising influence depends both on the valency of the ions and alkalinity of the medium.

The clotting of blood has generally been regarded as the conversion of soluble fibrinogen to insoluble fibrin under the action of an enzyme known as thrombin. We are of the opinion that thrombin may assist the process of clotting but it is not essentially the cause of the phenomenon. The clotting of blood is guided by the same forces which bring out the gelation of other organic and inorganic jellies. Fibrin has a high hydration tendency and yields an unstable colloidal suspension. The clotting of blood is guided by the characteristic unstable nature of fibrin, its concentration, and the nature and concentration of electrolytes present in blood, and all this has been so well regulated in blood, that as soon as the capillary action of blood-vessels and circulatory motion are stopped, jelly-forming forces begin to act and finally a solid clot is obtained in a few minutes. The presence of an excessive amount of coagulating electrolyte causes the agglomeration of particles, and the contraction of the clot and the synerised serum is squeezed out of the network. Such syneresis has been observed with various inorganic jellies, such as those of vanadium pentoxide, silicic acid, ferric arsenate, borate and various zirconium jellies. These jellies on ageing, lose markedly the hydration capacity, and on account of the agglomeration of particles give out the solvent.

In previous communications[1] from these laboratories, we have mentioned that the process of jelly formation is guided by the agglomeration and hydration tendencies of the particles. In presence of coagulating electrolytes, the charge on the jelly-forming sol decreases and the amount of hydration increases up to a limiting value. When the concentration of the electrolyte is increased, agglomeration of the particles begins, with the result that the jelly contracts and undergoes syneresis. The same is applicable to the blood clot also. Under the action of coagulating ions, blood forms a clot, and due to the presence of an excess of the same ions, its particles agglomerate and undergo contraction, and finally the serum is squeezed out.

Waele[2] has shown that the blood-fibrinogen exists in a highly buffered system, of which the pH, however, is subject to variations. He has also observed that fibrinogen is precipitated at pH 5-6, forms a gel at pH 7-9, and remains dissolved at pH 10. This dissolution of fibrinogen can be explained on the view that it is stabilised by the adsorbtion of similarly charged OH' ions from the alkaline medium. The observations of Herzfeld and Klinger[3] that acids accelerate the precipitation of fibrin and alkalis exert an inhibitory action can also be explained on the same basis. As we have mentioned in a previous paper,[4] the clotting tendency of blood is most marked near the neutral point. On the acid side and alkaline side, the charge on the blood is increased and hence the hydration tendency is less. Stuber and Heim[5] have observed that the coagulating action of fatty acids increases with the increasing number of carbon atoms in the acids, i.e., in the decreasing order of the dissociation constants. The fall in the coagulating action of the lower members of the series is due to the fact that comparatively larger amounts of hydrogen ions are given out in the presence of these acids and the medium becomes acidic, whereby the charge on the plasma is increased and the system is stabilised.

Summary

1. The influence of different concentrations of potassium chloride, calcium chloride, ammonium sulphate, potassium fluoride, potassium oxalate, sodium acetate, tartrate, citrate, and hydroxide on the extent of syneresis of blood clot has been studied.

2. It has been observed that in all the cases, the amount of syneresis decreases as the concentration of the electrolytes is increased. In some cases, the syneresis is totally stopped and in a few cases, the electrolytes prevent the clotting of blood.

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[1] J. Indian. Chem. Soc., 6, 391 (1929).
[2] Ann. physiol. physico chim. biol., 3, 94 (1927).
[3] Biochem. Z., 71, 391 (1915).
[4] Loc. cit.
[5] Biochem. Z., 77, 333 (1916).

3. The influence of electrolytes is explained on the view that blood has a high tendency of adsorbing similarly charged ions from the salts, and thus the electric charge on blood is increased and it is stabilised. The stabilising influence of the salts is in the following order:

Sodium citrate > potassium oxalate > NaOH > K_2F_2 > $CaCl_2$ KCl > Am_2SO_4.

4. It has been shown that the stabilising influence of fluorides, citrates or oxalates is not due to the removal of calcium ions from the blood, but it is due to the stabilising influence of anions which are largely adsorbed by blood.

5. The syneresis and clotting of blood are guided by the same forces which give rise to the syneresis and formation of inorganic and organic jellies.

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June, 1930.

STUDIES ON THE POROUS DISC METHOD OF MEASURING OSMOTIC PRESSURE[1]

BY F. T. MARTIN AND L. H. SCHULTZ

Introduction

The osmotic pressure of a solution because of its magnitude, should be the most sensitive method available for determining the escaping tendency of the solvent.

The use of a semipermeable membrane, in making this measurement, is difficult because there is no certainty that it will act as a simple sieve. Furthermore it is practically impossible to obtain a membrane impermeable to all ions.

The method of Frazer and Patriek[2] in which tension is exerted on the solvent by means of a porous disc is not beset by these difficulties. It is more straightforward from a theoretical standpoint and so long as the solute is nonvolatile the true escaping tendency of the solvent is certainly being measured. The Donnan membrane equilibrium is also eliminated making the accurate measurement of the osmotic pressure of colloidal solutions a possibility.

On the other hand, while the membrane is eliminated in the porous disc method, other difficulties arise. Air-free or nearly air-free conditions must prevail. The temperature must remain quite constant and a great many other small sources of error must be eliminated.

It was the object of this investigation to study the porous disc method of measurement and to remove, as far as possible, the various difficulties encountered. To this end the original method of Townend was considerably modified and several pieces of special apparatus were developed.

The Thermostat

A drawing of the thermostat, used in this work, is shown in Figure 1. The main bath was a copper tank a meter high and a meter in diameter. It was insulated with "ozite" and was provided with a window about 9 centimeters wide and 41 centimeters long. The propeller, run by the motor M, stirred the water upward.

The thermoregulator T consisted of a long helix of ¼" copper tubing filled with toluene prepared by the method of Beal and Souther.[3] It was provided with an oscillating contact as described by Gouy,[4] and sparking was avoided at the contact by using a radio tube as a relay.[5]

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[1] This paper is abstracted from two dissertations submitted by the authors to the Board of University Studies of the Johns Hopkins University as part of the requirement for the degree of Doctor of Philosophy.

[2] R. V. Townend: J. Am. Chem. Soc., 50, 2958 (1928).

[3] J. Am. Chem. Soc., 49, 1994 (1927).

[4] J. Phys., 6, 479 (1897). Also Sligh: J. Am. Chem. Soc., 42, 60 (1920).

[5] Beaver and Beaver: Ind. Eng. Chem., 15, 359 (1923).

The bath was continuously cooled with water at a constant temperature flowing at a constant rate from a small secondary thermostat thru the coil C. The heat input thru the heater H was governed by the regulator T.

When necessary the water in the small thermostat was cooled with water from a silica gel refrigerator.

The main thermostat was kept at about 27°, the secondary thermostat at about 21° and the water in the refrigerator tank at about 5°. When the

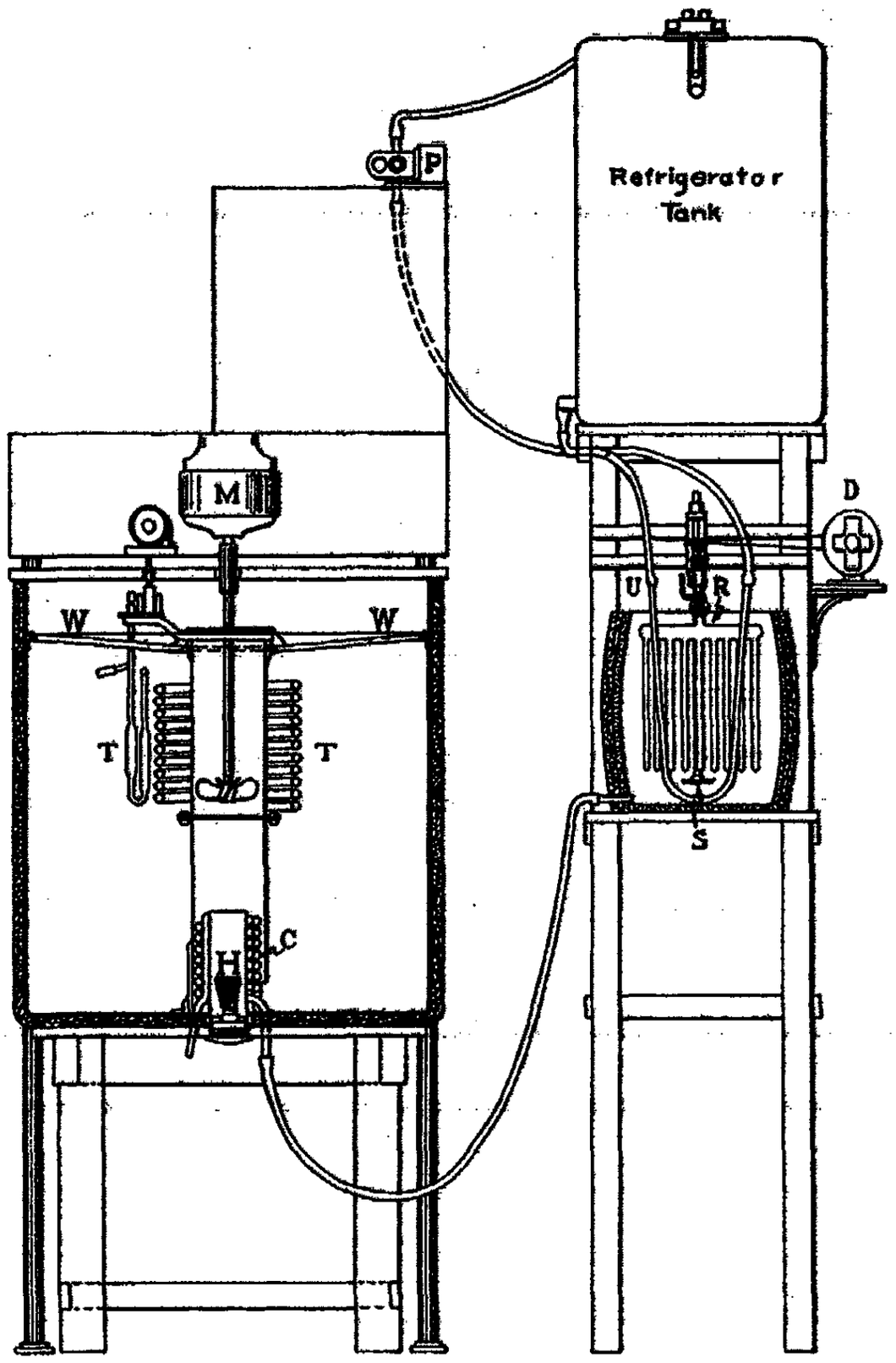

FIG. 1

bath was operating properly a Beckmann thermometer that could be read to 0.001° indicated no change in temperature altho it was tapped vigorously with a special "tapper".

Glass Apparatus and Method of Procedure

The glass apparatus is shown in Fig. 2. The tube 1 led to a mercury vapor diffusion pump backed by a Nelson oil pump. The pumps were protected by the trap 2 which could be surrounded by a mixture of solid carbon dioxide and ether.

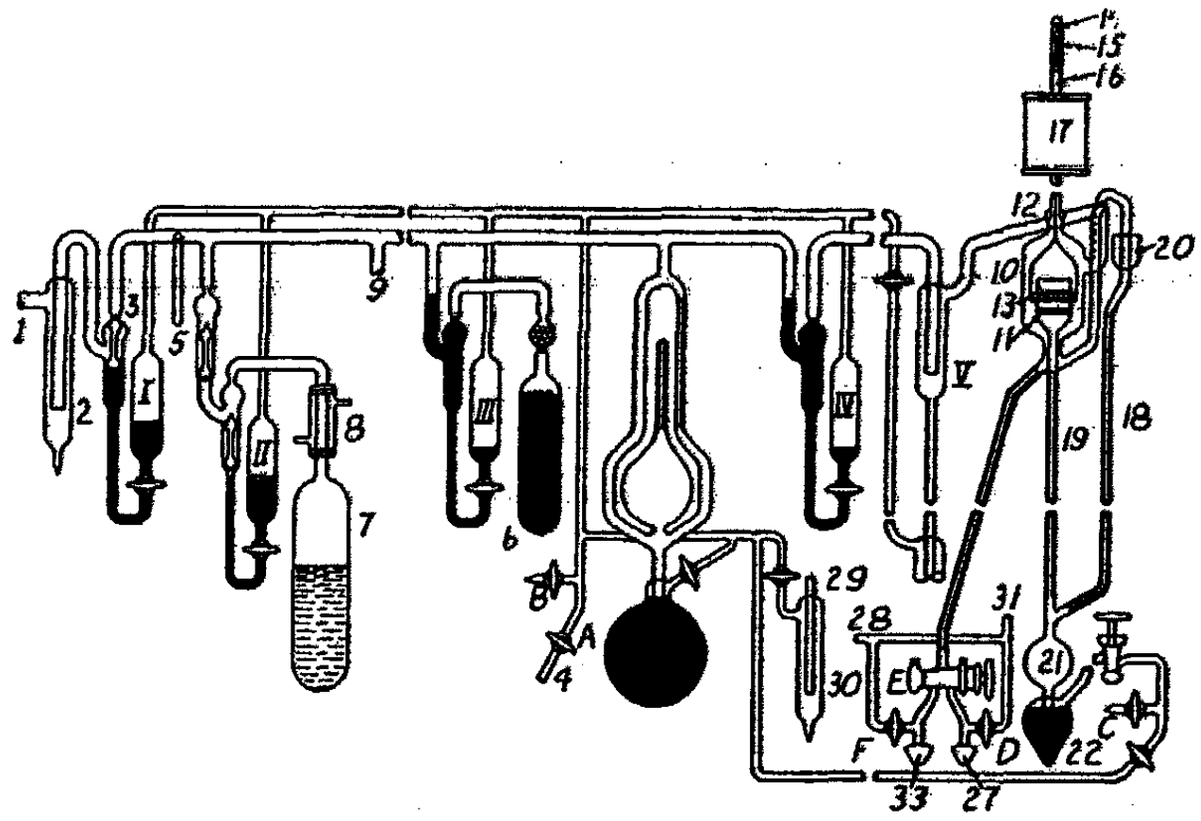

Fig. 2

The mercury cut-offs I, III, and IV were each provided with a stopper 3 which fit into a ground seat when the mercury was raised. Atmospheric pressure could be exerted on the mercury in the left hand limb of these cut-offs while a vacuum was maintained to the right. These cut-offs together with the McLeod gauge etc. were operated by means of a "secondary system" which could be evacuated with a Hyvac oil pump thru the tube 4 and the stopcock A. Air entered the secondary system thru stopcocks B and C.

It was necessary to remove practically all permanent gases from the system before satisfactory measurements could be made. Only under these conditions would the water stick to the disc. Permanent gases also interfered with the process of distillation whereby contact was made between the pure solvent and the solution. This was especially true when vapor was passing from the solution thru the disc into the solvent.

Owing to the fineness of the pores of the disc the removal of air from it was extremely slow, especially as no means were provided for baking the disc while it was being evacuated.

The vacuum pumps reduced the pressure of the gases in the system to less than 1×10^{-5} mm. A more complete removal of permanent gases was

accomplished by exposing the system to the cocoanut charcoal contained in bulb 6. The charcoal was prepared by evacuating and heating it to 480° for four or five hours. When opened to the disc it was immersed in liquid air. After 28 days of such treatment (during which time the accumulation of air on standing progressively diminished) a pressure of 10^{-4} mm. developed in two days. The disc as finally used was deaerated 42 days.

Air-free Water. It was, of course, necessary to use air-free water under the disc. Ordinary distilled water was boiled to ¼ its volume to remove most of the air. It was then introduced into the bulb 7 (and another similar bulb at 9) thru a side arm (not shown) which was then connected to a vacuum and sealed off while the water was boiling thru it. The bulbs were kept warm and the water was continuously refluxed by using the small condenser 8. The vapor and accumulated air were removed from time to time by expanding them into the outer system. Four hours after introduction the pressure of the accumulated air was 2.5×10^{-5} mm. After 86 days of deaeration, the air which accumulated in five days gave a pressure in the system of 2×10^{-5} mm. This water was entirely satisfactory for use under the disc.

Freezing and sublimation methods of deaeration were also tried, but we found none of them as good as the above procedure.

The Osmometer. The cut-off IV was just outside the thermostat and was used to protect the osmometer. Another cut-off V inside the bath and under water kept water vapor from getting out of the apparatus in the thermostat.

The main part of the apparatus was the osmometer. It consisted of a flask 10 made of pyrex tubing 7.5 cm. in diameter. Inside this was a sort of funnel holding the porous disc 11.

The flask 10 was fitted with a ground glass stopper 12 that could be mercury sealed. The joint was not greased. The stopper had a long tube sealed to it which stuck up out of the thermostat. It contained the mechanism for operating the platinum gauze stirrer 13 by means of the solenoid 17 and a suitable commutator.

The manometer for measuring the osmotic pressure consisted of the capillary tubes 18 and 19.

The Porous Disc. The porous disc was made of a special clay and ground[1] pyrex glass. Both clay and pyrex were passed thru a 200 mesh sieve. Equal parts by weight were then carefully mixed and water was added to make a not too stiff paste. From this the discs were molded in a plaster of Paris mold. They were about 3 cm. in diameter and 2 mm. thick. It may be mentioned that a mixture containing 75% pyrex was unsatisfactory.

A layer of fine sand was now placed on the bottom of a large porcelain crucible. After making the surface of this sand quite flat the disc was carefully placed on it and covered with more sand which was made flat on top. Another disc could now be laid on this surface and covered with sand.

In this way as many as four discs could be placed in a horizontal position in the crucible. Besides making it possible to bake four discs at once, this

[1] Townend: J. Am. Chem. Soc., 50, 2961 (1928).

arrangement made the heating of the discs more even, their cooling slower, and minimized warping.

The crucible was now heated in a small electric pot furnace, and the temperature being slowly raised to 950°, which is somewhat above the melting point of pyrex. It was held at this temperature for 45 minutes when the current was turned off and the discs were allowed to cool in the furnace.

The baked discs were very hard and quite porous and it was usually unnecessary to grind their faces to get rid of imperfections. However, it was very important to grind the edges of the discs smooth on a large grindstone. If this was not done the discs could not be sealed into pyrex funnels, but if they were ground properly, this operation was very easy and successful.

The discs after being sealed into their funnels were tested by filling the space under the disc with water. A capillary tube also filled with water was then attached and its other end was dipped into mercury. Air was now blown over the disc and if the mercury rose in the capillary to more than the height required for the apparatus, the disc was satisfactory.

Cleaning the Osmometer. The measurements of osmotic pressure were carried out on dilute aqueous solutions of potassium chloride. The concentration of the solutions could not exceed 0.007 molar because of the dimensions of the apparatus. As it was desired to carry the determinations of osmotic pressure to solutions of extreme dilution, great care was taken to thoroughly cleanse the disc, the osmometer and the mercury used in it. The osmometer assembly was washed successively with a mixture of nitric and chromic acids, dilute nitric acid, and conductivity water until a sample of the washings draining thru the disc in two days showed a specific conductance of 1.3×10^{-6} mohs. A check sample of the same water a little better protected from the air had a conductance of 1×10^{-6} mhos.

The mercury used was first treated in turn with dilute nitric acid and distilled water in a dropping column. It was then redistilled and washed repeatedly with conductivity water.

Preparation for making a Measurement. To prepare for making a measurement, air-free water was first distilled from the bulb 7 to the top of the capillary 18 by allowing cold water to flow into the cup 20. Thence the air-free water ran down 18 to the bulb 21. When a little more than was sufficient to fill the space under the disc had collected, the water was forced up thru the disc, by regulating the air pressure over the mercury in the bulb 22, until the mercury in the tube 19 was one or two centimeters below the top of the capillary portion. The excess water on top of the disc and in the tube 18 was then distilled into the condenser tube 5 by surrounding it with ice.

When necessary additional water could be added to that under the disc by carefully introducing small portions into the bulb 21 and then forcing them up thru the capillary 19 at the top of which the water would pass around the mercury.

Once the water was stuck to the disc the level of the mercury in the outer capillary could be changed at will resulting in the application of various tensions to the column under the disc. The level of the mercury meniscus in

the capillary 19 varied slightly when the tension was changed due to readjustment of the water surfaces in the capillaries of the disc to the position of equilibrium.

Preparation of the Solution. The potassium chloride used for preparing the solutions was "Kahlbaum for analysis" and was twice recrystallized from conductivity water with pure hydrogen chloride.

The conductivity water was made by distilling ordinary distilled water containing neutral permanganate. The still was of the type described by Dexter[1] and consisted of a large pyrex flask with a block-tin cap connected to a pyrex settling column by a block-tin tube. The condenser was also of block-tin. The flask was heated electrically. The water obtained from this still in one operation and without taking any special precautions usually had a conductivity of 10^{-6} mohs.

Since the solution cup held about 60 cc. and the highest concentration to be used was 0.007 molar, approximately 32 mg. of salt were dissolved in 150 cc. of conductivity water. The solution was slowly boiled down to about 65 cc. in a pyrex flask on an electric heater in order to remove air from it.

Introduction of the Solution into the Osmometer. The hot solution was put into the "solution introducer" Fig. 3. This consisted of a bulb 23 for holding the solution and a mercury reservoir 24 which was set in a wooden block 25. The whole was supported from a large tripod by three springs in the manner indicated by the arrows. The neck of the bulb 23 had a seat 26 ground to fit the stopper 27 (Fig. 2). By means of thumb nuts fastened to the springs the "solution introducer" could be brought up to the stopper 27 and after a little manipulation the ungreased joint could be sealed with mercury.

The vapors above the warm solution were removed by evacuating several times thru the stopcock D and the tube 28 (Fig. 2) which was connected to the tube 29 thru pressure tubing. The Hyvac pump was protected by the trap 30 which was surrounded by solid carbon dioxide. Tube 32 (Fig. 3) was connected thru a two-way stopcock and suction tubing to tube 31 (Fig. 2) so that the space over the mercury in bulb 24 (Fig. 3) was evacuated at the same time as the space above the solution.

When no air bubble was observed, on forcing the solution up against the stopcock E (Fig. 2) the liquid was allowed to cool and was then forced up thru the stopcock E into the osmometer until its surface in the flask 10 was a little above the level of the disc. The solution was then stirred and further deaerated for two days by occasionally removing the vapors from the osmometer by expanding them into the outer evacuated system. To avoid possible splashing of the solution it was never opened directly to the pumps.

Analysis of the Solutions. Owing to changes in the concentration of unknown magnitude during the process of deaeration it was necessary to analyse the solution after removal from the osmometer following the determination of the osmotic pressure. Samples for analysis were removed without admitting air. It was thus possible to prepare a new dilution by distilling air-free water

[1] J. Am. Chem. Soc., 44, 2468 (1922).

into the portion of the solution not removed. This was done by cooling the osmometer cell with a stream of ice water and slightly warming one of the air-free water bulbs. In this way it was found possible to make determinations on a whole series of dilutions with one salt without the annoyance of repeatedly having to deaerate the solution before use.

Electrical conductivity was chosen as a suitable means of determining the concentration of the small portion of dilute solution available for analysis.

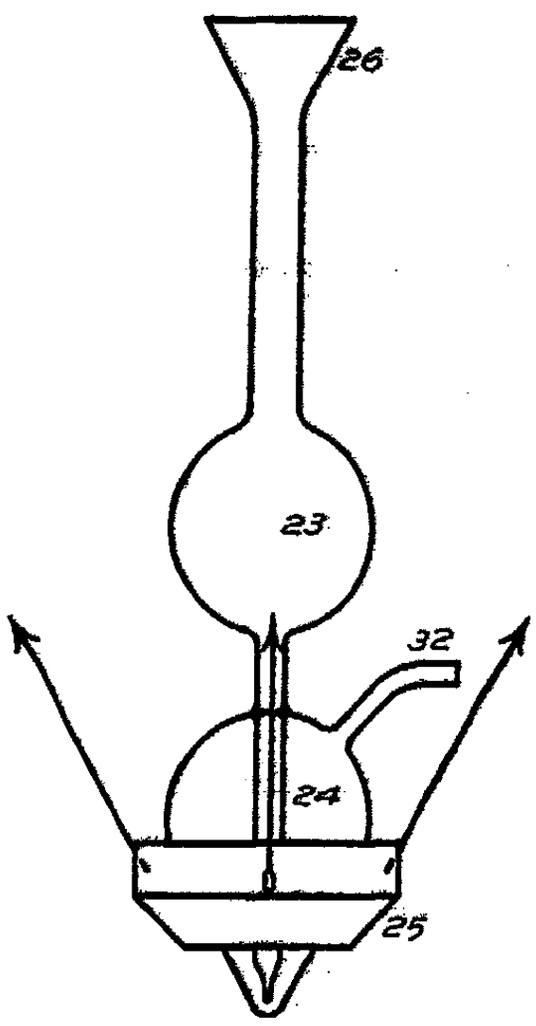

FIG. 3

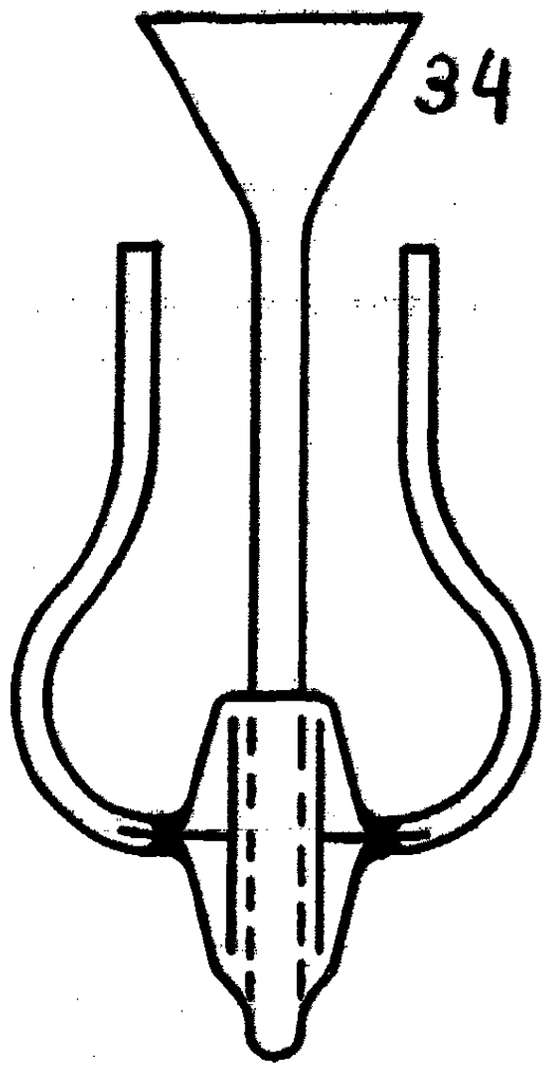

FIG. 4

A cell of pyrex glass (Fig. 4) having a volume of about 15 cc. was constructed. It was provided with a seat 34 ground to fit the stopper 33 (Fig. 2). When this ungreased joint was sealed with mercury the cell could be evacuated thru the stopcock F (Fig. 2) and the solution was dropped into it thru stopcock E. Before taking out the sample a small portion of solution was removed to flush out the stopcock E and the lower parts of the capillary tube above.

The conductivity of the sample was referred to a curve of conductivities for different standard solutions of the salt. These known solutions were measured in the same cell under conditions duplicating as nearly as possible the actual experimental procedure described above. At low concentrations the widest deviation of the standard conductivities from a regular curve was one and one-half per cent. All measurements of conductivity were corrected to the same temperature.

Measurements. Osmotic pressures were determined by estimating the tension exerted on the pure water under the disc at which distillation to or from the solution did not take place or, in other words, that tension at which there is no movement of the mercury meniscus in the capillary under the disc. By observing the rate of movement up or down of this meniscus when different tensions were applied, the required data were obtained. The tension was considered as being made up of the difference in height between the two mercury meniscuses added to the height of solution above the inner mercury meniscus in terms of water height all reduced to terms of height of mercury at zero degrees centigrade. All positions were read by a cathetometer on which they could be duplicated within 0.04 mm. The average of three readings was used for each position and the rate of movement was generally determined from five or six positions observed at about one hour intervals. Owing to the large surface the solution height was determined but once for each dilution as the amount of transfer of the solvent by distillation was extremely small. Because of occasional shifting of the entire apparatus it was necessary to observe, in connection with each set of readings, the height of a point of reference on the glass and make a correction when such shifts were noted. The largest sudden change in elevation of the entire apparatus observed was 0.2 mm. The probable cause of the shifting of the apparatus was that the thermostat tank, the bottom of which was made of copper, and was a meter in diameter, rested on a mat of ozite felt and may have been inclined to buckle.

The data needed in the determinations were height of the solution, height of the two mercury meniscuses, height of the reference point, time of each reading, and temperature of the bath. In case of a change in temperature greater than 0.002 degree the series was stopped and another not commenced until close regulation was restored.

The first experiments resulted in greater distillation from the disc than could be accounted for by the solutions in the osmometer. It was found that where the tube containing the spring suspension for the stirring device passed through the surface of the water in the bath there was a fog of condensed moisture. Though the room temperature was kept higher than that of the bath and the latter was covered with a lid, the evaporation from the surface of the water in the bath lowered the temperature sufficiently to cause distillation in the evacuated system. An air-tight housing over this part improved matters and results were more satisfactory but still too high. Later inspection showed that condensation was taking place even in some of the immersed tubes especially those nearest the central chimney. It was thought, despite fairly good stirring, that water cooled at the surface might stream down onto the apparatus and cause distillation. The entire bath was covered with liquid paraffin oil to stop surface evaporation and again the results showed noticeable improvement. There was still, however, reason to believe that the results were being influenced by non-uniformity of temperature perhaps from water pouring out of the top of the central chimney. Some improvement was noted after erection of a baffle to shield the apparatus from the currents of water directly from the chimney. Stirring downward was not feasible with the

apparatus as constructed. A reconstruction of the apparatus placing trap V as closely as possible to the osmometer would be a desirable change suggested by this experience.

Results. As previously stated the first trials were unsuccessful. The determinations reported here were made after most of the changes related in

TABLE I

Solution 0.0020 molar KCl Temperature 26.429°C

	Tension mm. mercury @ 0 C	Time, hours	Height of Meniscus millimeters	Rate of Distillation mm. per hour
A.	64.48	0	0	
		0.63	0.062	
		1.11	0.101	
		2.42	0.183	
		3.20	0.194	
		3.68	0.221	
		4.30	0.291	
		5.13	0.328	0.075
B.	82.40	0	0	
		0.87	0.014	
		1.42	0.075	
		1.97	0.088	
		4.48	0.114	
		4.89	0.120	
		5.70	0.175	
		6.23	0.190	0.028
C.	104.75	0	0	
		1.02	−0.024	
		1.92	−0.044	
		3.18	−0.116	
		3.88	−0.079	
		5.40	−0.119	
		6.63	−0.144	
		7.50	−0.171	−0.022
D.	122.94	0	0	
		1.90	−0.113	
		2.57	−0.112	
		3.12	−0.203	
		3.75	−0.214	
		4.65	−0.310	
		5.95	−0.330	
		6.23	−0.372	
		6.55	−0.394	−0.057

the preceding paragraph were carried out. As an illustration of the data and results, those data and results for the solution 0.0020 weight molar are given in Table I. The rates of distillation were calculated from the data by the method of moments. To show the relation of the individual coordinate points to the curves representing the calculated slopes and intercepts the results are shown graphically in Fig. 5. By reference to the scale it will be seen that the deviation of individual points from the curves is in very few cases greater than the limits of accuracy of the cathetometer readings.

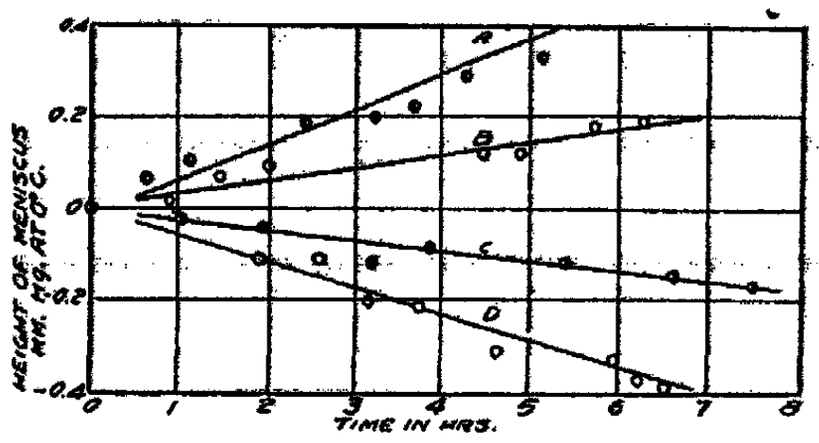

FIG. 5

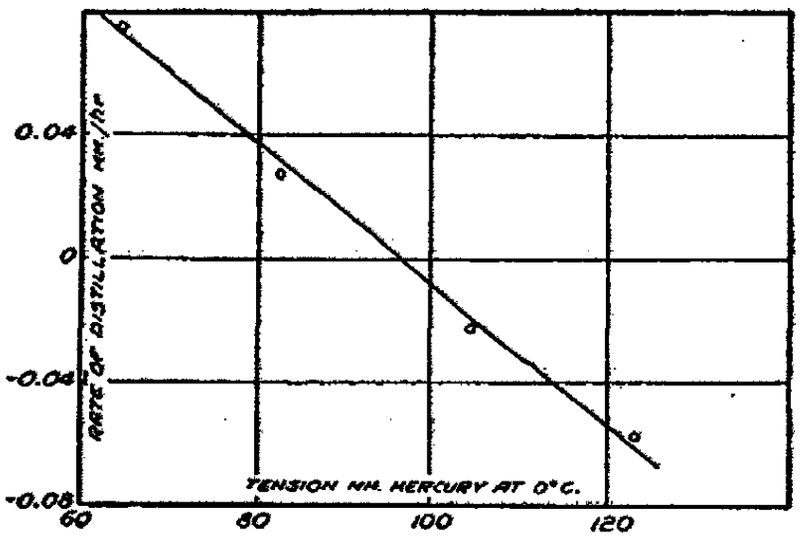

FIG. 6

Applying mathematical analysis to the rates and tensions given above, the calculated tension for zero rate of distillation, which should be the value of the osmotic pressure, is 96.5 mm. The graphic representation of these coordinate points and the curve drawn to the calculated slope and intercepts are shown in Fig. 6.

The results of five determinations on three solutions are shown in Table II. The ratio of the observed osmotic pressure to that calculated for a nondissociated nonhydrated solute is given along with the experimental results.

It will be noted, in Table II, that there is a tendency for the results to be higher than would be expected. Also they are somewhat inconsistent in the case of the second solution, which was run over a very extensive period of time without removal. The explanation is offered that these high values, which are

TABLE II

Concentration moles KCl/1000 grams water	Tension for zero rate of distillation	Ratio of tension of zero rate of calc. os. press. of nondissociated solute.
0.00504	187 mm.	1.986
0.00298	112.4 mm.	2.015
0.00298	111.5 mm.	2.005
0.00298	136.5 mm.	2.45
0.0020	96.5 mm.	2.58

the result of too great distillation from the disc and too little back into it, are caused by distillation taking place in other parts of the apparatus. As the vapor pressure, lowering for a 0.0020 molar solution due to solute, is around 0.001 mm., which is roughly that for a decrease of 0.001 degree in temperature, lack of uniformity of temperature throughout the apparatus seems to be the most probable cause of error.[1]

In conclusion the authors wish to express their appreciation to Professor J. C. W. Frazer and W. A. Patrick who suggested this research and under whose direction it was performed.

Summary: 1. The porous disc method for directly measuring osmotic pressure was applied to dilute solutions of potassium chloride with sufficient success to justify further work on it.

2. Errors in results were traceable to unequal temperatures within the apparatus and therefore suggested refinements in construction of the system.

3. Distillation was obtained at will in either direction with relation to the disc, which had not been found possible in preliminary work on this method.

[1] The above explanation of the error is strengthened by results of later work done by Clara E. Miller using the same apparatus with pure water in the solution chamber. Operating in the usual way distillation was observed taking place from the disc even when slight tensions were applied. The water was tested for purity after removal and gave conductance measurements, checking those of the fresh conductivity water used. The only cause for distillation in this case would have been difference in temperature in different parts of the system.

THE ADSORPTION OF CHROMATE IONS BY COLLOIDAL ALUMINUM HYDROXIDE

BY BEN H. PETERSON AND KEITH H. STORKS

A great deal of research has been done on the adsorption and coagulating properties of electrolytes on colloidal suspensions of metallic hydroxides.[1] Many attempts have been made to formulate an equation which would express the relation between the amount of the coagulating ion adsorbed and the amount of the colloid of which the well known Freundlich isotherm is the most familiar.[2] The coagulation or precipitation values of different electrolytes on such colloidal systems have also been intensively studied in an attempt to find a relation between the valence of the coagulating ion, the mass of the colloid, and the effect of the associated ions. The actual mechanics of coagulation, that is, what actually happens to so reduce the stability of the system that the particles coalesce is rather difficult to picture. It has been shown,[3] that if the potential or charge on the colloidal particle is reduced below a certain value, the particles will adhere and coagulation take place. It hardly seems reasonable that this neutralization of the charge by adsorption of oppositely charged ions should be the same type of adsorption as that occurring *after* the coagulation of the system has taken place. If the mechanism of the adsorption which actually causes the coagulation is different from that which occurs on the surface of the coagulated particle, the adsorption isotherms as usually obtained may not have any significance in any theory attempting to explain the coagulating power of electrolytes.

A search of the literature did not reveal any data on adsorption at concentrations below that required for coagulation, although in many cases the isotherms are extrapolated to zero concentration of the electrolyte. If the above hypothesis be true, it follows that the adsorption isotherms obtained at concentrations less than and greater than that required for complete coagulation will show a break at that point where one type of adsorption ceases and the other begins. It was to test this hypothesis that the following experiments were performed.

Experimental

Aluminium hydroxide was precipitated from a purified sample of the chloride with ammonia. This was washed by decantation with distilled water until dispersion began. The partially purified precipitate was then

[1] Weiser: J. Phys. Chem., 28, 232 (1924); Gann: Kolloidchem. Beihefte, 8, 125 (1916); Weiser and Middleton: J. Phys. Chem., 24, 639 (1920); Sen: J. Phys. Chem., 31, 419, 525 (1927); Weiser: "The Hydrous Oxides" (1926); Ghosh and Dhar: "Studies on Adsorption," A series of researches published in J. Phys. Chem. during 1927-1929.

[2] Freundlich: "Kapillarchemie" (1922); Swain and Urquhart: J. Phys. Chem., 31, 231-76 (1927).

[3] Powis: Z. physik. Chem., 89, 91, 186 (1915).

dialyzed electrically using a potential drop of 80 volts until a moderately sensitive galvanometer placed in series gave only a slight deflection. This treatment yielded a product very free from adsorbed ions of any sort. The purified hydroxide was then dispersed in conductivity water and peptized with a few drops of hydrochloric acid. The positive suspension so prepared remained evenly dispersed during the three weeks it was allowed to stand before any samples were taken. Enough of the suspension for a complete run was transfered to a separate flask and 150 cc. samples transferred to each of twelve glass stoppered bottles. An equal volume of conductivity water was placed in an equal number of similar flasks to serve as blanks, and the suspensoid and water flasks paired. To each sample and corresponding blank was then added 50 cc. of a solution of potassium chromate of varying concentrations, each pair, suspensoid and blank, containing the same amount of electrolyte. The concentrations of the potassium chromate was so arranged that coagulation took place at about Flask No. 5. The entire set-up was allowed to stand three weeks to insure equilibrium. The residual chromate was determined by electrometric titration according to the method of Eppley and Vosburg[1] using a standard solution of ferrous sulphate. An aliquot part of the blank was titrated first and then an equal volume of the supernatant liquid in the cases where the colloid settled readily. Where coagulation was incomplete, the colloid was removed by ultra filtration using a special Berkfeld filter cone. The first few cc. of the filtrate so obtained was discarded in order to avoid any error on account of adsorption by the cone itself. Preliminary experiments showed no adsorption after the first few cc. had filtered through. The concentration of the chromate in the blank being known, the concentration of the residual solution from which the colloid had been removed could be calculated as:

$$\frac{\text{cc. } FeSO_4 \text{ for residual soln}}{\text{cc. } FeSO_4 \text{ for blank}} \times \text{Conc. blank} = \text{Conc. Res. Soln.}$$

and from this value the amount of chromate adsorbed could be determined by difference. The mass of the colloid was determined gravimetrically from samples taken at the beginning of the run.

Experimental Results

The results are recorded in the Table as, millequivalents chromate left unadsorbed, "C", millequivalents adsorbed, "X", in columns I and II. In column III are given the values of X/M, and in column IV the values for log. "C". In column V are given the values of log. X/M. The star marks the sample containing the lowest concentration of chromate that coagulated completely. M, is the mass of the colloid.

[1] Eppley and Vosburg: J. Am. Chem. Soc., 44, 2148 (1922).

TABLE

Al_2O_3 per sample, "M", equals 0.09988 gms.

No.	"C"	"X"	X/M	log. "C"	log. X/M
1	0.23538	0.16407	1.64267	9.37157−10	0.21556
2	0.31472	0.16522	1.65419	9.49729−10	0.21859
3	0.39783	0.16210	1.62295	9.59970−10	0.21032
4	0.64844	0.15146	1.51642	9.81187−10	0.18081
5#	0.72941	0.15048	1.50661	9.86297−10	0.17800
6	0.78843	0.17145	1.71656	9.89676−10	0.23467
7	0.85551	0.18436	1.84581	9.93223−10	0.26618
8	0.93005	0.18981	1.90038	9.96851−10	0.27885
9	1.00516	0.19469	1.94924	0.00225	0.28986
10	1.18422	0.21561	2.15869	0.07343	0.33419
11	1.46059	0.23920	2.39847	0.16453	0.27929
12	1.71443	0.28532	2.85663	0.23411	0.45585

These results are plotted as X/M against C in Fig. 1 and as log. X/M × 10 against log. C × 10 in Fig. 2.

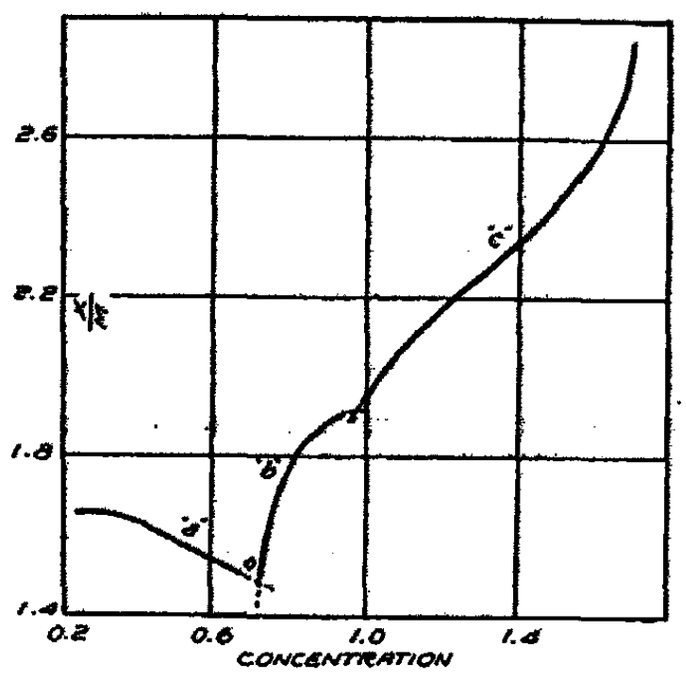

FIG. 1
Adsorption of Chromate Ions by Aluminum Hydroxide

Discussion of the Results

The curves shown in Figs. 1 and 2 show three distinct parts and have been labeled "a", "b" and "c". "a" represents the data obtained at concentrations below the coagulation value of the added electrolyte, terminating at point "o" which was the last sample to be coagulated. The section marked "b" was unexpected. The supernatant liquid was clear to the Tyndall beam, showing complete coagulation. Section "c" marks the isotherm as usually obtained. Two additional sets of data on suspensions similarly prepared,

respectively three months and three years old showed the same type curves except the section "b" was more extended. These data are not recorded as the results are similar.

The hypothesis suggested in the introduction seems amply borne out by the results of these experiments, at least on colloid suspensions which are charged. If the mechanics of adsorption were the same in the uncoagulated and coagulated regions the curves would be continuous, i.e., there would be no sudden break. The break shown, so extreme as to even reverse the slope, indicates that the type of adsorption by the coagulated system is entirely different from the type of adsorption at concentrations below the coagulation values of the added electrolyte. An explanation for the section "b" is suggested. It is well known that the coagulation of a charged suspensoid takes place before the charge is completely neutralized. "b" may represent a combination of the neutralization adsorption represented by "a" and the surface adsorption as represented by "c".

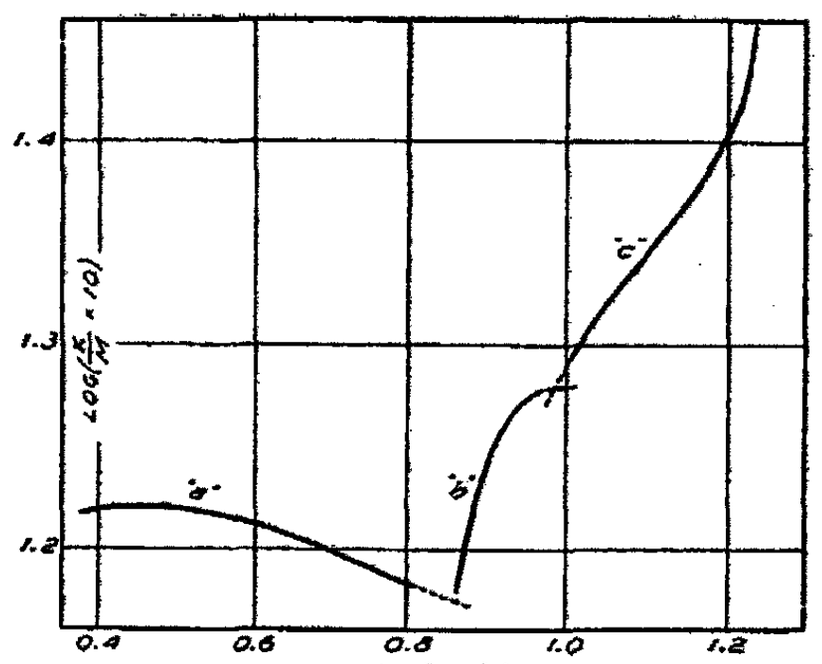

FIG. 2
Logarithm of the Adsorption Isotherms

Summary

1. The adsorption of potassium chromate by colloidal aluminum hydroxide has been determined at concentrations above and below that required for complete coagulation.

2. The results show three separate and distinct types of adsorption for which the explanation is offered: "a" represents a neutralization adsorption, that is, the neutralization of the positive charge on the suspensoid particle. "c" represents surface adsorption, not electrical in type and "b" represents a combination of these two types, "a" and "c".

3. The extrapolation of adsorption data to zero concentration of the adsorbed substance is not always justified.

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VARIATION OF EXTINCTION COEFFICIENT OF SOLUTIONS WITH TEMPERATURE. II

BY A. K. BHATTACHARYA AND N. R. DHAR

In a previous publication[1] from these laboratories it has been shown that the extinction coefficient of several coloured solutions and mixtures of different solutions markedly increase with rise in temperature.

In this communication we are submitting the results obtained with several other reacting mixtures.

For the measurement of the extinction coefficients, a Hilger-Nutting Spectrophotometer was used. To isolate any particular region of the spectrum for ease of comparison, a shuttered eyepiece was employed. The source of light was a 100 c.p. point-o-lite lamp working at 220 volts. Two similar, neutral-tint glass cells with optically-plane parallel ends were used, one for the solution whose extinction coefficient had to be observed and the other for an equal volume of distilled water so that the comparison might be made under identical conditions of original light intensity.

The time taken in actually reading the scale after the comparison of the two spectra did not exceed 45 seconds and precautions were taken to ensure constancy of temperature during this interval.

In the cases of reacting mixtures, titrations were carefully made to test that no appreciable change takes place at the lower and the higher temperatures during the very short time taken to read the scale on the photometer.

The following experimental results were obtained:—

1. *Neocyanin* (Kodak)—M/7176
Thickness of the cell—1 cm.
Spectral region—λ = 5490 Å

Temperature in °C.	Reading on the density scale	Extinction coefficient
10	0.84	0.84
40	0.86	0.86
70	0.90	0.90

2. *Ferric thiocyanate.*
10 c.c.—N/250 ferric chloride
10 c.c.—N/50 ammonium sulphocyanate
Spectral region λ = 5490 Å

10	0.72	0.72
40	0.73	0.73
70	0.75	0.75

[1] J. Phys. Chem., 32, 1834 (1928).

3. *Sodium cobaltinitrite*—M/80.8
Spectral region λ = 5670 Å

Temperature in °C.	Reading on the density scale	Extinction coefficient
10	0.85	0.85
40	0.86	0.86
70	0.88	0.88

4. *Sodium malonate and iodine.*
10 c.c.—N/2.69 sodium malonate
10 c.c.—N/100 iodine
Spectral region λ = 5200 Å

10	0.54	0.54
40	0.56	0.56
70	0.575	0.575

5. *Sodium tartrate and iodine.*
10 c.c.—N/2.42 sodium tartrate
10 c.c.—N/100 iodine
Spectral region λ = 5490 Å

10	0.48	0.48
40	0.50	0.50
70	0.515	0.515

6. *Citric acid and chromic acid.*
10 c.c.—6.75 N citric acid
10 c.c.—N/44.4 chromic acid
Spectral region λ = 5000 Å

10	0.51	0.51
40	0.52	0.52
70	0.535	0.535

7. *Lactic acid and chromic acid.*
10 c.c.—N/4.72 lactic acid
10 c.c.—N/44.4 chromic acid
Spectral region λ = 4800 Å

10	0.595	0.595
40	0.61	0.61
70	0.63	0.63

8. *Citric acid and potassium permanganate.*
10 c.c.—N/5 citric acid
5 c.c.—N/50 potassium permanganate
5 c.c.—N/69 manganous sulphate
Spectral region λ = 5000 Å

10	0.57	0.57
40	0.58	0.58
70	0.60	0.60

9. *Tartaric acid and potassium permanganate.*

5 c.c.—N/5.36 tartaric acid
10 c.c.—N/98.45 potassium permanganate
5 c.c.—N/69 manganous sulphate
Spectral region 4800 Å

Temperature in °C.	Reading on the density scale	Extinction coefficient
10	0.48	0.48
40	0.50	0.50
70	0.515	0.515

Discussion

In all the cases investigated above it may be observed that the extinction coefficients increase with increase in temperature. One thing however is to be noted that the increase in extinction coefficient is not marked unless the variation of temperature is great. We are of the opinion that there is increase in absorption for even small rise of temperature but this is too small to be observed.

These results can be explained from the point of view of the change of hydration of the solutes, at higher temperatures. The amount of hydration of a solute is likely to decrease on increase of temperature and this frequently leads to changes in the absorption. As the solvates become simpler on increase of temperature the absorption of light is likely to increase. It is generally found that the effect of increasing the temperature of the solution is the same as that of increasing the concentration of the solute. In both the cases there is an widening of the absorption bands—that is the absorption of light increases owing to the solvates becoming simpler (Compare H. C. Jones "The Nature of Solutions", page 331). Consequently the increased quantum yield on the increase of temperature of the reacting substances appears to be associated with the increase in the light absorption on increase of temperature.

Summary

1. The extinction coefficients of solutions of neocyanin, ferric thiocyanate, sodium cobaltinitrite, and mixtures of solutions of sodium malonate and iodine, sodium tartrate and iodine, citric acid and chromic acid, lactic acid and chromic acid, citric acid and potassium permanganate and tartaric acid and potassium permanganate appreciably increase with increase of temperature.

2. An explanation for this phenomenon has been put forward from the point of view of the change of hydration of the solutes at higher temperatures.

3. This increase in the extinction coefficient with temperature partly explains the frequent increase in the quantum yield with temperature.

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June, 1930.

PHOTO-CHEMICAL DECOMPOSITION OF HYDROGEN PEROXIDE IN AQUEOUS SOLUTION IN PRESENCE OF SODIUM NITRO-PRUSSIDE. I

BY M. QURESHI

As is well known, an aqueous solution of hydrogen peroxide, free from dust particles and catalytic influences due to the surface of the containing vessel, is insensitive to the visible light. This is, however, not the case with a solution of hydrogen peroxide, to which a relatively small quantity of a mixture of potassium ferrocyanide and ferricyanide has been added. In the latter case, hydrogen peroxide suffers decomposition in the visible light with a brisk evolution of oxygen. This was discovered by Kistiakowsky,[1] who also found that the decomposition follows the unimolecular law and continues with undiminished velocity after the illumination ceases. According to the same author, an insolation of one minute in sunlight is sufficient to produce the maximum rate of decomposition. It has been further shown by Weigert[2] that the reaction takes place in the dark as well, when the solution of potassium ferrocyanide is first illuminated alone and afterwards added to the solution of hydrogen peroxide. Obviously, in the case studied by Kistiakowsky potassium ferrocyanide or ferricyanide, on illumination, gives rise to some catalyst, which remains effective in the dark. But the exact nature of this 'dark' catalyst is not yet definitely known. It may be of a colloidal nature, as suggested by Kistiakowsky, or it may be simply $Fe^{...}$ ions, that are known to act catalytically in the thermal decomposition of hydrogen peroxide. There is a further possibility of both the catalysts appearing and working simultaneously. Any decision on this point must await the results of further experiments. In the meantime, it may be of interest to report another case of a similar nature, which throws some light on the nature of the catalyst, responsible for the after-effect in the photo-chemical decomposition of hydrogen peroxide.

While observing the decomposition of sodium nitro-prusside in the visible light, it occurred to the present writer to try the effect of nitro-prusside compounds on the photo-chemical decomposition of hydrogen peroxide. As the nitro-prusside compounds are decomposed by light with the formation of Prussian blue, it was thought very likely that an aqueous solution of hydrogen peroxide, to which a few drops of sodium nitro-prusside have been added, would be sensitive to the visible light, owing to the colloidal Prussian blue, formed as a result of the photo-chemical decomposition of the latter compound. These expectations came out to be true. An aqueous solution of hydrogen peroxide, to which a few drops of a freshly prepared solution of sodium nitro-prusside had been added, was fairly stable in the dark for long

[1] Z. physik. Chem., 35, 431 (1901).
[2] Ann. Physik, (4) 24, 261 (1907).

intervals of time. When the same solution was exposed in glass vessels to the light of a metal filament lamp or a quartz mercury vapour lamp, decomposition set in after a short time and continued with a brisk evolution of oxygen after the light was shut out. A few experiments are described below.

Experiment No. 1

One c.c. of a solution of sodium nitro-prusside (M/10), prepared in the dark, was added to one c.c. of 33% hydrogen peroxide, and the mixture made up to 100 c.c. by the addition of dust-free conductivity water. The process of mixing, which was carried out in a semi-dark room, did not take more than a minute. One portion of this mixture was transfered to a small, thoroughly cleaned, Erlenmeyer flask, placed in a thermostat, and exposed to the light of a quartz mercury lamp. The flask was closed by a cork, carrying a valve and an arrangement for pipetting out one c.c. of the mixture. The remaining portion of the mixture was transferred to a second flask, similar to the first, but painted black from outside for comparitive experiments in the dark. After an exposure of 10 minutes, the light was shut out and the course of the reaction followed in both the flasks by withdrawing one cc. of the mixture at noted intervals of time and titrating against potassium permanganate. The results are stated below. The values of the velocity constant ($K \times 10^5$), given in the last column of the table, have been calculated on the basis of the uni-molecular formula: $K = 1/t \log_{10}(a/(a-x))$.

TABLE I

(a) Rate of decomposition after exposure

Concentration of hydrogen peroxide = 0.1 molar approx).
Concentration of sodium nitro-prusside = 0.001 molar.
Time of exposure = 10 minutes.
Temperature = 30°.

Time (in minutes)	Permanganate titer (c.c.)	Velocity constant ($k \times 10^5$)
0	20.2	
19	19.3	104
38	18.4	109
69	16.7	136
117	14.7	115

(b) Rate of decomposition in the dark

0	20.2	—
15	20.2	—
34	20.1	11
57	20.1	—
80	20.0	9

Experiment No. 2

In this experiment, the concentration of hydrogen peroxide was nearly half of that in the first experiment, but the time of exposure was increased to

15 minutes. Other conditions were the same as in the first experiment. For titrations, a burette, graduated to 1/50 c.c. with a certificate of N. P. L. was used.

TABLE II

(a) Rate of decomposition after exposure

Concentration of hydrogen peroxide = 0.05 molar (approx.)
Concentration of sodium nitro-prusside = 0.001 molar.
Time of exposure = 15 minutes.
Temperature = 30°.

Time (in minutes)	Permanganate titer (in c.c.)	Velocity constant ($k \times 10^4$)
0	8.58	—
21	8.02	139
45	7.26	180
65	6.85	126
91	6.32	134

(b) Rate of decomposition in the dark

0	9.28	—
51	9.20	7
76	9.14	11
141	9.02	9

Experiment No. 3

The mixture, exposed to light, appeared to possess a pale blue colour and showed Tyndall effect. The mixture, kept in the dark, however, neither developed blue colour nor showed Tyndall effect, but on standing for twenty-four hours deposited a precipitate of ferric hydroxide.

Experiment No. 4

On adding a few drops of a solution of nitro-prusside, that had been separately illuminated for half an hour, to an aqueous solution of hydrogen peroxide, evolution of oxygen took place in the dark. The course of this reaction was not followed quantitatively.

The above experiments, though preliminary in character, are sufficient to establish the following conclusions:

(1) An aqueous solution of hydrogen peroxide, to which a few drops of a solution of sodium nitro-prusside are added, is sensitive to the visible light.

(2) The decomposition of hydrogen peroxide, under the above conditions, continues after the illumination ceases. (photo-chemical after-effect).

(3) During the illumination, very probably colloidal Prussian blue is formed, which acts as a catalyst in the dark reaction.

Further experiments on the effect of the variation of intensity of illumination and temperature on this reaction are in progress and will be reported in due course.

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NOTE REGARDING THE COLLOIDAL NATURE OF CUPRAMMONIUM SOLUTION*

BY ALFRED J. STAMM[1]

The nature of the complex salts of copper and ammonia, and the reason for their intense blue color is one of considerable interest. Earlier investigations on the lowering of the freezing point,[2] vapor pressure depression,[3] distribution coefficient,[4] and change in viscosity[5] all showed that four ammonia radicals are combined with one copper to form the complex ion $Cu(NH_3)_4^{++}$. This relationship of copper to ammonia is not exact, however. According to Dawson,[6] dilution of the solution or decreasing the ammonia concentration relative to that of copper causes the equilibrium between the components to be displaced so that the ratio of combined ammonia to copper diminishes. Copper finally precipitates from solution as copper hydroxide.

Bhatnagar, Goyle, and Prasad[7] have recently shown that this deviation from the true stoichiometric relationship and the intense blue color of the solutions may be explained on the assumption that for all concentrations and proportions of ammonia and copper, part of the copper is colloidally dispersed as copper hydroxide. The amount of colloidal copper hydroxide present and its degree of dispersion, which affects the color of the solution, will vary with the relative concentrations of the constituents and the method of preparation. These investigators have further substantiated their theory by comparing four properties of copper hydroxide sols with those of cuprammonium solutions, namely the absorption spectra, cataphoresis, dialysis, and flocculation with electrolytes. In all cases the data indicate that the cuprammonium solutions contain some colloidally dispersed copper hydroxide.

The author had occasion, in connection with his study of the dispersion of cellulose in cuprammonium solvent,[8] to make a brief study of the colloidal nature of cuprammonium solvent itself, using the ultracentrifuge apparatus of Prof. The Svedberg.[9] In this study the concentration gradients existing in the sedimenting systems were determined by the new index of refraction method developed by Ole Lamm[10] in this laboratory.

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* Contribution from the Laboratory of Physical Chemistry of the University of Upsala.

[1] Fellow of the Rockefeller Foundation. Chemist on leave from the U. S. Forest Products Laboratory, Madison, Wis.

[2] Reychler: Bull. 3, 13, 387 (1895).

[3] Gaus: Z. anorg Chem., 25, 259 (1900).

[4] Dawson: J. Chem. Soc., 89, 1668 (1906).

[5] Blanchard: J. Am. Chem. Soc., 26, 1315 (1904).

[6] Dawson: J. Chem. Soc., 95, 371 (1909).

[7] Bhatnager, Goyle and Prasad: Kolloid-Z., 44, 79 (1928).

[8] Stamm: J. Am. Chem. Soc. 52 3047, 3068 (1930).

[9] Svedberg, "Colloid Chemistry," pp. 146-167 (1928).

[10] Lamm: Z. physik. Chem., 138, 313 (1928); 143, 177 (1929).

The cuprammonium solution was prepared by drawing CO_2-free air slowly through a tall cylinder containing concentrated ammonia (sp. gr. 0.91) and strips of electrolytic copper foil for 6 hours. The copper concentration was determined by evaporation of 2 cc. portions, igniting and weighing as the oxide. The ammonia concentration was determined by titrating a diluted portion against 0.1 N HCl using methyl orange as an indicator. The stock solution contained 1.28 per cent copper and 22.0 per cent ammonia.

With the high-speed oil-turbine centrifuge a definite sedimentation of a polydisperse material was observed using the above stock cuprammonia solution. The sedimentation velocity ranged from 5×10^{-12} cm./sec. per cm./sec.^{2} to 10 to 100 times this value. The upper limit of the sedimentation velocity was not determined, as the author was primarily interested in the finer dispersion. This sedimentation value could have been definitely obtained by making measurements with the centrifuge operating at a lower speed.

If it is assumed that the colloidal material present is simple $Cu(OH)_2$, the density of which is 3.37, the particle size range can be calculated using Stokes' law of settling. This gives a particle size range from 6.5 mμ in diameter to more than 20.0 mμ. Unfortunately, the percentage of the total copper concentration that is colloidally dispersed can not be definitely determined without the knowledge of the relationship existing between the sol concentration and the refractive index. It is very likely less than 10 per cent of the total copper concentration, however.

Conclusions

It has been shown with the aid of the ultracentrifuge that cuprammonium solutions do contain a material in colloidal dispersion. This colloidal material is undoubtedly a copper hydroxide sol, according to the deductions drawn from the data of Bhatnagar, Goyle and Prasad.[7] This sol is polydisperse and contains particles ranging in diameter from 6.5 mμ to more than 20.0 mμ for the concentration investigated.

The author wishes to express his sincere thanks to Prof. Svedberg for the use of the ultracentrifuge equipment of this laboratory, and for the help which he always freely gave towards the carrying out of this research.

NEW BOOKS

A Comprehensive Treatise on Inorganic and Theoretical Chemistry. *By J. W. Mellor. Vol. X. 25 × 17 cm., pp. x + 958. London and New York: Longmans, Green and Co., 1930. Price: $20.00.* The tenth volume of this series deals with sulphur and selenium. The sulphur cycle is discussed on p. 9. "W. Lindgren has well emphasized the fact that in nature a large part of the sulphur is continually in movement, changing from sulphide to sulphate with local reversions to native sulphur, and from sulphate back to sulphide. He follows the cycle somewhat as follows: All active volcanoes give off enormous quantities of hydrogen sulphide some of which is oxidized to form sulphur dioxide and then the trioxide. The resulting sulphuric acid descends to the earth with rain to form sulphates by reacting with the basic rocks. A part of the hydrogen sulphide is reduced to native sulphur. All intrusions contain sulphur compounds part of which are fixed as metal sulphides—*e.g.* pyrites—which fill veins or impregnate adjacent rocks; or else as sulphates—*e.g.* barytes and anhydrite. Some of the silicated waters which come to the surface carry hydrogen sulphide in soln., and this gives rise to accumulations of native sulphur about the vent of springs.

"When the basic sulphide rocks are exposed at the surface, they are oxidized to soluble sulphates—*e.g.* iron, aluminum, magnesium, zinc, calcium, potassium, and sodium—which find their way to the sea. The less soluble sulphates—*e.g.* lead sulphate or the basic iron sulphates—linger behind. In the average river waters, sulphates are present in relatively large amounts, and enormous quantities are discharged into the ocean, so that the sulphates would predominate over the chlorides in the waters of the sea were it not for the continuous reduction of sulphates to sulphides along the littoral—particularly muddy shores rich in organic matter. Sulphur as iron sulphide is plentiful in shore deposits, and in some deep closed basins, like the Black Sea, similar reducing conditions obtain at the bottom, and the mud at the bottom is rich in iron sulphide.

"The evaporation of sea-water or lake-water in closed basins results in the deposition of calcium sulphate which forms nearly all the known beds of gypsum. When meteoric waters loaded with hydrocarbons act on calcium sulphate, the sulphate is reduced to sulphur. The sulphate may be similarly reduced by bacterial activity.

"The muds and silts, rich in iron sulphide, largely as marcasite, are compressed, raised, and folded by geological processes to form shales and sandstones. The sulphide is then attacked by oxidizing soln., converted into soluble sulphates and again carried back to the sea. The meteoric waters circulating at deeper levels, extract sulphates from uplifted sediments—limestone, slate, or silt—near the surface, and, lower down, the sulphides of hydrogen, iron, zinc, lead, copper, cadmium, cobalt, or nickel. The sulphides may be deposited elsewhere as in the zinc and lead sulphide deposits on the limestone of the Mississippi Valley."

At 600° calcium sulphite decomposes reversibly in two stages, p. 18. $4\,CaSO_3 = CaS + 3\,CaSO_4$ and $CaS + 3\,CaSO_4 = 4\,CaO + 4\,SO_2$. "The so-called plastic sulphur of Imbert, for use in agriculture, is not the viscous or plastic sulphur indicated in the next section but is a mixture of sulphur with 0.05 percent of ox-gall," p. 20. "Royer said that if a hot saturated solution of sulphur in turpentine be cooled rapidly, monoclinic sulphur is formed, and rhombic sulphur if cooled slowly," p. 24. "The Thomsen Chemical Co. prepared colloidal sulphur by grinding it with a colloid—say, 50 parts of sulphur, 5 of glue, and 50 of water; other protective colloids can be used—extract of soap bark, Irish moss, gum tragacanth, or gum arabic. The solution is not precipitated by sulphuric acid, and is used as an insecticide," p. 40. "The various methods for determining the molecular weight of sulphur show that, in all probability, this element, in the solid, liquid, or vaporous state (at a low temperature) has the complex molecule S_8," p. 59.

"According to J. Bohm, when flowers of sulphur are kneaded in ordinary water, the floating portions removed, and the immersed portions left in an open vessel covered with

only a small quantity of water, sulphuric acid is produced, whereas if the flowers of sulphur are kept in spring-water, and the air is excluded, hydrogen sulphide is formed after a short time. Flowers of sulphur have been kept for a month or longer in well-water, daily changed, immediately produce hydrogen sulphide, and, after a few days, the water, if its volume does not greatly exceed that of the flowers of sulphur, gives with a solution of a lead salt, a black precipitate, and with barium chloride, a moderate turbidity. In sealed tubes, with flowers of sulphur not very well adapted for the production of hydrogen sulphide, the formation of the gas is permanently hindered by the presence of air, even in small quantity. The same effect is produced by any acid or by phenol; carbon disulphide prevents the action only when the flowers of sulphur have been well mixed with a few drops of it. Flowers of sulphur thus treated, and then freed from the admixed substance, also those which have been boiled or frozen for some days, do not recover the power of immediately producing hydrogen sulphide till they have digested for some time in spring-water, daily renewed. In distilled water, no hydrogen sulphide is evolved, and even flowers of sulphur highly capable of generating this gas, lose the power of immediately producing it, even in spring-water, if they have been washed with pure water and kept for some time. In distilled water mixed with a little chalk, much less hydrogen sulphide is formed, than under similar conditions in spring-water, and a large quantity of chalk prevents the formation of the gas, even under circumstances otherwise favourable. The same is true in a still higher degree for gypsum, and for a considerable quantity of charcoal-powder freed from air by boiling. In the latter case the liquid, which in most cases is faintly alkaline, is strongly clouded by barium chloride. Hydrogen sulphide is also formed on boiling sulphur in water," p. 91.

"Sulphur has no action on the skin, but some of it may be converted into hydrogen sulphide which acts as a mild vascular stimulant and with some persons produces eczema; some sulphur may be converted into sulphurous and sulphuric acid which act as irritants. If taken internally, most of it passes out in the faeces unaltered; but a small proportion is converted in the intestine into hydrogen sulphide and other sulphides. These have a mild laxative effect, which is sometimes accompanied by a flatus of hydrogen sulphide which makes sulphur an undesirable laxative. Excessive amounts of sulphides and hydrogen sulphide may produce symptoms of asphyxia, and paralyze the nervous and muscular systems. . . . According to L. C. Maillard, colloidal sulphur, prepared by the interaction of hydrogen sulphide and sulphur dioxide, is completely and rapidly absorbed by rabbits when introduced into the aesophagus. Within twenty four hours, somewhat less than half is eliminated with the urine as mineral sulphates, and a portion in the form of organic sulphates. The normal amount of the latter is increased by 5-13 per cent. after the ingestion of sulphur, but the proportion falls below normal when this is withdrawn from the diet. About half of the sulphur is excreted in an incompletely oxidized condition, probably in organic combination, since no sulphur, hydrogen sulphide, or sulphur dioxide is formed on treating the urine with acid. It may be supposed that substances are formed by the conjugation of compounds of the type $R.SO_2.OH$ with phenols, and that more highly oxidized compounds escape combination in this way. L. Sabbatani showed that when the hydrosol is injected subcutaneously, hydrogen sulphide is formed only very slowly. After interperitoneal injection it is formed more rapidly, but yet not sufficiently quickly for it to be detectable in the expired air. When injected intravenously, it is readily formed, and for this reason the hydrosol of sulphur is very toxic. As the sulphur aggregates become larger, the toxicity diminishes. The dog can tolerate relatively large doses when the sulphur is introduced into the stomach. With the larger doses vomiting occurs, and the animal rapidly recovers. The sulphur is more toxic under the same conditions in rabbits, as these animals cannot vomit. A little more than 0.1 grm. per kilo. of body-weight can produce death. This dose can be well tolerated when introduced intraperitoneally or subcutaneously, although larger doses can act toxically. When given intravenously, doses of 0.0065-0.0203 grm. are toxic, the toxicity depending on the rate at which the sulphur is introduced," p. 104.

T. M. Lowry points out that optical activity occurs in a trisubstituted sulphonium ion, although it does not exist in the analogous molecule of ammonia. "No analogous difference exists between the electronic formula for the two groups since in each case the central atom carries three pairs of shared electrons with one 'lone pair' to complete the octet. The contrast is, therefore probably due to the existence in the nitrogen-compound of a mobility of atomic or molecular structure, similar to that which makes it easy to form a double or triple bond between elements of the first short period, whereas this is difficult or impossible in elements of the later periods," p. 111.

The reaction between sulphur dioxide and hydrogen sulphide occurs practically completely at the glass surface which therefore acts as a contact catalyst; each of the reacting gases being activated when adsorbed and the reaction taking place between the activated molecules. Quam said that dry sulphur dioxide reacts vigorously with liquid hydrogen sulphide. H. B. Baker found that liquid alcohol and liquid sulphur dioxide can liberate sulphur from the dried mixed gases, whereas carbon tetrachloride is inert. "According to D. Klein, immediate action is produced by water, ethyl alchool, *isobutyl* alcohol, *iso*amyl alcohol, acetone, propyl acetate, benzaldehyde, and carvone. A slower decomposition occurs with methyl ethyl ketone, acetonitrile, propionitrile, valeronitrile, phenylacetonitrile, methyl benzoate, isobutyl acetate, and ethyl ether. On the other hand, carbon disulphide, acetyl chloride, benzoyl chloride, ethyl chloride, and carbon tetrachloride are quite inert. There appears to be no connection between the dielectric capacity or association factor of a liquid and its activity as a catalyst in this reaction. Many of the active liquids are known to form compounds with hydrogen sulphide, notably the nitriles, the aldehydes, and carvone. E. Matthews also found that in order to bring about the decomposition of a mixture of sulphur dioxide and hydrogen sulphide in either the gaseous or the liquid state, the addition of a third substance in the liquid phase is necessary. There is no rigid relationship between the values of the dielectric constants of substances and their chemical activity as measured by their ability to bring about the interaction of hydrogen sulphide and sulphur dioxide. Hydrogen sulphide and sulphur dioxide when in liquid state do not react vigorously. The activity of a substance in causing decomposition is dependent on the solubility of the two gases in the substance when liquid, or on the solubility of the solids in the liquid mixture of the two gases," p. 135.

"The aqueous solution of hydrogen sulphide and the gas are poisonous, but less poisonous than chlorine or bromine. Toward the end of the eighteenth century a number of accidental deaths occurred in Paris due to the gases from the sewers; and in 1785 M. Hallé reported on the conditions but did not recognize hydrogen sulphide as the cause of the poisoning. . . . . Mitchell and Davenport say that hydrogen sulphide is one of the most toxic gases, and is comparable to hydrogen cyanide with respect to rapidity of action and concentration producing death. The action depends upon the concentration—0.005 percent is sufficient to produce poisoning, while a continued exposure to a concentration of 0.02 percent during several days may produce death," p. 145. In this last respect it is not like hydrogen cyanide the effect of which is not cumulative.

Mellor calls Schützenberger's acid hyposulphurous instead of hydrosulphurous acid, p. 167. "The effect of passing from weakly acid to strongly acid solution is to lower the oxidation potential of ferric-ferrous chlorides and phosphates, and to raise that of sulphur dioxide. The oxidation potential of cupric-cuprous chloride is actually raised by an increase in potential up to about 6.5 N, after which it decreases," p. 202.

"F. C. Calvert found that a solution 1:1000 does not affect protoplasmic life or fungi. According to M. Ogata, sulphurous acid under all conditions is a powerful poison; a solution with only 0.04 per cent. produced, after a few hours, a dyspnoea and darkening at the cuticle. The injurious action is mainly on the blood where the absorbed acid is converted into sulphuric acid. This action was not observed with sulphites. Diluted blood, decolorized with sulphur dioxide, shows no spectral absorption bands. H. Kionka found that relatively small proportions of sulphur dioxide in the atmosphere proved fatal. Doses of 0.02-0.04 grm. of sodium sulphite injected into frogs paralyze the heart, the central, and to some extent the peripheral nervous system. Dogs fed on the salt, or on food preserved by its use, suffer

from injuries to various organs, especially the lungs and kidneys; there is local irritation of the stomach, and a fall of blood pressure, and haemorrhages tend to occur. The use of the salt as a preservative is most reprehensible.... The trees in an atmosphere containing sulphur dioxide, as occurs, for instance, in the neighborhood of smelting works, suffer severely. According to J. Schroder, the coniferae suffer more injury than ordinary foliaged trees. The number of stomata on the leaves bears no proportion to the amount of gas taken up. The sulphur dioxide disturbs the normal relation between absorption and transpiration of water, and the water taken up goes to the veins, and is not transmitted further. A decrease in the amount of the gas caused less disturbance in the amount of transpired water, though no simple proportion between the amount of the gas and of decrease was indicated. The amount of sulphur dioxide taken up by the leaves in the dark and with a lower temperature and moister air, is smaller and its injurious effects much lews marked than in the light and with higher temperature and moister air; therefore the same amount of sulphur dioxide in the air is much less injurious to plants during the night than in the daytime. The amount of sulphur dioxide absorbed by pine-leaves is smaller than that absorbed by trees with ordinary foliage for equal surfaces, and as its effect on transpiration is less in the case of the pine, the cause of the greater injury to pine trees in nature must be due to the longer duration of the leaves, whereby the injury accumulates in them, whilst in trees with annual leaves the hurt to one year's foliage would have only an indirect influence on that of the following year. The alder, sycamore, ash, and especially maple, best withstand the action of smoke containing sulphur dioxide; next the pines suffer more than other trees, owing to the fact that, although their sensitiveness at first is less than that of other trees, their power of restoring lost leaves is much less," p. 242.

When a sodium mercuric sulphite solution is heated, there is a separation of mercury which first appears as a bright rolling cloud, suggesting a precipitate of great volume, an effect apparently due to metallic reflection of light. This cloud then melts away, leaving a relatively minute, very dark grey deposit of mercury at the bottom of the vessel; the bright cloud becomes, so to speak, a rain of mercury, p. 297.

Reference is made, p. 338, to the use of vanadium pentoxide as a catalyst in the contact sulphuric acid process; but the author says that platinum is the only catalyst of technical importance, p. 339.

"Sulphuric acid is poisonous to man, and a fatal case of the poisoning of an adult by 3.8 grms. of acid was reported by R. Christison, and this is the smallest lethal dose on record. When externally applied, the concentrated acid may produce phenomena resembling scalds or burns; the destruction of the tissue may not be deep seated if the acid is quickly washed off. The skin is at first coloured white, and at a later period brown, and part may appear as if it had been dissolved. When administered internally, there is immediate and great suffering; the tongue and throat swell and inflame so that saliva cannot be swallowed. The acid attacks the mucous membrane of the gullet, and stomach. There may be excessive vomiting and retching. Pieces of mucous membrane may be expelled. The bowels are usually constipated, and the urine contains an excess of sulphates and often albumen with hyaline casts of unriniferous tubes. The pulse is small, the breathing slow, the extremities may be affected with convulsions and cramps, and death may follow in 24-36 hrs., or be more protracted and painful. In bad cases, the sulphuric acid may dissolve the stomach and pass into the peritoneum producing effects like a penetrating wound in the abdomen. In chromic poisoning by small doses W. Starkoff showed that it acts as a specific poison on the blood. R. Kobert mentioned that drunkards addicted to Schnapps may show symptoms of chronic poisoning because this liquor is acidified with sulphuric acid to give it a sharp taste," p. 440.

"According to H. Schulze, camphor readily absorbs sulphur dioxide and thereby liquefies, and the absorbed gas escapes when the liquid is exposed to air. Chlorine gas has no action on camphor, but is greedily absorbed by the above liquid until saturated, and a solution of camphor in sulphuryl chloride is formed, which can be easily separated and obtained pure by distillation. This action cannot be due to the mere condensation of the sulphurous anhydride and its action in the liquid state on the chlorine for these two gases do not com-

bine even when condensed and cooled to −20°; but, on the other hand, in presence of camphor the reaction takes place even at −20°. Sulphurous anhydride combines in large proportion with and liquefies glacial acetic and formic acids; these acids are scarcely attacked by chlorine if sunlight is excluded, but the sulphurous compounds greedily absorb chlorine with formation of sulphuryl chloride, the acetic and formic acids remaining almost unacted on; thus their mode of action seems to resemble that of camphor. Alcohol and acetone also absorb quantities of sulphur dioxide; chlorine passed through these liquids acts on the alcohol and acetone, and in proportion as this proceeds the sulphurous anhydride escapes without being acted on. Other absorbents of sulphurous anhydride are sulphuryl chloride itself, and liquid sulphur trioxide. Chlorine passed into the latter solution does not yield a trace of sulphuryl chloride, no more than it does with the former. Turpentine absorbs sulphur dioxide, but it does not effect the union of this body with chlorine. Carbon bisulphide and chloroform absorb chlorine, but the solution is not acted on by sulphur dioxide. It cannot be supposed that the action of camphor, or acetic or formic acids, is due to their combining momentarily with chlorine, and then passing it over to the sulphur dioxide *in statu nascendi*, for the first two undergo substitution to a slight extent only and the last is completely decomposed into carbonic anhydride and hydrochloric acid," p. 668.

The author does not commit himself on the question whether perselenates have or have not been formed electrolytically, p. 852; on the question whether one has $SeO_3.2HCl$ or $SeOCl_2.H_2O$, p. 913.

Wilder D. Bancroft

Introduction to Physiological Chemistry. *By Meyer Bodansky. Second edition, rewritten and reset. 23 × 15 cm; pp. ix + 542. New York: John Wiley and Sons, 1930. Price: $4.00.* The first edition was reviewed four years ago (31, 1106). In this new edition two chapters have been added, one dealing with the composition of foodstuffs and the other devoted to a brief consideration of the composition of milk and of certain tissues, including bone, cartilage and muscle.

"The lactones of the sugar acids are relatively stable and some have been prepared in crystalline form. Levene is of the opinion that in a solution of sugar acids, all theoretically possible lactones are formed. In a freshly prepared solution the unstable lactones are said to predominate; but, after a short time, only the stable forms are present in measurable quantities," p. 45. "Until recently it was generaly believed that the sugar in animal nucleic acid (thymonucleic acid) was an hexose; but, according to recent observations, it is desoxyaldopentose, namely, *d*-2-ribodesose," p. 56. "Mannose is the constituent sugar of the mannans, a group of polysaccharides widely distributed in plants, but which are especially abundant in the endosperm of the seed of the tagua palm. Recently, Levene and Mori reported mannose to be a constituent of ovomucoid, a conjugated protein which occurs in egg white," p. 57.

"Arachidonic acid, and possibly tetracosapentenoic acid, $C_{24}H_{36}O_2$, are said to occur in the brain, where the highly unsaturated fatty acids seem to be present in greater proportion than in other tissues," p. 74.

"The synthesis of proteins in the plant can take place in the dark, provided there is an adequate supply of carbohydrate and potassium," p. 99. Vickery and Osborn give nine reasons for believing that the peptide binding, .C(:O).NH., is the principle linkage existing between the amino acids in the protein molecule. The ninth reason, p. 101, is as follows: "Pepsin alone liberates as a rule about 20 percent of the total amount of amino nitrogen which can be obtained by the complete hydrolysis of a protein. Erepsin acting on a peptic digest can liberate as much as 70 percent more. Since there is every reason to believe that the latter enzyme acts only upon peptide bonds, it is obvious that by far the greater part of the total possible amino nitrogen of a protein has its origin in such bonds."

The author calls attention to the fact, p. 102, that "certain facts seem to point to the possibility that the protein molecule is not merely a single large polypeptide. This type of structure is believed to be inconsistent with the changes which protein undergoes in the process of denaturation by alcohol or heat. Nor is it possible to explain the insolubility in

water of many proteins on the basis of a polypeptide structure. [Neither of these objections seems to have any value.] An even greater obstacle in accepting the peptide bond as being the sole link between amino acids is the behavior of pepsin towards polypeptides. Pepsin does not act on polypeptides, nor for that matter on any synthetic products formed from amino acids. In fact, it is not known which bonds in the protein molecule are attacked by this enzyme."

"Rawlins and Schmidt have titrated casein, fibrin, gelatin, and edestin with certain basic dyes, methylene blue, safranine Y, and induline scarlet and found that the union between protein and basic dye occurred in stoichiometric proportions," p. 110. People have also titrated lead acetate with sodium eosinate and found stoichiometric relations; but they did not have lead eosinate after all. The experiments of Bancroft and Barnett with ammonia and hydrogen chloride gas on proteins are mentioned without comment, p. 114. The purification of urease by Sumner and of pepsin by Northrop are mentioned, p. 126. "Attempts to correlate our knowledge of enzyme action have resulted in the formulation of two main rival theories. Bayliss has advanced a colloid chemical point of view. According to this, the substances which react are first absorbed on the surface of the enzyme particles. The chemical reaction then takes place at the interface. Though this chemical reaction may be subject to the law of mass action,—namely, that the rate of reaction at any moment is proportional to the concentration at the moment of the reacting substances, still it is the adsorbed portion of the substances which is the controlling factor.

"The Michaelis school, on the other hand, has assumed that enzyme and substrate unite chemically, as ions would, to form an intermediate substance and that the rate of reaction is proportional to the concentration of this intermediate enzyme-substrate compound. These assumptions imply that the substances involved act as if they were in homogeneous solution. A good exposition of Michaelis' theory and the work upon which it is based is given by Waldschmidt-Leitz," p. 126.

"Proteins, therefore, are foods when absorbed in the usual way as amino acids, and poisons when introduced directly into the blood. One of the most violent poisons known is ricin, the protein of the castor bean. The injection of a protein that is foreign to the tissues of an animal results in the excretion of most of it in the urine. If the injection is repeated a few days later, no ill effects ensue. Continued injection of small amounts of a given protein at short intervals establishes an immunity for that protein, due, it is believed, to the formation of a precipitin, in the presence of which the foreign protein is precipitated. If, however, the second injection is administered several weeks after the first, severe shock is induced. This phenomenon is termed *anaphylaxis* and has among its symptoms a marked fall in blood pressure and a reduction in the coagulability of the blood. According to some investigators anaphylactic shock and peptone shock are essentially the same, the former being due to the development in the sensitized animal of an enzyme capable of converting the foreign protein in question into proteoses and peptones. 'Serum-sickness' frequently occurs in individuals sensitized against horse-serum proteins, and develops after the injection of antitoxins, such as diphtheria antitoxin. Under these conditions typical anaphylactic shock may occur and may terminate fatally," p. 181.

"The protein content of the plasma amounts to about 7 percent in man. The proteins may be separated into several fractions, the method most commonly employed consisting in salting out the fractions with varying concentrations of certain inorganic salts. From the work of Howe and others, it appears that the precipitation of the protein fractions occurs with some regularity. Thus, in a 0.75 molar solution of sodium sulfate, fibrinogen separates out. Euglobulin is salted out in a 1.00 molar solution. In a solution that is 1.25 molar, fibrinogen, euglobulin, and the so-called pseudoglobulin I are precipitated. All the globulins are separated from the albumins in a 1.50 molar solution, the last of the globulin fractions being pseudoglobulin II. Similarly various albumin fractions are precipitated in concentrations above 1.50 molar. While Howe recognizes the probability that the precipitates of protein may not be chemical identities, he has nevertheless suggested the grouping of the albumins into five fractions: V, VI, VII, VIII, and IX, which are precipitated in 1.75, 2.00, 2.25, 2.50, and 2.75 molar solutions of sodium sulfate, respectively," p. 216.

"In one particular is there less confusion than formerly, and this is with regard to the origin of blood sugar from liver glycogen, but not from muscle glycogen. The process glycogen ⇄ glucose occurs in the liver and the sugar thus formed is liberated into the systematic circulation. Reconversion of this sugar into glycogen occurs in the muscles, where, as we have seen, the reaction glycogen ⇄ lactic acid takes place. The lactic acid formed during muscular contraction is for the most part reconverted into glycogen during the recovery phase, but a small amount of lactic acid escapes into the blood. Even in a state of rest, the blood contains lactic acid, which has been estimated to vary between 5 and 20 mg. per 100 cc. of blood. In moderate exercise the blood lactic acid increases. For example, walking at a rate of 3.5 miles per hour was found by Hill, Long and Lupton to cause the lactic acid content of the blood to increase from 20.9 mg. (the concentration before the period of exercise) to 36.6 mg. per 100 cc. Somewhat more strenuous exercise, namely walking at the rate of 4.1 miles per hour, produced an increase of from 21.4 mg.. the initial value, to 58.9 mg. per 100 cc.," p. 284.

"Now, what we are primarily interested in here is the fate of the lactic acid which escapes into the blood, for, it is seen, this occurs to some extent even in the resting condition and is much increased during exercise. A small portion of the lactic acid is excreted in the urine and the amount lost in this way may be considerable during violent exercise, but the larger proportion is returned to the liver, there to be resynthesized into glycogen. Thus, as Cori and Cori have pointed out, a sugar molecule can go through a complete cycle in the body; it can in turn be liver glycogen, blood sugar, muscle glycogen, blood lactic acid, and again liver glycogen. An abundance of evidence has accumulated in support of this idea but only a small portion of the literature can be referred to here. For example, the question as to whether muscle glycogen is converted directly into glucose has been virtually settled. When the liver is removed, the blood sugar rapidly falls to very low levels, as shown by the work of Bollman, Mann and Magath. As the muscle contains considerable amounts of glycogen and as this does not prevent the hypoglycemia and does not disappear to any great extent, it is concluded that muscle glycogen is not readily converted into glucose.

"It is well known that epinephrin, ether anesthesia and asphyxia produce hyperglycemia. But, as has been shown by Soskin, if the abdominal viscera, including the liver, are removed, hyperglycemia does not develop under these conditions despite the fact that there is glycogen in the muscles.

"There remains to be considered some of the evidence for the transformation of lactic acid into glycogen in the liver. It is to be supposed that in severe liver damage, as in phosphorus poisoning, the liver would lose its ability to convert lactic acid into glycogen and that there would be an increased excretion of lactic acid in the urine. This is actually the case. More direct evidence is that of Parnas and Baer, who observed glycogen synthesis in the turtle liver, perfused with sodium lactate. Similar observations have been made by many others, although occasionally negative results have been reported. Abramson, Eggleston and Eggleston were unable to demonstrate the synthesis of glycogen in the liver from racemic sodium lactate in dogs under amytal anesthesia. On the other hand, Izume and Lewis observed glycogen deposition in the liver of fasting rabbits injected subcutaneously with sodium lactate, and more recently Cori and Cori, working with rats, found that if sodium *d*-lactate is fed by mouth or injected subcutaneously, glycogen is deposited in the liver. Sodium *l*-lactate, though absorbed from the intestine at the same rate as the *d*-isomer, hardly formed any liver glycogen. Cori and Cori state that of the *d*-lactate absorbed in three hours, 40-95 per cent was retained as liver glycogen and none was excreted in the urine, whereas 30 per cent of the *l*-lactate absorbed was recovered in the urine," p. 285.

"Holmes, Gerard and Solomon have shown that during rest in oxygen there is no change in the glycogen or lactic acid content of nerve. The 'free sugar,' on the contrary, decreases in amount with time. In rabbit nerves, at 37°C., the decrease is 36 mg. percent for the first hour and progressively less during later periods. In bullfrog nerves, at 22° C., the rate of 'free sugar' is constant for at least nine hours at 6 mg. percent, per hour. This is 50 percent more than can be oxidized by all the oxygen used by the nerve at rest. The fate of this sugar is unknown," p. 287.

Wilder D. Bancroft

Colloids. *By H. R. Kruyt. Translated by H. S. van Klooster. Second edition. 23 × 15 cm; pp. xi + 280. New York: John Wiley and Sons, 1930. Price: $3.50.* The first edition of this book appeared in 1927 and was reviewed (32, 316). The general plan is the same as the earlier edition, the revision having been limited to bringing the text up to the level of 1929. General headings of the sections are: general introduction, suspensoids, emulsoids, and special cases. Practically the entire book is devoted to aqueous suspensoids and emulsoids, the special cases being intermediate between these. There is therefore little to be found concerning systems in which liquids other than water, solids, or gases are the dispersion media. The whole problem of catalysis with its large commercial importance is omitted, as are also any references to such colloidal systems as foams, fogs, smokes, etc.

"Color is indeed a characteristic property of colloidal solutions. A dilute solution of ferric chloride is slightly yellow; when this solution is poured into boiling water, a colloidal solution of Fe_2O_3 is formed by hydrolysis, and thus with the same amount of iron, a deep red liquid is produced. Sols show strong coloration, and have more pronounced absorption bands than the corresponding molecularly or ionically dispersed systems.

"It is obvious that some relation exists between the size of the dispersed particle and the light absorption. The phenomenon of the change in color from red to blue, exhibited by a gold sol at the beginning of coagulation, has been known for years and has led to the search for a direct connection between light absorption and size of particle. This relation, however, can evidently be simple only when the shape of the particles is comparable, i.e., when we are dealing, for instance, with spherical particles of different radius. When a sol flocculates, however, the particles coagulate in the form of warty lumps so that not merely the radius but also the shape of the surface and the density of the particle taken as a whole are changed. This is no doubt an important factor in the case of the gold sol, because we are not at all sure that a highly dispersed gold sol is red and a slightly disperse sol blue. On the contrary, it is quite possible to prepare a blue gold sol which is more dispersed than one that looks red.

"Zsigmondy found that, in general, a sol consisting exclusively of primary particles appears red, while the agglomeration of such spherical particles to multiple particles causes a change to blue. All blue gold sols, therefore, have undergone coagulation to some extent," p. 132. The discussion of ultrafiltration contains these paragraphs:

"This forced dialysis, or osmosis (depending on the point of view), is sometimes useful for preparatory purposes. On page 112 we saw, for instance, that such a separation of the intermicellar liquid serves a definite purpose. It has been wrongly assumed, however, that ultrafiltration in itself affords a means of determining the size of the particles. By choosing different concentrations of collodion solution, membranes of different degrees of permeability are obtained, and this has been considered to be due to different degrees of porosity of the membranes, the latter acting as sieves.

"This assumption, however, appears to be largely incorrect. Filter and membrane action is only to a limited extent comparable with the action of a sieve, and is much more dependent on the adsorption at the capillary wall than on the mechanical dimensions of the pores. For instance, a positively charged colloid cannot be filtered through a negatively charged filter paper, when the latter is rather thick; a negative sol, however, passes through easily. This question will be reconsidered later. Bechhold has reported a close connection between the concentration of his membranes and the size of the particles held back by them, but this fact in itself does not prove anything regarding the sieve mechanism of the ultrafilter. It is also possible that the adsorbability runs parallel with the particle size. If we could consider substances that are comparable as regards their adsorbability and their electro-adsorbability, a direct connection between the size of the particles and the nature of the ultrafilters might add something to our knowledge of the size of the particles; but a comparison of completely dissimilar substances, on the basis of their behavior toward ultrafilters, does not permit any conclusion regarding the size of the particles." p. 159.

"There is, however, a special reason which has led many investigators to look upon emulsoids as molecularly dispersed systems, more particularly, as electrolyte solutions; this is the fact that a great many properties of protein solutions may be explained by considering these solutions as systems of *amphoteric electrolytes*. This train of thought will be

fully considered in the next chapter and shown to be incorrect. It may be pointed out at this place that a discussion of emulsoids in terms of ionically dispersed systems must necessarily conflict with typically colloidal properties of these systems. We do not know any electrolyte solutions that scatter light in a corresponding manner (Tyndall effect), show no lowering of the freezing point or rise of the boiling point, and produce, for such minute concentrations, such exceedingly viscous solutions. The fact that protein solutions do not pass through dialysis membranes might possibly be explained on the basis of a large number of atoms in the molecule, but the other properties mentioned here cannot be connected with large molecular weight without leaving the domain of general chemical experience," p. 190.

In the preface to the first edition, reprinted in the second is found: "As is indicated on the title page, this book is intended for use as a textbook. In other words, it is the author's purpose to offer a main line of orientation to students who wish to become acquainted with the general trend of Colloid Chemistry or who desire to undertake research in this particular branch of Chemistry." Any textbook must necessarily be limited in the choice of subjects and in the exhaustiveness of their treatment. This one appears to bear out the statement: "Completeness has nowhere been the aim, but the arguments are constantly advanced." If one is content to accept the limitations chosen by Kruyt, one finds that this is a satisfactory textbook for the material covered. It is clear, readable, well supplied with references to the literature, and utilizes repeatedly the device of teaching, by an illustration or compact word-picture, the state of things as Kruyt believes them to exist in colloidal systems. For many readers this making of pictures after the argument has substantiated the picture proves a valuable aid in the retention of the concept proposed.

Herbert L. Davis

The Fundamentals of Chemical Thermodynamics. *By J. A. V. Butler. 19 × 13 cm; pp. xi + 207. London: Macmillan and Co., Limited, 1928.* In the preface the author says: "I have tried to present the subject in a logically precise yet simple form, having in mind not only the student who intends to specialize in Physical Chemistry, but also that class of chemistry students which has only a very moderate knowledge of mathematics and little sympathy with mathematical methods.... The present volume, containing the 'elementary theory,' is based mainly on cyclic processes. A second part is in preparation, which will deal with the more advanced parts of the subject, mainly on the basis of thermodynamic functions."

The subject is treated under the general heads: the first law of thermodynamics; the second law of thermodynamics; changes of state; solutions, homogeneous gaseous reactions; the galvanic cell; electrode potentials; concentration cells and activities; electrolysis. The book is concise; it is pretty well written; and it can be recommended to students.

There are some things which should be changed in the next edition. Kirchhoff's name is misspelled throughout and Julius Thomsen suffers. Arragonite is probably a typographical error. In this country we should mean something different from what Mr. Butler does by the statement, p. 88, that "in general, an increase of pressure favours the state with the smallest volume." No student will see how one measures an electromotive force rather than a potential drop with a potentiometer, p. 109. This should be made clear or should be omitted. It is probable that the student will also be bothered a good deal by the thermionic work function, p. 124. Calomel should be written Hg_2Cl_2, p. 133, and the German spelling of cation is unfortunate, p. 143. Faraday was an Englishman.

On p. 79 is an illustration of how difficult it is to say just what one wishes to. The author has moved "the semipermeable piston up (gainst pressure P) until a quantity of solvent equal to that which gives one mol of the vapour has passed through it. If ΔV is the decrease in the volume of the solvent [solution?], the work done is $P\Delta V$."

The author spoils it all by saying four lines lower that "it should be observed that ΔV is the volume of the solution containing that quantity of solvent which gives one mol of the vapour." If we had a solution containing benzene and toluene in the ratio of 78:92 in grams, the volume through which the piston would move to push out 78 grams of benzene would

be less than one half the volume of the solution containing 78 grams of benzene, if we ignore the difference between the molecular volumes of benzene and toluene.

The activity coefficient of ten-molal hydrochloric acid is 10.55 and of sixteen-molal acid is 43.2, p. 161. As the author says, "the activities and activity coefficients are quantities which express the actual behaviour of substances in solution, without asserting that it is due to one effect or another. If the ions combine to form molecules to any extent, the effect on the behaviour is included in the activity," p. 167.

Wilder D. Bancroft

Polar Molecules. *By P. Debye. 23 × 15 cm; pp. 172. New York: Chemical Catalog Company, 1929. Price: $3.50.* In the preface the author says: "This book contains a survey of questions treated in connection with the conception of polar molecules as being systems having a distribution of electrical charges which can be characterized by a permanent electric moment. Since the appearance in 1912 of my first article many contributions on the experimental side of the problem have shown that absolute measurement of polarity based on this idea may successfully by used to determine the geometrical arrangement of the atoms in a molecule. On the theoretical side the introduction of the quantum theory in its most modern form has made it possible to develop in detail the connection existing between polarity and the phenomena of dispersion and absorption, especially in the infra-red. An interesting example of the inter-dependence of experiment and theory also resulting from the electrical definition of polarity is exhibited in the field of the electrical saturation phenomena, analogous to ferromagnetism," p. 3.

The chapters are entitled: fundamental electrostatic field relations; polarizability and molecular structure; measurements of polarity and its connection with chemical structure; the constitution of simple polar molecules; anomalous dispersion for radio frequencies; electrical saturation effects; dielectric phenomena and quantum theory; energy levels and wave mechanics; rotating molecules; dispersion and absorption of polar gases.

"The word polarity has been used in different ways to express molecular properties more or less connected with the actual arrangement, or the mobility of, the charges of which molecules are supposed to consist. All definitions have, in common, the feature that they are based on the fundamental picture according to which a molecule may be represented as a system of electric charges, and at the outset it is not at all necessary to decide as to whether those charges have to be taken as discrete units, or if the natural phenomena can be better represented by introducing a continuous distribution, more in agreement with the picture in modern quantum theory. The fundamental proposition being the electrical viewpoint, it is obvious that we may expect to advance our knowledge of molecules by studying more closely their behavior under the influence of a disturbing electric field. This field may be an external field, subject to our control, or may be the field created by other neighboring molecular systems. In the last case we will ultimately obtain an electrical theory of the equation of state; in the first case we are dealing with dielectric and optical properties. As the last named properties can be treated most simply, and still give us much insight into the molecular structure, we will in this treatise confine our attention chiefly to these dielectric and optical properties alone. A brief review of certain features of classical electrical theory will give the necessary foundation," p. 7.

When discussing the dielectric constants of ionic solutions, the author says, p. 112: "If, therefore, the water contains a number of ions, there will be a region around each ion which contains electrically saturated water. If we now superpose a small homogeneous external field in order to measure the dielectric constant of the electrolyte solution, the regions of the water surrounding the ions will be made more or less inactive due to their saturation. A very rough picture of this occurrence will be obtained if each ion with its surrounding water is replaced by a spherical cavity, the radius of which depends on the distance over which the saturation effect is appreciable," p. p. 112.

For small concentrations of an electrolyte the apparent dielectric constant decreases with increasing concentration, which is accounted for by the saturation, p. 114. "At higher concentrations it is found that the dielectric constant comes back to, and surpasses,

the value for the pure solvent. The qualitative picture proposed to explain this concentration effect is that, at higher concentrations, an appreciable number of doublets may be formed by the coupling of positive and negative ions, and that these doublets will give an increase in the dielectric constant by their orientation. The question of a chemical interaction, resulting in a relatively permanent and definite coupling, being necessary, or of the coupling due to the interionic electric forces being sufficient, has not yet been treated," p. 144

"The whole subject of saturation in ionic solutions and connected phenomena has been treated in a highly hypothetical way. On the other hand the existing experiments are far from satisfactory. . . . The table shows clearly the big differences, even in magnitude, of the different experimenters. . . . The valency relation is satisfied most completely by the values of Sack, less completely by those of Skancke and Schreiner and of Walden and his collaborators, and not at all by those of Deubner. It is doubtful whether these differences can be explained by the differences in frequency. The fact is that no definite conclusions with regard to any theory can be drawn from the measurements in their present condition. Old methods will have to be improved and new methods introduced," p. 122.

The reviewer does not like the word "hydroiodic", p. 40; that seems to be a case of misguided purism.

Wilder D. Bancroft

Reference Book of Inorganic Chemistry. *By Wendell M. Latimer and Joel H. Hildebrand. 22 × 15 cm; pp. viii + 643. New York: The Macmillan Company, 1929.* In the preface the authors say: "This book represents the fulfillment of a plan, long cherished, of providing a volume of descriptive chemistry to complete the series begun with "Principles of Chemistry" by Hildebrand, which adheres strictly to its title, and continued with the "Course in General Chemistry" by Bray and Latimer, which presents a laboratory course. The rather radical experiment in teaching general chemistry, begun in the University of California in 1912, has been somewhat hampered by the lack of a reference book on descriptive chemistry employing the language and the point of view adopted for our instructional scheme.

"This 'Reference Book of Inorganic Chemistry' has been written as a reference book rather than a text. The authors have sought to present essential chemical facts briefly, clearly, and in due relation to other facts and principles. The instructor using it will have to map out his own course, following whatever order of arrangement appeals to him. The numbering of paragraphs will make it possible for him to assign for study material selected from any desired portion of the book. We feel that many teachers will welcome the greater freedom thus afforded of developing their own pedagogical methods," p. v.

The chapters deal with: hydrogen; the inert gases; oxygen; alkali metals; alkaline earth metals; boron and aluminum; copper, silver, and gold; zinc, cadmium, and mercury; gallium, indium, and thallium; the halogens; nitrogen, phosphorous, arsenic, antimony, and bismuth; sulphur, selenium, and tellurium; carbon; silicon; the metals of Group IV; vanadium, columbium, and tantalum; chromium, molybdenum, tungsten, and uranium; manganese; iron, cobalt, and nickel; platinum and the palladium metals; scandium, yttrium and the rare earth metals; the radioactive metals.

This is far from being a pandemic chemistry; but it is a step in the right direction, and metals are taken up on p. 27. The book is distinctly an interesting one and well worth reading. The authors are a bit shaky on the difference between an adjective and an adverb, and the reviewer questions the statement, p. 280, that "excess of alkali hydroxide dissolves the precipitate [of chromic hydroxide] with the formation of chromites, but the hydroxide or hydrated oxide is precipitated upon boiling." Even for freshmen the reviewer would prefer a different wording in regard to ozone, p. 25. "The silent electrical discharge is the principal commercial method of forming ozone. This involves the action of electrons shot off from high-potential surfaces upon oxygen molecules."

One does not quite see why the crystal form of sodium nitrate should be sandwiched in between the method of making potassium nitrate and the fact that the alkali nitrates decompose when heated, p. 42.

Apart from a few infelicities, the authors are very much to be congratulated on this book. There is an immense amount of information packed into it, and it is presented in a clear and readable fashion.

Wilder D. Bancroft

Le Soufflage du Verre. *By Henri Vigreux. 16 × 11 cm., pp. 276. Paris: Librairie Dunod, 1930. Price: 35 francs.* It is somewhat surprising that opportunities for learning glass blowing even by advanced students in physics and chemistry scarcely exist in England and reliance has to be placed upon self education and experience. Under these conditions any book which describes methods of glass blowing which really can be followed and acted upon would prove invaluable. There are but few text books on this subject and nearly all of these suffer from the defect that it is difficult to follow the directions. Dr. Vigreux's little book on glass blowing is a good book although it might be regarded from the English point of view as somewhat old fashioned. The directions given in the book are clear and intelligible. It contains an interesting history of early operations in glass, continues with practical methods for making first simple and then more complex apparatus and terminates somewhat surprisingly with cements, X-ray bulbs and artificial eyes. This book is already in its third edition and is to be warmly commended both to physicists and to chemists.

Eric K. Rideal

Optical Rotatory Power. *A General Discussion held by the Faraday Society. 25 × 16 cm; pp. ii + 197. London: Gurney and Jackson, 1930. Price: 10 shillings, 6 pence.* This volume is a separate issue of that part of the Transactions of the Faraday Society which contains the papers read at the general discussion held in London during last April and the comments that arose from the papers. The papers are classified on four groups, the physical basis of optical rotation, apparatus and methods, the rotatory power of solutions and finally the chemical aspects of rotatory power. In all there are twenty one papers together with an introduction and a concluding summary by Professor Lowry.

Reading through this volume gives one a very good impression of the present position of many of the diverse problems that await solution in this subject. The majority of the papers are summaries of investigations already published and, as such, will be of the greatest value. To the reviewer two of the most interesting are those of Kuhn and of Wolf. The former is a simplified exposition of Kuhn's theory of the physical basis of rotatory power which appeared in the *Zeitschrift für physikalische Chemie* last year; it is presented in an extremely able way and can be followed by those who do not possess an extensive mathematical equipment. The latter, that of Wolf, deals with the question of free rotation in saturated carbon compounds, and indicates a new method of investigating the extent of the freedom of rotation. As Wolf points out, classical stereochemistry was based on three postulates, of which two, constancy of atomic distances and constancy of valency angles, have been justified as first approximations by all recent methods of physical investigation. The third postulate, free rotation, however, has had to be abandoned in a few cases by even the most classical of stereochemists, so that this preliminary account of a physical investigation into the extent of free rotation is of the greatest interest. *T. W. J. Taylor*

Biological Applications of Absorption Spectrophotometry. *16 × 24 cm; pp. 12. London: Adam Hilger Ltd., 1930. Issued gratis.* The study of absorption spectra has in recent years occupied an important place in biochemical investigation, particularly with regard to vitamin A and vitamin D. Very interesting results have also been obtained with proteins, blood sera, biological pigments and the respiratory ferments. There are probably few fields of research in which hasty deductions and inadequate technique present greater dangers, and this publication is useful both in calling attention to the possibilities of absorption spectrophotometry and to the need for accuracy in gathering data and care in interpretation.

R. A. Morton

Erratum

Owing to an oversight on the part of the editor the legends were omitted from the cuts in the article by Levene and Rothen (34, 2567).

Fig. 1. The concentration of mandelic acid is 0.05N throughout, except in the case of $Ca(OH)_2$ where the concentrations are indicated in brackets on the curve.

Fig. 2. The concentration of sodium mandelate is constant and equal to 0.05N.

Fig. 3. The concentration is 0.05N in mandelic acid and in HCl.

THE STATISTICAL TREATMENT OF REACTION-VELOCITY DATA. I.

A Critical Review of Current Methods of Computation*

BY LOWELL J. REED AND EMERY J. THERIAULT

Introduction

In the study of reaction-velocity, although analyses and manipulations of unusual difficulty are frequently carried through, and a high order of mathematical skill is demanded, it is nevertheless true that, almost without exception, no attempt is made to estimate the degree of confidence which may be placed on the final results. In the absence of appropriate precision values it appears doubtful whether, in most cases, a decision can ever be reached concerning the validity of the proposed theories which prompt these laborious investigations..

In illustration of the point in question, let it be assumed that the critical increment for a given reaction is 50,000 ± 3,000. Such a deviation does not appear improbable in certain published results. Now, given the value of K_∞ from theoretical or other considerations, let the validity of a particular theory be tested by comparing a value of K_T calculated by the formula

$$K_T = K_\infty e^{\frac{-50,000 \pm 3,000}{RT}} = K_\infty e^{\frac{-50,000}{RT}} . e^{\frac{\pm 3,000}{RT}}$$

with an observed value of the velocity constant at the same temperature. When the temperature on the absolute scale is 328°, the numerical value of the term $e^{\frac{\pm 3,000}{RT}}$ is $10^{\pm 2.0}$, that is, the calculated value might be multiplied or divided by 100 without violence to the data. With this degree of latitude in the adjustment of the calculated value of K_T, the proof or disproof of proposed mechanisms of molecular behavior is obviously impossible.

In other directions a disregard of accepted statistical procedures has led to conclusions which must be accepted with caution. Thus the unimolecularity of the inversion phenomenon, for a long time the classical illustration of a "unimolecular" process, has been questioned on grounds of systematic divergencies in the velocity constants computed by the usual methods (cf. Pennycuick, 1926). Explanations based on the increasing activity of the sucrose or of the hydrogen-ion have been offered to account for increasing values of K, but no satisfactory theory appears to have been advanced to cover cases in which the trend in the K values is decidedly downward. In

* From the Department of Biostatistics of the School of Hygiene and Public Health of the Johns Hopkins University, Paper No. 144, and the Stream Pollution Investigation Laboratory, United States Public Health Service.

all of these studies, no account appears to be taken of the fact that, especially in work of the highest precision, a trend in the K values must inevitably be obtained when the usual methods of computation are employed.

In the main the statistical discussion which follows will be limited to a consideration of unimolecular reaction-velocity data. In the present paper it will be shown that the various methods in vogue for the calculation of velocity constants will by no means give equivalent results.

In a separate paper a detailed presentation will be given of a statistical procedure developed by us and already applied to the derivation of velocity constants in biochemical oxygenations (Theriault, 1927). The procedure in question will be expanded to cover cases where constant errors must be eliminated from the observations and appropriate methods for the derivation of precision values will also be given.

1. Nomenclature

For a unimolecular process, the differential equation representing the rate of reaction is

$$\frac{dY'}{dt'} = K(L'-Y') \tag{1}$$

or,

$$\frac{dZ'}{dt'} = -KZ' \tag{1a}$$

depending on whether attention is focused on the amount of material, Y', which has decomposed or on the amount of material, $Z' = L'-Y'$, which remains undecomposed at the time t'. The integration of these expressions between the concentration limits ($Y' = L'-Z'$) and ($Y_0' = L'-Z_0'$) and the corresponding time limits t' and t_0' gives

$$K = \frac{1}{t'-t_0'} ln \frac{L'-Y_0'}{L'-Y'} \tag{2}$$

or,

$$K = \frac{1}{t'-t_0'} ln \frac{Z_0'}{Z'} \tag{2a}$$

In equations (2) and (2a) the following significance attaches to the various symbols:

Y' = Amount of material decomposed (transformed, inverted, diffused, etc.) at the time t'.

Y_0' = Amount of material decomposed at the time, t_0'.

$Y'-Y_0'$ = Amount of material decomposed during the time interval $(t'-t_0')$.

L' = Amount of undecomposed material present when t' = zero; the limiting value of Y'.

$L'-Y_0' = Z_0'$ = Amount of undecomposed material present when $t' = t_0'$.

$L'-Y' = Z'$ = Amount of undecomposed material present at the time t'.

t' = Time which has elapsed since the start of the reaction.

t_0' = Time at which the observations were begun measured in terms of time elapsed since the start of the reaction.

For the purpose of placing equations (2) and (2a) in a more convenient form, it may be assumed in any given experiment that the observed quantities were

$$t = t' - t_0'$$
$$Y = Y' - Y_0'$$
and, $$L = L' - Y_0' = Z_0' \qquad (3)$$

Substituting in (2) and (2a)

$$K = \frac{1}{t} ln \frac{L}{L-Y} \qquad (4)$$

or,

$$K = \frac{1}{t} ln \frac{L}{Z} \qquad (4a)$$

Equations (4) and (4a) might also have been derived on the equivalent assumption that t_0' and Y_0' in equations (2) and (2a) were equal to zero. For the purposes of the present discussion it will be convenient, however, to assign to L, Y and Z the significance denoted by (3).

In addition to equations (4) and (4a), use will also be made of the expressions

$$Y = L(1-e^{-Kt}) \qquad (5)$$

and, $$Z = L e^{-Kt} \qquad (5a)$$

obtained by solving for Y and Z in equations (4) and (4a).

2. The Usual Methods of Computation

Given a series of timed observations, $Y_1, Y_2, \ldots, Y_n$, of a supposedly unimolecular process, together with the corresponding times $t_1, t_2, \ldots, t_n$ and the experimentally determined value of L, the usual procedure in deriving the average value, $\overline{K}$, of K is, first of all, to calculate a series of K values, such as

$$K_1 = \frac{1}{t_1} ln \frac{L}{L-Y_1}$$
$$K_2 = \frac{1}{t_2} ln \frac{L}{L-Y_2} \qquad (6)$$
$$\ldots\ldots\ldots\ldots,$$
$$K_n = \frac{1}{t_n} ln \frac{L}{L-Y_n}$$

If the series of K values obtained does not manifest an ascending or descending tendency, $\bar{K}$ is then found by taking the simple arithmetical average of $K_1, K_2, \ldots, K_n$.

An objection frequently raised against this procedure is that in deriving the values K_1, K_2, etc., the observation L is used n-times as frequently as the equally reliable observations $Y_1, Y_2, Y_3, \ldots, Y_n$. It may also be objected that the values of K in (6) are by no means possessed of an equal degree of reliability. Thus, during the early stages of the reaction, when the value of Y is small, the ratio $L/(L-Y)$ is nearly unity. Conversely, in the later stages of the reaction, the value of Y approaches to that of L and the ratio in question approaches infinity. In either case the logarithm of the ratio will be disproportionately affected by otherwise unimportant errors in the estimation of either L or Y. The conclusion appears warranted that in averaging the values of K derived by means of equations (6), some system of weighting should be employed.

It is of more consequence perhaps that even when Y is determined with great accuracy, a series of ascending or descending values of K must inevitably be obtained when equations (6) are used, unless L is entirely free from error. As L, in general, will always be affected by some experimental error, the above statement implies that when the method of computation under discussion is employed no chemical reaction can appear unimolecular throughout its course, provided that Y has been determined with sufficient precision. Thus, let it be assumed that Y has been determined with a high degree of precision so that the trend in the K values deduced under (6) is not masked by relatively large errors of observation. Let it be assumed that, if possible, L has also been determined with an equal degree of precision so that the true value, L′, of L differs from L by the small quantity s. In order to obtain the correct values of K_1, K_2, etc., use should therefore be made of the corrected expression

$$K = \frac{1}{t} ln \frac{L'}{L'-Y}$$

If, instead of this equation, use is made of the uncorrected expression,

$$K = \frac{1}{t} ln \frac{(L'+s)}{(L'+s)-Y} = \frac{1}{t} ln \frac{L}{L-Y}$$

the correct value of the fraction

$$\frac{L'+s}{(L'+s)-Y} = \frac{L}{L-Y}$$

will only be obtained when Y is zero. With increasing values of Y (and t) the numerator of the fraction will remain constant while the denominator decreases. The numerical value of the fraction will therefore increase disproportionately with time if s is negative and it will decrease too rapidly if s is positive. The logarithm of the fraction will show a corresponding increase or decrease. As the result of a constant error in L, an ascending or de-

scending series of K values will therefore be obtained depending on whether the value of L is smaller or greater than its true value. From similar considerations it may readily be shown that a trend in the K values must result when the times t_1, t_2, t_3, etc., or the observations Y_1, Y_2, Y_3, are affected by constant errors superimposed on the usual plus or minus errors of observations.

An excellent example of the difficulty in question is afforded by the work of Pennycuick (1926). Using methods of utmost refinement, Pennycuick attempts to show that the inversion of sugar cannot be represented accurately by a formula of the unimolecular type, the basis for this conclusion being the presence of a decided trend in the K values computed by three different formulae. In explanation of this trend it is stated: "The decrease in water content and the increase in hydrogen-ion activity during inversion, are sufficient to explain the steady increase of the coefficients."

Scatchard (1926), accepting Pennycuick's findings in regard to a systematic divergence in the K values, points out that equation (1a) defining a unimolecular process does not apply to the values in question as the expression cannot be integrated unless K is given in terms of t. By a graphical method, Scatchard then deduces the following empirical relation between K and t

$$K = K_1 (1 - 0.03\, e^{-0.01}\,)$$

and by substitution in equation (1a) he derives the modified formula

$$\log \frac{Z_1}{Z_2} = K_1(t_2 - t_1) \left[1 - \frac{3}{t_2 - t_1} (e^{-0.01t_1} - e^{-0.01t_2}) \right]$$

When certain empirical allowances are made for constant time errors, the individual measurements are said to conform to the above formula with a mean deviation of 0.2 to 0.5 per cent, "so the agreement with the theory is as good as could be expected." Scatchard concludes: "The evidence for the increase in the hydrogen-ion activity appears sound, but these results indicate that there must be some compensating tendency to diminish the rate." The trend in the K values is ascribed to inefficient mixing. "Five hours does not appear too long for this process."

It will be shown in a subsequent section that, when appropriate methods of computation are used, the data of Pennycuick conform with great fidelity to the classical unimolecular expression.

In the light of the preceding discussion it would appear that, in work of the highest precision, the usual test for unimolecularity, namely the possibility of deriving a series of K values which do not manifest a trend, must be discarded. In less precise work, definite conclusions as to the unimolecularity of a process cannot, in general, be drawn. In such work a trend in the K values will nevertheless exist although it may be masked by counterbalancing positive or negative errors in the estimation of Y. In the presence of a trend the procedure of averaging a series of K values is open to serious objections, as the most reliable value of K may correspond not to the average of all the K values but rather to the first or last values in the series, depending on the

sign of the constant error. In this sense the procedure of rejecting either the initial or the terminal results in a series of K values is obviously unsound (cf. Wobbe and Noyes, 1926).

As an alternative method of deriving the average value of K, use is also made of the "chain" or "short-time interval" formulae:

$$K_1 = \frac{1}{t_2 - t_1} ln \frac{L - Y_1}{L - Y_2}$$

$$K_2 = \frac{1}{t_3 - t_2} ln \frac{L - Y_2}{L - Y_3} \qquad (7)$$

$$K_{n-1} = \frac{1}{t_n - t_{n-1}} ln \frac{L - Y_{n-1}}{L - Y_n}$$

If the logarithms, $ln(L-Y_1)$, $ln(L-Y_2)$, etc., in (7) are replaced by the symbols, N_1, N_2, etc., the average value of K is,

$$\overline{K} = \frac{1}{n-1}\left(\frac{N_1 - N_2}{t_2 - t_1} + \frac{N_2 - N_3}{t_3 - t_2} \cdots \frac{N_{n-1} - N_n}{t_n - t_{n-1}}\right) \qquad (8)$$

In deriving the set of equations represented by (7) it is sometimes assumed (cf. Pennycuick, 1926, p. 11) that the individual values of K have been found by the subtraction of two expressions such as

$$K_{n-1} = \frac{1}{t_{n-1}} ln \frac{L}{L - Y_{n-1}}$$

and,

$$K_n = \frac{1}{t_n} ln \frac{L}{L - Y_n}$$

with the result

$$K_n t_n - K_{n-1} t_{n-1} = ln \frac{L - Y_{n-1}}{L - Y_n} \qquad (9)$$

If it be now assumed that $K_n = K_{n-1}$, it follows that

$$K = \frac{1}{t_n - t_{n-1}} ln \frac{L - Y_{n-1}}{L - Y_n} \qquad (10)$$

As the value of L is fixed, the transition from (9) to (10) is evidently forced. More logically, the set of equations given under (7) may be regarded as the result of substitution in (2); that is, the terms t_0' and Y_0' are successively assigned the values

$$t_1, Y_1 ; t_2, Y_2 ; \text{etc.}$$

As to the merits of equations (7), it is to be noted that, as in the corresponding equations (6), the observation L is repeated n-times as frequently as the observations Y_1, Y_2, etc. Another objection relates to a cancellation effect which will briefly be discussed.

Let it be assumed that the observations have all been equally spaced in respect to time, so that

$$(t_2-t_1) = (t_3-t_2) \ldots\ldots = (t_n-t_{n-1}) = \Delta t$$

Under this condition, equation (8) reduces to the simple form

$$\overline{K} = \frac{N_1-N_n}{(n-1)\Delta t} = \frac{N_1-N_n}{t_n-t_1} = \frac{1}{t_n-t_1} \ln \frac{L-Y_1}{L-Y_n}$$

that is, only the first and last observations are considered in deriving the average value of K (cf. Wagner, 1923, p. 132).

In this case, it is obvious that errors of any order of magnitude in the estimation of the intermediate values, $Y_2, Y_3, \ldots, Y_{n-1}$, would be without influence in the final result. The data of Daniels and Johnston (1921, p. 64; their experiment No. 25) afford an example of this method of calculation. On the basis of 6 observations equally spaced at one-minute intervals, they compute 5 values of K by means of equations (7). They then deduce the average value of K by the formula

$$\overline{K} = \frac{K_1 + K_2 + K_3 + K_4 + K_5}{5}$$

$$= \frac{337 + 288 + 329 + 434 + 337}{5 \times 10^3} = 345 \times 10^{-3}$$

Using equation (2) and neglecting the intermediate observations, the result is the same, namely

$$\overline{K} = \frac{2.303}{7-2} \log \frac{32.6 - 18.6}{32.6 - 30.1} = 345 \times 10^{-3}$$

The cancellation effect in question is also apparent in all of the other data presented by Daniels and Johnston (1921) even though the time intervals may vary in a given experiment. Thus, in their experiment No. 23, the first nine observations are separated by one-minute intervals while the remaining three observations are spaced 2 minutes apart. Equation (8) accordingly assumes the form

$$\overline{K} = \frac{2.303}{11}\left(\log \frac{L-Y_1}{L-Y_8} + \frac{1}{2} \log \frac{L-Y_8}{L-Y_{11}}\right)$$

$$= \frac{2.303}{11}\left(\log \frac{319.5 - 128.2}{319.5 - 299.4} + \frac{1}{2} \log \frac{319.5 - 299.4}{319.5 - 316.5}\right)$$

$$= 291.3 \times 10^{-3}$$

a result which accords exactly with the true average* of the eleven K values

* The average value given by Daniels and Johnston ($K = 290.0 \times 10^{-3}$) is apparently in error. The value 291.3×10^{-3} accords with the true average of their figures. The difference may arise from minor typographical errors or else it may be due to the use of some system of weighting.

given by Daniels and Johnston, although only three observations were used in the computation. It is obvious that, in general, a "chain" formula should not be used in determining the average value of K. Neither should such a formula be employed as a means of detecting a trend in the value of K, as the trend, although present, will be masked by the occurrence of alternate high and low values of K whenever a relatively large error occurs in the observations.

In passing, it may be noted that "chain" formulae are generally used when the times, t_1, t_2, etc., are known to be affected by an appreciable constant error. A constant error in the determination of t_1, t_2, etc., will evidently cancel out when expressions such as (t_2-t_1), etc., are used. However, even when the observations are not equally spaced, this procedure gives undue weight to the initial and final observations. It is also to be noted that, at best, this method of computation neglects another important source of constant error, namely the constant error in L.

3. Miscellaneous Methods of Computation

Guggenheimer (1926) considers that the procedures thus far discussed are justifiable only when the value of L has been determined with appreciably greater precision than the other observations, Y_1, Y_2, etc. However, "Not infrequently it is inconvenient or even impossible to observe the end-point (L) directly at all; in such cases it is usual to obtain a value for it by extrapolation. If this is done by any straightforward method the value of L obtained will, at best, be no more accurate than any of the directly observed values of Y. The best value of K will not then be obtained by any of the usual methods which give great weight to L." To obviate the difficulty in respect to the undue weighting of L, Guggenheimer proposes that n readings Y_1, Y_2, Y_3, etc., be made at the times t_1, t_2, ..., t (without any restrictions as to the intervals) and that n more readings Y_1', Y_2', etc., be made at the times (t_1+r), (t_2+r), ... (t_n+r) each a constant time r after one of the previous set. "Provided that r is several times as great as the time of half-completion of the reaction, the accuracy will be of the same order as in taking n ordinary readings and further taking n readings of the end-point spread over an interval of time equal to that spent on the ordinary readings; in fact, it is equivalent to obtaining a very accurate end-point and using it in the usual manner."

Sheppard (1926; cf. Sheppard and Mees, 1907) has shown that if two observations only are to be made, it may be advantageous to select them in such a manner that $t_2 = 2t_1$. Then, using equation (4)

$$K = K_1 = \frac{1}{t_1} ln \frac{L}{L-Y_1} \tag{11}$$

$$K = K_2 = \frac{1}{2t_1} ln \frac{L}{L-Y_2} \tag{12}$$

The assumption $K = K_1 = K_2$ is justifiable if only two observations are at hand, provided that the value of L is not fixed. On dividing (11) by (12) and solving for L, the result is

$$L = \frac{Y_1^2}{2Y_1 - Y_2} \tag{13}$$

Equation (13) gives L in terms of the two observations Y_1 and Y_2. By substitution in (11) or (12), the value of K may therefore be determined. This method of computation has also been discussed by Smith (1926) who states that the procedure can be extended to bimolecular reactions. This extension, however, is not formulated by Smith.

Guggenheimer (1926) considers that it would be a more natural procedure, instead of eliminating K, to eliminate L. Thus, using equation (5), let two observational equations be

$$Y_2 = L\left(1 - e^{-2Kt_1}\right) \tag{14}$$

and,

$$Y_1 = L\left(1 - e^{-Kt_1}\right) \tag{15}$$

By division,

$$\frac{Y_2}{Y_1} = \frac{1 - e^{-2Kt_1}}{1 - e^{-Kt_1}} = 1 + e^{-Kt_1}$$

From which,

$$K = \frac{1}{t_1} ln \frac{Y_1}{Y_2 - Y_1} \tag{16}$$

Equation (16) gives the value of K in terms of two observations Y_1 and Y_2 and without reference to L.

The procedures just described are evidently designed for use in orientation experiments where approximate values of K or L are desirable or in cases where the direct estimation of L is inconvenient or impossible. The results obtained will evidently possess a minimum of reliability as the computation, without resort to weighting, must be restricted to the minimum number of possible observations, namely two, corresponding to the two constants L and K in equations (4) or (5). In special cases approximate values of K and L may even more readily be obtained by the use of nomographical charts (Buchanan, 1926) or by mechanical means (Latshaw, 1925).

Schmid (1926) has proposed a method of calculating K which possesses certain points of interest. Starting with the set of equations

$$\begin{aligned} K_1 &= \frac{N_1 - N_2}{t_2 - t_1} \\ K_3 &= \frac{N_3 - N_4}{t_4 - t_3} \\ K_5 &= \frac{N_5 - N_6}{t_6 - t_5} \end{aligned} \tag{17}$$

where $N_1 = \ln(L - Y_1)$; $N_2 = \ln(L - Y_2)$, etc. Schmid apparently assumes that the relative weights of the individual values K_1, K_3, etc., are $(t_2 - t_1)$, $(t_4 - t_3)$, etc. The weighted average of K then becomes

$$\bar{K} = \frac{(t_2-t_1)(K_1) + (t_4-t_3)(K_3) + (t_6-t_5)(K_5)}{(t_2-t_1) + (t_4-t_3) + (t_6-t_5)} \qquad (18)$$

On substituting from (17) in (18), there results the simple formula

$$\bar{K} = \frac{N_1-N_2 + N_3-N_4 + N_5-N_6}{-t_1 + t_2 - t_3 + t_4 - t_5 + t_6} \qquad (19)$$

It is claimed by Schmid that his formula involves a minimum of arithmetical work; also that the precision with which K is determined is equal to that attainable by the method of least-squares. The system of weighting implied in Schmid's formula is obviously arbitrary.

Rice, Fryling and Wesolowski (1924), in extension of the work of Rice and Kirkpatrick (1923), have proposed a system for weighting the values of K obtained by equations (6) when the observed quantity is $Z = L-Y$. Assuming that t is relatively free from error, they first derive the partial derivatives of K with respect to Z and L in the expression

$$Z = Le^{-Kt}$$

and so obtain

$$\frac{\delta K}{\delta L} = \frac{1}{tL}$$

and,

$$\frac{\delta K}{\delta Z} = \frac{1}{tZ}$$

From which the partial fractional errors in K become

$$\left(\frac{\delta K}{K}\right)_L = \frac{\delta L}{KtL} = \frac{\delta L}{L} \div \ln \frac{L}{Z} \qquad (20)$$

and,

$$\left(\frac{\delta K}{K}\right)_Z = \frac{\delta Z}{KtZ} = \frac{\delta Z}{Z} \div \ln \frac{L}{Z} \qquad (21)$$

On the tacit assumption that the absolute error in Z will be of the same order of magnitude as that in L, they then express $\delta Z/Z$ in terms of $\delta L/L$. Thus,

$$\frac{\delta Z}{Z} = \frac{\delta L}{Z} = \frac{\delta L}{L} \cdot \frac{L}{Z}$$

Substituting in (21),

$$\left(\frac{\delta K}{K}\right)_Z = \frac{\delta L}{L}\left(\frac{L}{Z}\right) \div \ln \frac{L}{Z} \qquad (22)$$

The total (fractional) error in K is then assumed to be given by the square root of the sum of the squares of the partial fractional errors; so that, using (20) and (22),

$$\frac{\Delta K}{K} = \sqrt{\left(\frac{\delta K}{K}\right)_L^2 + \left(\frac{\delta K}{K}\right)_Z^2} = \frac{\delta L}{L} \frac{\sqrt{1 + \left(\frac{L}{Z}\right)^2}}{\ln \frac{L}{Z}} \qquad (23)$$

$$= \frac{\delta L}{L} \cdot F(L,Z) = \frac{\delta Z}{L} \cdot F(L,Z)$$

Somewhat arbitrarily, the quantity F(L,Z) is then defined as the weight of K. On plotting this function against the fraction, $1 - Z/L$, of material which has reacted, the conclusion is reached that the maximum relative weight of K is reached when a unimolecular reaction is 66 per cent completed.

In criticism of the system of weighting proposed by Rice, Fryling and Wesolowski, it may be objected that, at best, such procedures are applicable only to series of K values which do not show a trend. As already shown, this condition will rarely be satisfied when an accurate series of observations is made. Otherwise stated, such treatments make no allowance for the presence of constant errors.

In another direction, the procedure proposed by Rice, Fryling and Wesolowski is open to the objection that, unless each value of L in equations (6) represents an independent observation (cf. Guggenheimer, 1926), the error δL will be a constant throughout a series of calculations. On the other hand, δY may be regarded as an error which is equally likely to be positive or negative. It is only when L is a quantity affected by plus or minus errors that the step represented by equation (23) would be justifiable.

If L is regarded as a true constant, the differentiation of the expression

$$Y = L(1 - e^{-Kt})$$

gives,

$$\Delta Y = L\, t\, e^{-Kt} \cdot \delta K$$

From which

$$\Delta K = \frac{\delta Y}{L(te^{-Kt})}$$

It follows that, for minute variations in K, the error ΔK will be a minimum when the function $t\, e^{-Kt}$ is a maximum. Such a maximum will occur when

$$\frac{d(t\, e^{-Kt})}{dt} = e^{-Kt} - K\, t\, e^{-Kt} = 0$$

From which, when ΔK is a minimum,

$$K = 1/t$$

Using equation (5), it may readily be shown that, under the assumed conditions, the fraction of material used up will be

$$Y/L = 1 - e^{-1} = 1 - \frac{1}{2.71} = 0.632$$

If the assumption regarding the constancy of L is ever justified, it would appear that a velocity constant will be determined with a maximum of precision when the period of observation is so selected that the reaction has proceeded to the extent of 63.2 per cent. On the same basis the weight of a given value of K might be expressed in terms of the function $t\,e^{-Kt}$. Such a procedure would evidently be inapplicable to ascending or descending series of K values.

If L and Z are both regarded as variables the following treatment should apply. For convenience, the equation

$$Z = L\,e^{-Kt}$$

will first be placed in the equivalent form

$$Kt = ln\,\frac{L}{Z} = ln\,L - ln\,Z$$

From which,

$$t\Delta K = \frac{\delta L}{L} - \frac{\delta Z}{Z}$$

Now, if it is assumed that the error in L is of the same order of magnitude as that in Z, we may write

$$Kt.\,\frac{\Delta K}{K} = \frac{\delta L}{L} - \frac{L}{L}\cdot\frac{\delta L}{Z} = \frac{\delta L}{L}\,(1 - \frac{L}{Z})$$

Substituting the value of Kt and transposing, it follows that

$$\frac{\Delta K}{K} = \frac{\delta L}{L}\cdot\frac{(1 - L/Z)}{ln\,L/Z} \qquad (23a)$$

Equation (23a) may be compared with equation (23). The difference between these two functions arises from the fact that there is correlation in errors between the two terms $(\delta K/K)_Z$ and $(\delta K/K)_L$, whereas the formulation of equation (23), based on the theorem relating to the square root of the sum of the squares of partial fractional errors, presupposes the absence of such correlation. The difficulty is avoided by deriving $\Delta K/K$ directly as shown above.

If L and K are regarded as quantities affected by errors of observation and if t is free from error, the partial differentiation of equations (4) and (4a) gives, respectively,

$$\Delta Y = (1 - e^{-Kt})\,.\,\delta L + L\,t\,e^{-Kt}\,.\,\delta K$$

and,

$$\Delta Z = \quad e^{-Kt}\,.\,\delta L - L\,t\,e^{-Kt}\,.\,\delta K \qquad (24)$$

By substitution in these equations of the approximate values of K and L, it would be possible to estimate the effect on Y or Z of arbitrarily selected values of δL and δK and so obtain some idea of the precision with which Y or Z must be determined in order to secure a given degree of precision in K or L. Conversely, and with particular reference to the treatment proposed by Rice, Fryling and Wesolowski, if ΔZ if regarded, say, as the difference

between an observed quantity, Z, and a calculated quantity Z′ obtained by substituting known values of K and L in (4a), then the value of δK (and δL) could be found by elimination from two equations such as (24). However, if more than two equations are available, the solution becomes indeterminate and resort must be made to the method of least-squares.

4. Attempted Applications of Least Squares

The shortcomings of the procedures thus far discussed have prompted at least three writers to attempt a solution of the problem by the application of the least-squares criterion.

Moesveld (1923) has discussed the least-squares treatment of data pertaining to reactions of the second or higher orders. For such reactions,

$$\frac{dY}{dt} = K(A-Y)^a(B-Y)^b(C-Y)^c(D-Y)^d \text{ etc.}$$

For the special case, $A = B = C \ldots\ldots = L$ and $a = b = c \ldots\ldots = n$

$$\frac{dY}{dt} = K(L-Y)^n$$

The integration of this expression gives

$$K = \frac{1}{(n-1)t}\left(\frac{1}{(L-Y)^{n-1}} - \frac{1}{L^{n-1}}\right)$$

For the supposedly fourth-order reaction which Moesveld uses as an example,

$$K = \frac{1}{3t}\left(\frac{1}{(L-Y)^3} - \frac{1}{L^3}\right)$$

From which,

$$\frac{1}{(L-Y)^3} = 3Kt + \frac{1}{L^3}$$

or,
$$W^3 = K't + W_0^3 \qquad (25)$$

where,
$$W^3 = \frac{1}{(L-Y)^3};\ W_0^3 = \frac{1}{L^3};\ K' = 3K$$

Moesveld then places equation (25) in the form

$$Y = af_1 + bf_2 \qquad (26)$$

where,
$$Y = W^3;\ a = 3K;\ f_1 = t;\ b = W_0^3;\ f_2 = 1$$

As will be shown elsewhere, the least-squares solution of a series of equations such as (26) gives the following values for the constants a and b

$$a = \frac{n\,.\,\Sigma f_1 Y - \Sigma f_1\,.\,\Sigma Y}{n\Sigma f_1^2 - (\Sigma f_1)^2} \qquad (27)$$

$$b = \frac{\Sigma f_1^2\,.\,\Sigma Y - \Sigma f_1\,.\,\Sigma f_1 Y}{n\Sigma f_1^2 - (\Sigma f_1)^2} \qquad (28)$$

For the purpose of simplifying the computations, Moesveld recommends that the periods of observation be selected in such a manner that $\Sigma f_t = \Sigma t = o$. This is accomplished by making an uneven number of observations and by spacing the observations symmetrically in respect to the middle observation. If the center of coordinates is then referred to the middle observation, the term $\Sigma f_t = \Sigma t$ will be of the form

$$-\frac{(n-1)}{2} \ldots -6\ -5\ -4 \ldots\ldots o \ldots\ldots +4\ +5\ +6 \ldots\ldots \frac{n-1}{2} = o$$

Whenever this arrangement is possible,

$$a = \frac{\Sigma f_t Y}{\Sigma f_t^2} = {}_3K \tag{29}$$

$$b = \frac{\Sigma Y}{n} = \frac{1}{L^3} \tag{30}$$

As claimed by Moesveld, the computation of K and L using equations (29) and (30) is less laborious than the usual computation by means of equations (27) and (28). However, it must be noted that, in general, a precise arrangement of the periods of observation according to Moesveld's scheme could be only accomplished with very slow reactions. Moreover, the use of equation (25) as a basis of computation introduces the quantity

$$Y = W^3 = \frac{1}{(L-Y)^3}$$

although in Moesveld's experiments the quantity actually observed (resistance method) was $W = 1/(L-Y) = 1/Z$. No account is taken by Moesveld of the possible effect of this substitution on the least-squares treatment.

The difficulty in question appears to have been partly recognized by Wagner (1923), who proposed a system for weighting the observational equations. Considering the special case of the second-order reaction represented by the equation

$$1/(L-Y) = Kt + 1/L$$

or,

$$1/Z = Kt + J$$

Wagner assumes that the standard deviation, σ, of Z does not depend on the magnitude of Z. For the standard deviation of $1/Z$ he deduces σ/Z^2 and for the weight of any observational equation he writes $p = Z^4$. The weighted observational equations used by Wagner are accordingly of the type

$$Z_1^4 (1/Z_1 - Kt_1 - J) = o$$

or, in general,

$$p (1/Z - Kt - J) = o$$

where p denotes the weights Z_1^4, Z_2^4, etc. His normal equations are

$$a\Sigma f_1^2 Z^4 + b\Sigma f_1 Z^4 - \Sigma f_1 Z^4 = o$$

$$a\Sigma f_1Z^3 + b\Sigma Z^4 - \Sigma Z^3 = 0$$

where $a = K$ and $b = J = 1/L$. From this he deduces

$$a = K = \frac{\Sigma Z^4 \cdot \Sigma f_1Z^3 - \Sigma f_1Z^4 \cdot \Sigma Z^3}{\Sigma Z^4 \cdot \Sigma f_1^2Z^4 - (\Sigma f_1Z^4)^2}$$

$$J = 1/L = \frac{\Sigma f_1^2Z^3 \cdot \Sigma Z^3 - \Sigma f_1Z^4 \cdot \Sigma f_1Z^3}{\Sigma Z^4 \cdot \Sigma f_1^2Z^4 - (\Sigma f_1Z^4)^2}$$

For the standard deviation ("mittleren Fehler;" mean error) of K, Wagner gives

$$\sigma_K = \sigma_y \cdot \sqrt{\frac{\Sigma Z^4}{\Sigma Z^4 \cdot \Sigma f_1^2Z^4 - (\Sigma f_1Z^4)^2}}$$

Wagner (p. 135) also considers the question of how a given number of observations should be arranged so as to obtain the most precise value of K. When 5 observations are to be made at two different concentrations, the concentrations Z_1 and Z_2 should be related in the sense that $Z_2 = 0.456\ Z_1$ and 4 of the 5 observations should be made at the concentration Z_2. It is stated that a fixed spacing of the observations is necessary only for the detection of systematic trends. The derivation of the factor, 0.456, is not given.

Before presenting any criticism of the statistical procedures proposed by Moesveld and by Wagner, it should first be recalled that in applying the Gaussian method of solution to a set of observational equations, it is generally necessary to place the equations in the linear form, $Y = af_1 + bf_2 + cf_3$, etc. It should also be borne in mind that the least-squares treatment is inapplicable to the solution of observational equations unless the observational and, accordingly, the residual errors are known to follow the normal curve of error. Thus, in the equation

$$Z = 1/(Kt+J)$$

used by Wagner, let it be assumed that the errors in the directly observed quantity Z are normally distributed. It follows that the residual errors, r_1, r_2, etc., represented by the expression

$$r = Z - 1/(Kt+J)$$

will also be normally distributed. This last equation, however, is not in the linear form and, if the distribution of the residual errors is not to be disturbed, it could only be placed in the linear form by the linearization of the term $1/(Kt+J)$. This difficulty is avoided by Wagner through the use of observational equations of the type

$$1/Z = Kt + 1/L$$

Now this expression (and the similar expression

$$1/Z^3 = 3Kt + 1/L^3$$

used by Moesveld) may be linearized by replacing $1/Z$ (or $1/Z^3$) by Y. For Wagner's equation, however, the expression for the residual errors becomes

$$r' = 1/Z - Kt + 1/L$$

and the condition imposed regarding the symmetrical distribution of the residual errors is obviously disturbed. Weighting of the observational equations does not satisfactorily correct the difficulty. For the bimolecular reaction in question, the problem could be simplified by making direct observations on the quantity $1/Z$. Moesveld has done this by using an electrical resistance method, but his further treatment is invalidated by the use of an equation in which the quantity presumably affected by the usual plus and minus errors is $1/Z^3$. For Moesveld's data the equation representing the residual errors should be

$$r'' = 1/Z - \sqrt[3]{3Kt + 1/L^3}$$

In this equation, the possibility of applying the Gaussian method of solution would depend on the linearization of the term under the radical sign.

For these and other reasons the statement by Moesveld that his treatment can be extended to unimolecular equations is to be accepted with caution. Thus, the equation

$$K = 1/t \; ln \; L/(L-Y)$$

may be linearized by placing it in the form

$$ln \; (L-Y) = ln \; L - Kt$$

This expression is obviously of the type

$$Y' = a + bf_2$$

This transformation could be used when the quantity directly observed was $ln \; (L-Y)$, provided that the errors in $ln \; (L-Y)$ are symmetrically distributed. In general, it could not properly be used when the course of the reaction was followed by direct measurements of Y or $L-Y$.

Summary

1. The usual test for unimolecularity, namely, the possibility of deriving a consistent series of K values, should be discarded.

2. The least-squares procedures which have been described in the chemical literature are inapplicable to unimolecular data.

3. Proposed systems for the weighting of unimolecular constants are inapplicable in the presence of constant errors.

4. Appropriate methods for the derivation of weighted constants from observational equations of the unimolecular type will be described in a separate paper.

References

Buchanan, R. E., (1926): Nomogram for the determination of generation time and velocity coefficient for rates of growth or death. Iowa State College, J. Sci., 1, (1), 63-65.

Daniels, F., and Johnston, E. H., (1921): The thermal decomposition of gaseous nitrogen pentoxide. A monomolecular reaction. J. Am. Chem. Soc., 43, 53-71.

Guggenheimer, E. A., (1926): On the determination of the velocity constant of a unimolecular equation. Phil. Mag. (7) 2, 538-43.

Latshaw, M., (1925): A simple tangimeter. J. Am. Chem. Soc., 47, 793-4.

Moesveld, A. L. Th., (1923): Über die Berechnung von Geschwindigkeitskonstanten. Z. physik. Chem., 103, 481-5.

Pennycuick., S. W., (1926): The unimolecularity of the inversion process. J. Am. Chem. Soc., 48, 6-19.

Rice, F. O., and Kirkpatrick, Jr., M., (1923): The measurement of reaction velocity and the temperature coefficient of reaction velocity. J. Am. Chem. Soc., 45, 1402-5.

Rice, F. O., Fryling, C. F., and Wesolowski, W. A., (1924): The relation between the temperature coefficient and the mechanism of a chemical reaction. J. Am. Chem. Soc., 46, 2410-13.

Scatchard, G., (1926): The unimolecularity of the inversion process. J. Am. Chem. Soc., 48, 2259-63.

Schmid, G., (1926): Über die Berechnung von Geschwindigkeitskonstanten. Z. physik. Chem., 119, 8-18.

Sheppard, S. E., (1926): Some consideration of the reaction constant equation, and a simple method of determining the endpoint. Phil. Mag. (7) 2, 448. Priority claim; cf. Smith (1926).

Sheppard, S. E., and Mees, C. E. K., (1927): "Investigation on the theory of photographic processes," p. 65; cit. Sheppard (1926).

Smith, R. C., (1926): Some considerations of the reaction-constant equation, and a simple method of determining the end-point. Phil. Mag. (7) 1, 496-9.

Theriault, E. J., (1927): The oxygen demand of polluted waters. Public Health Bulletin No. 173, Appendix IV, pp. 174-185.

Wagner, C., (1925): Über die Berechnung von Geschwindigkeitskonstanten. Z. physik. Chem., 115, 130-6.

Wobbe, S. E., and Noyes Jr., W. A., (1926): Photochemical studies: IV. The thermal decomposition of anhydrous oxalic acid and its relation to the photochemical decomposition. J. Am. Chem. Soc., 48, 2856-68; cf. Table III, p. 2864.

THE FICTIVE VOLUMES OF SODIUM SULPHATE IN AQUEOUS SOLUTIONS OF SULPHURIC ACID AND OF IODINE IN AN AQUEOUS SOLUTION OF POTASSIUM IODIDE

BY R. E. GIBSON

Introduction

The fictive volume v_2 of a solute in a solution of any concentration may be defined as the increase in volume produced by the introduction of one gram of the solute into an infinitely large volume of that particular solution. If V is the total volume of the solution and m_2 the mass of solute in that volume, v_2 is defined by the equation

$$v_2 = \left(\frac{\partial V}{\partial m_2}\right)_{p,t,m_1}$$

The partial molal volume is the fictive volume multiplied by the assumed molecular weight of the solute. If v_0 is the specific volume of the pure solute in the liquid state and if the solute and solvent form ideal solutions over the whole range of concentration, then $v_2 = v_0$. If, however, the solutions are not ideal, the expression $(v_0 - v_2)$ may be taken as a measure of the departure from ideality or of the specific interaction between solute and solvent.[1]

In particular, strong attractive forces between solvent and solute will result in $(v_0 - v_2)$ having a large positive value while repulsive forces between molecules of solvent and solute will lead to negative values for $(v_0 - v_2)$. If $(v_0 - v_2)$ is zero, we can say that the molecules of solute are no more or no less strongly attracted to molecules of solvent than they are to themselves.

In this paper I propose to examine the fictive volumes of two solutes in solutions in which chemical-compound formation, the result of intense interaction between solvent and solute, has been presumed to take place. In the first case sodium sulphate is the solute and the solvent consists of 5 and 10 per cent solutions of sulphuric acid. As the ratio of H_2SO_4 to water is kept constant throughout each series, the sulphuric acid solution may be taken as the solvent. It will be shown that in this system there are distinct peculiarities in the fictive volume-concentration curves which may be connected with the formation of $NaHSO_4$ in solution.

In the second case a concentrated solution of potassium iodide is used as solvent and iodine is the solute.

Experimental

Part 1. The first part of the experimental work consisted in determining accurately at 25° the specific volumes of two series of solutions, Series I, solutions of Na_2SO_4 in 4.818 per cent aqueous sulphuric acid, and Series II, solutions of Na_2SO_4 in 9.333 per cent aqueous sulphuric acid.

[1] For discussion see J. H. Hildebrand: "Solubility," 62 ff. (1924).

The aqueous sulphuric acid was made from J. T. Baker's C.P. Analyzed H_2SO_4 and stored in five-litre Resistance Glass bottles provided with glass syphon, stopcock, and trap for excluding atmospheric moisture. In the preparations of the solutions of sodium sulphate, the anhydrous salt, obtained by recrystallization and subsequent dehydration of J. T. Baker's C.P. Analyzed sodium sulphate, was weighed by difference in a 100 cc stoppered flask and to it was added the requisite amount of sulphuric acid solution. The whole was then weighed, thoroughly mixed and kept at a temperature above 25° so that no air bubbles might form in the pycnometer.

The specific volumes were determined by a pycnometer method. The apparatus was that used and described in a previous paper[1] and the same technique was adhered to throughout. The pycnometer was recalibrated with pure water and its volume was found to be the same as before—55.0373 millilitres. The weight of the water content was 54.8762 grams as against an average of 54.8756 grams for the previous work.

The solutions of sulphuric acid were not analyzed, as their densities, combined with the tables of density as a function of concentration of Domke[2] gave an excellent method of determining the concentration of H_2SO_4. Before and after each series the specific volume of the sulphuric acid solution used was determined. The results agreed well, thereby giving the assurance that no change had taken place in the sulphuric acid during the work.

The experimental results are given in Tables I and II. The weighings are all corrected to vacuum, due regard being paid to the meteorological conditions at the time of the experiment. As I have now a fair confidence in the method, I duplicated the determination on only one Na_2SO_4 solution. The result was satisfactory, as a glance at the 6th and 7th rows in Table III will show.

TABLE I

Specific Volumes of Solutions of Na_2SO_4 in 5% H_2SO_4
Experimental Results at 25°

Weight of salt	Weight of solution	Concentration per cent (x_2)	Weight of soln. in pycnometer	Specific volume (v)
		0	56.6230	0.971981_1
		0	56.6233	0.971977
0.9975	102.3168	0.9749	57.0462	0.964771_1
2.0036	102.4381	1.9559	57.4779	0.957524
3.6054	100.0582	3.6033	58.2229	0.945278
5.0284	102.8749	4.8879	58.8312	0.935657
5.0073	102.4592	4.8871	58.8206	0.935667
11.2984	109.8719	10.2833	61.4846	0.895121_1
15.9422	104.2579	15.2911	64.1376	0.858108
20.9849	101.9319	20.5871	67.1031	0.820172
20.1725	87.2351	23.1243	68.5810	0.802504

[1] R. E. Gibson: J. Phys. Chem., 31, 496 (1927).
[2] Landolt-Börnstein: "Physikalisch-chemische Tabellen," 397 (1923).

TABLE II

Specific Volumes of Solutions of Na_2SO_4 in 10% H_2SO_4
Experimental Results at 25°

Weight of salt	Weight of solution	Concentration per cent (x_2)	Weight of soln. in pycnometer	Specific volume (v)
		0	58.3041	0.943957
		0	58.3040	0.943958
1.2018	103.2458	1.1640	58.8003	0.935989
2.0869	100.5386	2.0758	59.1955	0.929742
3.5075	104.5824	3.3538	59.7559	0.921022
5.5054	105.7186	5.2076	60.5889	0.908360
10.8726	109.2192	9.9548	62.8289	0.875974
15.8660	111.6128	14.2152	64.9817	0.846954
20.5285	113.3373	18.1127	67.0648	0.820646
26.0016	116.6655	22.2873	69.4085	0.792937
26.0549	104.2839	24.9846	70.9808	0.775372
30.0904	105.6213	28.4890	73.0915	0.752981

Part 2. In the second half of the experimental work measurements were made of the specific volumes of a series of solutions of iodine in a concentrated solution of potassium iodide, prepared by dissolving J. T. Baker's C.P. Analyzed KI, twice recrystallized, in air-free distilled water. The density of the solution was accurately determined as 1.52106, which according to the International Critical Tables[1] corresponds to a solution containing 48.72 per cent of KI. The solutions of iodine were prepared by successive dilution starting from Solution I, the most concentrated, which was prepared by dissolving a weighed amount of Merck's Reagent Iodine in the KI solution. The next solution was prepared by mixing weighed amounts of Solution I and the standard KI solution and so on for subsequent dilutions. Care was taken to preserve the solutions from contamination or evaporation at any stage in the investigation. Exactly the same apparatus was used but a special technique was required for introducing the concentrated iodine solutions into the pycnometer. The experimental results are recorded in Table VII. Unfortunately, there was not a sufficient amount of the standard potassium iodide solution left at the end of the series to admit of a check determination of its density.

Calculation of Results

For each series of sulphate solutions two simple equations were found adequate to express the results. These equations, which express the specific volume v as a function of the weight per cent of Na_2SO_4 in the solution, x_2, are as follows:

Series I

Eqn.(1) $v = 0.971980 - 0.00743x_2$

Eqn.(2) $v = 0.895127 - 0.007514(x_2 - 10.2833) + 0.00002(x_2 - 10.2833)^2$

Series II

Eqn.(3) $v = 0.943957 - 0.006820x_2$

Eqn.(4) $v = 0.875664 - 0.006830(x_2 - 10) + 0.000010(x_2 - 10)^2$

[1] "International Critical Tables," 3, 88.

Equations (1) and (3) hold for the more dilute solutions from 1 to 15 per cent and the quadratic equations (2) and (4) apply to the concentrated solutions (15 to 30 per cent Na_2SO_4). Values of v calculated from these equations are given in Tables III and IV and the divergence from the experimental results is given in the columns marked "Obs.-calc." These differences, when plotted against x_2, gave the usual deviation curve by the help of which the values at even concentrations were calculated. In both series it was desirable to have the two equations overlap so that a check on the interpolation calculations might be made.

TABLE III

Interpolation Data for Calculation of Specific Volumes of Solutions of Na_2SO_4 in 5% H_2SO_4. Check Determinations brought to Same Concentration

x_2	v	v (obs) Final value	v calc. from Eqn. 1	obs.-calc. × 10^6	v calc. from Eqn. 2	obs.-calc. × 10^6
0	0.971981	0.971980	0.971980	0		
	0.971977					
0.9749	0.964771	0.964771	0.964736	35		
1.9559	0.957524	.0957524	0.957448	76		
3.6033	0.945272	0.945272	0.945207	65		
4.8879	0.935658	0.935660	0.935663	−3		
	0.935661					
10.2833	0.895127	0.895127	0.895575	−448	0.895127	0
15.2911	0.858101	0.858101	0.858367	−266	0.858100	1
20.5871	0.820178	0.820178	0.819018	1160	0.820250	−72
23.1243	0.802504	0.802504	0.800167	2337	0.802598	−94

TABLE IV

Interpolation Data for Calculation of Specific Volumes of Solutions of Na_2SO_4 in 10% H_2SO_4

x_2	v observed	v calc. from Eqn. 3	obs.-calc. × 10^6	v calc. from Eqn. 4	obs.-calc. × 10^6
0	0.943957	0.943957	0		
1.1640	0.935989	0.936018	−29		
2.0758	0.929742	0.929780	−38		
3.3538	0.921022	0.921084	−62		
5.2076	0.908360	0.908441	−81	0.908674	−314
9.9548	0.875974	0.876065	−91	0.875973	− 1
14.2152	0.846954	0.847010	−56	0.847010	− 56
18.1127	0.820646	0.820428	218	0.820831	−185
22.2873	0.792937	0.791958	979	0.793129	−192
24.9846	0.775372			0.775413	− 41
28.4890	0.752981			0.752617	364

As a check on the interpolations for Series I, a cubic equation was fitted to the results. The deviations were smaller and the equation was useful over the whole range, but the results were exactly the same as those recorded in TableV. The specific volumes at even concentrations of sodium sulphate are given in Tables V and VI.

TABLE V

Specific Volumes of Solutions of Na_2SO_4 in 5% H_2SO_4

x_2	v Equation 1	v Equation 2	v Weighted mean
0	0.971980		0.971980_0
1	0.964589		0.964589_0
2	0.957196		0.957198
3	0.949769		0.949770
5	0.934814		0.934814
10	0.897244	0.897241	0.897244
15	0.860226	0.860228	0.860228
20	0.824318	0.824313	0.824313
23		0.803363	0.803363

TABLE VI

Specific Volumes of Solutions of Na_2SO_4 in 10% H_2SO_4

x_2	v Equation 3	v Equation 4	v Weighted mean
0	0.943957		0.94396
1	0.937115		0.93712
2	0.930278		0.93028
3	0.923442		0.92344
5	0.909777	0.909774	0.90978
10	0.875664	0.875664	0.87566
15	0.841619	0.841629	0.841625
18	0.821391	0.821402	0.82140
20		0.808047	0.80805
25		0.775274	0.77527
28		0.756084	0.75608
30		0.743428	0.74343

The fictive volumes of Na_2SO_4 in the various solutions may now be calculated, as v_2, the fictive volume of the salt, is given by the equation

$$v_2 = (100 - x_2)\, dv/dx_2 + v.$$

Approximate values of dv/dx_2 were found by the differentiation of equations 1, 2, 3 and 4. These approximate values were corrected by adding the slopes of the deviation curves at the appropriate points. The corrected values of dv/dx_2 are recorded in Tables VII and VIII which illustrate the calculations

and give the final values of the fictive volumes at even concentrations. The results in Table VII were confirmed from calculations made from the cubic equation which has already been mentioned.

In Table X is shown the agreement between the observed values of the specific volumes of iodine solutions of different concentrations and those calculated from the equation

$$v = 0.65685 - 0.004173x_2$$

It is remarkable that a linear equation applies so exactly over so large a range of concentration. The last column of this table shows the fictive volumes of iodine at various concentrations as calculated by the method already described.

TABLE VII

Calculation of Fictive Volumes of Na_2SO_4 in Solutions containing 5% H_2SO_4

x_2	$dv/dx_2 \times 10^2$ (Eqn. 1)	$dv/dx_2 \times 10^2$ (Eqn. 2)	$dv/dx_2 \times 10^2$ (Weighted mean)	$x_1\, dv/dx_2$	v	v_2
0	0.7372		0.7372	0.7372	0.9720	0.2348
1	0.7391		0.7391	0.7317	0.9646	0.2329
2	0.7410		0.7410	0.7262	0.9572	0.2310
3	0.7441		0.7441	0.7218	0.9498	0.2280
5	0.7508		0.7508	0.7133	0.9348	0.2215
10	0.7466	0.7461	0.7464	0.6718	0.8972	0.2254
15	0.7320	0.7310	0.7310	0.6213	0.8602	0.2389
20	0.7080	0.7105	0.7105	0.5685	0.8243	0.2558
23		0.6960	0.6960	0.5359	0.8034	0.2675
25		0.6862	0.6862	0.5147	0.7897	0.2750

(These are confirmed by results from cubic equation.)

TABLE VIII

Fictive Volumes of Na_2SO_4 in Solutions containing 10% H_2SO_4

x_2	$dv/dx_2 \times 10^2$ (Eqn. 1)	$dv/dx_2 \times 10^2$ (Eqn. 2)	$dv/dx_2 \times 10^2$ (Weighted mean)	$x_1\, dv/dx_2$	v	v_2
0	0.6840		0.6840	0.6840	0.9440	0.2600
1	0.6838		0.6838	0.6770	0.9371	0.2601
2	0.6837		0.6837	0.6700	0.9303	0.2603
3	0.6835		0.6835	0.6630	0.9234	0.2604
5	0.6830	0.6824	0.6827	0.6486	0.9098	0.2612
10	0.6816	0.6822	0.6820	0.6138	0.8757	0.2619
15	0.6795	0.6773	0.6780	0.5763	0.8416	0.2653
18		0.6710	0.6710	0.5502	0.8214	0.2712
20		0.6643	0.6643	0.5314	0.8080	0.2766
25		0.6455	0.6455	0.4841	0.7753	0.2912
28		0.6354	0.6354	0.4575	0.7561	0.2986

TABLE IX

Specific Volumes of Solutions of Iodine in 48.7% KI
Experimental results at 25°

Weight of Iodine	Weight of solution	Concentration per cent (x_2)	Weight of solution in pycnometer	Specific volume (v)
		0	83.7152	0.65744
5.2128	95.4703	5.4601	86.8124	0.63398
12.0908	121.0945	9.9846	89.4644	0.61519
17.9998	120.0390	14.9950	92.6112	0.59428
25.8572	129.2853	20.0001	95.9874	0.57338
33.9294	135.8123	24.9826	99.5953	0.55261
42.0891	141.5455	29.7354	103.3054	0.53276
52.4860	150.1190	34.9629	107.7049	0.51100
58.2987	145.6945	40.014	112.3395	0.48992
67.6814	150.5092	44.9683	117.2967	0.46921
70.2798	146.0359	48.1250	120.6860	0.45604

TABLE X

Observed and Calculated Specific Volumes of Iodine Solutions.
The fictive volumes of iodine in solution

Concentration per cent x_2	v (observed)	v (calculated)	obs.-calc. $\times 10^5$	Fictive volume v_2
5.4601	0.63398	0.63407	−9	
9.9846	0.61519	0.61519	0	0.2396
14.9950	0.59428	0.59428	0	0.2396
20.0001	0.57338	0.57339	−1	0.2395
24.9826	0.55261	0.55260	+1	0.2396
29.7354	0.53276	0.53277	−1	0.2396
34.9629	0.51100	0.51095	+5	0.2396
40.0140	0.48992	0.48988	+4	0.2395
44.9863	0.46921	0.46920	+1	0.2396
48.1250	0.45604	0.45603	+1	0.2396

Discussion of Results

The chief features of interest revealed by a study of the sulphate solutions may be seen in Fig. 1. The specific volume of liquid Na_2SO_4 at room temperature is not known so v_s, the specific volume of solid Na_2SO_4, is used instead of v_0 and its value is 0.375. The expression $(v_s - v_2)$ is plotted as ordinate and the mol fraction of Na_2SO_4 in the solution is abscissa. The mol fraction rather than the weight fraction was used in order to facilitate comparison of equimolal concentrations of different materials. Curve A refers to sodium sulphate in pure water, curve B, to sodium sulphate in the 4.818 per cent H_2SO_4 solution, and curve C, to the salt in the 9.333 per cent solution of sulphuric acid.

The course of curve A is fairly typical of the way in which the fictive volumes of salts in aqueous solutions vary with concentration.[1] The contraction on solution, $(v_s - v_2)$, is greatest at zero concentration and diminishes steadily as the concentration increases. The very high value of $(v_s - v_2)$ in the dilute solutions may be attributed to two causes (a) attraction between the Na_2SO_4 and H_2O molecules and (b) the depolymerization of water which follows as a result of the reduction in the activity of the simple water molecules by the presence of a salt, a process which takes place with decrease in volume.

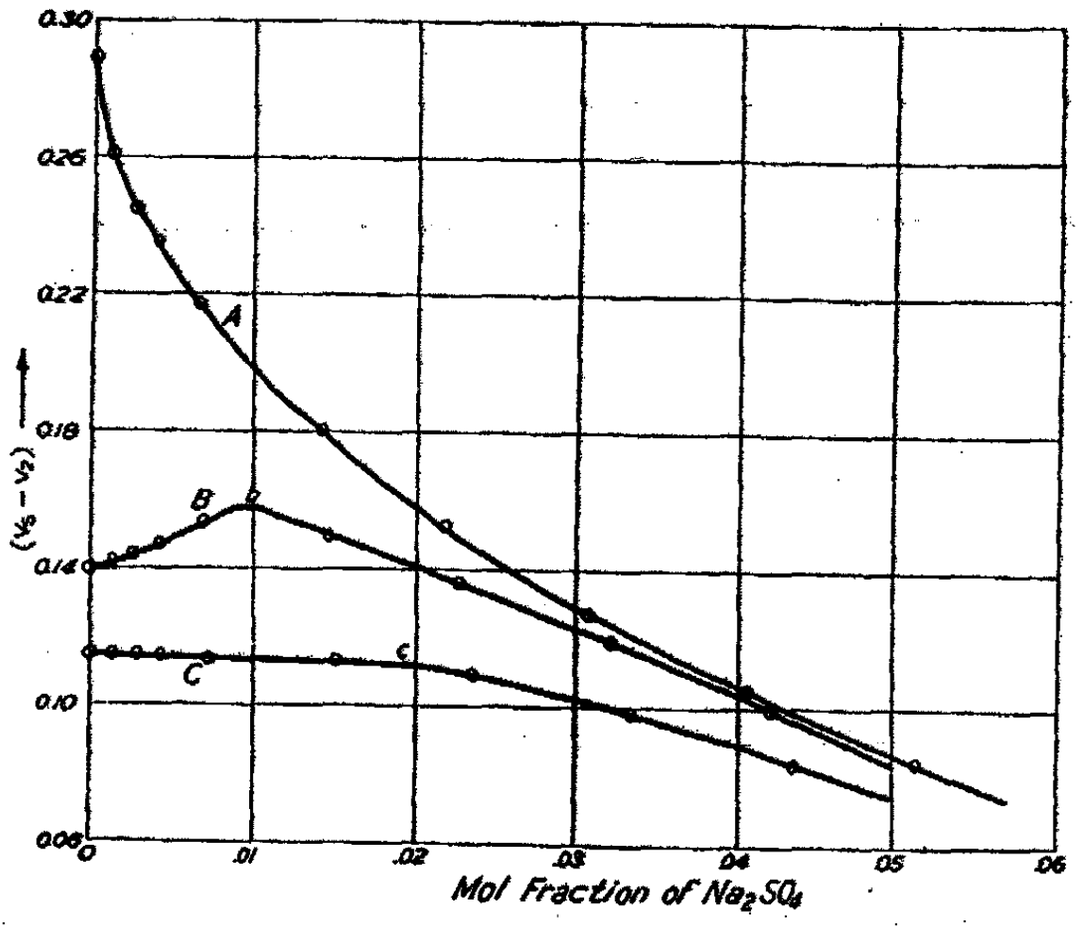

FIG. 1

The differences between the specific volume of solid Na_2SO_4 and the fictive volumes of Na_2SO_4 in solutions in (A) Water, (B) 5 per cent H_2SO_4, (C) 10 per cent H_2SO_4 as functions of the mol fraction of Na_2SO_4 in solution.

Turning to curves B and C we notice that the higher the concentration of sulphuric acid in the solvent, the smaller is the value of $(v_s - v_2)$ at zero concentration. Undoubtedly the addition of sulphuric acid reduces the polymerization of water so that when Na_2SO_4 is added to the solution the contraction due to this effect alone is lessened.

A very interesting question now arises—why do not curves B and C start downward toward the concentration axis at zero concentration as curve A does, and what is the significance of the points b and c where these curves finally do acquire a negative slope. At the point b the mol fraction of H_2SO_4 in the solution is 0.0091 and at c the mol fraction of H_2SO_4 in the solution is 0.018. These figures are approximately the same as the values of the mol

[1] The data for this curve are taken from Gibson: loc. cit.

fractions of sodium sulphate in the solutions represented by the points b and c. The curves therefore undergo an abrupt change in slope at the points where the solutions contain equimolecular amounts of sodium and hydrogen sulphate or the correct proportions for the production of $NaHSO_4$. It is assumed in explanation that the reaction $Na_2SO_4 + H_2SO_4 \rightarrow 2NaHSO_4$ is accompanied by a decrease in volume and that, as the concentration of Na_2SO_4 rises, the reaction proceeds to an increasing extent reaching a maximum when the two sulphates are present in equimolecular concentration.

While it cannot be claimed that the curves in Fig. 1 give absolutely convincing evidence of the compound formation in solution, the case is put forward as an example of some interest where a function derived from an intensive property of the solution as a whole may be linked with the possibility of the compound formation in the solution.

The sulphate results led to an investigation of the question whether this mode of attack might furnish any evidence of the alleged combination of iodine and potassium iodide to form potassium triiodide in solution. The discussion as to what happens in solutions of iodine in aqueous potassium iodide has been admirably summarized by Jones[1] who concluded that the evidence is overwhelmingly in favor of the formation of triiodide. Nevertheless, the results of this investigation cannot be interpreted as giving any evidence in favor of the formation of KI_3; but on the other hand point to the conclusion that if KI_3 is formed it must be in very small amount—which does not agree with figures which are given as the equilibrium constant of the triiodide reaction.

In order to include in the range of experiments a solution in which there should be equimolecular amounts of I_2 and KI it was necessary to employ a very concentrated solution of KI (48.7 per cent). Such a solution would contain equimolecular amounts of I_2 and KI when the concentration of iodine was 42.68 per cent. The last column of Table X shows that over a range of concentrations extending from 10 to 48 per cent of I_2 the fictive volume of iodine in the solution is constant at a value of 0.2396 cc. per gram. There is a complete absence of any singularity around 42.7 per cent. It should be noted that it was not possible to make reliable estimates of v_2 below 10 per cent as an insufficient number of points were observed. The constancy of the fictive volume over this large range of concentration precludes any large interaction between the iodine and the potassium iodide. Data on the specific volume of liquid iodine at 25° are lacking. At 19°C the specific volume of solid iodine is 0.2036.[2] If we assume that iodine expands roughly 10 per cent on melting, the specific volume at 25° of liquid iodine is about 0.22 cc. The specific volume of liquid iodine at 183° is given as 0.2698 by Drugman and Ramsay[3] which leads to an estimate of 0.23 as the specific volume at 25° if the coefficient of expansion of iodine is not far from that of bromine (1.1×10^{-3}). It would seem that v_0, the specific volume of liquefied iodine, is

[1] Grinnell Jones: J. Phys. Chem., 34, 673 (1930).
[2] "International Critical Tables," 3, 21.
[3] Drugman and Ramsay: J. Chem. Soc., 77, 1228 (1900).

not far from 0.23 at 25°. Hence the value of the expression (v_0-v_2) for iodine in a 48.7 per cent solution of KI is of the order of −0.01 or probably numerically less. The conclusion is that when iodine dissolves in concentrated solutions of iodine in aqueous potassium iodide the volume change is very small, being, if anything, a slight expansion. In other words, from the point of view of volume relations, the concentrated solutions of iodine in aqueous potassium iodide which have been examined approximate closely to a requirement of ideal solutions, namely, that (v_0-v_2) shall be zero at all concentrations. It must be emphasized that in this work only large effects were sought. To investigate the existence of small changes in v_2 it would have been necessary to extend the accuracy of the specific-volume measurements to the sixth decimal place—a task which is particularly difficult with solutions containing a volatile component like iodine. The results given here, however, show that the specific interaction between molecules of iodine and of potassium iodide as measured by volume changes is not appreciably greater and in fact may be less than the interaction of molecules of iodine among themselves in the liquid state.

Summary

From measurements of the specific volumes of two series of solutions of sodium sulphate, in the first series approximately 5 per cent aqueous H_2SO_4 and in the second approximately 10 per cent H_2SO_4 being the solvent, the fictive volumes of Na_2SO_4 in these solutions were calculated. The curves showing the relation between a constant minus the fictive volume and the concentration exhibited peculiarities which were linked with the formation of $NaHSO_4$ in solution. Measurements of the specific volumes of iodine in a 49 per cent solution of potassium iodide showed that in solutions containing from 10 to 50 per cent of iodine the fictive volume of the iodine is independent of the concentration of iodine and is close in value to the most probable estimate of the specific volume of liquid iodine at 25°.

Geophysical Laboratory,
Carnegie Institution of Washington,
July, 1930.

STUDIES ON ELECTROKINETIC POTENTIALS. VIII

Ion Antagonism*

BY HENRY B. BULL AND ROSS AIKEN GORTNER

Historical

It has long been recognized by biologists that electrolytes which are individually toxic to cell life are no longer toxic when present in the proper ratios with certain other electrolytes. That this is true has been demonstrated by Loeb,[1] Sztück,[2] Berger,[3] Lillie,[4] and others.

Osterhout[5] has shown the existence of ion antagonism between NaCl and $CaCl_2$ by studying the electrical conductance of *Laminaria* tissue in the presence of NaCl and $CaCl_2$ solutions. With NaCl the conductivity of the tissue was increased; with $CaCl_2$ it was decreased. When the salts were present in the ratio of 100 molecules of NaCl to 1 of $CaCl_2$ the conductance of tissue indicated increasing permeability.

Neuschloss[6] reports a marked ion antagonism in the effect on the surface tension of lecithin sols. The alkalies, alkali earths, and aluminum increase the surface tension of lecithin sols to a maximum. This maximum is considerably depressed upon the addition of another electrolyte. He reports that a maximum effect is secured when the ratio of uni-univalent cation mixture is 1:1, uni-bivalent 20:1, and uni-trivalent 100:1. An exception is encountered with Na and K which have their maximum effects in a ratio of Na to K of 1:20 or K to Na of 1:20.

Freundlich and Scholz[7] believe that the ion antagonism encountered in sols in the test tube is closely related to the biological action of electrolytes. It is also their belief that purely electrical influences of pronounced ion antagonism cannot be produced; for ionic antagonism a hydration influence is always necessary.

Weiser[8,9,10,11] has done considerable work on ion antagonism in colloidal systems. He does not agree with Freundlich and Scholz that emphasis should be placed on the hydration influences but maintains rather that the electrical effects play the major role. He seems to feel that there are two factors which influence the precipitating power of a mixture of electrolytes on a colloidal system. These are: (1) the effect of each precipitating ion on the adsorption of the other and (2) the stabilizing action of the ion having the same charge as the colloidal particles. Weiser compares the cell membrane to a copper ferrocyanide membrane. He thinks that the membrane consists of myriads of

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small particles which adsorb water strongly, forming a true colloidal system which is capable of reversible coagulation, and that all the work on the effect of electrolyte mixtures on colloidal systems should apply.

Clowes[12] worked on the problem of emulsion inversion as influenced by different ions. He concludes that the mono-valent cations, in general, favor the oil-in-water emulsion and that di- and tri-valent cations favor the water-in-oil emulsion. There appears to be a marked antagonism between Na and Ca, both in respect to the type of emulsion and their effect upon the interfacial tension of oil-water. NaCl was found to increase the interfacial tension between olive oil and a solution of NaOH or Na oleate or a mixture of both. $CaCl_2$ in the presence of $Ca(OH)_2$ was found to increase the interfacial tension. Here again an ion antagonism was found when the ratio of Ca to Na was 1 to 100. Clowes suggests that the cell membrane is also an emulsion which is capable of inversion, and depending on whether or not we have Ca or Na we get an oil-in-water emulsion which is permeable or a water-in-oil which is impermeable to water-soluble materials. At the proper concentrations Na and Ca ions antagonize each other, and we have an inversion point at which neither type of emulsion predominates.

Harkins and Zollman[13] repeated the work of Clowes in so far as the ion effects upon interfacial tension of oil-water systems are concerned, and using exact physico-chemical technic demonstrated a marked lowering of interfacial tension in pure solutions of NaCl, an increased interfacial tension in pure solutions of $CaCl_2$, and an ion antagonism between Na and Ca so that no changes in interfacial tension occurred in the proper mixtures of NaCl and $CaCl_2$.

Simms[14] reports the effect of neutral salts on the pH of a glycine solution. He finds an ion antagonism between NaCl and KCl; NaCl and $MgCl_2$; NaCl and $CaCl_2$; $CaCl_2$ and $MgCl_2$. The fact that ion antagonism was observed in a non-colloidal system is very suggestive.

Experimental

The apparatus and technic were identical with those of our previous paper[15] and involved only slight modifications from those used by Martin and Gortner[16] which in turn were a modification of Briggs'[17] methods.

Salt	Equivalent ratio	Milli-equivalents per liter	Mg per liter
Na_2SO_4	0.5	0.0075	0.53
Na_2HPO_4	3.0	0.0450	8.06
$NaHCO_3$	30.0	0.4500	37.80
NaCl	89.5	1.3428	78.49
KCl	4.3	0.0645	4.81
$CaCl_2$	3.4	0.0510	3.75
$MgCl_2$	2.6	0.0390	3.96

The dilute physiological salt solution was made up to contain the salts in the same ionic ratios as in blood plasma. The dilutions were made from the stock solutions shown on the preceding page.

The cation concentration of the dilute physiological salt solution in the streaming cell was increased progressively until 0.2×10^{-3} N was reached. At this point sufficient $MgCl_2$ was added to make the solution 0.05×10^{-3} N in respect to Mg and in addition to the amount of Mg already in solution. This solution was streamed through the diaphragm, then sufficient $CaCl_2$

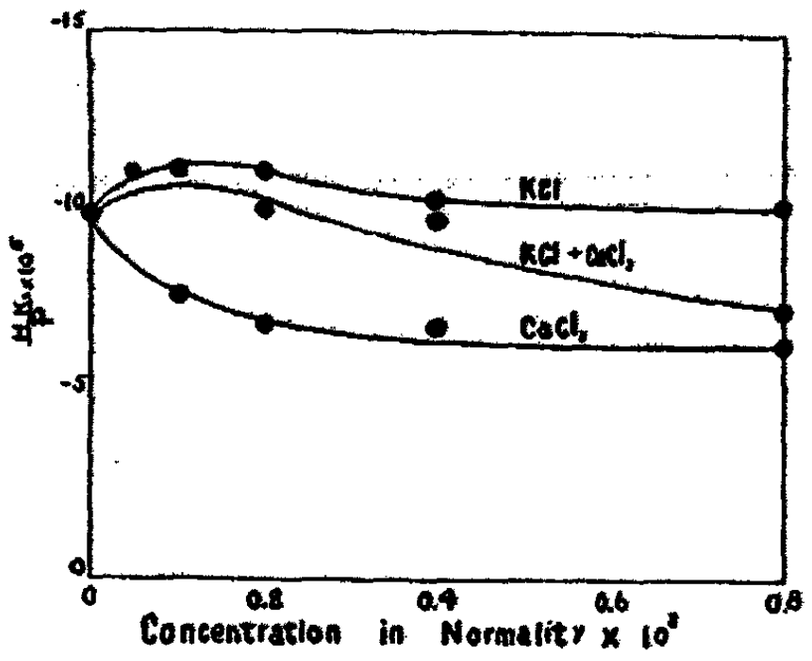

FIG. 1
Showing the effect of KCl and $CaCl_2$ and of mixtures of these salts on $H\kappa_s/P$.

was added to the solution to make it 0.05×10^{-3} N in respect to Ca in addition to that already in solution.

The same technic was employed with the K and Na in the ratio of 20:1 and also with the Na and Ca in the ratio of 100:1, as with the dilute physiological salt solution.

The data are given in Tables I to XIV and Figs. 1 through 9. The concentration is always expressed in terms of the total cation equivalency. As with all the results reported in this paper, the individual datum is the average of six determinations, three made while streaming the liquid in one direction and three in the reverse direction. For comparative purposes the data for each curve are multiplied by an appropriate factor so that the value of $H\kappa_s/P$ for zero salt concentration is reduced to 10×10^{-5}.

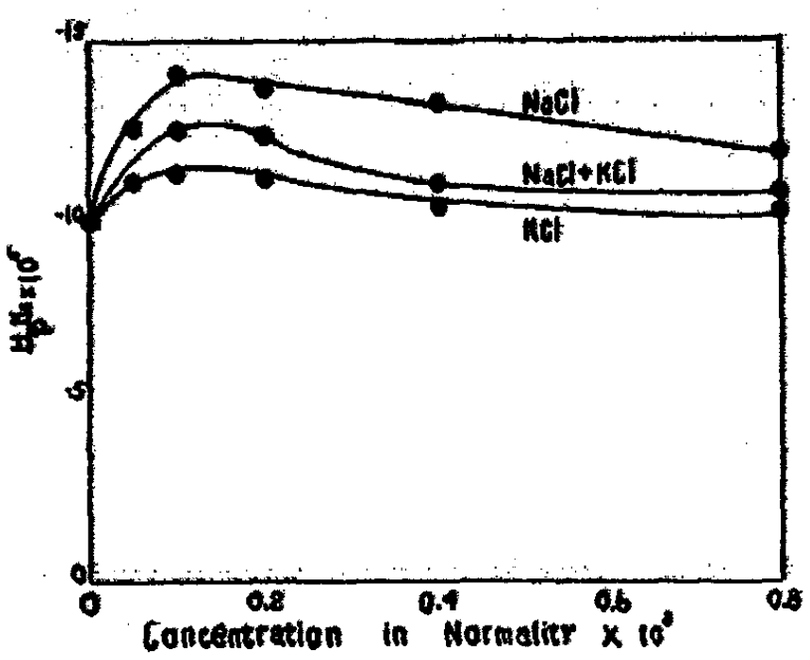

FIG. 2

Showing the effect of NaCl and KCl and of mixtures of these salts on $H\kappa_a/P$.

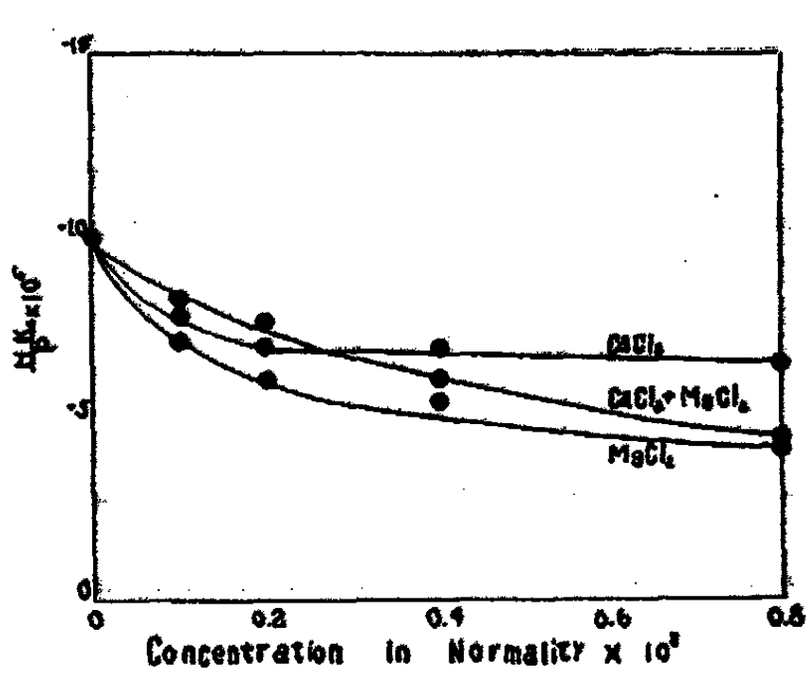

FIG. 3

Showing the effect of $CaCl_2$ and $MgCl_2$ and of mixtures of these salts on $H\kappa_a/P$.

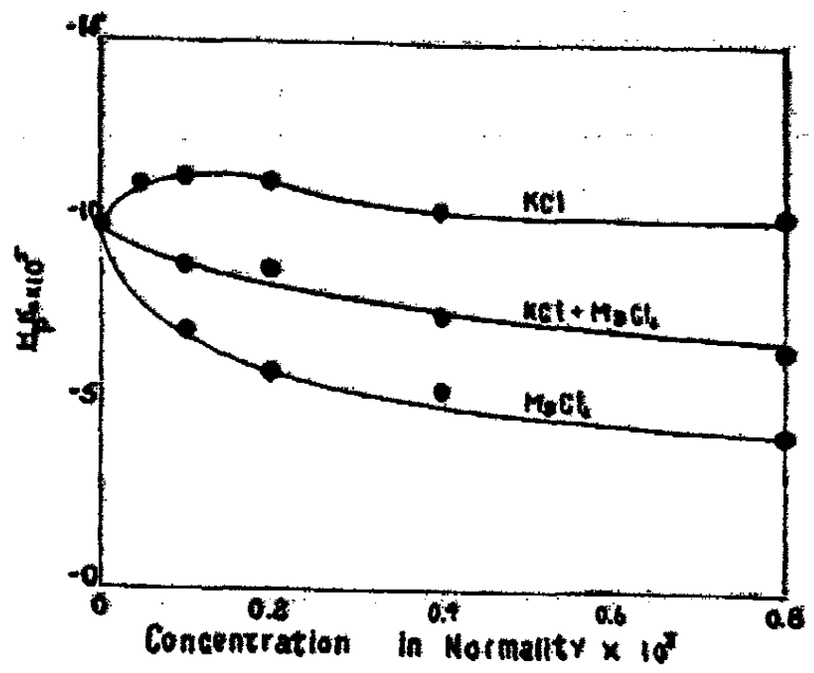

FIG. 4

Showing the effect of $MgCl_2$ and KCl and of mixtures of these salts on $H\kappa_s/P$.

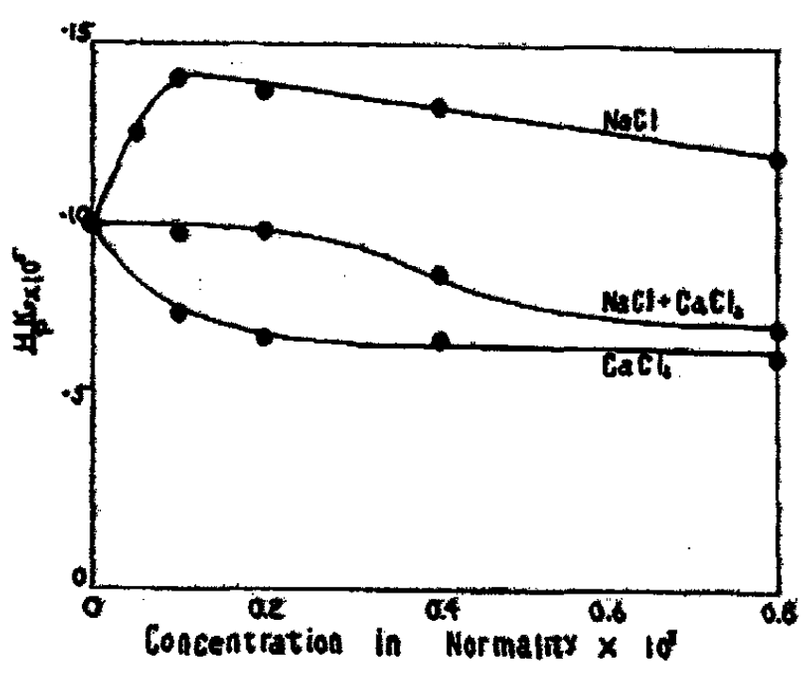

FIG. 5

Showing the effect of NaCl and $CaCl_2$ and of mixtures of these salts on $H\kappa_s/P$.

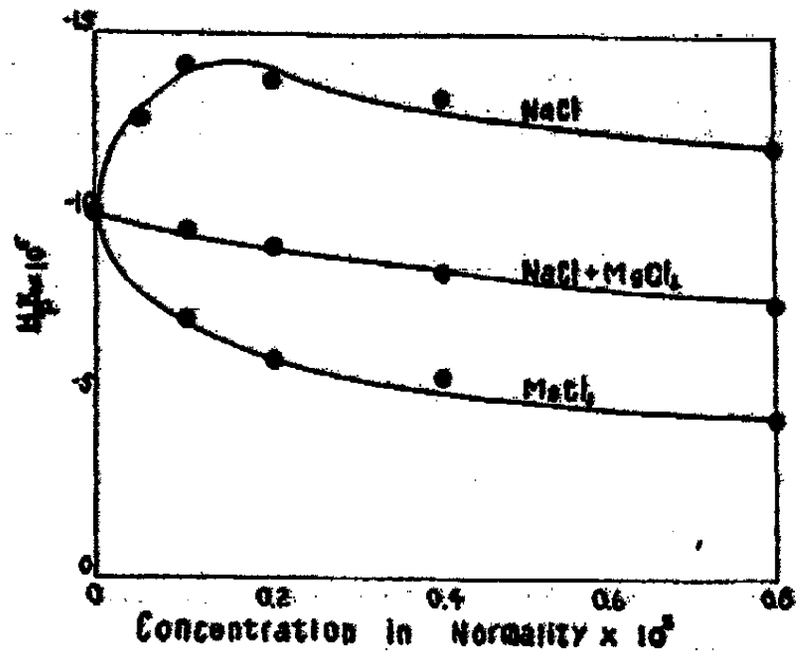

FIG. 6

Showing the effect of NaCl and $MgCl_2$ and of mixtures of these salts on $H\kappa_s/P$.

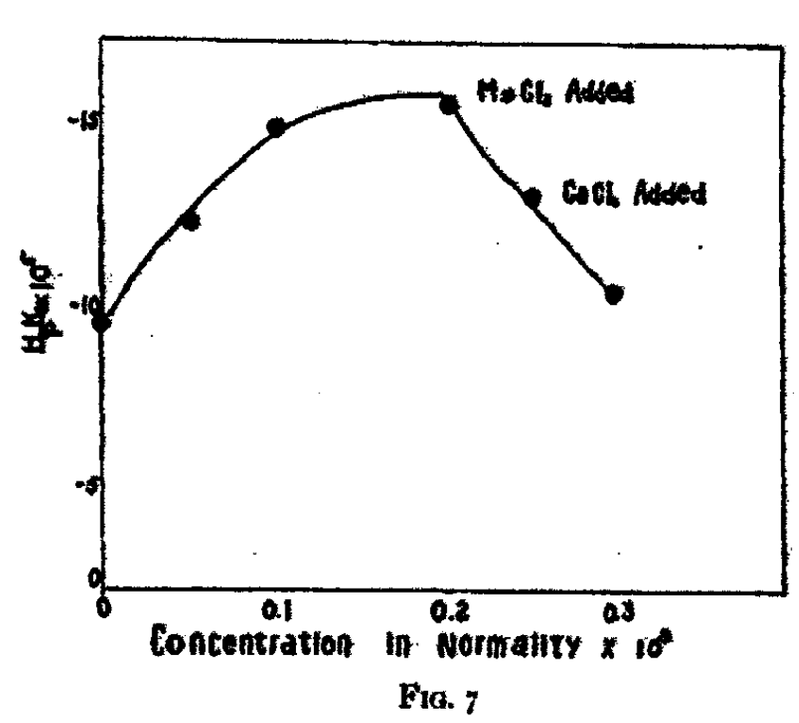

FIG. 7

Showing the effect of $MgCl_2$ and $CaCl_2$ upon the ζ-potential in a dilute physiological salt solution.

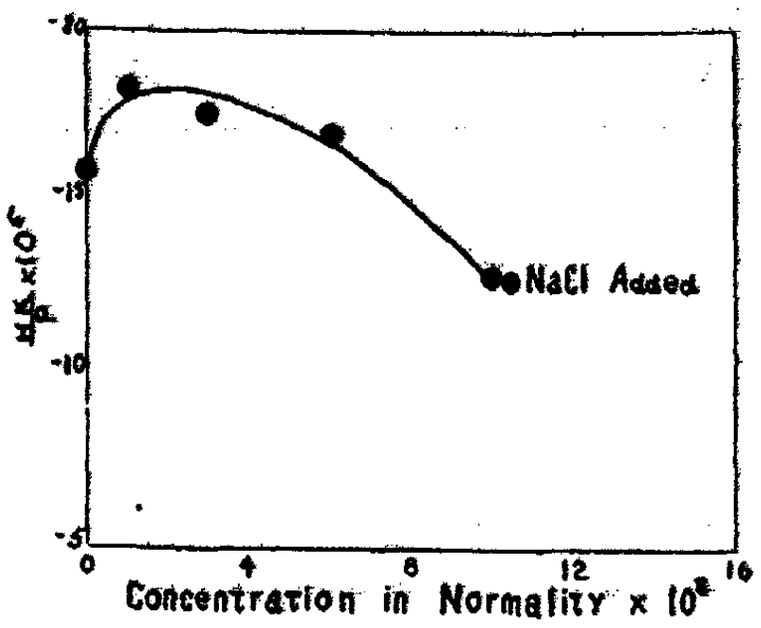

FIG. 8

Showing the effect of the addition of NaCl to KCl in the ratio of 1 to 20 on the electrical potential at a cellulose-aqueous interface.

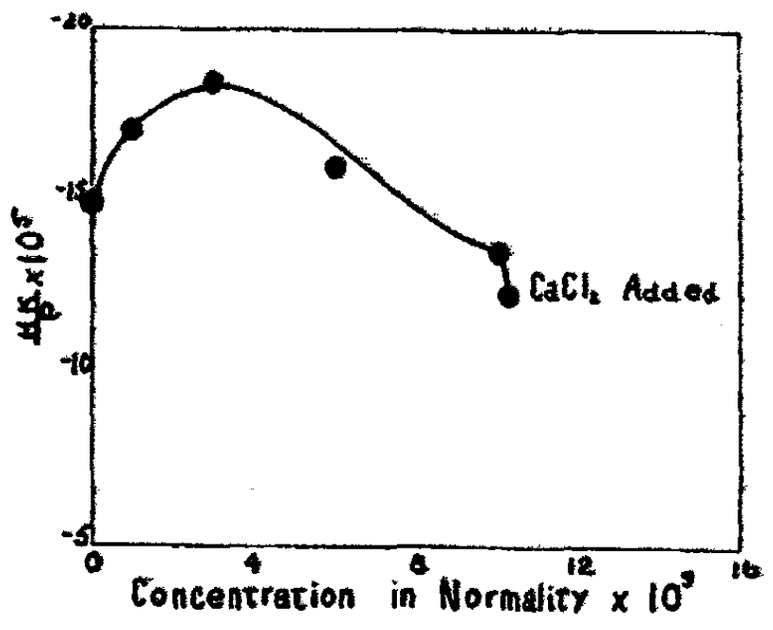

FIG. 9

Showing the effect of the addition of $CaCl_2$ to NaCl in the molecular ratio of 1 to 100 on the electrical potential at a cellulose-aqueous interface.

TABLE I

Data for $MgCl_2$

Concentration $MgCl_2$	Pressure cm. Hg	$\frac{H\kappa_0}{P} \times 10^5$	Pressure cm. Hg	$\frac{H\kappa_0}{P} \times 10$
0.00	61.3	−15.5	57.2	−15.5
	78.1	−15.5	79.6	−15.5
	75.5	−15.5	78.3	−15.3
		Average $H\kappa_0/P = -15.48 \times 10^{-5}$		
0.10×10^{-3}	66.3	−10.5	74.5	−11.4
	80.9	−11.1	81.7	−11.1
	73.9	−11.5	75.7	−10.7
		Average $H\kappa_0/P = -11.05 \times 10^{-5}$		
0.20×10^{-3}	51.2	− 8.52	58.9	− 8.84
	80.6	− 9.95	80.6	− 9.42
	78.5	− 9.76	78.9	− 9.45
		Average $H\kappa_0/P = -9.32 \times 10^{-5}$		
0.4×10^{-3}	60.5	− 8.83	63.0	− 8.05
	80.9	− 8.72	81.4	− 8.50
	79.5	− 8.60	79.3	− 8.24
		Average $H\kappa_0/P = -8.50 \times 10^{-5}$		
0.8×10^{-3}	50.1	− 6.90	61.8	− 5.10
	80.6	− 6.94	81.3	− 6.75
	76.5	− 6.68	78.1	− 6.52
		Average $H\kappa_0/P = -6.75 \times 10^{-5}$		
1.6×10^{-3}	81.9	− 2.69	66.9	− 3.10
	80.7	− 2.00	81.1	− 2.71
		Average $H\kappa_0/P = -2.62 \times 10^{-5}$		

TABLE II

Data for $CaCl_2$

Concentration $CaCl_2$	Pressure cm. Hg	$\frac{H\kappa_s}{P} \times 10^5$	Pressure cm. Hg	$\frac{H\kappa_s}{P} \times 10^5$
0.00	77.2	−13.7	68.3	−13.4
	72.0	−13.8	72.9	−13.6
	69.5	−14.0		
		Average $H\kappa_s/P = -13.7 \times 10^{-5}$		
0.1×10^{-3}	63.5	−10.5	51.8	−11.6
	74.9	−10.4	73.7	−10.5
			78.4	−10.5
		Average $H\kappa_s/P = -10.7 \times 10^{-5}$		
0.2×10^{-3}	53.8	− 9.80	57.9	−10.1
	76.9	− 9.45	76.9	− 9.4
	82.3	− 9.20	82.9	− 9.3
		Average $H\kappa_s/P = -9.55 \times 10^{-5}$		
0.4×10^{-3}	80.3	− 9.2	52.2	−10.8
	82.8	− 9.3	73.1	− 9.5
	75.5	− 9.2	80.4	− 9.2
		Average $H\kappa_s/P = -9.55 \times 10^{-5}$		
0.8×10^{-3}	59.0	−10.0	66.0	− 9.5
	78.2	− 8.9	80.2	− 8.5
	83.5	− 8.0	82.9	− 8.4
		Average $H\kappa_s/P = -8.90 \times 10^{-5}$		
1.6×10^{-3}	70.5	− 9.0	67.8	− 9.5
	79.0	− 8.8	80.3	− 8.6
	82.3	− 8.7	76.4	− 8.6
		Average $H\kappa_s/P = -8.87 \times 10^{-5}$		

TABLE III

Data for KCl

Concentration KCl	Pressure cm. Hg	$\frac{H\kappa_s}{P} \times 10^5$	Pressure cm. Hg	$\frac{H\kappa_s}{P} \times 10^5$
0.00	51.9	−13.0	51.6	−11.5
	78.4	−12.6	83.0	−12.4
			78.2	−12.6
		Average $H\kappa_s/P = -12.4 \times 10^{-5}$		
0.05×10^{-3}	77.4	−13.8	80.6	−13.8
	82.4	−13.8	77.2	−13.8
	76.0	−13.6		
		Average $H\kappa_s/P = -13.8 \times 10^{-5}$		
0.10×10^{-3}	48.7	−15.1	59.1	−12.4
	82.2	−14.3	77.4	−14.1
	76.1	−14.3	84.4	−14.2
		Average $H\kappa_s/P = -14.01 \times 10^{-5}$		
0.20×10^{-3}	36.7	−13.7	63.3	−13.1
	79.0	−14.3	82.4	−14.2
	85.5	−13.9	78.2	−14.4
		Average $H\kappa_s/P = -13.9 \times 10^{-5}$		
0.4×10^{-3}	81.2	−12.7	50.3	−12.50
	66.8	−12.4	82.9	−12.95
	71.4	−13.5	72.2	−13.40
		Average $H\kappa_s/P = -12.9 \times 10^{-5}$		
0.8×10^{-3}	41.6	−11.75	53.2	−13.7
	76.7	−12.3	76.8	−12.6
	83.3	−12.2	68.7	−13.4
		Average $H\kappa_s/P = -12.8 \times 10^{-5}$		

TABLE IV

Data for NaCl

Concentration NaCl	Pressure cm. Hg	$\frac{H\kappa_s}{P} \times 10^5$	Pressure cm. Hg	$\frac{H\kappa_s}{P} \times 10^5$
0.00	71.9	−10.23	75.9	− 9.85
	75.1	− 9.90	79.1	− 9.70
	78.9	−10.02	72.0	− 9.70
		Average $H\kappa_s/P = -9.90 \times 10^{-5}$		
0.05×10^{-3}	70.3	−12.80	69.7	−12.84
	78.5	−12.34	74.7	−12.50
	73.9	−12.45	78.6	−12.58
		Average $H\kappa_s/P = -12.6 \times 10^{-5}$		
0.10×10^{-3}	72.9	−13.90	74.1	−14.30
	75.7	−13.85	76.5	−14.40
	79.7	−13.70	73.5	−15.50
		Average $H\kappa_s/P = -14.1 \times 10^{-5}$		
0.2×10^{-3}	71.3	−14.0	72.9	−13.8
	75.1	−13.8	75.9	−13.6
	79.0	−13.7	79.2	−13.6
		Average $H\kappa_s/P = -13.75 \times 10^{-5}$		
0.4×10^{-3}	69.5	−13.4	73.2	−13.3
	74.7	−13.4	76.9	−13.0
	78.3	−13.5	80.2	−13.1
		Average $H\kappa_s/P = -13.30 \times 10^{-5}$		
0.8×10^{-3}	61.5	−12.40	71.7	−11.6
	70.1	−12.45	75.7	−11.6
	77.7	−12.35	82.1	−11.2
		Average $H\kappa_s/P = -11.95 \times 10^{-5}$		
1.6×10^{-3}	67.8	−10.02	75.2	−11.6
	74.8	−10.20	79.2	−11.6
	80.5	−10.25	82.3	−11.8
		Average $H\kappa_s/P = -10.90 \times 10^{-5}$		

TABLE V

Data for $MgCl_2$ and $CaCl_2$ in 1:1 ratio

Concentration $MgCl_2$	Concentration $CaCl_2$	Pressure cm. Hg	$\frac{H\kappa_s}{P} \times 10^5$	Pressure cm. Hg	$\frac{H\kappa_s}{P} \times 10^5$
0.00	0.00	73.3	−12.45	71.6	−11.82
		71.4	−12.20	80.7	−12.20
		77.4	−12.26	74.0	−12.40
			Average $H\kappa_s/P = -12.2 \times 10^{-5}$		
0.05×10^{-3}N	0.05×10^{-3}N	72.7	−10.6	62.2	−11.0
		81.3	− 9.9	74.6	− 9.9
		76.3	− 9.7		
			Average $H\kappa_s/P = -10.22 \times 10^{-5}$		
0.1×10^{-3}N	0.1×10^{-3}N	53.4	− 9.16	59.5	− 9.70
		63.4	− 9.20	74.0	− 9.32
		66.7	− 9.25	70.8	− 9.25
			Average $H\kappa_s/P = -9.32 \times 10^{-5}$		
0.2×10^{-3}N	0.2×10^{-3}N	68.3	− 7.26	70.7	− 6.85
		74.4	− 7.85	76.7	− 7.50
		69.9	− 7.62	70.0	− 7.62
			Average $H\kappa_s/P = -7.45 \times 10^{-5}$		
0.4×10^{-3}N	0.4×10^{-3}N	54.9	− 5.20	62.1	− 4.37
		69.1	− 5.95	70.6	− 5.72
		82.8	− 6.12	84.0	− 5.42
			Average $H\kappa_s/P = -5.46 \times 10^{-5}$		
0.8×10^{-3}N	0.8×10^{-3}N	75.3	− 3.38	56.8	− 4.85
		79.7	− 4.83	82.4	− 5.10
		82.0	− 5.12	78.2	− 5.06
			Average $H\kappa_s/P = -4.72 \times 10^{-5}$		

TABLE VI

Data for Mixture of $MgCl_2$ and KCl in Equivalent Ratio of 1:1

Concentration $MgCl_2$	Concentration KCl	Pressure cm. Hg	$\frac{H\kappa_s}{P} \times 10^5$	Pressure cm. Hg	$\frac{H\kappa_s}{P} \times 10^5$
0.00	0.00	52.0	−13.20	61.9	−12.30
		69.9	−13.35	69.4	−13.37
		82.3	−13.18	81.8	−13.75
		Average $H\kappa_s/P = -13.2 \times 10^{-5}$			
0.05×10^{-3}N	0.05×10^{-3}N	64.1	−11.8	45.9	−10.2
		79.1	−12.3	66.3	−11.7
		76.0	−12.4	81.2	−12.3
		Average $H\kappa_s/P = -11.8 \times 10^{-5}$			
0.10×10^{-3}N	0.10×10^{-3}N	56.8	−11.1	62.2	−11.5
		69.2	−11.8	81.4	−11.6
		79.6	−11.9	82.3	−12.3
		Average $H\kappa_s/P = -11.7 \times 10^{-5}$			
0.2×10^{-3}N	0.20×10^{-3}N	49.6	− 9.80	64.7	− 8.50
		78.8	−10.40	78.2	−10.30
		83.1	−10.50	81.9	−10.60
		Average $H\kappa_s/P = -10.0 \times 10^{-5}$			
0.40×10^{-3}N	0.40×10^{-3}N	60.7	− 9.00	65.9	− 7.94
		78.5	− 9.00	80.3	− 9.00
		81.3	− 9.15	75.2	− 9.10
		Average $H\kappa_s/P = -8.86 \times 10^{-5}$			
0.80×10^{-3}N	0.80×10^{-3}N	59.1	− 5.95	78.2	− 7.20
		81.9	− 7.60	82.7	− 7.60
		77.1	− 8.45	75.1	− 8.05
		Average $H\kappa_s/P = -7.48 \times 10^{-5}$			

TABLE VII

Data for Mixture of $CaCl_2$ and KCl in Equivalent Ratio of 1:1

Concentration $CaCl_2$	Concentration KCl	Pressure cm. Hg	$\frac{H\kappa_s}{P} \times 10^5$	Pressure cm. Hg	$\frac{H\kappa_s}{P} \times 10^5$
0.00	0.00	77.2	−11.10	82.6	− 9.10
		81.4	−11.10	86.7	− 9.12
		86.0	−11.10	76.4	− 9.05
		Average $H\kappa_s/P = -10.1 \times 10^{-5}$			
0.05×10^{-3}N	0.05×10^{-3}N	75.6	−11.3	80.2	−11.42
		80.5	−11.2	84.7	−11.50
		85.0	−11.0	75.1	−11.97
		Average $H\kappa_s/P = -11.4 \times 10^{-5}$			
0.1×10^{-3}N	0.1×10^{-3}N	78.8	−10.18	81.1	−10.12
		82.4	−10.05	86.2	−10.13
		86.6	−10.03	72.8	−10.50
		Average $H\kappa_s/P = -10.15 \times 10^{-5}$			
0.2×10^{-3}N	0.2×10^{-3}N	68.5	− 9.77	79.8	− 9.22
		77.7	−10.00	85.6	− 9.60
		85.2	−10.22	72.0	−10.17
		Average $H\kappa_s/P = -9.83 \times 10^{-5}$			
0.4×10^{-3}N	0.4×10^{-3}N	85.8	− 7.73		
		81.0	− 7.70		
		73.4	− 7.85		
		Average $H\kappa_s/P = -7.76 \times 10^{-5}$			

TABLE VIII

Data for Mixture of NaCl and $MgCl_2$ in Equivalent Ratio of 1:1

Concentration NaCl	Concentration $MgCl_2$	Pressure cm. Hg	$\frac{H\kappa_s}{P} \times 10^5$	Pressure cm. Hg	$\frac{H\kappa_s}{P} \times 10^5$
0.00	0.00	72.7	−11.20	81.0	−10.00
		79.6	−11.34	84.1	− 9.95
		85.5	−11.38	87.4	−10.32
		Average $H\kappa_s/P = -10.7 \times 10^{-5}$			

TABLE VIII (Continued)

Data for Mixture of NaCl and $MgCl_2$ in Equivalent Ratio of 1:1

Concentration NaCl	Concentration $MgCl_2$	Pressure	$\frac{H\kappa_s}{P} \times 10^5$	Pressure	$\frac{H\kappa_s}{P} \times 10^5$
0.05×10^{-3}N	0.05×10^{-3}N	71.9	−10.25	81.8	−10.28
		79.9	−10.22	84.0	−10.27
		85.1	−10.28	76.8	−10.00
		Average $H\kappa_s/P = -10.22 \times 10^{-5}$			
0.1×10^{-3}N	0.1×10^{-3}N	74.8	− 9.75	74.9	− 9.60
		80.9	− 9.75	81.2	− 9.60
		84.8	−10.00	86.1	− 9.60
		Average $H\kappa_s/P = -9.75 \times 10^{-5}$			
0.2×10^{-3}N	0.2×10^{-3}N	79.1	− 9.15	81.8	− 8.90
		82.5	− 9.07	87.0	− 8.86
		86.8	− 9.15	77.7	− 9.20
		Average $H\kappa_s/P = -9.05 \times 10^{-5}$			
0.4×10^{-3}N	0.4×10^{-3}N	74.0	− 8.12	80.6	− 8.05
		80.5	− 8.23	84.1	− 7.96
		86.0	− 8.26	88.5	− 7.82
		Average $H\kappa_s/P = -8.07 \times 10^{-5}$			
0.8×10^{-3}N	0.8×10^{-3}N	72.4	− 6.27	80.6	− 6.62
		79.7	− 6.30	86.0	− 7.02
		86.1	− 6.25	75.6	− 6.90
		Average $H\kappa_s/P = -6.55 \times 10^{-5}$			

TABLE IX

Data for Mixture of NaCl and $CaCl_2$ in Equivalent Ratio of 1:1

Concentration NaCl	Concentration $CaCl_2$	Pressure cm. Hg	$\frac{H\kappa_s}{P} \times 10^5$	Pressure cm. Hg	$\frac{H\kappa_s}{P} \times 10^5$
0.00	0.00	66.1	− 9.90	63.5	−10.00
		76.5	−10.00	70.0	− 9.75
		79.3	− 9.90	74.8	− 9.65
		Average $H\kappa_s/P = -9.86 \times 10^{-5}$			
0.05×10^{-3}N	0.05×10^{-3}N	58.4	−10.35	51.5	− 9.48
		68.9	−10.23	63.8	− 9.02
		73.7	−10.20	70.9	− 9.10
		Average $H\kappa_s/P = -9.72 \times 10^{-5}$			

TABLE IX (Continued)

Data for Mixture of NaCl and $CaCl_2$ in Equivalent Ratio of 1:1

Concentration NaCl	Concentration $CaCl_2$	Pressure	$\frac{H\kappa_s}{P} \times 10^5$	Pressure	$\frac{H\kappa_s}{P} \times 10^5$
0.1×10^{-3}N	0.1×10^{-3}N	41.1	− 9.75	48.1	− 9.84
		60.9	− 9.62	73.7	− 9.65
		69.5	− 9.72	68.3	− 9.70
		Average $H\kappa_s/P = -9.71 \times 10^{-5}$			
0.2×10^{-3}N	0.2×10^{-3}N	67.8	− 8.35	62.8	− 8.65
		58.1	− 8.33	70.7	− 8.76
				69.9	− 8.78
		Average $H\kappa_s/P = -8.57 \times 10^{-5}$			
0.4×10^{-3}N	0.4×10^{-3}N	66.9	− 7.90	75.0	− 7.20
		75.0	− 7.75	79.8	− 6.67
		78.2	− 7.80	69.1	− 5.64
		Average $H\kappa_s/P = -7.15 \times 10^{-5}$			
0.8×10^{-3}N	0.8×10^{-3}N	70.9	− 6.13	77.3	− 6.07
		76.9	− 6.10	81.4	− 6.33
		80.3	− 6.15	60.5	− 6.63
		Average $H\kappa_s/P = -6.24 \times 10^{-5}$			

TABLE X

Data for Mixture of NaCl and KCl in Equivalent Ratio of 1:1

Concentration NaCl	Concentration KCl	Pressure cm. Hg	$\frac{H\kappa_s}{P} \times 10^5$	Pressure cm. Hg	$\frac{H\kappa_s}{P} \times 10^5$
0.00	0.00	59.9	−12.3	48.9	−10.7
		77.5	−11.9	78.8	−11.9
		78.3	−11.8	81.1	−12.3
		Average $H\kappa_s/P = -11.8 \times 10^{-5}$			
0.05×10^{-3}N	0.05×10^{-3}N	61.7	−14.7	53.4	−14.6
		78.9	−14.8	82.1	−14.9
		82.8	−14.6	79.2	−15.1
		Average $H\kappa_s/P = -14.8 \times 10^{-5}$			

TABLE X (Continued)

Data for Mixture of NaCl and KCl in Equivalent Ratio of 1:1

Concentration NaCl	Concentration KCl	Pressure	$\frac{H\kappa_s}{P} \times 10^5$	Pressure	$\frac{H\kappa_s}{P} \times 10^5$
0.10×10^{-3}N	0.10×10^{-3}N	62.5	−14.5	59.1	−13.4
		78.1	−14.5	77.5	−14.6
		82.3	−14.6	71.2	−16.5
		Average $H\kappa_s/P = -14.7 \times 10^{-5}$			
0.20×10^{-3}N	0.20×10^{-3}N	78.0	−12.90	54.4	−10.90
		80.0	−13.05	81.0	−12.90
		77.6	−13.00	81.4	−13.30
		Average $H\kappa_s/P = -13.03 \times 10^{-5}$			
0.4×10^{-3}N	0.40×10^{-3}N	52.2	−13.00	54.1	−12.30
		78.8	−12.80	78.6	−12.90
		82.8	−12.85	81.2	−12.60
		Average $H\kappa_s/P = -12.72 \times 10^{-5}$			
0.8×10^{-3}N	0.8×10^{-3}N	65.4	− 8.55	54.2	− 7.20
		81.2	− 9.98	82.0	− 9.95
		81.8	− 9.70	84.2	−10.25
		Average $H\kappa_s/P = -9.27 \times 10^{-5}$			

TABLE XI

Summary of Ion Antagonism Data

$H\kappa_s/P \times 10^5$

Concentration in Cation Equiv.	$MgCl_2$	$CaCl_2$	NaCl	KCl
0.00	−15.48	−13.70	− 9.90	−12.4
0.05×10^{-3}			−12.60	−13.8
0.10×10^{-3}	−11.05	−10.70	−14.10	−14.01
0.20×10^{-3}	− 9.32	− 9.55	−13.75	−13.9
0.40×10^{-3}	− 8.50	− 9.55	−13.30	−12.9
0.80×10^{-3}	− 6.76	− 8.90	−11.95	−12.8
1.60×10^{-3}	− 2.62	− 8.87	−10.90	−13.6

	$MgCl_2$ $CaCl_2$	$MgCl_2$ KCl	$MgCl_2$ NaCl	$CaCl_2$ KCl	$CaCl_2$ NaCl	KCl NaCl
0.00	−12.2	−13.20	−10.70	−10.10	−9.86	−11.80
0.05×10^{-3}						
0.10×10^{-3}	−10.2	−11.80	−10.22	−11.40	−9.72	−14.80
0.20×10^{-3}	− 9.32	−11.70	− 9.75	−10.15	−9.71	−14.70
0.40×10^{-3}	− 7.45	−10.00	− 9.05	− 9.83	−8.57	−13.03
0.80×10^{-3}	− 5.46	− 8.86	− 8.07	− 7.76	−7.15	−12.72
1.60×10^{-3}	− 4.72	− 7.48	− 6.55		−6.24	− 9.27

TABLE XII

Data for Dilute Physiological Salt Mixture

Cation concentration × 10^4	Pressure cm. Hg	H/P	Pressure cm. Hg	H/P
0.0	82.7	−3.911	82.5	−3.860
	84.9	−3.904	84.8	−3.879
	86.8	−3.934	86.2	−3.915
	Average H/P = −3.900	$H_{K_s}/P = -9.75 \times 10^{-5}$		
0.05	77.6	−3.279	73.3	−3.342
	81.6	−3.290	78.3	−3.339
	84.9	−3.303	83.8	−3.323
	Average H/P = −3.312	$H_{K_s}/P = -12.57 \times 10^{-5}$		
0.10	82.5	−3.060	83.9	−3.116
	84.1	−3.049	85.0	−3.094
	86.1	−3.072	86.2	−3.091
	Average H/P = −3.08	$H_{K_s}/P = -15.172 \times 10^{-5}$		
0.20	75.5	−2.304	82.4	−2.326
	80.0	−2.287	84.6	−2.304
	85.2	−2.300	86.2	−2.302
	Average H/P = −2.305	$H_{K_s}/P = -15.85 \times 10^{-5}$		
0.20*	81.0	−1.629	83.6	−1.590
	83.35	−1.625	85.1	−1.603
	87.1	−1.618	86.8	−1.624
	Average H/P = −1.6148	$H_{K_s}/P = -13.29 \times 10^{-5}$		
0.20**	81.7	−1.187	73.0	−1.205
	84.7	−1.186	78.5	−1.223
	88.5	−1.163	83.9	−1.269
	Average H/P = −1.205	$H_{K_s}/P = -10.73 \times 10^{-5}$		

* plus 0.05×10^{-4} N $MgCl_2$

** plus 0.05×10^{-4} N $MgCl_2$ and 0.05×10^{-4} N $CaCl_2$

TABLE XIII

Data for Mixture of NaCl and KCl in the Equivalent Ratio of 1:20

Concentration	Pressure cm. Hg	H/P	Pressure cm. Hg	H/P
0.0	48.6	−6.759	66.5	−6.661
	65.1	−6.589	73.5	−6.639
	73.7	−6.499	79.7	−6.637
	Average H/P = −6.6306	$H\kappa_s/P = -15.93 \times 10^{-5}$		
0.1×10^{-3} KCl	58.3	−3.927	70.8	−3.707
	69.6	−3.829	77.7	−3.758
	78.3	−3.767	81.6	−3.792
	Average H/P = −3.796	$H\kappa_s/P = -18.38 \times 10^{-5}$		
0.3×10^{-3} KCl	62.5	−2.008	63.7	−1.781
	73.7	−1.953	73.4	−1.744
	80.1	−1.953	80.7	−1.753
	Average H/P = −1.8653	$H\kappa_s/P = -17.65 \times 10^{-5}$		
0.6×10^{-3} KCl	65.1	−1.105	65.9	−1.107
	66.0	−1.038	73.9	−1.123
			79.7	−1.122
	Average H/P = −1.099	$H\kappa_s/P = -17.06 \times 10^{-5}$		
1.0×10^{-3} KCl	61.9	−0.5573	62.7	−0.6060
Series 1	72.5	−0.5448	70.6	−0.6232
	77.7	−0.5469	78.0	−0.5897
	66.5	−0.6165	66.4	−0.5120
	76.5	−0.5424	74.6	−0.5160
	80.7	−0.5452	80.1	−0.4931
	Average H/P = −0.5577	$H\kappa_s/P = -12.715 \times 10^{-5}$		
1.0×10^{-3} KCl	63.0	−0.5555	64.8	−0.6327
Series 2	72.1	−0.5200	71.5	−0.6573
	78.4	−0.5165	80.1	−0.6054
	71.3	−0.5539	70.5	−0.5957
	77.1	−0.5317	76.4	−0.6020
	81.7	−0.5263	81.8	−0.5806
	Average H/P = −0.5731	$H\kappa_s/P = -13.18 \times 10^{-5}$		
1.0×10^{-3} KCl	62.3	−0.5698	66.4	−0.5195
$.05 \times 10^{-3}$ NaCl	71.2	−0.5758	75.0	−0.5066
	79.3	−0.5674	81.2	−0.4987
	60.7	−0.5848	67.9	−0.5301
	70.3	−0.5832	75.6	−0.5555
	77.3	−0.5821	80.4	−0.5534
	Average H/P = −0.5522	$H\kappa_s/P = -12.75 \times 10^{-5}$		

TABLE XIV

Data for Mixture of NaCl and $CaCl_2$ in Molecular Ratio of 1:100

Concentration	Pressure cm. Hg	H/P	Pressure cm. Hg	H/P
0.0	71.9	−7.065	66.0	−6.636
	78.1	−6.888	75.4	−6.446
	76.2	−6.797	80.7	−6.332
	Average H/P = −6.694	$H\kappa_s/P = -14.95 \times 10^{-5}$		
0.1×10^{-3} NaCl	75.4	−3.872	74.5	−3.369
	79.3	−3.883	78.7	−3.437
	82.7	−3.863	83.2	−3.383
	Average H/P = −3.634	$H\kappa_s/P = -17.116 \times 10^{-5}$		
0.3×10^{-3} NaCl	71.7	−2.280	67.3	−2.184
	77.1	−2.243	76.9	−2.197
	82.3	−2.205	81.3	−2.195
	Average H/P = −2.2173	$H\kappa_s/P = -18.49 \times 10^{-5}$		
0.6×10^{-3} NaCl	58.1	−1.187	68.1	−1.167
	68.5	−1.168	76.3	−1.186
	78.5	−1.133	80.9	−1.162
	Average H/P = −1.1671	$H\kappa_s/P = -15.979 \times 10^{-5}$		
1.0×10^{-3} NaCl	70.1	−0.6704	69.7	−0.7317
	75.7	−0.6472	74.1	−0.7422
	80.1	−0.6367	78.4	−0.7716
	68.0	−0.7058	65.9	−0.7132
	74.7	−0.6827	74.5	−0.6711
	79.4	−0.7052	81.0	−0.6666
	Average H/P = −0.6953	$H\kappa_s/P = -13.63 \times 10^{-5}$		
1.0×10^{-3} NaCl 0.02×10^{-3} $CaCl_2$	63.1	−0.6814	69.5	−0.6906
	73.1	−0.6429	76.2	−0.6692
	80.6	−0.5955	80.5	−0.6708
	84.0	−0.6666	70.5	−0.6241
	74.6	−0.6300	76.1	−0.6438
	81.7	−0.6609	81.7	−0.6365
	Average H/P = −0.6510	$H\kappa_s/P = -12.317 \times 10^{-5}$		

Discussion

The results show, in general, an averaged effect of the individual salts in a mixed salt solution upon the surface potential. Thus the curve for KCl and NaCl is clearly simply a component curve of the individual curves for KCl and NaCl. There is a slight suggestion of antagonism between $CaCl_2$ and $MgCl_2$ below a concentration of 0.2×10^{-3}, but it is very doubtful if the results are clear enough to warrant one considering that this is a case of ion antagonism. In any event, it is certainly very slight. Other than this, somewhat doubtful case, we may state definitely that in the concentrations investigated there are no ion antagonistic effects on the surface potential.

The results with dilute physiological salt solution indicate clearly the absence of ion antagonism between $MgCl_2$ and $CaCl_2$, as influencing the electrokinetic potential.

In interpreting these results it is to be remembered that the concentrations used are very much less than those usually employed in observing ion antagonism in biological systems. These low concentrations were necessarily employed since the specific conductivity becomes large in more concentrated solutions and thus invalidates streaming potential measurements.

Summary

1. The surface potential at a cellulose-aqueous solution interface has been measured for solutions of NaCl, KCl, $CaCl_2$, $MgCl_2$, NaCl with KCl, NaCl with $CaCl_2$, NaCl with $MgCl_2$, KCl with $CaCl_2$, KCl with $MgCl_2$, and $CaCl_2$ with $MgCl_2$ up to a total cation normality of 0.8×10^{-3}.

2. With the possible exception of $CaCl_2$ and $MgCl_2$ the results obtained for the mixtures of the salts are more or less an average of the results obtained for the salts separately.

3. There is no antagonism between $MgCl_2$ and $CaCl_2$ in a 0.2×10^{-3} N diluted physiological salt solution.

4. There is no antagonism, as affecting the electrokinetic potential, between KCl and NaCl in the ratio of 20:1, or between NaCl and $CaCl_2$ in the molecular ratio of 100:1.

Literature Cited

[1] J. Loeb: "Artificial Parthenogenesis and Fertilization," (1913).

[2] J. Sztück: Experimentelle Beiträge zu einer Theorie der antagonistischen Ionenwirkungen, Jahr. Bot., 52, 85-142 (1913).

[3] Eva Berger: Unterschiedliche Wirkungen gleicher Ionen und Ionengemische auf verschiedene Tierarten, Pflügers' Archiv, 223, 1-39 (1929).

[4] Ralph S. Lillie, The Relation of Ions to Ciliary Movement, Am. J. Physiol., 10, 419-443 (1904).

[5] W. J. V. Osterhout: "Injury, Recovery, and Death, in Relation to Conductivity and Permeability" (1922).

[6] S. M. Neuschloss: Untersuchungen über antagonistische Wirkungen zwischen Ionen gleicher Ladung, Kolloid-Z., 27, 292-306 (1920).

[7] H. Freundlich and P. Scholz: Über die Flockung durch Elektrolytgemische, Kolloidchem. Beihefte, 16, 267-284 (1922).

[8] H. B. Weiser: Adsorption by Precipitates. VI., J. Phys. Chem., 28, 232-244 (1924).

[9] H. B. Weiser: The Antagonistic Action of Ions in the Neutralization of Sols, J. Phys. Chem., 30, 20-33 (1926).

[10] H. B. Weiser: The Antagonistic Actions of Ions in the Neutralization of Sols II., J. Phys. Chem., 30, 1527-1537 (1926).

[11] H. B. Weiser: Ionic Antagonism in Colloid Systems, Colloid Symposium Monograph, 4, 354-373 (1926).

[12] G. H. A. Clowes: Protoplasmic Equilibrium. I. Action of Antagonistic Electrolytes on Emulsions and Living Cells, J. Phys. Chem., 20, 407-451 (1916).

[13] W. D. Harkins and H. Zollman: Interfacial Tension and Emulsification. I. The Effect of Bases, Salts, and Acids upon the Interfacial Tension between Aqueous Sodium Oleate Solutions and Benzene. II. Extremely Small Interfacial Tensions Produced by Solutes, J. Am. Chem. Soc., 48, 69-80 (1926).

[14] H. S. Simms: Chemical Antagonism of Ions. IV. Effect of Salt Mixtures on Glycine Activity, J. Gen. Physiol., 12, 783-792 (1929).

[15] H. B. Bull and R. A. Gortner: Studies on Electrokinetic Potentials. VI. Electrical Phenomena at Interfaces, Eighth Colloid Symposium Annual, J. Phys. Chem., 35, January issue (1931).

[16] W. McK. Martin and R. A. Gortner: Studies on Electrokinetic Potentials, V. Interfacial Energy and the Molecular Structure of Organic Compounds. I. Electrokinetic Potentials at Cellulose-Organic Liquid Interfaces, J. Phys. Chem., 34, 1509-1539 (1930).

[17] D. R. Briggs: The Determination of the ζ-Potential on Cellulose—A Method, J. Phys. Chem., 32, 641-675 (1928).

THE DIRECT MEASUREMENT OF THE ADSORPTION OF SOLUBLE SUBSTANCES BY THE BUBBLE METHOD*

BY DAVID M. GANS AND WILLIAM D. HARKINS

1. Introduction

While there is conclusive evidence that practically all true films of insoluble substances on water are monomolecular, it is possible that with some soluble substances the amount in the surface corresponds to a polymolecular film. However, the values calculated from the adsorption equation in its "corrected form"

$$u = -\frac{r}{RT}\frac{\delta\gamma}{\delta \ln a} \qquad (1)$$

indicate that such films as produced by soluble substances are only one molecule in thickness.

Additional evidence for the monomolecular theory is given by the values thus far obtained for the amount of soap adsorbed at the oil-water interface in emulsions. Thus Griffin,[1] van der Meulen and Rieman,[2] and Harkins and Beeman[3] have all obtained values which agree with the theory. The direct method used by them has not, however, attained a very high degree of accuracy.

A different type of direct method devised by Donnan and Barker[4] gives in its latest form results of a different order. Thus McBain and Davies[5] passed bubbles of gas through solutions of amyl alcohol and of paratoluidine in water, collected the films from the bubbles, and found that the excess in the surface corresponds to a bi- or tri-molecular film. Similar work by Harkins and Gans[6] with the much less soluble nonylic acid had, however, indicated a monomolecular film.

By the "direct" bubble method, McBain and Davies obtained an area of 14 sq. Å per molecule adsorbed from the more concentrated solutions of paratoluidine, while Gans and Harkins[7] by the use of Equation (1) calculated the mean molecular area as twice as large, or 28.5 sq. Å. In making this calculation the writers assumed the correctness of the values for the activity of paratoluidine as obtained by McBain, Wynne-Jones and Pollard[8].

* Contribution from Kent Chemical Laboratory of the University of Chicago.

[1] Griffin: J. Am. Chem. Soc., 45, 1648 (1923).

[2] Van der Meulen and Rieman: J. Am. Chem. Soc., 46, 876 (1924).

[3] Harkins and Beeman: Colloid Symposium Monograph, 5, 27 (1927); J. Am. Chem. Soc., 51, 1674 (1929).

[4] Donnan and Barker: Proc. Roy. Soc., 85A, 557 (1911).

[5] McBain and Davies: J. Am. Chem. Soc., 49, 2230 (1927). Since the completion of the work here presented, several papers on this subject by McBain and his coworkers have appeared: Laing, McBain and Harrison: Colloid Symposium Monograph, 6, 63 (1928); McBain and DuBois: J. Am. Chem. Soc., 51, 3534 (1929).

[6] Harkins and Gans: Colloid Symposium Monograph, 5, 40 (1927).

[7] Gans and Harkins: J. Am. Chem. Soc., 52, 2289 (1930).

[8] McBain, Wynne-Jones, and Pollard: Colloid Symposium Monograph, 6, 57 (1928).

However, any inaccuracy in the activities cannot be sufficient to make the two methods agree.

It is evident that the present status of our knowledge of the thickness of such films from soluble substances is altogether unsatisfactory and is confusing even to the expert in this field. Further work is essential to explain the disagreement, and to decide between the following alternatives which may be considered:

1. The adsorption equation is correct and some unknown error is inherent in the "direct" method of McBain and Davies.

2. Neither the adsorption equation nor the direct method gives the true values. Probably then the correct results are intermediate.

3. The method of McBain and Davies gives correct results, and the adsorption equation has not been derived by a correct method.

In this connection it is important to keep in mind what is almost universally forgotten, that the "adsorption" Equation (1) is not Gibbs' equation for adsorption. His equation

$$d\gamma = -SdT - u_1 d\mu_1 - u_2 d\mu_2 \qquad (2)$$

contains the two unknown adsorptions, u_1 and u_2, and thus cannot be solved unless a relation between them can be found. McBain and Davies consider that even Gibbs' equation is incorrect and that it should include an electrical term, as follows:

$$d\gamma = -SdT - u_1 d\mu_1 - u_2 d\mu_2 \quad \ldots . \quad -edV \ . \ (3)$$

It seems apparent, however, that the electrical term should not be included for an experiment in which thermodynamic equilibrium is attained, and in which there is no difference of applied potential between the liquid and the gas. Thus, if from the thermodynamic standpoint Equation (1) is correctly derived it is correct without the inclusion of the above mentioned electrical term, and if it is incorrectly derived the inclusion of the electrical term will not make it correct.

It is, then, obvious that if the bubbles in the experiments of McBain and Davies are so highly charged that the term $-edV$ becomes large, then their method should not give the adsorption for an ordinary plane surface, and this would mean that the film is polymolecular only when a large potential is applied through the surface. Our opinion is that no such high potential difference at the surface exists, and that the term $-edV$ is in general negligible and should not be included.

Since the results of McBain and Davies were not in accord with our results in which the less soluble nonylic acid was used, it seemed advisable to repeat their work on amyl alcohol and paratoluidine in order to determine the effect of other variables, such as the size of the bubbles. The apparatus was similar to that used earlier in this laboratory[6] except that the form of collecting tube for the films was that used by McBain and Davies.

2. Apparatus and Procedure

The apparatus employed for the direct determination of adsorption in the air-solution interface is shown in Fig. 1, which is drawn to scale. The liquids in the various parts of the diagram are all samples of the same aqueous solution of the substance under investigation. The uniform bubbles in the regular stream pictured in the adsorption tube 34 pass along this tube to the point 37, where they rise in the inverted U-tube, while the solution around them drains downward. These bubbles which contain in their surfaces the solute adsorbed in their passage through the adsorption tube 34, travel single-file

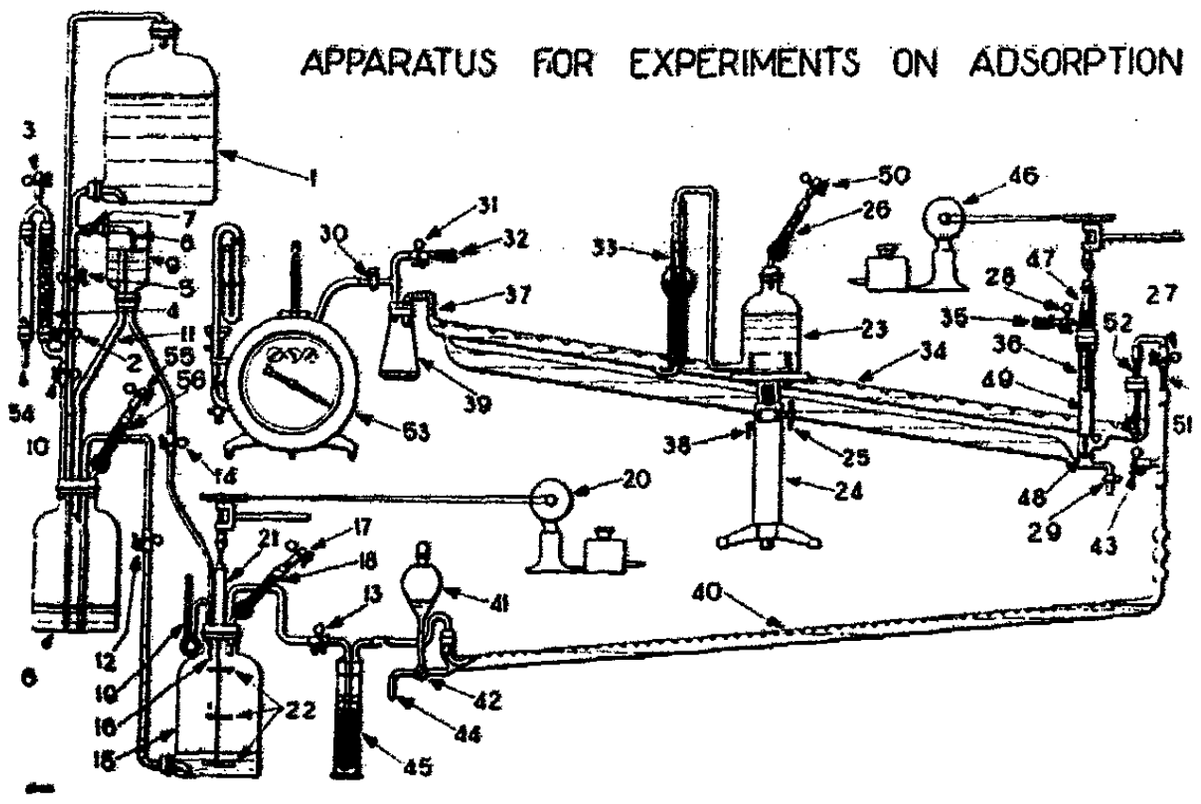

FIG. 1

around the U-tube, burst, and the resultant liquid drops down into flask 39. The solution which collects in this flask is therefore more concentrated (with organic solutes) than that in tube 34. The air within the bubbles passes on through the wet-test meter 53.

If the collection of the films is to be kept efficient, the level of the solution at point 37 must be kept constantly at the proper height. This is accomplished by reservoir 23, which is connected with the adsorption tube 34 through tube 33. When the level has fallen appreciably at point 37, it is brought back to its initial position by reservoir 23, which is raised by means of the rack and pinion 24. The mercury seal 33 permits a change of elevation over a 12 cm. range, while a small quantity of air trapped by the four tubes which form the seal keeps the solution from contact with the mercury.

Adsorption may set up various non-uniformities in concentration within tube 34. Such changes are prevented by the use of the small pump 48, operated by motor 46 through the mercury seal 47. The pump creates a gentle counter-current against the stream of bubbles in tube 34 and mixes the solution in this tube with that in the larger tube just beneath. A suffi-

ciently uniform concentration is thus maintained. At the left side of the apparatus, the two tubes are sealed together far enough from point 37 to avoid any disturbances in the collection of the films. Tube 34 is inclined to such an extent that each bubble remains within it for a period of several times that required for complete adsorption.

The air which forms the bubbles is completely saturated with respect to the solution before it arrives at the bubble-forming tip 52. This saturation is secured first by fifteen minutes of vigorous stirring of both air and solution in bottle 15, in which the air is under a pressure sufficiently above that of the atmosphere to ensure its passage through the entire apparatus. Then the air goes through the Fisher-Milligan wash-bottle 45, which almost completes the saturation. To make saturation certain, the air finally passes through the saturation tube 40 in bubbles that burst at the top of the tube. This tube contains solution of the same concentration as that in the adsorption tube 34.

The pressure in bottle 15 is maintained at a constant value by means of the unvarying head of solution between bottles 9 and 15. As air leaves bottle 15, solution from bottle 9 enters through tip 16 to take its place.

The procedure followed in each determination will be made clear by a more detailed description of the apparatus. It will be noticed in particular that the solution in tubes 34 and 40 come in contact with nothing but air, glass and gold-plate.

Reservoir 1, which communicates with the atmosphere through soda-lime tube 4, contains about six liters of the solution under investigation. A thin stream of solution enters bottle 9, which is under atmospheric pressure. The level in this bottle is maintained constant by a slight overflow down the sides of the wide tube 11. Some of the solution runs into bottle 15 through tip 16 until the increased pressure in bottle 15 stops the flow. This pressure, which amounts to 5 cm. of mercury above atmospheric, remains constant throughout the experiment. By means of the small motor 20, operating through the mercury seal 21, the air in the bottle is stirred vigorously for fifteen minutes before each experiment, in order to saturate the air with the vapor from the solution.

Both the adsorption tube 34 and the saturation tube 40 are filled with the solution, the latter through bulb 41, and the former through reservoir 23, the contents of which can be drawn over into tube 34 by suction at tube 32, with the necessary clamps closed. The tubes are emptied, the solutions well mixed, and the tubes refilled. This operation is again repeated, until the tubes contain solutions of the same concentration. At this time, wash bottle 45 is well rinsed and filled with solution.

Motor 46 is started, and maintains a slow counter-current of solution down tube 34 during the experiment, as described above. Next a 100 c.c. sample of the contents of the adsorption tube is drawn over into flask 39 and poured into a glass-stoppered flask labelled A.

Clamp 13, heretofore closed, is opened, and air enters bottle 45 and thence tube 40 in a stream of small bubbles. This air, saturated with respect to the

solution, emerges from the collapsing bubbles, goes through capillary 51, which is necessary for proper operation, and passes down tube 52, which is of thick-walled glass, flattened and ground at the lower end. Each bubble formed at this tip escapes upward on reaching its proper size, and encounters a gold-plated brass baffle plate, which deflects it forward along tube 34. At this time, reservoir 23 is kept so low that the bubbles burst below point 37, and the liberated air enters a fresh flask 39 and finds its exit through meter 53.

The apparatus is now in working order. The stream of bubbles is stopped by closing clamp 27, the level of the solution is carefully adjusted to point 37, the meter is read, the time noted, and the bubbles started. Upon reaching the outlet at point 37, the bubbles mount in rapid succession, pushing each other along and draining until nothing but a thin envelope is left around each. These films pass around the inverted U-tube, collapse at its end, and drop down into flask 39, while the enclosed air passes on through the meter. During the experiment, the level is maintained at such a point 37 that the collection of films is most efficient. At frequent and regular intervals, the time of formation of a convenient number of bubbles, usually 100, is determined with a stop-watch. The rate of rotation of the pump is also measured, but was found not to affect the results noticeably. The time each bubble takes to traverse the entire length of the adsorption tube is about 15 seconds.

After enough solution for the analyses has been collected in flask 39, the stream of bubbles is stopped, the exact time again noted, stopcock 30 closed, and motor 46 stopped. The liquid in flask 39 is poured into a weighed glass-stoppered container, labelled B, and its weight is later determined. Without delay, flask 39 is replaced and about 100 cc. of the solution closest to the outlet is drawn over. This solution, which contains any adsorbed solute that may have been skimmed off from each bubble in its passage up the inverted U-tube, is placed in a glass-stoppered flask labelled C. The contents of tube 34 are withdrawn through outlet 29, and after a thorough mixing a 200 cc. sample is separated and placed in a glass-stoppered flask labelled D. About 100 cc. of the solution in tube 40 is also set aside in a glass-stoppered flask labelled E. By means of a suction pump attached to tube 54, the solutions distributed in the left-hand half of the apparatus may be drawn back up into reservoir 1.

From the measured rate of formation of the bubbles and the time of duration of the experiment, the number of bubbles formed is calculated. Since the total volume of air passed is recorded by the meter, the volume of each bubble is easily determined. Measurements of the shapes of bubbles of different volumes permit the calculation of the surface area of each bubble, and hence of the entire area exposed for adsorption. The analyses of the five samples of solution taken give data for the calculation of the total number of adsorbed molecules of solute carried over into flask 39 by the known adsorbing area. Thus is found the molecules of solute adsorbed on each square centimeter of surface and, reciprocally, the apparent surface area occupied by each adsorbed molecule in the surface region. The calculation of the adsorption will be discussed in detail below.

Determinations of the adsorption were made for various concentrations of *iso*amyl alcohol solutions for bubbles of one size, and for both *iso*amyl alcohol and *p*-toluidine solutions, for different sizes of bubbles but for only one concentration, suitably chosen for each solute. Four or five experiments were carried out for each concentration as well as for each size of bubbles. After every two or three experiments, the adsorption tube 34 and the saturation tube 40 were cleaned with hot dichromate cleaning solution and very thoroughly rinsed with distilled water. The inverted U-tube outlet was cleaned with particular care, as it was essential for proper collection of films that the solution should wet the glass at the outlet, as was observed also by McBain and Davies. Greater difficulties were met in this respect with the *p*-toluidine solutions than with those of *iso*amyl alcohol. In a clean outlet tube, however, the former substance gave less trouble, since the films of *p*-toluidine solutions were more stable than those of *iso*amyl alcohol solutions. Whenever the concentration of solution or the solute employed was changed, the entire apparatus was cleaned.

3. Analysis of Solutions

All solutions were analyzed in a Zeiss interferometer, equipped with both a 2 cm. and an 8 cm. cell. To obtain the accuracy necessary for this work, the interferometer was housed in a heat-insulated copper container supplied by a pump with water from an adjacent thermostat regulated at 25.0°C. The glass-stoppered flasks containing the solution to be analyzed were suspended for an hour in the copper container after which time the cell and the solutions were at the same temperature. The cell was filled directly from the flasks. This procedure made possible rapid and very accurate analyses.

After each analysis, the contents of the cell were removed by means of a rubber-tipped glass tube, attached to a suction pump. Since air sucked through the cell in this operation changed the concentration of the last few drops of solution adhering to the cell walls, these were thoroughly dried before the next analysis with a tightly rolled rod of filter paper.

The readings of the drum of the interferometer were calibrated with respect to each of the solutions used. The readings were determined for a series of solutions of each substance, compared against distilled water as the standard. The 2 cm. cell was used for this purpose. In Fig. 2 the calibration curves are given. By corrected reading is meant the reading of the drum when the solution is compared with distilled water, less the zero reading, when both sides of the cell are filled with water. The double curve for the more concentrated solutions arises from a gradual change in the color fringes in the interferometer spectrum, a change which ultimately shifts the apparently correct setting of the drum by the width of one entire order of the spectrum. This phenomenon is amply discussed in the literature.[9]

[9] Adams: J. Am. Chem. Soc., 37, 1181 (1915); Macy: *ibid.*, 49, 3070 (1927). A paper by Bartell and Sloan: *ibid.*, 51, 1637 (1929), which appeared since the completion of the present work, describes the use of an interferometer to measure changes in concentration produced by adsorption.

Each analysis was the average of five settings of the drum. In all cases, duplicate analyses were made. With rare exceptions, these checked each other to well within 0.5 of the smallest drum division. The stock solutions were analyzed in the 2 cm. cell. In order to obtain a much higher accuracy, the 8 cm. cell was employed to measure the concentrations of the five samples of solution, A to E, taken during each experiment, and, for these, a differential method was used, that is, the concentration of each was determined, not with water, but with solution D as the standard. It was shown that, for the same solution, the corrected reading for the 8 cm. cell was, within experimental error, 4.00 times that for the 2 cm. cell.

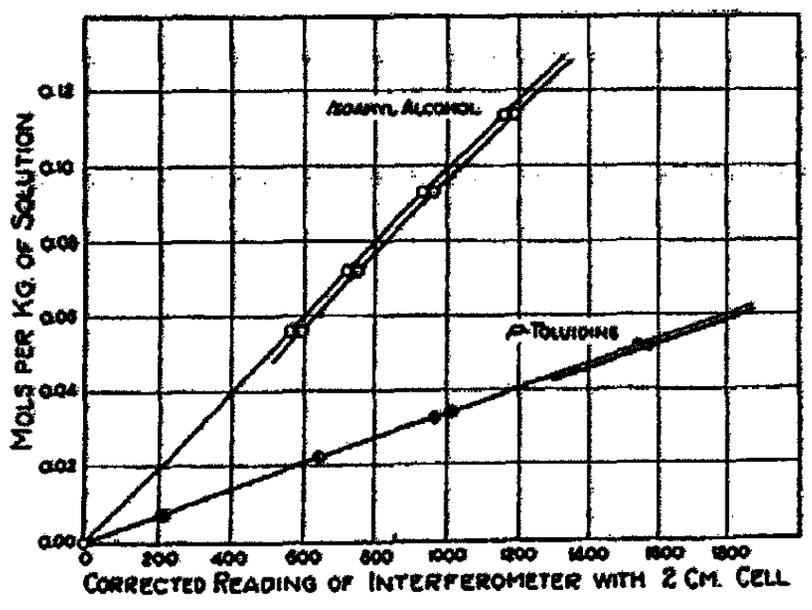

FIG. 2
Calibration curves for Zeiss interferometer

4. Calculation of the Adsorptions

The total volume of the adsorption tube 34 and the tube directly beneath and parallel to it was made so great that the lowering in the concentration of its contents arising from removal of solute by the films was just appreciable. The increase in concentration of solution B, consisting of the collapsed bubble films, was calculated with respect to the average concentration of the solution in the adsorption tube 34 during the experiment, that is, the average of the concentrations of solution A and solution D. This increase in concentration of solution B was corrected by the concentration of solution C relative to solutions A and D. Solution C, which may contain any of the adsorbed solute that may have been removed from the bubbles in their ascent up the right-hand part of the inverted U-tube, was in general found to be somewhat more concentrated than solution D, the final stock solution, and at times more concentrated also than solution A, the initial stock solution. Just what correction to apply on the basis of these differences depends upon the interpretation given of the phenomena occurring within tube 34 during the experiments. To study these, experiments with dyes were performed. A few drops of an aqueous solution of an intensely red dye were injected into various

parts of the adsorption tube in order to study the pumping action. On the basis of these experiments, it was decided that, if the collection of the films were perfect, the concentration of solution C would be closely that of the final stock solution D. The following equation was therefore employed to calculate the corrected increase in concentrations due to the films:

$$\Delta R = \left\{(B) - \frac{(A) + (D)}{2}\right\} + \left\{(C) - (D)\right\} \frac{100}{W_B} \qquad (4)$$

in which the symbol (B), for example, represents the concentration of solution B in the arbitrary scale divisions of the interferometer drum, while W_B is the weight of liquid collected from the bubbles, and 100 is the weight in grams of solution C. The quantity in the first brackets represents the increase in concentration found in the collapsed films, while the term which includes the second brackets corrects this increase for any skimming of the films as they mount up the outlet. Since the equation involves only differences of concentration, any arbitrarily selected concentration may be chosen as the zero. For convenience, (D) is chosen as zero, so that (A), (B), and (C) are simply the corrected drum readings relative to (D) as standard of comparison. ΔR is, then, the increase in concentration of solution B, expressed in the arbitrary drum divisions when the 8 cm. cell is used, calculated for the average concentration of the stock solution, and corrected for conditions under which the collection of films would be perfect.

McBain and Davies employed what would correspond to (C) − (A) instead of (C) − (D) in Equation (4) in calculating their results. In the one experiment which they list with sufficient detail to permit a recalculation of their results a difference of 19 per cent is introduced by the difference in the two methods of calculation. While the actual conditions in the tube fall between those assumed in our method of calculation and in that of McBain and Davies, we believe our equation gives much the better approximation to the truth. However, since (D) and (A) never differ greatly *in our experiments* since the adsorption tube has a total volume of two liters—in fact, since they only infrequently differed by more than the experimental error inherent in the interferometer—it is not surprising that the two methods of calculation yield the same average results for most of *our own* experiments.

The concentration of solution E was determined in order to demonstrate, which it did very satisfactorily, that the air, even before entering tube 40, was already saturated with the vapors from the solution.

The wet test meter, graduated in thousandths of a cubic foot, was calibrated and found to read an average of 2.1% too high. From the corrected volume of air that passed through the meter, there was subtracted the volume of solution B, collected in flask 39, since this solution displaced from the flask an equal volume of air which obviously did not originate from collapsed bubbles.[10] The volume thus obtained was the volume of the bubbles themselves.

[10] McBain and Davies do not seem to have applied this correction.

The surface area of each bubble could not be taken as that of a sphere of equal volume, for the bubbles were obviously not spherical. The bubbles, when in the inverted U-tube, take the form of cylinders, in which form McBain and Davies calculated their areas. But the bubbles assume this shape only in the last two seconds or so of their life. The shape attributed by us to the adsorbing surfaces is that which they possess some few centimeters before they strike the collecting end of the adsorption tube. The largest bubbles were to some extent blunted by their forward motion while the smallest retained an approximately spherical shape. The radius of the adsorption tube 34 was 1.2 cm. Under such an arch, the bubbles took on a form nearly that of an oblate spheroid. As close an estimate of the true

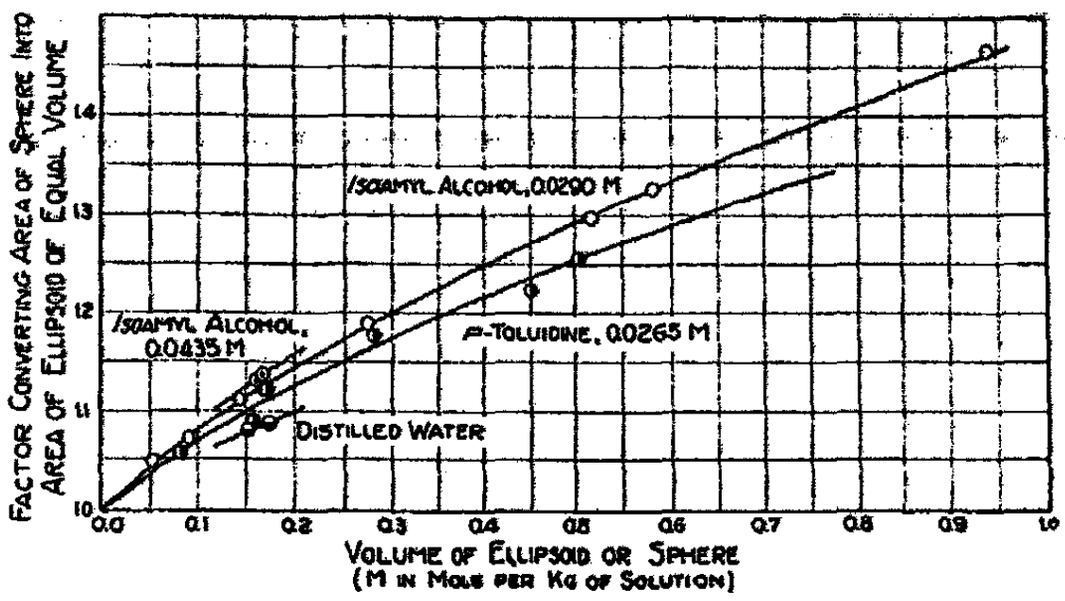

FIG. 3

Experimentally determined factor which converts calculated area of a sphere into actual area of ellipsoidal bubble of same volume, plotted against volume of bubble.

surface area of the bubbles as was possible under the circumstances was made by calculating the area of each bubble as that of an ellipsoid of equal volume. The eccentricity of such ellipsoids of various sizes was determined in a series of solutions by trapping the bubbles under an inverted vessel of optically plane glass and measuring their major and minor axes with a travelling microscope and a cathetometer, respectively. The measurements are summarized in Fig. 3. Interpolation between the curves was resorted to for concentrations different from those plotted.

The equation used in the calculation of the adsorption may now be derived. The total number of bubbles, N is,

$$N = \frac{100}{b} 60.0\ t$$

where b is the observed time in seconds required for the formation of 100 bubbles and t is the observed duration of the experiment in minutes. The total volume of the bubbles, V, is

$$V = 27.75\ M - W_B$$

where M is the recorded change in meter reading in thousandths of a cubic foot, 27.75 is the factor correcting this reading by the requisite 2 per cent and at the same time converting the volume into cubic centimeters, and W_B is the weight determined and, closely enough, the volume of the bubble films collected as solution B. The volume of each bubble, v, then is

$$v = V/N$$

and the area, s, of each as an oblate spheroid, is

$$s = 4.836\ v^{2/3}\ F$$

where $4.836\ v^{2/3}$ is the area of a sphere of volume v, while F is the factor, taken from Fig. 3, which converts this area into that of the proper ellipsoid of the same volume. The entire surface area exposed for adsorption is, then,

$$S = Ns.$$

The stock solution, which gives a corrected reading of R divisions against water as a standard, with the 2 cm. cell, corresponds to one containing m moles of solute per kilogram of solution, as determined from Fig. 2. The same solution, but in the 8 cm. cell, would give a corrected reading of 4.00 R divisions. The total number of mols of adsorbed solute which is carried over into solution B by the films is, then,

$$U = \frac{\Delta R}{4.00\ R} \cdot m \cdot \frac{W_B}{1000}$$

where $\Delta R/4.00\ R$ is the fractional increase in the concentration of solution B.

The adsorption u, in mols per square centimeter of surface, is

$$u = U/S$$

or, expressed in terms of the quantities directly measured,

$$u = \frac{0.01707\ m\ \Delta R\ W_B\ t^{2/3}}{RF\ \{b\ (27.75\ M - W_B)\}^{2/3}}.$$

When multiplied by Avogadro's number, u becomes u′, the adsorption in molecules per square centimeter of surface. The reciprocal of u′ is a, the mean surface area per adsorbed molecule in the surface region. In the calculation of this mean area, no assumption as to whether the film is polymolecular or monomolecular is involved.

5. Adsorption of Isoamylalcohol and Paratoluidine

Experiments were performed with *iso*amyl alcohol to determine the variation of the adsorption with the concentration of the solution for one size of bubble. For both *iso*amyl alcohol and *p*-toluidine, experiments were carried out to study the dependence of the adsorption upon the size of the adsorbing bubble. The size of the bubble was varied by changing the external diameter of the ground glass tip under which the bubble formation occurred. For each

size of bubble, a different inverted U-tube was sealed onto the adsorption tube at point 37. The external diameter of the tip, the internal diameter of the U-tube, and R, the corrected reading in drum divisions given by each solution against water as the standard in the 2 cm. cell are listed in Table I. The concentration m in mols per kilogram of solution, and the corresponding concentration in mols per kilogram of water, as well as the life of the bubbles, are also tabulated. Four to five experiments conducted with portions of the same solution comprise each series. Series A to G are for *iso*amyl alcohol, while series L and M are for *p*-toluidine.

The experiments themselves are listed in Tables II, III, and IV. In these, T signifies room temperature in degrees Centigrade. All of the other symbols have been explained in the derivation of Equation (4). ΔR is calculated by means of Equation (4). Table II shows the variation of the adsorption with the concentration of the solution of *iso*amyl alcohol, for what is closely enough a uniform average size of bubble. Table III contains the data

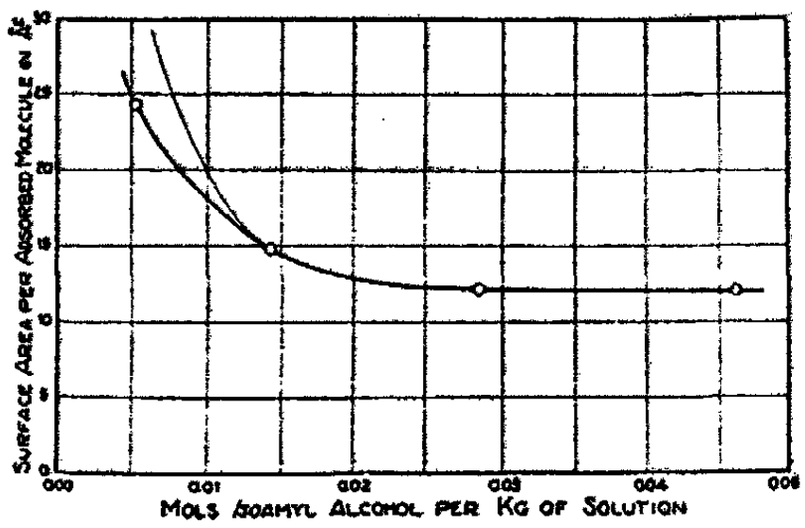

FIG. 4

Variation of molecular area with concentration of solution.

TABLE I

Series of Expts.	R	m	Mols per Kg. Water	External Diam. of Bubble Forming Tip in Cm.	Internal Diam of Bubble Collecting Tube in Cm.	Life of Bubbles in Secs.
A	53.3	0.0054	0.0054	0.90	0.65	15
B	140.9	0.0143	0.0143	0.90	0.65	15
C	282.3	0.0284	0.0285	0.90	0.65	15–18
D	457.5	0.0460	0.0462	0.90	0.65	13–15
E	290.9	0.0293	0.0294	0.90	0.56	16–18
F	292.1	0.0286	0.0287	0.60	0.43	18–20
G	300.7	0.0303	0.0304	1.88	0.90	11–12
L	781.2	0.0265	0.0266	0.90	0.57	15–17
M	756.1	0.0258	0.0259	1.88	0.90	11–13

A-G Solutions of Isoamyl Alcohol
L-M Solutions of Para-Toluidine

for the variation of the adsorption in isoamyl alcohol solutions with the size of the adsorbing bubble. The different concentrations, given in Table I under the same series letter, are very nearly identical, and were so chosen as to fall in the horizontal portion of the curve in Fig. 4, in which region the adsorption does not vary with change in concentration. In Table IV are collected data similar to those in Table III, but for solutions of *p*-toluidine, chosen in the region of concentrations in which, according to the work of McBain and Davies, the adsorption is at its maximum, unvarying value. In all of the derived columns in these tables, the calculations were initially

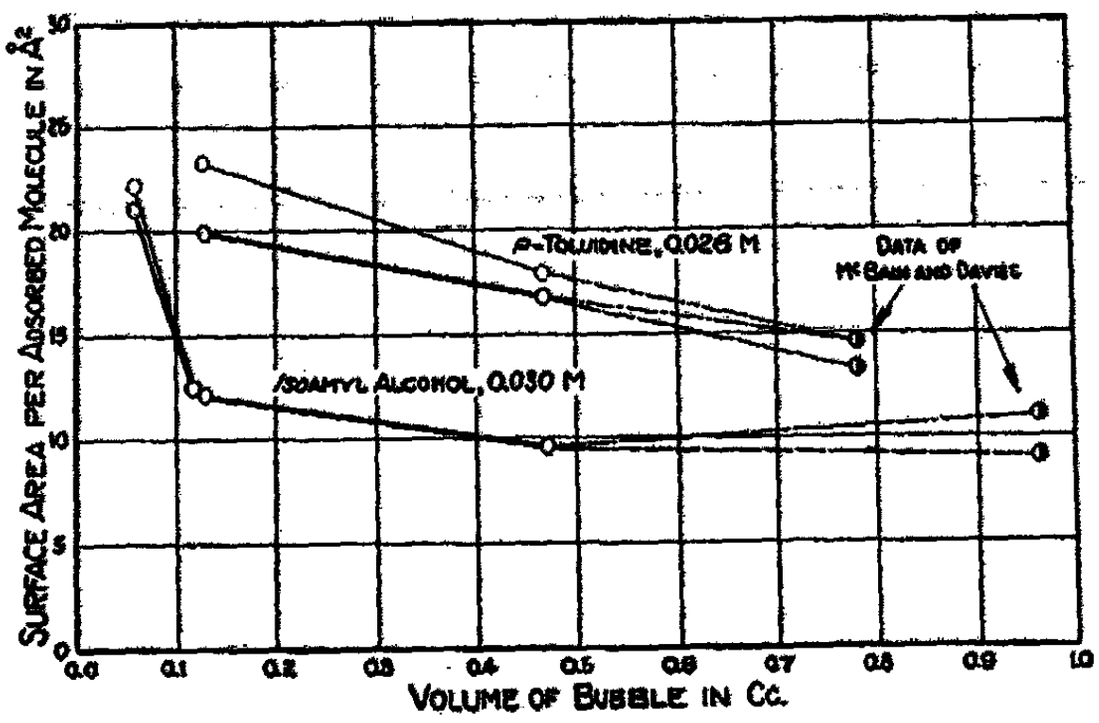

FIG. 5

Variation of molecular area with volume of bubble. Heavy full lines represent results calculated by method given in this paper; light full lines, by method of McBain and Davies. The four points on extreme right of figure represent data obtained by McBain and Davies.

carried out to one more place than is shown. The data in Table II are plotted in Fig. 4 as the heavy full line; the data of Tables III and IV, in Fig. 5 as the heavy full line. The lighter lines in these graphs represent the same data when calculated by the method of McBain and Davies. On account of the minuteness of the quantities measured, the sudden upward jump for the smallest size of bubble taken by the curve in Fig. 5 may be somewhat exaggerated.

The data of McBain and Davies for those two solutions which fall closest in concentration to the solutions here investigated are also included in Fig. 5. The lower point of each pair is the value as given by McBain and Davies, while the upper point in each case is the average value secured by a recalculation of their data, in which the bubble surfaces are considered as those of oblate spheroids, and not those of cylinders, the form accorded them by these investigators. Their data, if calculated by Equation (4), would probably fall between each pair of values in Fig. 5, so that their values on the whole agree very well with those now presented.

TABLE II

Adsorption of Isoamyl Alcohol at Various Concentrations

Series of Expts.	No.	T	t	b	N	M	W_s	v	F
A	1	26	15.0	30.7	2930	16.6	42.8	0.1425	1.082
A	2	28	15.0	26.6	3385	19.0	50.0	0.1410	1.081
A	3	28	15.0	35.0	2570	14.7	42.8	0.1420	1.082
A	4	28	15.0	28.5	3160	17.3	65.5	0.1330	1.074
							Average	0.1395	
B	1	28	15.0	29.6	3040	16.4	62.8	0.1290	1.081
B	2	28	15.0	32.7	2750	14.9	54.4	0.1305	1.082
B	3	27	15.0	24.2	3720	20.0	55.5	0.1345	1.085
B	4	27	15.0	23.0	3915	22.1	74.1	0.1380	1.087
							Average	0.1330	
C	1	27	15.0	36.4	2475	12.2	53.3	0.1155	1.088
C	2	26	15.0	34.5	2610	14.0	43.3	0.1325	1.100
C	3	26	15.0	34.6	2600	14.0	48.7	0.1305	1.099
C	4	26	15.0	35.0	2570	14.0	49.3	0.1320	1.100
C	5	26	15.0	37.2	2420	13.9	52.8	0.1380	1.103
							Average	0.1295	
D	1	24	20.0	28.0	4285	22.5	57.0	0.1325	1.116
D	2	23	20.0	26.0	4615	25.0	72.6	0.1345	1.118
D	3	28	15.0	22.7	3965	20.4	54.4	0.1290	1.114
D	4	28	15.0	21.3	4225	22.7	62.8	0.1340	1.118
D	5	28	15.0	21.6	4165	21.7	60.7	0.1300	1.114
							Average	0.1320	

Series of Expts.	No.	S	(A)	(B)	(C)	ΔR	u $\times 10^{10}$	u' $\times 10^{-14}$	a in Å^2
A	1	4185	0.3	2.6	0.0	2.5	6.5	3.9	25.4
A	2	4795	0.4	2.6	−0.1	2.2	5.8	3.5	28.4
A	3	3665	0.2	2.5	0.0	2.4	7.1	4.3	23.2
A	4	4235	0.6	2.4	0.0	2.1	8.2	5.0	20.1
								Average	24.3
B	1	4060	0.1	3.2	0.2	3.5	13.7	8.3	12.0
B	2	3705	0.0	2.7	0.2	3.1	11.5	7.0	14.3
B	3	5120	0.0	3.7	−0.1	3.5	9.7	5.9	17.1
B	4	5490	0.0	3.1	0.0	3.1	10.6	6.4	15.6
								Average	14.8
C	1	3085	0.2	2.1	0.9	3.7	16.1	9.7	10.3
C	2	3605	−0.1	2.9	0.4	3.9	11.8	7.1	14.0
C	3	3560	−0.1	3.1	0.4	4.0	13.8	8.3	12.0
C	4	3545	0.0	3.0	0.5	4.0	14.0	8.5	11.8
C	5	3440	0.0	2.7	0.4	3.5	13.5	8.2	12.2
								Average	12.1
D	1	6010	0.1	5.8	−0.1	5.6	13.4	8.1	12.4
D	2	6555	1.0	5.1	0.3	5.0	13.9	8.4	11.9
D	3	5455	−1.3	5.1	0.0	5.8	14.5	8.8	11.4
D	4	5990	−0.2	4.1	0.3	4.7	12.4	7.5	13.3
D	5	5760	0.4	4.5	0.8	5.6	14.8	9.0	11.1
								Average	12.0

TABLE III
Adsorption of Isoamyl Alcohol for Various Sizes of Bubbles

Series of Expts.	No.	T	t	b	N	M	W_s	v	F
C	1	27	15.0	36.4	2475	12.2	53.3	0.1155	1.088
C	2	26	15.0	34.5	2610	14.0	43.3	0.1325	1.100
C	3	26	15.0	34.6	2600	14.0	48.7	0.1305	1.099
C	4	26	15.0	35.0	2570	14.0	49.3	0.1320	1.100
C	5	26	15.0	37.2	2420	13.9	52.8	0.1380	1.103
							Average	0.1295	
E	1	25	45.0	42.7	6325	26.5	48.7	0.1085	1.083
E	2	27	45.0	59.5	4540	19.4	50.0	0.1075	1.082
E	3	28	40.0	32.5	7385	35.2	52.0	0.1250	1.093
E	4	29	41.0	40.4	6090	25.6	55.5	0.1075	1.082
E	5	28	35.0	32.7	6420	32.6	65.8	0.1305	1.099
							Average	0.1160	
F	1	28	90.0	60.8	8880	19.8	42.5	0.0570	1.049
F	2	27	90.0	52.8	10225	24.3	53.6	0.0605	1.052
F	3	26	90.0	51.2	10545	23.2	44.0	0.0570	1.049
F	4	26	105.0	52.4	12025	26.4	52.9	0.0565	1.049
F	5	26	90.0	48.0	11250	24.2	44.7	0.0555	1.048
							Average	0.0575	
G	1	25	25.0	68.0	2205	36.0	57.0	0.4270	1.258
G	2	28	15.0	42.0	2140	37.3	76.9	0.4470	1.269
G	3	27	20.0	53.6	2240	40.2	71.1	0.4665	1.276
G	4	27	20.0	60.0	2000	37.8	81.2	0.4840	1.282
G	5	27	15.0	54.0	1665	34.9	66.5	0.5410	1.307
							Average	0.4730	

Series of Expts.	No.	S	(A)	(B)	(C)	ΔR	u $\times 10^{10}$	u' $\times 10^{-11}$	a in Å'
C	1	3085	0.2	2.1	0.9	3.7	16.1	9.7	10.3
C	2	3605	−0.1	2.9	0.4	3.9	11.8	7.1	14.0
C	3	3560	−0.1	3.1	0.4	4.0	13.8	8.3	12.0
C	4	3545	0.0	3.0	0.5	4.0	14.0	8.5	11.8
C	5	3440	0.0	2.7	0.4	3.5	13.5	8.2	12.2
								Average	12.1
E	1	7540	0.0	8.9	0.2	9.3	15.1	9.2	10.9
E	2	5370	0.0	5.1	0.5	6.1	14.3	8.7	11.5
E	3	9770	0.0	7.4	0.5	8.4	11.3	6.8	14.7
E	4	7205	−0.3	6.7	0.3	7.4	14.4	8.7	11.5
E	5	8790	0.2	5.9	0.3	6.3	11.9	7.2	13.9
								Average	12.5
F	1	6680	0.0	3.3	0.7	5.0	8.0	4.9	20.5
F	2	8035	−0.3	4.5	0.2	5.1	8.6	5.2	19.3
F	3	7915	0.3	4.4	0.5	5.5	7.7	4.7	21.4
F	4	8985	0.0	4.4	0.6	5.5	8.2	5.0	20.2
F	5	8320	0.3	4.0	0.6	5.2	7.1	4.3	23.4
								Average	21.0
G	1	7610	0.1	6.3	1.4	8.8	16.6	10.1	9.9
G	2	7690	−0.4	5.5	0.9	6.9	17.4	10.5	9.5
G	3	8310	−0.2	6.0	1.3	7.9	17.0	10.3	9.7
G	4	7645	−0.2	5.0	1.2	6.5	17.4	10.5	9.5
G	5	6995	−0.3	6.1	0.8	7.5	18.0	10.9	9.2
								Average	9.6

TABLE IV
Adsorption of Para-Toluidine for Various Sizes of Bubbles

Series of Expts.	No.	T	t	b	N	M	W_B	v	F
L	1	25	31.0	48.6	3825	19.7	46.1	0.1310	1.087
L	2	27	40.0	52.2	4600	22.2	59.2	0.1210	1.081
L	3	24	30.0	56.2	3335	18.0	53.6	0.1340	1.089
L	4	24	40.0	45.6	5265	27.7	74.3	0.1320	1.088
L	5	23	45.0	47.0	5745	30.0	71.9	0.1325	1.088
							Average	0.1300	
M	1	24	37.0	60.0	3700	58.0	69.4	0.4155	1.215
M	2	25	30.0	62.0	2905	48.3	59.2	0.4415	1.225
M	3	25	30.0	49.2	3660	61.3	73.9	0.4445	1.229
M	4	25	25.0	58.4	2570	48.8	61.9	0.5035	1.248
M	5	26	30.0	51.6	3490	72.2	81.7	0.5510	1.269
							Average	0.4710	

Series of Expts.	No.	S	(A)	(B)	(C)	ΔR	u $\times 10^{10}$	u' $\times 10^{-11}$	a in Å^2
L	1	5185	0.7	11.8	0.1	11.6	8.8	5.3	18.9
L	2	5885	1.2	9.3	0.1	8.9	7.6	4.6	21.7
L	3	4590	0.6	7.5	0.4	7.9	7.8	4.7	21.1
L	4	7180	0.3	9.9	0.0	9.7	8.7	5.3	19.0
L	5	7850	1.2	11.7	0.0	11.1	8.8	5.3	18.7
								Average	19.9
M	1	12120	0.8	20.7	0.1	20.4	10.0	6.0	16.6
M	2	9975	0.6	19.9	0.7	20.8	10.5	6.4	15.7
M	3	12670	1.7	20.2	1.4	21.2	10.6	6.4	15.7
M	4	9810	0.4	16.2	0.3	16.5	8.9	5.4	18.6
M	5	14390	0.6	17.5	1.7	19.5	9.4	5.7	17.5
								Average	16.8

Both the experiments reported and those of McBain and Davies show that the adsorption in the gas-solution interface, as measured by the method described, increases with concentration until it reaches a constant value which is much greater than corresponds to a monomolecular film. However, the present experiments indicate that the adsorption decreases with the size of the adsorbing bubble, and may approach, as the bubble is made smaller, the values given by the adsorption equation, correctly used, and by experiments with insoluble films.

Attempts to work with bubbles smaller than those listed were unsuccessful. Even when a uniform stream was secured, the bubbles would stick at the outlet. They seemed too small to mount rapidly enough into the inverted U-tube at the collecting end of the adsorption tube, despite the fact that the vertical distance through which each bubble had to rise was made relatively quite small. When the internal diameter of this collecting tube was made large enough to permit the bubbles to rise with the minimum freedom necessary for any collection of films, the bubbles would not drain properly but would carry over between them enough liquid to start a syphoning of the

contents of tube 34 into flask 39. The films arising from the largest size of bubbles drained at point 37 with the least difficulty and seemed in general to carry over less solution per unit area of adsorbing surface than the smaller sizes of bubbles.

The internal diameter of the inverted U-tube in the apparatus of McBain and Davies was 1.30 cm. These workers showed that when their bubbles were so large as to form cylinders over 1.1 cm. in length in this tube, only the front and rear end of each cylinder seemed to move forward, while the sides of the cylinder pressed too firmly against the walls of the tube to be able to move. They found the adsorption to decrease with increase in length of the cylinder, once the bubble exceeded the length of 1.1 cm. This phenomenon was also studied in the present case with an inverted U-tube which was 0.90 cm. in internal diameter. The results are presented in Table V. It appears that bubbles of volume greater than 0.55 cc. formed cylinders in this tube

TABLE V

Variation of Adsorption with Volume of Bubble for One Size of Film-Collecting Outlet

Series of Expts.	No.	N	v	S	u $\times 10^{10}$	u' $\times 10^{-11}$	a in Å^2
G	1	2205	0.427	7610	16.6	10.1	9.9
G	2	2140	0.447	7690	17.4	10.5	9.5
G	3	2240	0.467	8310	17.0	10.3	9.7
G	4	2000	0.484	7645	17.4	10.5	9.5
G	5	1665	0.541	6995	18.0	10.9	9.2
G	6	2360	0.579	10495	15.7	9.5	10.5
G	7	2440	0.593	11060	14.6	8.8	11.3
G	8	2220	0.625	10540	13.6	8.3	12.1
G	9	1830	0.728	9900	11.4	6.9	14.5

which were incapable of proper motion in the collecting tube. A bubble in the shape of a cylinder 0.90 cm. long and 0.90 cm. in diameter has a volume of 0.57 cc. Hence the observation of the investigators mentioned is corroborated. In the experiments here reported, the diameter of the outlet for each size of bubble was chosen as small as possible for efficient collection of films, but yet so large that the bubbles formed cylinders of diameter exceeding their length.

Blank experiments were performed from time to time to study the operation of the apparatus. The procedure followed in these was the same as in the normal experiments, except that at the beginning of the experiment, just after sample A had been taken, 100 cc. of the contents of the adsorption tube were sucked over into flask 39, while the level of the solution at point 37 was maintained so low during the experiment that no bubble films could get over into the flask. In this way, two effects were studied, for it could now be determined whether the air entering the adsorption tube was saturated with

respect to the solution, and, what is very important, whether this air, in passing over the solution in flask 39, affected its concentration. The results indicated that the air passing through the solution in the adsorption tube and over any solution in flask 39 did not change the concentration of either solution appreciably. Hence all concentration changes discovered in the normally conducted experiments were due solely to transportation of solute by adsorption.

6. Purification of Materials

By the use of the surface tension data in Volume V of International Critical Tables several substances were selected which are fairly soluble in water and which lower the surface tension of water markedly. *Iso*amyl alcohol, *p*-toluidine, *p*-cresol, and benzoic acid were chosen. Solutions of these which were 0.8 saturated, 0.4 saturated, and 0.2 saturated were prepared and the stability of the foam produced by each under the same conditions of vigorous shaking was observed. Although *p*-cresol behaved well in the most dilute solution, *iso*amyl alcohol and *p*-toluidine were selected as being more suitable for this type of work. The most stable films were given by *p*-toluidine. These two substances were employed also by McBain and Davies.

The *iso*amyl alcohol was obtained from the Eastman Kodak Co. It was shaken with a saturated aqueous solution of sodium bisulfite, washed well with water, and refluxed for three hours over 3 N sodium hydroxide solution. Then, after thorough washing, first with water and finally with dilute hydrochloric acid, it was twice refluxed over fresh lime for two hour periods and distilled over a third portion of fresh lime. It was redistilled, and the fraction coming over in the interval 130.2°-130.5°C under a pressure of 748 mm. of mercury was used. (International Critical Tables: 130.5°C.). The density of this alcohol, d_4^{20}, was 0.81038, while its surface tension at 20.0°C, determined by the drop-weight method, was 23.73 dynes per cm. It contained 20 per cent of the optically active isomer.

The *p*-toluidine used was the best procurable from the Eastman Kodak Co. It was dissolved in ether, and the solution was washed with water and then dried over anhydrous sodium sulfate. The solution was filtered and dry hydrogen chloride was passed into it. The hydrochloride precipitated was isolated by filtration, washed well with ether, and the *p*-toluidine was liberated with a slight excess of sodium hydroxide solution. The *p*-toluidine was further purified by steam distillation. The snow-white solid obtained was sucked dry on a filter and finally dried *in vacuo* over phosphorus pentoxide for several days. It melted at 43.2°C. (International Critical Tables: 43.7°C.)

All of the solutions were prepared with distilled water. The solutions of *p*-toluidine turned faintly amber after several days standing. However, Experiment L_1 was performed one hour after the solution was prepared, and Experiment L_2, one hour later, while the solution was still colorless. Experiment L_5 was conducted after the solution had aged five days. The results of these experiments demonstrate that the slight coloration observed had no appreciable effect.

7. Conclusion

The direct dynamic method for determining adsorption in the gas-liquid interface yields results for such substances as *p*-toluidine and *isoamyl* alcohol which are definitely greater than those derived from the inexact form of the adsorption equation. In fact, the adsorbed solute cannot lie entirely in a monomolecular film if the results for the larger bubbles are correct, as a comparison of the values listed in Table VI will show. However, the values lead to the conclusion that the adsorption decreases as the size of the adsorbing bubble decreases and may approach the value for each solute which is obtained from experiments with insoluble films.

TABLE VI

Surface Areas of Molecules in Sq. Å

a. Direct Measurement of Adsorption		
Volume of Bubble in cc.	0.13	0.47
Molecular Area for *p*-Toluidine	21	17
Molecular Area for Isoamyl Alcohol	13	10
b. Measurements of Insoluble Films		
Benzene Ring perpendicular to Surface		23.8[1]
Normal Alcohols		21.6[2]

Summary

1. Direct measurements by the bubble method of the adsorption of *p*-toluidine and of *isoamyl* alcohol in the air-solution interface are described.

2. Results in partial agreement with those of McBain and Davies, in that they represent an adsorption in excess of that deduced from the adsorption equation and that predicted by measurements of insoluble films, are obtained. However, the adsorption secured in our measurements is in general smaller than that obtained by McBain and Davies. Differences in the methods of calculation obscure the experimental discrepancy.

3. Evidence is presented which shows that the adsorption appears to decrease as the adsorbing bubbles grow smaller, and may approach the value for each solute which is obtained from the adsorption equation and from experiments with insoluble films.

4. The disagreement between the adsorptions expected and those found is discussed.

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[1] Adam: Proc. Roy. Soc., 103, 676 (1923).
[2] Adam: Proc. Roy. Soc., 101, 452 (1922); 106, 694 (1924).

THE CHEMICAL REACTIVITY OF THE FUSED BASES

I. The Action of the Alkali Amides upon Electropositive Metals[1]

BY W. CONARD FERNELIUS[2] AND F. W. BERGSTROM

In an earlier series of investigations[3] one of us has examined the action of liquid ammonia solutions of the ammono bases, potassium and sodium amides, upon a number of elements. It was found that an electropositive metal, such as magnesium, reacts in the sense of the equation,

$$_2NH_3 + Mg + {}_2KNH_2 = Mg(NHK)_2 \cdot {}_2NH_3 + H_2$$

to form potassium ammono magnesiate and hydrogen, just as zinc reacts with an aqueous solution of potassium hydroxide to form potassium zincate and hydrogen,

$$Zn + {}_2KOH = Zn(OK)_2 + H_2$$

Whereas such a reaction in water is fairly rapid, the analogous reaction in liquid ammonia is slow, enabling the observer to gain an idea of the steps involved and the intermediate products. Thus it was found that magnesium first reacts with a liquid ammonia solution of potassium amide to liberate potassium, which is detected by the opaque blue color of its dilute solution and the coppery lustre of the highly concentrated solution,[4] the reaction probably proceeding in accordance with the equation,

$$Mg + {}_2KNH_2 \rightleftharpoons Mg(NH_2)_2 + {}_2K.$$

To understand this apparently anomalous displacement of one metal by a less electropositive metal, one has but to recall that dilute solutions of the alkali metals in liquid ammonia are ionic in character,[5] the positive ions being the normal ions of the alkali metal while the negative ions are solvated electrons, e^-. Since potassium amide forms potassium, K^+, and amide, NH_2^-, ions, the reaction of a solution of this substance with magnesium is but a reaction between four ions, K^+, NH_2^-, Mg^{++} and e^-, in accordance with the equation,

$$_2K^+ + {}_2NH_2^- + Mg^{++} + {}_2e^- \rightleftharpoons Mg(NH_2)_2 + {}_2K^+ + {}_2e^-$$

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[1] This paper is a portion of a dissertation submitted to the department of chemistry and the committee on graduate study of Stanford University by Mr. W. C. Fernelius in partial fulfillment of the requirements for the degree of Doctor of Philosophy. Presented at the Swampscott meeting of the American Chemical Society, September 1928.

[2] Royall Victor Fellow in Chemistry, 1927-8.

[3] Bergstrom: J. Am. Chem. Soc., 45, 2788 (1923); 46, 1545 (1924); 47, 1836 (1925); 48, 2848 (1926); 50, 652 (1928); J. Phys. Chem., 30, 12 (1926).

[4] Although magnesium dissolves slightly in liquid ammonia, the color intensity of the solution is so much less than that of a solution of potassium that there can be no confusing the two. Furthermore, a concentrated solution of potassium has a very coppery luster. Cf. J. Am. Chem. Soc., 45, 2789 (1923).

[5] Kraus: J. Am. Chem. Soc., 43, 749 (1921) and previous articles.

Since magnesium amide, $Mg(NH_2)_2$, has a very low solubility in ammonia, it is precipitated and there remains in solution only K^+ and e^- ions, which together constitute a solution of metallic potassium.

The potassium resulting from the equilibrated condition noted above reacts with the solvent to regenerate potassium amide,

$$2K + 2NH_3 = 2KNH_2 + H_2$$

the magnesium serving as a catalyst for this reaction. Furthermore, the amide of the less electropositive metal, being an amphoteric base reacts with the alkali metal amide to form an ammono metallate,[1] in accordance with the equation,

$$Mg(NH_2)_2 + 2KNH_2 = Mg(NHK)_2 \cdot 2NH_3.$$

Purpose of the Investigation

In view of this interesting behavior of the alkali metal amides in liquid ammonia solution it was deemed worth while to extend the study of such reactions to the fused state where the temperature and concentration of the amide would be much greater and where solubility or insolubility in liquid ammonia would not be a factor influencing the course of the reaction. Furthermore, there is at the present time no really satisfactory or comprehensive theory of fusions in the alkali bases and any study pointing toward the formulation of such a theory is valuable. This work was stimulated by an observation of Professor E. C. Franklin that a piece of magnesium ribbon plunged into molten sodium hydroxide has drops of a blue liquid adhering to it upon withdrawal. Such behavior indicates the liberation of metallic sodium in accordance, probably, with the equation,

$$Mg + 2NaOH \rightleftharpoons 2Na + Mg(OH)_2.$$

Historical: The Action of the Amides upon the Elements

Following the discovery of sodium and potassium amides by Gay-Lussac and Thénard, these investigators found that several metals were attacked by potassium amide.[2] Davy, working contemporaneously, studied in a superficial manner the reaction of potassium amide with tellurium and arsenic.[3] Ephraim[4] examined the reactions of sodium amide with sulfur, bromine, iodine and magnesium as well as with a large number of oxides, sulfides, chlorides and ternary salts. Winter[5] observed that an energetic reaction occurred when yellow phosphorus was warmed with sodium amide. Wöhler

[1] One will recall that the phenomenon of amphotericity of the basic amides is much more general than the similar property of the basic hydroxides. Not only is there an aluminate, zincate, plumbite, stannite and stannate of potassium, but also a cuprite, a cadmiate, a magnesiate, a calciate, a bariate and even a sodiate in the ammonia system. Furthermore these compounds are for the most part definitely crystalline and easily obtained in a pure condition.

[2] Gay-Lussac and Thénard: "Recherches physico-chimiques," 1, 341 (1811).

[3] Davy: Phil. Trans., **1810**, 27.

[4] Ephraim: Z. anorg. Chem., **44**, 185 (1905).

[5] J. Am. Chem. Soc., **26**, 1484 (1904).

and Stang-Lund[1] have electrolyzed fused sodium and potassium amides and determined their specific conductivity and decomposition voltages. McGee[2] has also determined the specific conductance of molten sodium amide.[3]

Apparatus and Manipulation

In designing an apparatus for studying fusion reactions there were numerous factors which had to be taken into consideration. It can safely be said that no single technique so far employed has been entirely satisfactory in all

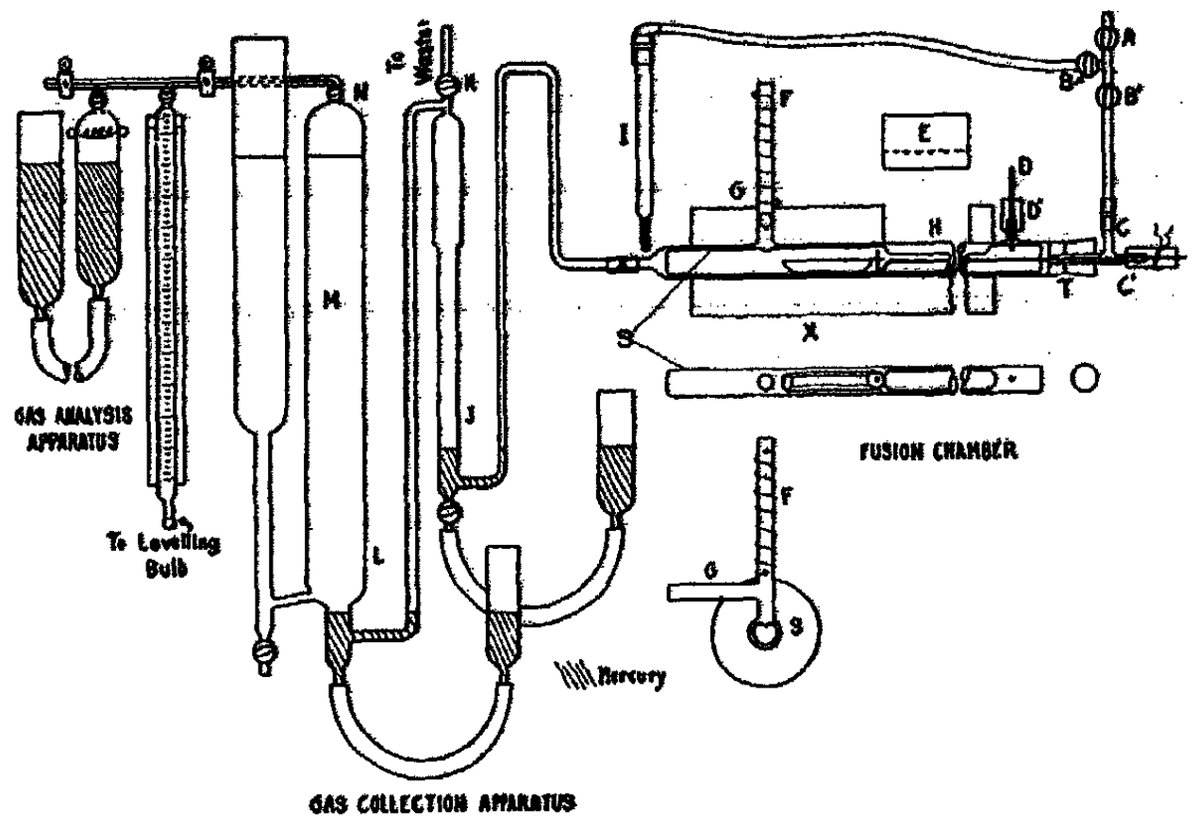

FIG. 1

of its details. The apparatus finally chosen for this investigation is shown in Fig. 1. It was designed so that the amide fusions could be carried out in a current of ammonia in the complete absence of air and moisture. The fusion chamber (DEFG) consists of a pyrex tube (27 mm. diameter by 60 cm. long, with side arms of 12mm. tubing, as shown) wound with number 27 chromel wire to serve as a heating unit[4] and insulated with 85% magnesia pipe covering. A length of three quarter inch monel metal tubing, *S*, is inserted in the

[1] Wöhler and Stang-Lund: Z. Elektrochemie, 24, 261 (1918).

[2] McGee: J. Am. Chem. Soc., 43, 586 (1921).

[3] Other important references dealing with the fused alkali amides are Beilstein and Geuther: Ann., 108, 88 (1858); Baumert and Landolt: 111, 1 (1859); Drechsel: J. prakt. Chem., (2) 16, 201 (1877); Wislicenus: Ber., 25, 2084 (1892); Titherly: J. Chem. Soc., 65, 504 (1894); 71, 469 (1897); De Forcrand: Compt. rend., 121, 66 (1895); Dennis and Browne: J. Am. Chem. Soc., 26, 587 (1904); Ruff and Goerges: Ber., 44, 502 (1911); Miles: Proc. Roy. Soc., Edinburgh, 35, 134 (1915); Kraus and Cuy: J. Am. Chem. Soc., 45, 712 (1923); Guntz and Benoit: Bull., (4) 41, 434 (1927). There exists also a voluminous literature on the use of sodium amide in organic chemistry.

[4] The pyrex tube was wound for the entire length covered by the magnesia insulation—including the section E. These windings are not shown in Fig. 1. The two terminals of the wire were tied to glass knobs fused to the glass at the ends of the insulated portion.

furnace to serve as a sheath to protect the glass from the corrosive amide which is often spattered or spilled from the fusion boat, X, during the course of a reaction. The upper part of the monel tube on the right was milled away to a depth of about one third its diameter and over about half of its length, to enable the observer to view the molten amide in the boat. Likewise, there is a hole in the metal directly underneath the glass tube F through which materials are introduced into the fusion boat. A short length of one eighth inch monel rod, inserted through the tight rubber sleeve, D′, and through a small hole drilled in the metal sheath served to keep the sheath in position. A long monel rod H (1/8 inch in diameter) hooked at one end and working through the rubber sleeve C′ is used to place the fusion boat, a nickel combustion boat 13x75 mm. in size, at any desired position within the fusion chamber. The space E of the insulation is arranged so that it may be removed to enable one to view the interior of the chamber. A resistance heating unit is wound on F, and the side tube G, sealed to F, may also be used for the introduction of materials into the furnace. J is a mercury bubbler which gives a visual measure of the amount of gas passing through the apparatus. The large tube M is filled with dilute air-free sulfuric acid and serves both as an ammonia scrubber and as a gas collector. The apparatus for gas analysis is connected through a capillary with the top of the gas collector, M.

The technique employed when using this apparatus is perhaps best described by giving the log of a typical run. After thoroughly cleaning and drying both the chamber and the sheath, the latter is inserted in the furnace and locked in position. The boat, previously cleaned inside and outside with emery cloth[1] is attached to the manipulative rod, H, placed in the chamber and then moved directly beneath the vertical filling tube, F. All stoppers are now fitted into position and the inlet tube C connected to the pure ammonia line,[2] A-B′, and a slow stream of ammonia admitted to sweep out foreign gases within the system. Stopcock K is open during this time so that all gases are vented to the waste. The heating current for the main furnace is now turned on.[3] The ammonia stream is continued for twenty minutes and during this time the stoppers F and G are removed for a sufficient length of time to insure the removal of all air that may be in these tubes.

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[1] Neither fused amides themselves nor the products of their reaction with the strongly electropositive elements attack or discolor the nickel boats to any noticeable extent. The reaction products of the more electronegative elements, however, exhibit a definite corrosive action upon the nickel. Particularly is this true of tin, lead, arsenic and antimony fusions which leave a rather tightly adherent film of brown-black material clinging to the boat. Phosphorus and the elements of the sulphur group give reaction products which discolor the nickel to a considerable extent, but do not appear to attack it seriously.

[2] The ammonia used is the commercial anhydrous product dried over sodium according to the method of Franklin and Kraus: Am. Chem. J., 23, 285 (1900).

[3] The amount of current passing through the furnace is regulated by means of a lamp resistance. The maximum temperature attained by the furnace is a function of the heating current. Having determined therefore the relation between the maximum temperature and the heating current once and for all, it was possible to dispense with temperature measuring instruments during the course of an experiment. This allowed the use of a smaller furnace.

The alkali metal can now be introduced into the fusion boat. For this purpose an injector tube, I, was prepared by sealing a fine capillary to a wider tube which snugly fits the interior of F. Freshly cut alkali metal a little in excess of the quantity it was desired to introduce into the boat (about a gram) is placed in the injector tube and this latter is connected by means of a rubber tube to the pure ammonia line at B. By closing B′ and opening B air in I was displaced with ammonia. After this was accomplished, ammonia was again directed through the furnace by closing B and opening B′. The tube I was placed inside of F with the end of the capillary about on a level with the top of the boat, and a current passed through the externally wound resistance to melt the alkali metal. After the metal was molten, I was tapped a few times to disengage the melt from the oxide crust. Then, by closing B′ and slowly opening B, the pure molten metal was forced by ammonia pressure through the capillary into the fusion boat, leaving the oxide behind. The injector was then weighed with rubber caps over both ends. Subtracting this weight from the weight of the same when it contained the alkali metal gave the weight of the metal in the boat.

This process completed, the vertical heating unit is shut off, the injector removed and F once more tightly stoppered. The boat is now withdrawn to the fusion space—that portion of the chamber between F and the removable cover, E. This region is the hottest and also the only one where there is absolutely no danger of any spattered material reaching the glass walls. Here the metal is quickly converted to the amide—usually within a half hour. A clear light yellow melt is sufficient indication that the reaction is complete, although, when gases are being collected it is better to run the exit ammonia stream through the acid tower for a time to see that no acid insoluble gases are present in the line. If the reaction that is to be carried out is very vigorous, or if it is desired to collect the gases given off during the reaction quantitatively the amide is allowed to cool, the boat moved under F and the reacting substance added through F or G, the entrance of air into the tube of course being prevented by the current of ammonia passing through F or G into the atmosphere. Then, with F and G tightly stoppered, the boat is withdrawn into the fusion space, stopcock K closed, and the furnace heated to the desired temperature. If a quantitative collection of the gases given off during the reaction is not desired, the solid reactant is added directly to the molten amide in a similar fashion.

Following the completion of the fusion the boat is withdrawn to the cooler part of the furnace—that portion outside of the insulation—and permitted to solidify. Unless otherwise specified, all reactions were carried out at 375°-400°.

The nickel boat containing the cooled melt was now sealed in an ammonia reaction tube according to the methods previously developed by Franklin and co-workers[1] and the products there washed with liquid ammonia and pre-

[1] Franklin: J. Am. Chem. Soc., 27, 831 (1905); 29, 1275 (1907); 35, 1460 (1913); J. Phys. Chem., 15, 510 (1911); 16, 694 (1912); Fitzgerald: J. Am. Chem. Soc., 29, 1694 (1907); Bohart: J. Phys. Chem., 19, 539 (1915).

pared for analysis. In those cases where all of a solid element does not react with the amide, the difference in density of the element and the insoluble reaction product is usually sufficiently great to enable one to carry the precipitate in suspension to the opposite leg of the reaction tube without carrying over any of the unreacted element. In order to transfer the boats to the ammonia tube, a "conveyor", made by sealing a stopcock on the closed end of a wide test tube, was slipped over the end of the pyrex furnace tube, after removal of the stopper, T. Then, with a current of ammonia passing through the conveyor, the end of the furnace was lowered to allow the boat to slide from the furnace into the conveyor, which was at once tightly stoppered. Ammonia pressure to the extent of about twenty centimeters of mercury was allowed to build up within the tube before the stopcock was closed. No apparent harm results if the fusion products be preserved for several days in such containers.

The technique just described for conducting amide fusions and treating the reaction products has several distinct merits: (1) chemically pure amides are used; (2) the temperature of the fusion chamber can be regulated at will by varying the amount of current passing through the heating unit; (3) any gases other than ammonia evolved during the reactions are quantitatively collected; (4) the melt can be examined optically at any time and the color changes, formation of precipitates, intensity of reaction, etc. determined; (5) the atmosphere in which the fusion is carried out can be changed at will; (6) at no time does the melt come in contact with glass or air and suffer contamination and (7) the use of liquid ammonia, the parent solvent of these nitrogen compounds, to extract the melt does not destroy the reaction products as does water. The disadvantages of the apparatus are (1) the small size of the boats employed prevents one from obtaining any but the smallest amounts of reaction products; (2) the spattering of the melt during some reactions clouds the window after a time, and (3) long time fusions in such an apparatus are inconvenient and wasteful of ammonia.[1] Furthermore, the slow decomposition of the fused amides into their elements introduces a somewhat uncertain blank correction into the analyses of gases evolved during the fusion process. Since the decomposition of the amides produces an alkali metal which reacts with the ammonia atmosphere in the furnace to form an amide and hydrogen, the net reaction should amount to a decomposition of the ammonia into three volumes of hydrogen and one of nitrogen. The heated metal of the sheath may also decompose some ammonia catalytically into its elements. In blank runs the ratio of hydrogen to nitrogen approximated the theoretical value of 3 to 1.

[1] The second objection is removed by enlarging the furnace sufficiently to allow a thin pyrex tube to be placed around the milled portion of the monel sheath. This tube can be readily replaced when it becomes clouded. It was found convenient also to move the filling tubes, *F* and *G*, to the edge of the uninsulated portion, *E*. This permitted one to see the fusion at the moment the solid reactant was introduced.

Discussion

In general it can be said that the reactions of the fused alkali amides resemble very closely their reactions in liquid ammonia solution. In some cases, however, there are very interesting differences. The reaction of magnesium with fused potassium amide will serve as an admirable example of the reaction of an electropositive metal with a fused alkali amide. Immediately upon adding magnesium to fused potassium amide, the melt becomes blue[1] and globules of potassium form and float about on the surface of the melt. A white precipitate, visible through the clear melt, and disappearing on subsequent heating indicates the presence of magnesium amide. On continuing the fusion in an atmosphere of ammonia, the potassium is converted into amide and the melt becomes clear. When the potassium amide is dissolved by liquid ammonia, potassium ammono magnesiate, $Mg(NHK)_2 \cdot 2NH_3$, remains behind.[2]

The extent of the displacement of sodium from the molten amide by magnesium was approximated by conducting the reaction in an atmosphere of nitrogen and extracting the cooled melt with liquid ammonia. In order to arrive at a relationship between the liberated sodium and the magnesium entering the reaction, it was necessary to apply a number of relatively large corrections to the actual weight of extracted sodium, so the values in the fifteenth column of Table I (Experimental part) are to be regarded as more or less close approximations. Nevertheless it will be seen that almost two atoms of sodium are liberated for each atom of magnesium entering the reaction.

The only other metals to liberate alkali metal in sufficient quantity to color the melt blue were calcium and aluminum. Calcium does not react as vigorously with fused potassium amide as might be expected. A heavy white precipitate of potassium ammono calciate, $CaNK \cdot 2NH_3$, remains after the excess of potassium amide is washed away with liquid ammonia.

Aluminum in the form of wire is not attacked as vigorously by fused potassium amide as is magnesium. Nevertheless, very small globules of potassium could occasionally be seen darting about the surface of the bluish-

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[1] Practically every investigator who has prepared the amides of the alkali metals by passing ammonia gas over the fused metals has reported the formation of a blue colored solution which loses its color when acted upon by an excess of ammonia. Davy: Phil. Trans., 1809, 42; Beilstein and Geuther: Ann., 108, 89 (1858); Baumert and Landolt: 109, 3 (1859); Titherley: J. Chem. Soc., 65, 504 (1894); 71, 469 (1897); Rengade: Compt. rend., 140, 1184 (1905); Wöhler and Stang-Lund: Z. Elektrochemie, 24, 261 (1918); Guntz and Benoit: Bull., (4) 41, 434 (1927). McGee: J. Am. Chem. Soc., 43, 586 (1921) did not observe this color although the present investigation has repeatedly shown it. From the analogy to the blue colored solutions of the alkali metals in liquid ammonia and the amines, Titherley: J. Chem. Soc., 65, 510 (1894), argued that this color was due to a solution of the alkali metal in the fused amide and this view appears to be correct.

[2] Ephraim (Z. anorg. Chem., 44, 185 (1905)) studied the reaction of magnesium with fused sodium amide and concluded that magnesium nitride, sodium, and hydrogen were formed. His experimental technique would not have distinguished between magnesium nitride and potassium ammono magnesiate.

The question of whether or not the ammono magnesiate exists in the anammonous form in the molten amide cannot be settled without further experimentation. It seems possible that the salt exists as $Mg(NHK)_2$, since the evolution of ammonia has been observed upon adding magnesium to fused sodium amide in an atmosphere of nitrogen.

green molten amide and the aluminum was slowly converted into a white or gray mass insoluble in the fusion. This precipitate, which remained when the potassium amide was dissolved out with liquid ammonia, did not prove to be definite in composition. It is perhaps best to regard it, provisionally, as consisting of ammonous aluminum nitride which has adsorbed potassium amide, since the known compound resulting from the action of potassium amide on ammonous aluminum nitride,[1] potassium ammono aluminate, is readily soluble in liquid ammonia.[2]

Beryllium is dissolved slowly by fused sodium amide with the production of sodium ammono berylliate, $BeNNa \cdot 2NH_3$, which may be readily extracted from the melt by liquid ammonia. Zinc slowly reacts with fused potassium amide to give potassium ammono zincate, $Zn(NHK)_2 \cdot 2NH_3$, which is sparingly soluble in liquid ammonia. Impure cerium is slightly attacked by fused potassium amide. Finely divided metallic germanium[3] reacts readily with fused potassium amide to liberate hydrogen and form a product insoluble in liquid ammonia which may be either potassium ammono germanate, NGeNHK, or potassium ammono germanite, $Ge{=}NK \cdot NH_3$, since the percentage of potassium, nitrogen and germanium in the two compounds is almost identical. The atomic ratio of hydrogen evolved to the germanium added is about 3:1, indicating that the ammonia-insoluble reaction product consists of a mixture of germanate and germanite in the approximate ratio of 1:1, formed in accordance with the equations,[4]

$$Ge + KNH_2 + NH_3 = NGeNHK + 2H_2$$
$$Ge + KNH_2 + NH_3 = Ge{=}NK \cdot NH_3 + H_2.$$

In this connection, it may be recalled that when carbon is fused with sodium amide, either sodium cyanide or sodium cyanamide is formed, according to the conditions.[5]

Fused potassium amide converts mercury into a dilute potassium amalgam. Apparently the mercury itself is not attacked, but merely dissolves the potassium resulting from the very slow decomposition of potassium amide into its elements.[6]

Thorium and manganese are attacked slightly by fused potassium amide over a period of ten hours, but the reaction products were not obtained in

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[1] Bergstrom: J. Phys. Chem., 32, 436 (1928).

[2] Bergstrom: J. Am. Chem. Soc., 45, 2788 (1923); 46, 1548 (1924).

[3] The germanium oxide, from which the germanium was prepared by reduction, was a gift of the New Jersey Zinc Company.

[4] An ammono germanate of the approximate composition, NGeNHK, has been prepared in liquid ammonia by the action of potassium amide upon the product of ammonolysis of germanium tetrabromide. (Bergstrom: unpublished observations.)

[5] Sodium cyanide, a sodium ammono carbonite: Franklin: J. Phys. Chem., 27, 167 (1923); sodium cyanamide, a sodium ammono carbonate: Franklin: J. Am. Chem. Soc., 44,1495 (1922). English patents, 12,219; 21,732 (1894); German patents, 117,623; 124,977; 126,241 (1900); 148,045 (1901). Cf. Zentrallblatt, 75, I, 411 (1904).

[6] At temperatures much above 400°, the fused alkali amides acquire a pale bluish-green color, because of the presence of free alkali metal in solution. This color does not persist at lower temperatures in an ammonia atmosphere.

Wöhler and Stang-Lund (Z. Elektrochemie, 24, 261 (1918)) found that mercury has no action upon molten sodium amide.

amounts sufficient for identification. Copper, cadmium, thallium, titanium, zirconium, tantalum, chromium, nickel, platinum and iridium were not attacked by fused potassium amide. Of these metals, zirconium alone was in the form of a powder.[1] Other metals which have been reported as unattacked by fused potassium amide are iron, silver and gold.[2]

Sodium Hydroxide Fusions

In order to follow the parallelisms between the fused alkali bases of the water and ammonia systems, a few reactions were carried out in fused sodium hydroxide at a temperature of 400° in the amide-fusion apparatus. Sodium dissolves to a slight extent in fused sodium hydroxide, imparting a blue color to the melt. At first the major portion of the sodium floats on the melt, but with lapse of time the two appear to react and form an insoluble solid. The cooled melt was very hard and reacted vigorously with water to form a small amount of gas. This latter behavior would suggest the formation of sodium hydride.[3]

Magnesium under similar conditions gives a blue color to the solution near the strips of the metal and then dissolves completely within a short time. Le Blanc and co-workers[4] have examined the action of sodium and potassium hydroxide on a number of metals and have formulated the reaction with magnesium as one of the type reactions, thus

$$Mg + 2KOH = Mg(OH)_2 + 2K$$
$$Mg(OH)_2 = MgO + H_2O$$
$$2H_2O + 2K = 2KOH + H_2$$

Had they written in place of (2) above the following,

$$Mg(OH)_2 + 2KOH = Mg(OK)_2 + 2H_2O$$

which is as strongly supported by the experimental results, then the course of the reactions of the aquo and ammono bases on magnesium is the same.

Calcium reacts with fused sodium hydroxide in an atmosphere of nitrogen to form a blue melt and, with lapse of time, a white precipitate that is insoluble in the fused mixture. Since liquid ammonia fails to extract any soluble metal from the cold fusion, free sodium and calcium must be present in very low concentrations in spite of the bluish-green color of the melt at

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[1] Platinum is attacked very noticeably over long periods of time. Titherley: J. Chem. Soc., 65, 505 (1894); Dennis and Browne: J. Am. Chem. Soc., 26, 590 (1904); McGee: 43, 590 (1921).

[2] *Silver*, Miles: Proc. Roy. Soc. Edinburgh, 35, 134 (1915); Ruff and Goerges: Ber., 44, 502 (1911); Wöhler and Stang-Lund: Z. Elektrochemie, 24, 263 (1918). *Gold*, Franklin: unpublished observations. *Iron*: Wöhler and Stang-Lund: loc. cit.; Titherley: loc. cit.; De Forcrand: Compt. rend., 121, 66 (1895); Winter: J. Am. Chem. Soc., 26, 1486 (1904). Carbon in the iron, however, introduces cyanides into the amide. Szarvasy: J. Chem. Soc., 77, 606 (1900); Dennis and Browne: loc. cit. p. 589.

[3] Hevesy: Z. Elektrochemie, 15, 529 (1909), has shown that sodium dissolves in sodium hydroxide to the extent of twenty percent (by weight) at 480°. This high solubility may be due, in part at least, to hydride formation.

[4] Le Blanc and Bergmann: Ber., 42, 4728, 4743 (1909); Le Blanc and Weyl: 45, 2300, 2312 (1912).

the completion of the reaction. As hydrogen is formed when the cold fusion is hydrolyzed, a portion, at least, of the calcium appears to have been converted into hydride.

Aluminum wire does not appear to be attacked at all by fused sodium hydroxide in five hours time.

It seems worthy of mention at this point that the reactions of the fused alkali amides considered in the present paper do not require for their interpretation any assumption of acidic dissociation as has been made for the alkali hydroxides.[1] Rather, it would appear more logical to assume a normal dissociation into alkali metal ions and amide ions, $NaNH_2 \rightleftarrows Na^+ + NH_2^-$.

Experimental

Calcium and Potassium Amide. Preparation 1. A freshly cut piece of calcium (0.2 g.) was added to molten potassium amide and the fusion continued for six and one half hours. The white fusion product, which was disintegrated under liquid ammonia only after long and patient shaking, was thoroughly washed with fresh solvent. One half of 0.5141 g. gave 0.0723 g. nitrogen, while the other half gave 0.1089 g. CaO and 0.1892 g. K_2SO_4. The specimen was dried in a vacuum at 20°.

Preparation 2. was in all essentials a duplicate of the preceding. The specimen taken for analysis weighed 0.5764 g. when dried in a vacuum at 20° and 0.5749 g. when heated in a vacuum at 115°. One half of 0.5749 g. gave 0.0820 g. nitrogen while the other half gave 0.1287 g. CaO and 0.2100 g. K_2SO_4.

	Calc. for $CaNK \cdot 2NH_3$	Found	
		I	II
Ca	31.5	30.3	31.9
N	33.1	28.1	28.5
K	30.8	33.0	32.7

The results are in better agreement with a formula, $CaNK \cdot 1.5\ NH_3$.

Beryllium and Sodium Amide. The product of the fusion of metallic beryllium with sodium amide was washed several times with large volumes of liquid ammonia to remove the very soluble sodium ammono berylliate. In this operation some sodium amide was necessarily transferred in solution to the other leg of the reaction tube since its solubility is of the order of a gram a liter at ordinary temperatures. The leg of the reaction tube containing the boat was then opened, cleaned out and resealed with the other leg maintained at −40° in a bath of liquid ammonia.[2] The extracted material was then concentrated to a volume of a few cc. to precipitate the major portion of the sodium amide, and then the clear supernatant liquid was decanted into the clean leg of the reaction tube. The solid left after evaporation of the ammonia

[1] Fry and others: J. Am. Chem. Soc., 46, 2268 (1924); 48, 958 (1926); 49, 864 (1927); 50, 1122, 1138 (1928); 52, 153 (1930). Cf. Strain: 52, 1217 (1930).

[2] Franklin: J. Phys. Chem., 15, 510 (1911).

from this solution was prepared for analysis in the usual manner. The sodium analysis, as expected, runs a little high. One quarter of 0.7133 grams (dried in vacuum at 20°) gave 0.0856 g. nitrogen. A second quarter gave 0.0850 g. nitrogen while the remaining half gave 0.1062 g. BeO and 0.3474 g. Na_2SO_4.

Calc. for $Be(NH_2)NHNa \cdot NH_3$, Be 11.2, N 52.5, Na 28.8. Found, Be 10.8, N 48.0, Na 31.5.

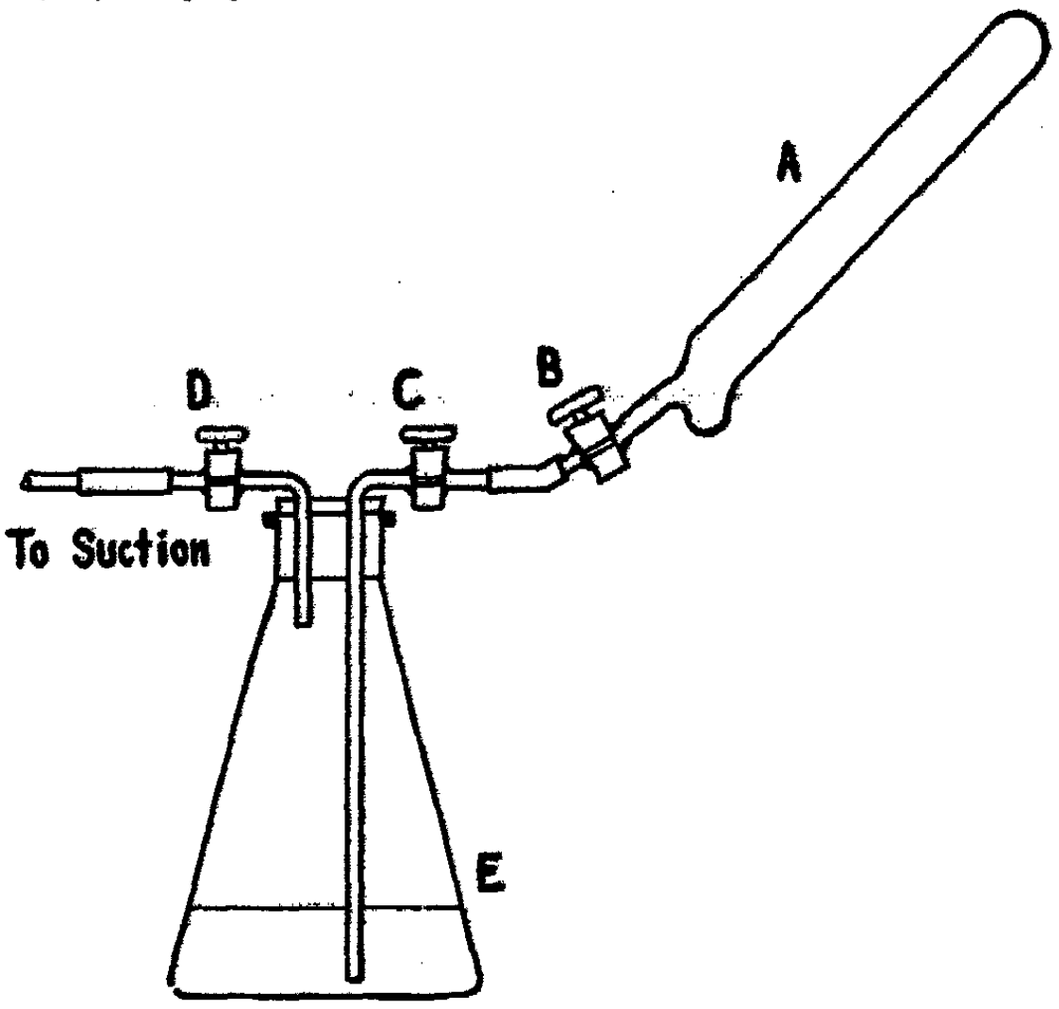

FIG. 2

The Initial Equilibrium between Sodium Amide and Magnesium. A weighed amount of polished magnesium ribbon was added to fused sodium amide in an atmosphere of nitrogen. In the resulting rapid reaction, metallic sodium was formed and floated in the form of a globule on the surface of the melt. The fusion was now quickly cooled and extracted with liquid ammonia until the washings were no longer colored blue—that is, until all of the alkali metal had been washed over. During these washings some sodium was converted to sodium amide and hydrogen by the combined catalytic action of the nickel of the boat and the solid sodium amide. To collect and measure this hydrogen the ammonia in the reaction tube was evaporated into a nitrometer containing dilute acid. The washings of the fusion, which contained metallic sodium, sodium amide and magnesium amide [the latter in the form of sodium ammono magnesiate, $Mg(NH_2)_2 \cdot 2NaNH_2$] were sealed off from the rest of the reaction tube and weighed, after drying in a vacuum.

When water was admitted to the specimen tube to hydrolyze its contents, considerable hydrogen pressure was developed. If this gas were allowed to

escape into the atmosphere, some ammonia would be lost, and since the exact amount of this ammonia was necessary in the calculations to follow, the released hydrogen was bubbled through dilute acid. The hydrolysate was then sucked from the reaction tube through this same dilute acid[1] (See Fig. 2), which was analyzed for nitrogen and magnesium. The weight of the sodium extracted is equal to the weight of the washings (Wt. of tube + sample, dried in a vacuum, less weight of tube empty and evacuated.) less the magnesium amide (calculated from the magnesium analysis) and the sodium amide (calculated from the nitrogen in excess of that present as $Mg(NH_2)_2$). The total amount of sodium liberated by the magnesium is equal to the amount extracted plus that converted to sodium amide during the washing. (Item 15) The following table is a summary of three determinations.

TABLE I

	I	II	III
(1) Wt. Na converted to amide	excess	2.5882	2.2059
(2) Wt. Mg introduced	0.0700	0.0833	0.0979
(3) Equivalent weight Na	0.1324	0.1576	0.1852
(4) Wt. solids extracted	0.2431	0.1024	0.1774
(5) Volume hydrogen, 0°, 760mm., cc.	34.0	36.7	21.9
(6) Corresp. wt. Na	0.0697	0.0752	0.0450
(7) Nitrogen analysis (grams)	0.0800	0.0069	0.0152
(8) Mg Analysis ($Mg_2P_2O_7$)	0.1148	0.0050	0.0238
(9) Magnesium amide, wt.	0.0581	0.0025	0.0120
(10) Nitrogen in $Mg(NH_2)_2$	0.0289	0.0013	0.0060
(11) Nitrogen in $NaNH_2$ (7)−(10)	0.0511	0.0056	0.0092
(12) Sodium amide, wt.	0.1424	0.0156	0.0256
(13) Total amides, wt. (9)+(12)	0.2005	0.0181	0.0376
(14) Wt. Na extracted (4)−(13)	0.0426	0.0843	0.1398
(15) Wt. Na liberated (6)+(14)	0.1123	0.1595	0.1848
(3) Wt. Na equivalent to Mg	0.1324	0.1576	0.1852

Magnesium and Potassium Amide. Four preparations were made by fusing small amounts of clean magnesium ribbon (0.08 g. in Prep. I to 0.40 gram in Prep. II) with an excess of potassium amide for periods of time ranging from one hour, Prep. I, to six hours, Prep. II. The high magnesium and low nitrogen analyses of preparation II are perhaps to be accounted for by an incomplete reaction of the primarily produced magnesium amide with the potassium amide, since there still remained some precipitate in the boat at the end of the fusion period.

[1] In Fig. 2 is pictured the apparatus customarily used for removal of solutions from an ammonia tube (Franklin: J. Phys. Chem., 15, 516 (1911), with the exception that the tube *C* terminates underneath the dilute acid in the flask. In operation, suction is applied at *D*, and the solution in *A* is slowly drawn through the acid in *E*. *B*, *C* and *D* are then closed. *A* is removed and partly filled with water by opening stopcock B, with the end of the stopcock capillary under water. This solution is drawn through *E* in the same manner and the process repeated to ensure the complete removal of the specimen from *A*. The partial vacuum in *E* is released by slowly opening *C* and then *D* to the atmosphere.

Preparation 1. One half of 0.2660 gram gave 0.0442 g. nitrogen while the other half gave 0.0930 g. $Mg_2P_2O_7$. The preparation was dried in a vacuum at 20°.

Preparation 2. One fifth of 2.0944 g. gave 0.1364 g. nitrogen. A second fifth gave 0.3009 g. $Mg_2P_2O_7$ and a third fifth gave 0.7765 g. of a mixture of $MgSO_4$ and K_2SO_4. Dried in vacuo at 20°.

Preparation 3. The analytical data for this specimen has been lost. The analyses though are correctly reported.

Preparation 4. One quarter of 0.7162 g. (dried in a vacuum at 20°) gave 0.0560 g. nitrogen, while a second quarter gave 0.1347 g. $Mg_2P_2O_7$.

	Calculated for $Mg(NHK)_2 \cdot 2NH_3$	Found			
		I	II	III	IV
Mg	14.5	15.3	15.7	15.9	16.4
N	33.7	33.2	32.6	33.2	31.4
K	47.0		48.3 (indirect)		

Zinc and Potassium Amide. Preparation 1. Four tenths of a gram of fine zinc shot was added to fused potassium amide, but no immediate reaction occurred, other than a darkening of the color of the fusion. Some of the zinc was still unattacked after two hours. The washed specimen, insoluble in liquid ammonia, was light grey in color. The specimen, dried in a vacuum at 20°, weighed 0.0748 g. From this 0.0197 g. nitrogen was obtained.

Preparation 2. This was a duplicate of the preceding, except that the fusion was continued for four hours. The specimen, dried in a vacuum at 20°, weighed 0.6722 g. One quarter gave 0.0446 g. nitrogen and a second quarter gave 0.1247 g. $Zn_2P_2O_7$.

	Calculated for $Zn(NHK)_2 \cdot 2NH_3$	Found	
		I	II
N	27.0	26.3	26.6
Zn	31.4		31.8

Cadmium and Potassium Amide. Cadmium in the liquid form (temperature of fusion 400°!) is very slightly attacked by fused potassium amide in a period of two hours.

Aluminum and Potassium Amide. Preparation 1. Upon adding 0.29 g. of aluminum wire to molten potassium amide there was an immediate reaction with the production of a blue melt. After five hours of heating there still remained a good deal of the aluminum. In an ammonia tube the white insoluble matter was separated from the aluminum wire and the former prepared for analysis. Subs., dried in vacuo at 20°, 0.1954 g. Heated in vacuo at 130°, 0.1943 g. One half gave 0.0323 g. nitrogen and the other half gave 0.1060 g. Al_2O_3 and 0.0208 g. K_2SO_4.

Preparation 2. In this experiment—a duplicate of the preceding—small globules of potassium could be seen on top of the melt after addition of the aluminum. During the fusion a grey precipitate appeared in the melt and

with time increased in amount. Time of fusion, five hours. The specimen, dried in a vacuum at 210°, weighed 0.2499 gram. One half gave 0.0400 g. nitrogen, while the other half gave 0.1334 g. Al_2O_3 and 0.0372 g. K_2SO_4.

Preparation 3. One half of 0.1056 g. (dried in a vacuum at 20°) gave 0.0164 g. nitrogen while the other half gave 0.0502 g. Al_2O_3 and 0.0261 g. K_2SO_4.

Calculated for	N	Al	K
AlN	34.2	65.9	0.0
$Al(NH_2)NHK$	37.1	23.9	34.6
Found			
I	33.0	57.5	9.6
II	32.0	56.6	13.4
III	31.0	50.4	22.2

Cerium and Potassium Amide. A half gram fragment of cerium dissolved in part in molten potassium amide (blue solution) and the liquid ammonia extraction gave a small amount of a grey precipitate, whose analysis did not correspond to a definite compound.

Thallium and Potassium Amide. Thallium, molten at the temperature of the fusion, 400°, was not attacked in four and one half hours.

Titanium, Zirconium, Thorium and Potassium Amide. Of these elements, the first two were not attacked at all in four hours. A short length of thorium rod (0.64 g) lost 20 mg. after five hours contact with fused potassium amide.

Germanium and Potassium Amide. Thirty and three tenths milligrams of germanium powder, prepared by reducing germanium oxide with hydrogen at 500°, was added to cold potassium amide and the mixture heated. Shortly afterward there was a vigorous evolution of gas which continued more slowly for one and one half hours and then ceased. The boat was examined at this time and found to contain a yellow solid with a clear supernatant liquid. The cooled melt was white and disintegrated readily in liquid ammonia to give a copious fine white precipitate. This was washed well with liquid ammonia but during the process it appeared to undergo a slight ammonolysis, as was inferred from the continued pale yellow or green color of the washings. (potassium amide in solution). Subs., dried in a vacuum at 20°, 0.5174 g. Heated in a vacuum at 110°, 0.5111 g. One quarter gave 0.0243 g. nitrogen. One half gave 0.1439 g. K_2SO_4. The germanium was separated by the method of Johnson and Dennis.[1] 190.2 cc of gases (standard conditions), collected during the fusion, consisted of hydrogen and nitrogen in the ratio of 13.69 to 1. Since the nitrogen was formed by the decomposition of ammonia in the presence of nickel and the fused amide, we must subtract the corresponding volume of hydrogen ($3 \times$Vol. N_2) plus the volume of nitrogen from the collected gases (190.2 cc) in order to find the hydrogen actually formed in the reaction between germanium and potassium amide. (138.4 cc.)

[1] Johnson and Dennis: J. Am. Chem. Soc., 47, 790 (1925).

Preparation 2. This was a duplicate of the preceding experiment except that 0.332 g. germanium was used. The preparation, dried in a vacuum at 20°, weighed 0.3433 g. Heated in a vacuum at 210° it lost 0.0082 g. One fifth of the heated specimen gave 0.0107 g. nitrogen, a second fifth gave 0.0109 g. nitrogen, and two fifths gave 0.0851 g. K_2SO_4. The gases (348.3 cc.) collected during fusion consisted of hydrogen and nitrogen in the volume ratio of 6.918 to 1, that is, there was 172.3 cc. or 0.0155 g. hydrogen in excess of that arising from the decomposition of the amide.

	Ge	N	K	H:Ge[1]
Calc. for Ge(NH)NK)	51.6	19.9	27.8	4:1
" " $Ge(NK)\cdot NH_3$	50.8	19.6	27.4	2:1
Found I		19.8	25.0	2.96:1
" II		17.7	27.8	3.36:1

The analyses refer to the specimens dried in a vacuum at room temperatures.

Tantalum and Potassium Amide. Sheet tantalum was not attacked at all by fused potassium amide in six hours.

Chromium and Potassium Amide. In two experiments chromium in the form of small lumps was fused with potassium amide for three hours, but the solutions obtained by hydrolyzing the melt and then acidifying gave no tests for chromium.

Manganese and Potassium Amide. Fused potassium amide attacks manganese (prepared by the thermite process) rather superficially over a period of six hours. The melt is colored a light brown. A small amount of precipitate, sparingly soluble in liquid ammonia, blackened in contact with the air, a behavior characteristic of potassium ammono hypomanganite,[2] $Mn(NHK)_2\cdot 2NH_3$.

Manganese and Sodium Amide. Manganese is only slightly attacked by fused sodium amide, but the cooled melt imparts a yellow color to liquid ammonia indicating the formation of some sodium ammono hypomanganite.

Summary

(1) An apparatus and technique have been developed for studying the reactions of the fused alkali amides.

(2) In general, the reactions of the electropositive elements with the fused amides are similar to the same reactions in liquid ammonia at room temperatures. The strongly electropositive elements react initially with the fused amides to liberate free alkali metal.

(3) Magnesium, beryllium, zinc and calcium dissolve in the alkali amides to give the corresponding ammono metallate. (i.e. compounds analogous to

[1] (Ratio of hydrogen evolved to the germanium reacting.)

[2] Bergstrom: J. Am. Chem. Soc., 46, 1553 (1924). It is better to call this derivative of divalent manganese a hypomanganite, rather than a manganite as was done in the article referred to.

potassium zincate, $Zn(OK)_2$.) Germanium appears to be converted to a mixture of potassium ammono germanite and germanate by fused potassium amide. Cerium, thorium and manganese are slightly attacked by fused potassium amide, while copper, cadmium, mercury, thallium, titanium, zirconium, tantalum, chromium, nickel, platinum and iridium are not attacked after several hours fusion.

(4) Sodium dissolves in fused sodium hydroxide to give a blue colored melt.

(5) The course of the reaction of the strongly electropositive metals with the fused alkali hydroxides appears to be essentially the same as that with the fused alkali amides.

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A PHYSICOCHEMICAL STUDY OF THE CARBOHYDRATE OCCURRING IN THE ROOT OF ARCTIUM LAPPA

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Introduction

Arctium Lappa (Burdock) is a coarse biennial weed which proliferates in Europe, Asia and North America.[1] The roots of this plant form a part of the vegetable portion of the Japanese dietary. The moist roots are sliced and cooked in fat.[2] The authors[4] have shown the carbohydrate to be absorbed and utilized by white rats as evidenced by increased glycogen storage in the liver. This fact was demonstrated also by showing that the root of Arctium Lappa exhibited a nitrogen-sparing action on dogs fed on a diet of protein. Its clinical value in the treatment of diabetes mellitus has been shown by one of us (J.K.) with Silver and Cohen.[5]

The authors have separated the polysaccharide (presumably) inulin from the root and have subjected it to a physicochemical study. The literature contains many references to the work on the inulin from dahlia and Jerusalem artichoke, but no reference was found to the properties of inulin from this source.

Tanret[6] investigated the physical and chemical properties of the inulin from Jerusalem artichoke and found the substance to consist of inulin, pseudo-inulin and inulenin. The value of the Jerusalem artichoke in the treatment of diabetes mellitus as evidenced by the classical experiments of Root and Baker[7] and also Carpenter and Root[8] stimulated a renewed interest in the properties of the carbohydrate from this root. Thus Irvine and Steele[9], Drew and Haworth[10] and also Haworth and Learner[11] have conducted recently extensive experiments on the structure of inulin from dahlia and the hydrolytic cleavage of this carbohydrate.

Furthermore, Jackson et al.[12] have studied the rate of hydrolysis of the artichoke inulin in their comprehensive investigations on the preparation of levulose.

A. Extraction of the Polysaccharide

The air-dried roots of the Arctium Lappa contain from 50 to 70 per cent of carbohydrate hydrolyzable into levulose. The dried root is reduced to about a No. 40 powder and extracted with ten volumes of boiling water. The aqueous extract is treated with a slight excess of solution of lead subacetate to precipitate the gums and resins. The filtrate is freed from lead salts by treatment with hydrogen sulphide. After filtration the solution is set aside at room temperature for several days until the separation of the carbohydrate is complete. The faintly yellow powder is separated by filtration and purified by dissolving in a small volume of hot water and precipi-

tating with alcohol. By repeating this precipitation process three times, a completely white powder is obtained. The substance is washed with alcohol and dried to a constant weight in a vacuum desiccator at 38°C. This inulin containing from 0.15 to 0.2 per cent of ash was employed in these studies.

B. Optical Rotation

At 28° the specific rotation of the inulin from Lappa was $[\alpha]_D$ −34.7°. The rotation was observed in solution containing 8 gm. of the carbohydrate in 100 cc. in a 200 mm. tube.

Although inulin requires heat for solution in water, it is readily soluble in alkali hydroxide solutions. Under the same conditions a solution of the substance in normal sodium hydroxide solution showed a $[\alpha]_D$ of −34.7°.

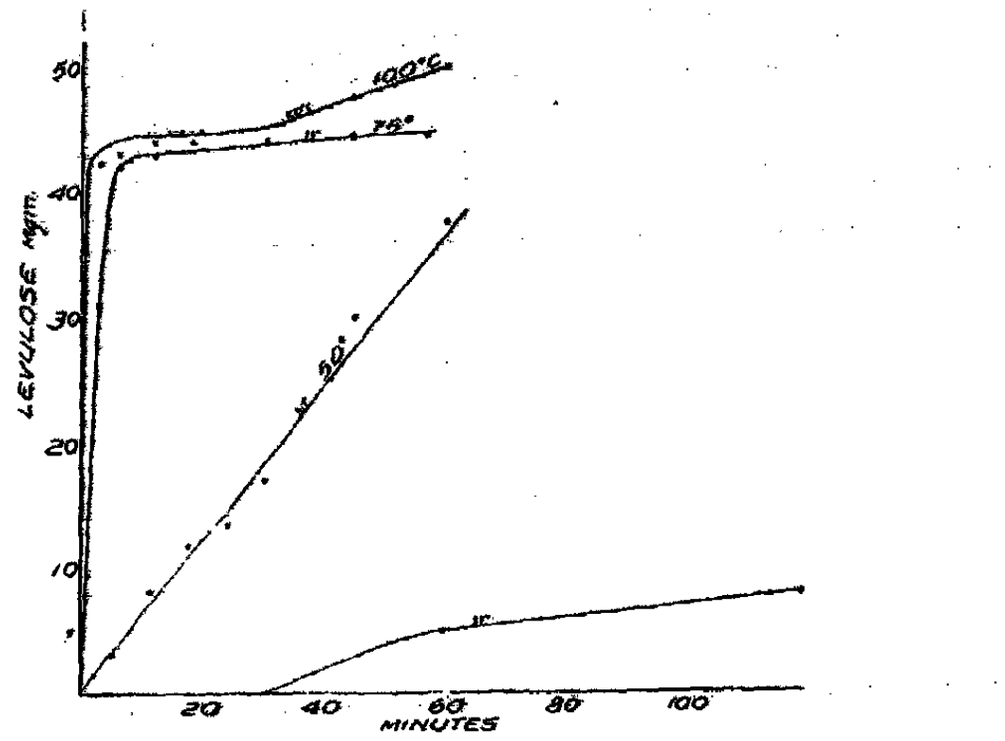
C. Hydrolysis—Influence of Temperature

The conditions under which the hydrolysis of inulin into levulose occurs is a matter of special importance in the utilization of this substance as a substitute carbohydrate in the treatment of diabetes. Okey[13] experimenting with the inulin from the Jerusalem artichoke, showed that this substance was partially hydrolyzed by the hydrochloric acid of the stomach and further this work demonstrated the presence of an inulase in the feces of normal patients fed a general diet.

TABLE I

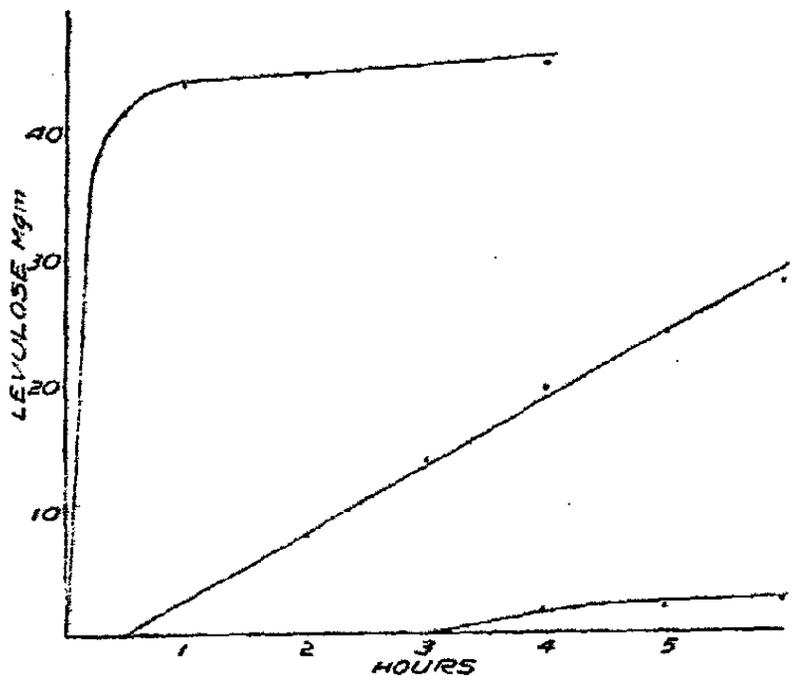
Hydrolysis of Inulin by Tenth-Normal Hydrochloric Acid at Various Temperatures

Temp.	Time min.	Levulose mgm.	Temp.	Time min.	Levulose mgm.
100°	1	41.9	75°	1	9.6
"	3	42.3	"	3	31.2
"	6	43.2	"	6	42.6
"	12	44.1	"	12	43.2
"	18	44.1	"	18	44.6
"	30	44.1	"	24	44.6
"	45	47.5	"	30	44.6
"	60	50.2	"	45	44.6
			"	60	44.2
50°	1	0.0	37°	30	0.0
"	3	1.5	"	60	5.1
"	6	3.0	"	120	8.2
"	12	8.2	"	180	14.1
"	18	11.8	"	240	19.9
"	24	13.1	"	300	24.0
"	30	17.2	"	360	28.6
"	45	30.8			
"	60	38.7			



GRAPH I

Influence of temperature upon the speed of hydrolysis of Inulin by 0.1N. HCl.



GRAPH II

Influence of concentration of HCl upon speed of hydrolysis of Inulin at 37°C.

The present authors studied the speed of hydrolysis of inulin from Burdock root as influenced by temperature and by concentration of acid.

Solutions of inulin in water (50 mgm. in 10 cc.) contained in tubes were placed in a constant temperature bath. Sufficient hydrochloric acid was added to make the total acid concentration tenth normal. After various time periods the hydrolysis was discontinued by the addition of sodium hydroxide solution. The reducing sugar formed was then determined by the Munson-Walker[14] method.

TABLE II

Influence of Concentration of HCl upon the Speed of Hydrolysis of Inulin at 37°C

Conc. HCl	Time min.	Levulose mgm.	Conc. HCl	Time min.	Levulose mgm.
1N.	30	41.8	0.1N.	30	0.0
1N.	60	44.1	0.1N.	60	5.1
1N.	120	44.7	0.1N.	120	8.2
1N.	240	45.6	0.1N.	240	19.9
0.01N.	180	0.0			
0.01N.	240	2.1			
0.01N.	300	2.1			
0.01N.	360	2.6			

Tables I and II show the results of these determinations which are also plotted in Graphs I and II.

The influence of various concentrations of hydrochloric acid upon the speed of hydrolysis is shown in Graph II.

D. Inversion Velocity Constant of Inulin from Burdock at 50°

Eight grams of inulin was dissolved in water and after adjusting the temperature to 50°, 10 cc. 1N. HCl was added and the solution was immediately made up to 100 cc. with water heated to 50°. Ten cc. portions of this solution were examined polariscopically at 30° after checking the hydrolysis by the neutralization of the acid.

The following general modification of the equation of a molecular reaction was employed:

$$K = 1/t \log_{10} \frac{R_0 - R_\infty}{R_t - R_\infty}$$

in which, R_0 is the reading before hydrolysis, R_∞ the reading after complete hydrolysis and R_t the reading at the time t. Table III shows the results of these determinations.

TABLE III

Inversion Velocity Constant

Time Min.	Rotation	Rt − R	$1/t \log_{10} \frac{R_0 - R_\infty}{R_t - R_\infty}$
0	−3.6	—	—
10	−4.4	3.5	$8\ 94 \times 10^{-3}$
20	−5.0	2.9	8.56×10^{-3}
30	−5.6	2.3	9.06×10^{-3}
40	−6.1	1.8	9.45×10^{-3}
50	−6.4	1.5	9.16×10^{-3}
60	−7.9	1.2	9.24×10^{-3}
		Mean	9.07×10^{-3}

For a series of five determinations under the same conditions the velocity constant of Coleman and Bell's C.P. inulin obtained from dahlia was 9.3×10^{-3}.

These data indicate that the hydrolysis of the inulin from Burdock follows essentially the course of an unimolecular reaction. Jackson et al.[13] found this condition to hold for hydrolysis of the carbohydrate in the expressed juice of the Jerusalem artichoke tubers.

E. Cryoscopic Measurements

A sample of inulin was dissolved in water using as little heat as necessary to effect solution. The concentration was 5 gm. in 25 gm. of water. The depression of the freezing-point of water produced by the presence of inulin as determinated by the Beckmann cryoscopic apparatus is given in Table IV.

TABLE IV

Cryoscopic Measurements

No. 1	0.19°	No. 4	0.23°
2	0.24°	5	0.26°
3	0.26°		
		Mean	0.24°

In the same concentration the mean depression of the solution of inulin from dahlia was determined to be 0.20°. Pringsheim and Fellner[15] determined the molecular weight of inulin from the dahlia tubers by direct measurement of the freezing point of its aqueous solution. They indicate that the molecule is composed of seven anhydrofructose units, which corresponds to a molecular weight of 1134. Drew and Haworth[10] by the boiling point method found the molecular weight of dahlia inulin to be 4000 in 4 minutes and to reduce regularly as the time increased being approximately 1200 in 17 minutes.

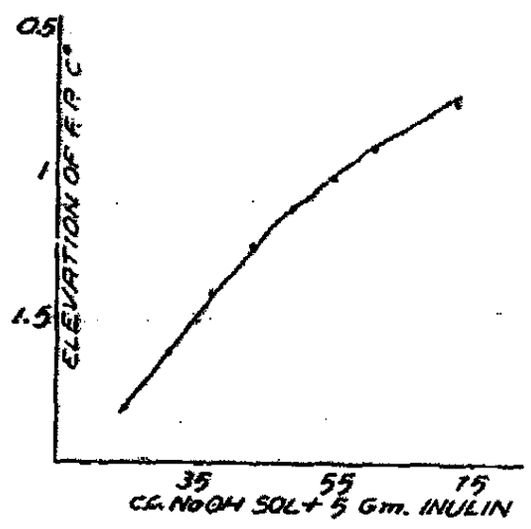
Using the well-known formula

$$M = \frac{C\ 100\ W}{\Delta w}$$

the present authors find the molecular weight of inulin from Burdock root to be 1550. Tanret[6] determined the molecular weight of inulin to be 4,827. We do not attach much significance to these data as actual molecular weights, yet it is of special interest to note that Tanret's molecular weight value for Inulenin from the Jerusalem artichoke is 1645 which agrees reasonably well with the value obtained with Burdock inulin.

Although it is generally supposed that levulose-free inluin will not reduce Fehling's Solution, in the experience of the authors it was quite impossible to obtain an inulin from Arctium Lappa which would not reduce the copper reagent after boiling for a short period (1.5 to 2 min.). Drew and Haworth[10] record the same experience and suggest that this reduction may be due to the

presence of open-chain molecules initially present, augmented by hydrolysis. In the preparation of the solutions for cryoscopic measurements heat must be employed to effect solution and invariably these solutions reduced the boiling copper reagent indicating partial degradation. Thus it is doubtful whether the values obtained even approximate the actual molecular weight of this substance. It was observed, however, that when solutions of the inulin from dahlia were prepared much more heat was required to effect a clear solution (85° to 95°) than was necessary in the case of dissolving of the inulin from Burdock root (65° to 75°). It is not unlikely that this physical property indicates a difference in molecular complexity. As mentioned before, inulin dissolves in alkali solution (solution gives a definite Tyndall cone) in the cold, hence, it was thought interesting to determine the action of dissolved inulin upon the freezing point of sodium hydroxide solution. Five grams of inulin were dissolved in 25 cc. of 1N.NaOH solution and freezing points of the diluted solutions determined. These results are given in Table V.



GRAPH III

Effect of dissolved Inulin upon the freezing point of N.NaOH.

TABLE V

Effect of Dissolved Inulin from Burdock upon the Freezing Point of 1 N. NaOH

No.	Gm. Inulin	cc. NaOH sol.	diff.
1	5	25	+ 1.82°
2	5	31	+ 1.61°
3	5	37	+ 1.41°
4	5	43	+ 1.25°
5	5	49	+ 1.13°
6	5	55	+ 1.03°
7	5	61	+ 0.93°
8	5	73	+ 0.79°
9	5	125	+ 0.60°

These data are plotted in Graph III definitely indicating that the elevation of the freezing point of a sodium hydroxide solution is a function of the concentration of inulin dissolved therein.

In another series of cryoscopic measurements, the influence of varying concentrations of sodium hydroxide upon a constant concentration of inulin was determined. These data are given in Table VI.

TABLE VI

Effect of Changes in Concentration of NaOH upon the Freezing Point of Inulin Solutions

No.	Inulin Gm.	Solvent cc.	diff.
1	1	25 cc. 1 N.NaOH	+0.60°
2	1	25 cc. 0.1 N.NaOH	+0.11°
3	1	25 cc. 0.01 N.NaOH	0.00°
4	1	25 cc. 0.001 N.NaOH	−0.02°

These results seem to indicate that in sodium hydroxide solutions between 0.1 N. and 1 N. concentration that inulin from Burdock enters into compound formation thus reducing the number of particles in solution. In concentrations of 0.01 N. sodium hydroxide and below this there seems to be no evidence of compound formation as shown by the freezing point determinations.

Nef[16] in his comprehensive studies of the action of alkalies upon monosaccharides postulates that these substances may react with oxygen to form acids. This investigator claimed that a solution of glucose in sodium hydroxide yields an equilibrium mixture of at least 93 different compounds. In view of the results obtained by the freezing point determinations of alkali solutions of the inulin from Burdock, it is not unlikely that the high hydroxyl-ion concentration causes a partial degradation of the inulin molecule into alkali consuming substances.

F. The Buffer Capacity of the Inulin from Burdock

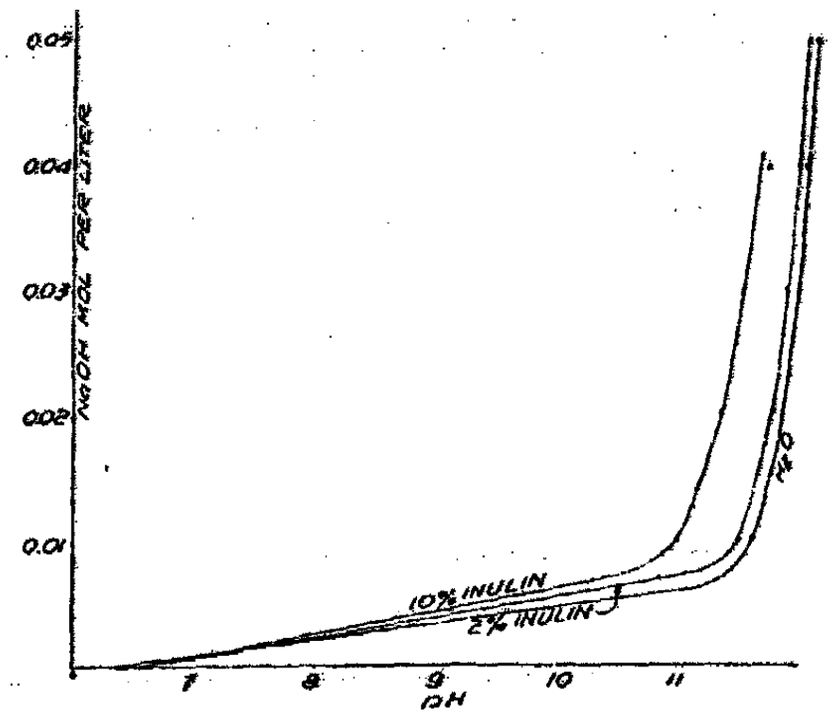
From the foregoing results of the cryoscopic measurements and in view of the work of Michaelis and Rona[17] who thru the determination of the dissociation constants of sugars, considered them as weak acids, the authors were prompted to determine the buffer capacity of this carbohydrate against alkalies. The method employed was devised by Van Slyke[18] and employed by one of the authors to measure the buffer capacity of acacia, tragacanth[19] and the extractive of digitalis leaves.[20] The pH values were measured electrometrically using a Wilson[21] electrode.

Graph IV shows the results of this experiment.

The solutions of the polysaccharide showed little capacity to change the hydroxyl-ion concentration of the alkaline solutions. With 10 per cent inulin solution pH 6.60 the addition of 0.01 mole of sodium hydroxide per liter changed the hydrogen-ion concentration to pH 11.06—in water pH 6.40 the same amount of alkali changed the pH to 11.55. For the 10 per cent inulin solution

$$\frac{\Delta B}{\Delta pH} = \frac{0.01}{4.46} = 0.002$$

As the curve between pH 6.60 and 11.06 is a straight line the "Van Slyke B" which is the differential ratio dB/dpH will have the same value.



GRAPH IV
Buffer capacity of Inulin from Burdock

Summary

Certain physicochemical characteristics of the carbohydrate from Arctium Lappa have been determined. The substance has the essential characteristics of an anhydrofructose molecule.

Bibliography

[1] D. M. R. Culbreth: "Manual of Materia Medica and Pharmacology," 615.
[2] Digest of Japanese Investigations on the Nutrition of Man—Kintaro Oshima: U. S. Dept. Agric. Bull., No. 159, 40 (1905).
[3] Inazo Nitobe: Am. J. Pharm., 72, 416 (1897).
[4] J. C. Krantz, Jr. and C. J. Carr: in press.
[5] A. Silver, B. Cohen, and J. C. Krantz, Jr.: in press.
[6] C. Tanret: J. Pharm. Chim., 27, 449 (1893); Compt. rend., 116, 1143 (1893).
[7] Root and Baker: Arch. Int. Med., 36, 126 (1925).
[8] Carpenter and Root: Arch. Int. Med., 42, 64 (1928).
[9] J. C. Irvine and E. S. Steele: J. Chem. Soc., 117, 1474 (1920).
[10] H. K. Drew and W. N. Haworth: J. Chem. Soc., 1928, 2690.
[11] W. N. Haworth and A. Learner: J. Chem. Soc., 1928, 2690.
[12] R. F. Jackson, C. G. Silsbee, and M. J. Proffitt: Scientific Papers Bureau of Standards, U. S., No. 519, 587 (1926).
[13] Ruth Okey: J. Biol. Chem., 39, 149 (1919).
[14] Munson and Walker: J. Am. Chem. Soc., 28, 163 (1906).
[15] Pringsheim and Fellner: Ann., 462, 231 (1928) through Drew and Haworth.
[16] J. U. Nef: Ann., 357, 214 (1907); 403, 204 (1914) through Gortner: "Outlines of Biochemistry," 519.
[17] L. Michaelis and P. Rona: Biochem. Z., 49, 232 (1913).
[18] D. D. Van Slyke: J. Biol. Chem., 53, 528 (1922).
[19] J. C. Krantz, Jr.: J. Am. Pharm. Ass'n., 18, 469 (1929).
[20] J. C. Krantz, Jr.: J. Am. Pharm. Ass'n., 19, 366 (1920).
[21] Wilson: Ind. Eng. Chem., 17, 74 (1925).

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THE HYPOTHETICAL POTASSIUM POLYIODIDES*

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Professor Grinnell Jones[1] believes in the existence of potassium tri-iodide as a stable solid phase at 25°, and gives definite reasons for his belief. "Johnson[2] evaporated solutions of iodine and potassium iodide over sulfuric acid and obtained lustrous, dark prismatic crystals, some of which were over two inches long, which were proved by analyses to have the composition represented by KI_3. He also determined the density of these crystals to be 3.498, which corresponded to a molecular volume of 120.1 cc., whereas the molecular volume of KI is 54.3 cc. and of I_2 is 51.34 cc., making a total of 105.64 cc. Therefore, unless Johnson made an error of nearly 15% in the determination of the density of his crystals, they could not have been a mixture of potassium iodide and iodine. He found the melting point to be 45°C. Wells, Wheeler and Penfield[3] also prepared solid KI_3 and determined the crystal angles and showed that it is monoclinic and determined the melting-point to 38°C. Foote and Chalker[4] obtain evidence of the formation of solid KI_3 from Phase Rule studies of the system $KI\text{-}I_2\text{-}H_2O$. Clark and Duane[5] have prepared solid crystals of KI_3 and confirm the observation of Wells and Penfield that it belongs to the monoclinic system and have studied the structure of the crystal by means of X-ray analysis with results proving that their crystals were not merely a mixture of KI and I_2. It should be noted, however, that Johnson is the only one of these investigators who reports analyses of the pure crystals.

"But in spite of this definite and circumstantial evidence of the existence of solid KI_3, Abegg and Hamburger,[6] Parsons and Corliss,[7] Parsons and Whittemore,[8] and Bancroft[9] deny the existence of solid KI_3 at 25°C. on the basis of Phase Rule studies of the system $KI\text{-}I_2\text{-}H_2O$. Abegg and Hamburger and Foote and Chalker state that a higher complex having the formula KI_7 exists in the solid state at 25°C., whereas Parsons and his collaborators deny the existence of any solid polyiodides of potassium at 25°C.

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* The experimental work was done in 1927-1929 and part of it was reported on at the Swampscott meeting of the American Chemical Society in 1928. The present article was written in September 1930, after having read the manuscript by Briggs and Geigle: J. Phys. Chem., 34, 2250 (1930).

[1] J. Phys. Chem., 34, 684 (1930).

[2] J. Chem. Soc., 31, 249 (1877).

[3] Z. anorg. Chem., 1, 442 (1892).

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

[5] J. Opt. Soc. America, 7, 472 (1923).

[6] Z. anorg. Chem., 50, 427 (1906).

[7] J. Am. Chem. Soc., 32, 1367 (1910).

[8] J. Am. Chem. Soc., 33, 1933 (1911).

[9] W. D. Bancroft: oral statement before the Division of Physical Chemistry at the Swampscott meeting of the American Chemical Society, September 1928.

"Berthelot[1] obtained crystals which he believed to be KI_3 but he found the heat of solution of these crystals to be the same as the heat of solution of equivalent quantities of KI and I_2 in the same amount of water, which indicates but does not necessarily prove that his crystals were a mixture rather than a compound.

"There are numerous references in the literature describing complex solid polyiodides[2] of rubidium, cesium, ammonium, and organic bases.

"There is thus an irreconcilable conflict of evidence in the literature as to the existence of solid KI_3. There are reports of four independent investigations in which it is claimed that solid KI_3 was obtained and in one or more of these researches the chemical analysis, density, melting point, crystal system and crystal angles, and internal structure as deduced from X-ray analyses were determined. On the other hand there are four separate investigations based on Phase Rule studies of the system KI-I_2-H_2O in which no evidence of the occurrence of KI_3 was found. The reviewer [Grinnell Jones] gives greater weight to the definite, circumstantial, positive evidence of the existence of solid KI_3 than to the negative evidence of those investigators who failed to find it. But even if it should eventually be definitely determined that KI_3 is unstable at 25°C., this fact—if it be a fact—would merely indicate that the vapor pressure of iodine from solid KI_3 exceeds that of pure iodine at 25°C; but would not disprove the existence of tri-iodide ions in solution. Evidence as to the existence of solid tri-iodides of cesium, rubidium and ammonium seems to be undenied. On the other hand, so far as the reviewer is aware, no one claims to have produced solid LiI_3 or NaI_3."

This is the strongest possible case that can be made out for the existence of potassium tri-iodide as a stable solid phase at 25°. The point at issue is whether phase rule methods are more or less reliable than other methods in this particular case. Before taking up that point, it will be well to eliminate the two sets of phase rule investigations which purport to show some such compound as KI_7. Professor Jones gives equal weight to Abegg and Hamburger, to Foote and Chalker, and to Parsons and his collaborators, which indicates an uncritical attitude.

Abegg and Hamburger studied the freezing-point curves for potassium iodide and iodine, and also determined the 25° isotherm for the ternary system KI-I_2-H_2O. Their data for the freezing-point curves are shown in Fig. 1, reproduced from the article by Briggs and Geigle.[3] Abegg and Hamburger found a eutectic at 80.5° and then a nearly horizontal branch, along which they assumed arbitrarily that KI_7 crystallized, because of what they assumed to be a maximum in the curve at or near the composition corresponding to KI_7. Since then, the true phase diagram has been determined by Briggs and Geigle and is shown in Fig. 2.

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[1] Compt. rend., 90, 841 (1880).

[2] J. W. Mellor: "A Comprehensive Treatise on Inorganic and Theoretical Chemistry," 2, 609 ff. (1922).

[3] J. Phys. Chem., 34, 2250 (1930).

"AB and BF are the liquidus (or solubility) curves for iodine and potassium iodide, respectively. EF is the boiling point curve for unsaturated solutions of potassium iodide in liquid iodine at approximately one atmosphere (740 mm). CBD is the eutectic boundary line and GFH is a similar line for systems consisting of salt, solution and vapor—which must in this case be practically pure iodine since the vapor pressure of potassium iodide is virtually zero at this temperature. Above the latter line, all mixtures of the two components exist in the form of salt and vapor as coexisting phases, while in the triangular area

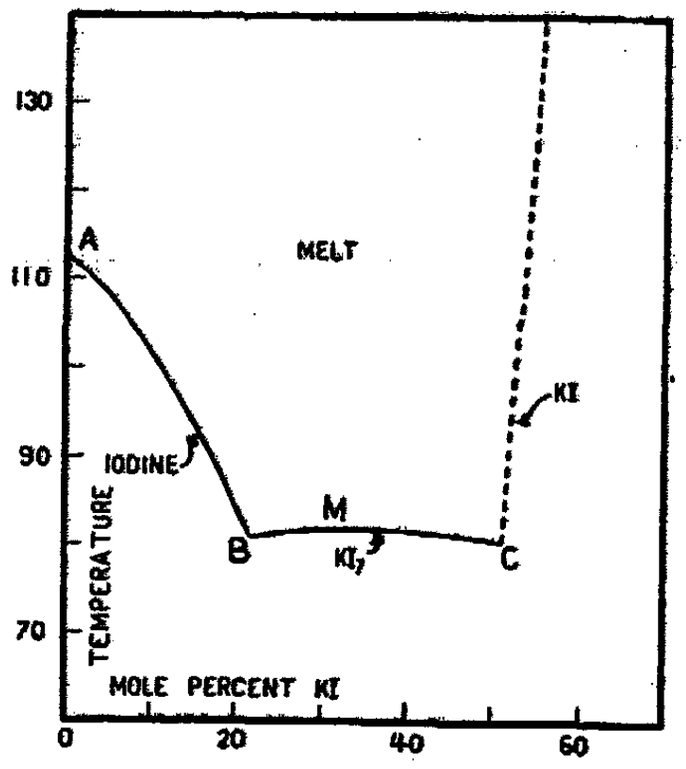

FIG. 1

The System KI-I_2 according to Abegg and Hamburger

EFG the coexisting phases are solution and vapor. The area AEFB, limited by the boundary lines AE, EF, FB, and AB, shows the conditions under which the two components exist as a single liquid phase—viz. as unsaturated solution. The remaining areas have their usual significance.

"The diagram as drawn applies, of course, to the system under a pressure of approximately one atmosphere. The lines AB and BF would be essentially the same for the system kept under the (variable) pressure of its own vapor, in which case the line BF could be followed upward either to the melting point of potassium iodide (680°) or to a critical point, the steepness of this line giving one reason to expect the latter. It is unlikely, however, that anything of importance would be learned by completing the diagram at high pressures and it would be in addition a difficult experimental problem.

"It is interesting to compare the present diagram—excluding the upper lines for systems in equilibrium with vapor—with the diagram as given by Abegg and Hamburger and by Kremann and Schoulz (Fig. 1). These investigators, for the reasons already given, missed entirely the real solubility

curve for potassium iodide, and as the result took part of the eutectic line (BMC in Fig. 1) to be the solubility curve of a compound (KI_7 or KI_4). They also placed the solubility curve for potassium iodide (the broken line in Fig. 1) in a quite erroneous position, though this was admittedly a pure guess on their part. The work of these investigators is a striking example of the danger of

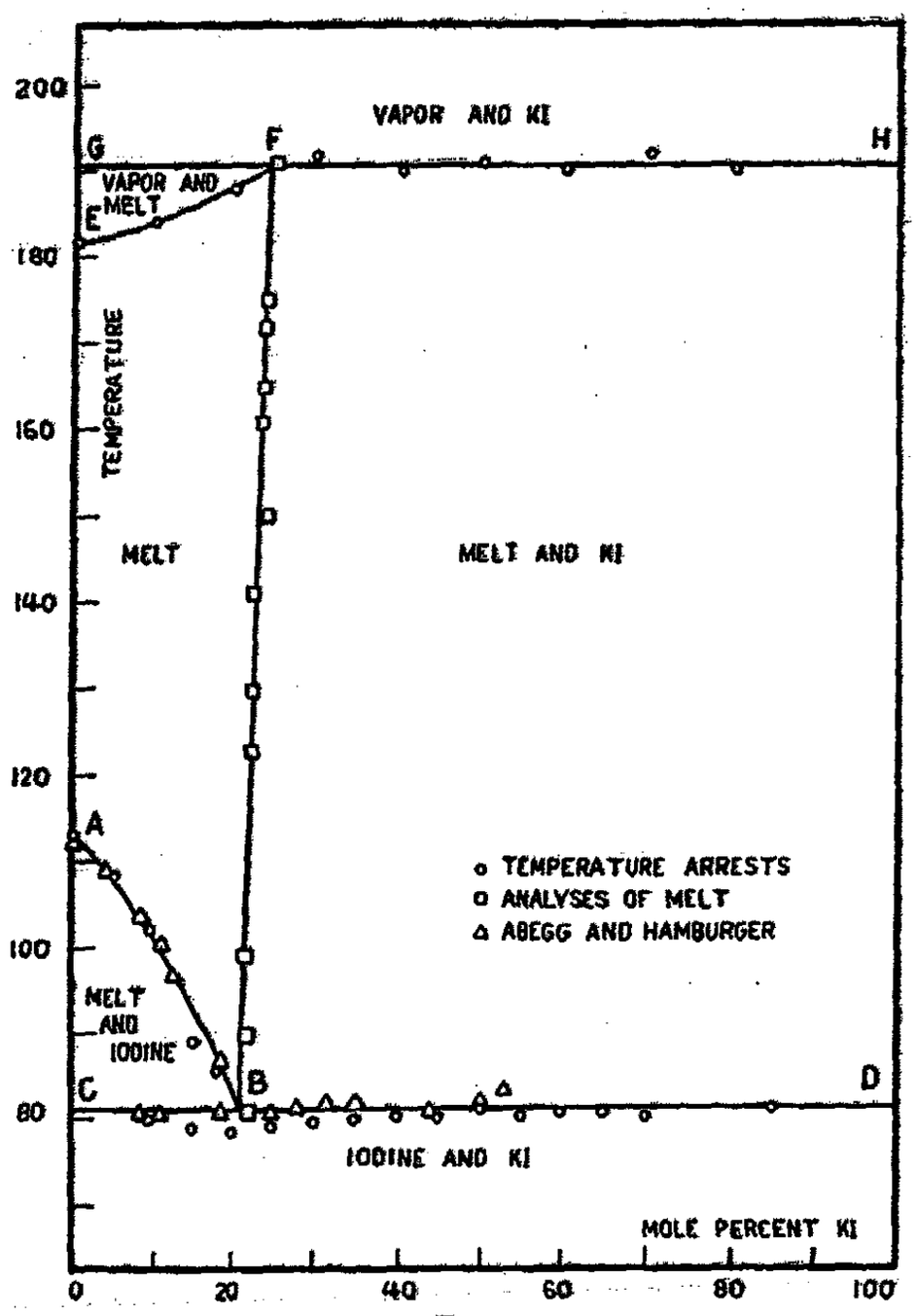

FIG. 2
Temperature-Composition Diagram for the System KI-I_2 at approximately 1 atm.

relying entirely upon temperature arrests, uncorroborated by other tests, in determining a phase diagram.

"The present work is of importance because of its bearing on the extremely controversial subject of the polyiodides of potassium. It proves definitely that there are no such polyiodides as stable phases in equilibrium with melt. Indeed, it may be stated that up to the present no one has presented strictly

trustworthy evidence that a polyiodide of potassium exists as a solid.[1] In the case of cesium, however, the evidence for the existence of polyiodides[2] is definite."

The three sets of observers, Abegg and Hamburger, Kremann and Schoulz, and Briggs agree that the eutectic temperature for potassium iodide and iodine lies between 80° and 81°. This bars out the observation by Johnson that potassium tri-iodide melts at 45°, and the corresponding observation

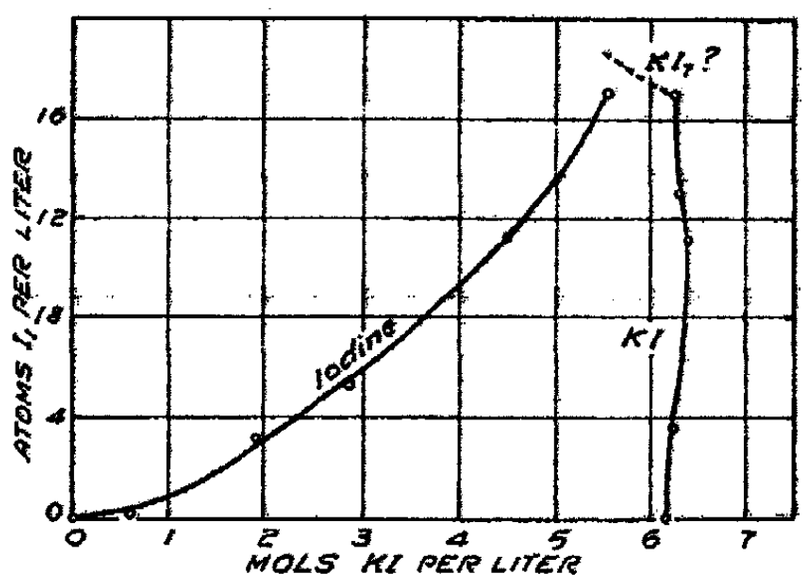

FIG. 3

Isotherm at 25° according to Abegg and Hamburger.

by Wells, Wheeler and Penfield that it melts at 38°. This had already been mentioned by Abegg and Hamburger.[3] "It is clear from the curves that no mixtures of iodine and potassium iodide melt below 80°. We must, therefore, recognize as false the melting-point determinations of Johnson[4] and of Wells and Wheeler[5] for KI_3, which gave melting-points of 45° and 38° respectively. Their preparations undoubtedly contained water. In fact we have observed a melting at 30° in the capillary for a pure sample crystallized from water, and one can force the melting-point of a potassium iodide-iodine mixture from 80° down to 40° merely by breathing on it." This was probably overlooked by Grinnell Jones.

The data of Abegg and Hamburger for the 25° isotherm of potassium iodide and iodine in water are given in Fig. 3. Abegg and Hamburger make the two arbitrary assumptions that a new phase occurs along the dotted line and that its composition is KI_7. There is not a scrap of evidence for either assumption; but people have believed it because Abegg and Hamburger said it loud and clear.

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[1] Cf. particularly Parsons and Corliss: J. Am. Chem. Soc., 32, 1367 (1910); Parsons and Whittemore: 33, 1933 (1911).

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

[3] Z. anorg. Chem., 50, 435 (1906).

[4] J. Chem. Soc., 31, 249 (1877).

[5] Am. J. Sci., (3) 43, 475 (1892).

Abegg and Hamburger[1] have some experiments with potassium iodide, iodine and benzene which really look as though they had KI_7 as solid phase. They started with a concentrated solution of iodine in benzene, and added varying amounts of potassium iodide until the concentration of iodine had fallen to a constant value. Knowing the amount of potassium iodide added and the amount of iodine that had been taken out of the solution, they could of course calculate the composition of the solid phase, which was apparently KI_7. They recognized the danger of moisture as introducing a second liquid phase and worked in sealed vessels. Since Dawson[2] had shown that iodine does not make potassium iodide soluble in benzene, there is no error on that score. On the other hand it is known that iodine forms a solid solution with benzene. If iodine forms a solid solution with benzene as it may, it is impossible to reason from the behavior in benzene to the behavior in water, because the solid phases would not be the same in the two cases. Since the results of Abegg and Hamburger with benzene do not check those of Parsons and Whittemore and of Scherer with water, and since their results have not yet been checked by anybody, it is safer not to lay too much stress on them for the present. It is very unfortunate under the circumstances that Abegg and Hamburger should have deduced the equilibrium of KI_7 with aqueous solutions from their benzene experiments instead of from the experiments with water. This is the more unfortunate because they were entirely wrong in their melting-point determinations.

Foote and Chalker appear to have found KI_3 and KI_7 as solid phases in aqueous solutions and Grinnell Jones says that positive results should be given preference over negative results. That is true in some cases; but there is no evidence of any precautions having been taken by Foote and Chalker. If KI_3 and KI_7 crystallized from their solutions, nobody should have any difficulty in getting these compounds. Apparently they also took no especial precautions to reach equilibrium, whereas Parsons and Whittemore did. Our experiments confirm those of Parsons and Whittemore and consequently we are forced to believe that the data of Foote and Chalker are inaccurate.

We can now consider the data obtained by Parsons and Whittemore.[3] They prepared solutions saturated with either iodine or potassium iodide in the presence of varying amounts of the other. In order to determine the solubility curves and corresponding solid phases for the system potassium iodide, iodine and water, various mixtures were prepared and placed in 100 cc bottles which were rotated in a thermostat at 25°. From time to time the bottles were removed for analysis and for the addition of more potassium iodide or iodine as the case might require, should examination show that the solid phase had all disappeared. This was continued until equilibrium was reached, some of the bottles being shaken for several months when necessary.

When equilibrium was reached, as shown by duplicate analyses made many days apart, a portion of the solid phase with adhering mother liquor

[1] Z. anorg. Chem., 50, 409 (1906).
[2] J. Chem. Soc., 85, 467 (1904).
[3] J. Am. Chem. Soc., 33, 1933 (1911).

was removed and analyzed. The results were plotted as a solubility curve and the prolongation of the lines drawn through points representing the compositions of a solution and the corresponding points representing the compositions of the solid phases with adhering mother liquor meet in a point representing the composition of the solid phase, so long as there is present one solid phase of constant composition. At the quadruple point with two solid phases, solution phase, and vapor phase, the solution can be shown to be in equilibrium with either pure component or with any mixture

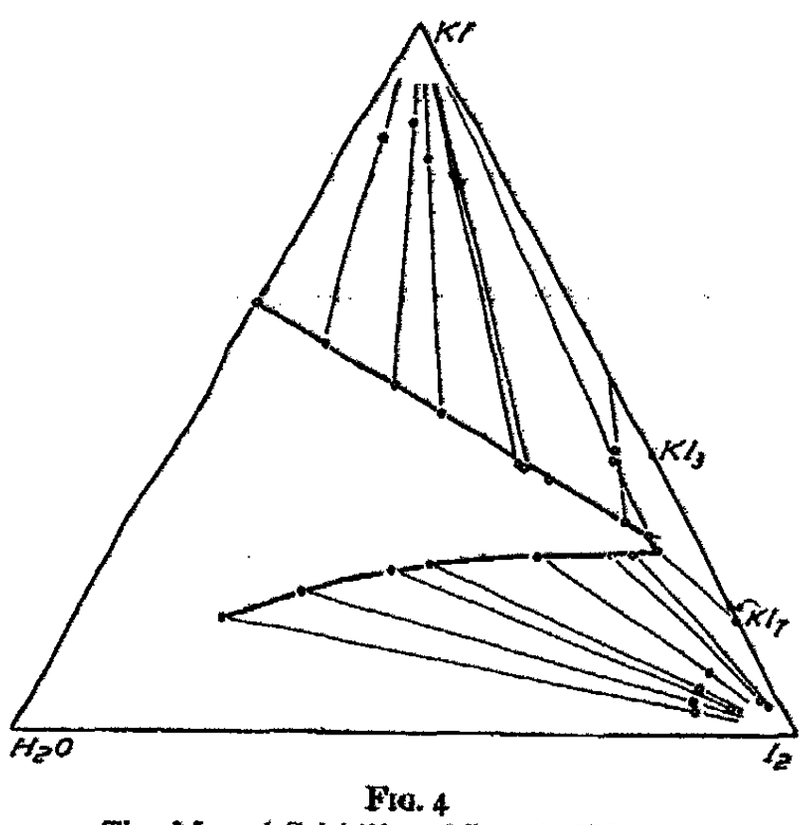

FIG. 4
The Mutual Solubility of I_2 and KI in H_2O.

of them. This work showed that the mutual solubility of potassium iodide and iodine, referred to a constant amount of water, increases with increasing amounts of each, though the percentage composition of potassium iodide in the ternary mixture decreases. At the quadruple point the solution phase contains about two and one-half mols of iodine per mol of potassium iodide.

Parsons and Whittemore assume that water does not enter into the composition of the solid phase and they plot their results on ordinary rectangular co-ordinates. There is no need of doing this and we have therefore plotted their data on a triangular diagram, Fig. 4, the numerical data being given in Table I.

There is evidently some mistake about the eighth analysis; but all the other data, including the ninth, show that potassium iodide and iodine are the only two solid phases. There is nothing that suggests KI_3, even remotely, not even the faulty No. 8. The eighteenth gives a solid phase corresponding pretty closely to KI_7—about 16 percent KI instead of about 18 percent; but this happens to be the quadruple point where the apparent composition of the solid phase can be varied at will from 100 percent iodine to 100 percent iodide. It was purely a coincidence that this particular experiment

TABLE I

Solubility of Iodine and Potassium Iodide in Water at 25°

Analysis of liquid phase			Analysis of solid phase with adhering mother liquor		
% KI	% I_2	% H_2O	% KI	% I	% H_2O
(a) In equilibrium with KI					
60.39	0.0	39.61	100.00	0.0	0.0
54.49	11.60	33.91	84.92	4.05	10.03
49.05	23.11	27.84	85.94	6.32	7.74
44.90	31.01	24.09	80.46	10.84	8.70
38.09	44.58	17.33	78.56	15.23	6.21
37.60	45.56	16.84	77.32	16.73	5.95
35.84	49.57	14.59	———	———	———
29.77*	62.81	7.42	39.99	56.10	3.91
27.86	66.48	5.66	38.78	56.27	3.95
(b) In equilibrium with iodine					
16.06	18.47	65.47	3.04	85.43	11.53
19.64	26.21	54.15	4.48	83.87	11.65
22.92	36.08	41.00	3.70	89.33	6.97
23.46	40.51	36.03	6.49	83.62	9.89
24.83	53.59	21.58	8.62	83.81	7.57
25.09	63.14	11.77	4.82	92.41	2.77
25.08	65.98	8.94	4.00	94.39	1.61

* [This one must be wrong so far as the solid phase is concerned.]

happened to come out with a composition approximately KI_7. Working as people often do, this solution could have been said to be in equilibrium with KI_7.

While these experiments would seem to be absolutely conclusive, there is one possible source of error. Let us assume, for the purposes of discussion, that potassium tri-iodide, though a stable phase, does not form readily and did not form in the experiments of Parsons and Whittemore. In that case a portion of their curve near the tip represents a metastable equilibrium. In that case the true isotherm consists of three branches as postulated by Abegg and Hamburger. This is not probable, because Johnson, Wells and Wheeler, and Foote and Chalker apparently took no particular pains and yet obtained what they called potassium tri-iodide. It is possible, however, and consequently an experiment was made to settle this question.

A solution corresponding approximately to the quadruple point on the curve of Parsons and Whittemore was made up synthetically. To this was added more potassium iodide and iodine so as to be certain of having an excess of both substances. The mixture was placed in a thermostat at 25° ± 0.1° and left there until the solution was in equilibrium both with the solid potassium iodide and the solid iodine. A titration of the saturated solution

by means of a standard sodium thiosulphate solution showed that the composition of the solution was practically identical with that given by Parsons and Whittemore. That confirmed their result. We then added crystals of Johnson's so-called tri-iodide prepared as he had prepared them. If the solution in the thermostat was in metastable equilibrium, the concentration must change on being seeded with what purported to be crystals of the stable phases. If the solution in the thermostat was in stable equilibrium, addition of Johnson's crystals would cause no change regardless of what they were.

After waiting several days the seeded solution was analyzed and was found not to have changed in composition. The solution was analyzed by diluting a weighed portion of the solution to 100 cc with 95% alcohol and titrating an aliquot portion of this alcohol solution with a standard solution of sodium thiosulphate, using starch as an indicator. The results are given in Table II along with some of the data of Parsons and Whittemore for comparison.

TABLE II

Analysis of Saturated Solution of KI and I_2

	G. sol. taken	Aliquot part	cc $Na_2S_2O_3$	% I_2	Mean
Solution before adding crystals:					
Dec. 14	2.4986	1/10	40.57	62.75	
Jan. 17	3.1762	1/10	53.29	64.87	
Feb. 15	6.2972	1/10	106.18	65.19	65.19
Mar. 2	3.6352	1/10	61.29	65.19	
Parsons and Whittemore				68.13	
Solution after adding crystals:					
Mar. 8	2.3779	1/10	40.09	65.18	65.19
Mar. 13	1.8783	1/10	31.67	65.19	

$Na_2S_2O_3$ = 0.30461 N

There is therefore no potassium tri-iodide as stable solid phase at 25° any more than there is in equilibrium with the melt. This being so, Johnson, Wells and Wheeler, and Clark either did not have potassium tri-iodide at all or had a metastable phase. This last does not seem probable.

Johnson states that he succeeded in obtaining lustrous, dark blue, prismatic crystals by evaporating slowly over sulphuric acid concentrated solutions of iodine in aqueous potassium iodide, which analysis showed to be the tri-iodide. He determined the KI by gentle heating of the crystals (dried over sulphuric acid) until potassium iodide alone remained. Then "in order to effect a more direct determination of the iodine, the crystals were dissolved in a little water (containing some potassium iodide to prevent precipitation of iodine) and the amount of the latter in excess of that required for the iodide was determined by a standard solution of sodium hyposulphite, starch being

used as indicator." The specific gravity of these crystals was found to be 3.498. The same compound has been obtained by Wells and Wheeler[1] and its crystallography determined.

Johnson describes KI_3 as "long prisms which are almost black, and exhibit a lustre resembling that of iodine; it is extremely deliquescent, and can be preserved only in an atmosphere dried by sulphuric acid; when it is exposed to ordinary air, a film of moisture is immediately deposited, the gradually increasing thickness of which causes a rapid succession of colors resembling those formed in the tempering of steel. After a short time it becomes a brown liquid. If crystals are exposed to light for even a few minutes, and then again allowed to dry over sulphuric acid, a film of potassium iodide, due to the efflorescence of iodine, forms on their surface, destroying their metallic lustre and after two or three repetitions of such treatment, even producing a whitish crust of that salt, which, however, exerts a protective influence upon the tri-iodide beneath."

Crystals the same as those described by Johnson and by Wells and Wheeler have been prepared according to the methods outlined by these authors. Solutions made by dissolving iodine and potassium iodide in the proportion of 60.4 iodine to 39.6 potassium iodide in as little water as possible were evaporated slowly over sulphuric acid at a low temperature. Due to the extremely deliquescent character of the crystals, it is impossible to transfer them from the desiccator to the balance without an increase in weight due to the absorption of moisture. There may also be water or mother liquor contained in minute cavities in the crystals. These crystals were dried from the mother liquor with filter paper, weighed quickly, and analyzed. The weighed crystals were dissolved in dilute aqueous potassium iodide and the free iodine determined by a standard solution of sodium thiosulphate, using starch as an indicator. Another weighed portion of the crystals was heated gently until potassium iodide alone remained and this white residue was then weighed. The analyses showed the crystals to have approximately the composition of KI_3, which is in agreement with the analyses of Johnson. The data are given in Table III along with some of the analyses of Johnson for comparison. The crystals used for the three samples are from three different crystallizations. The fact that the iodine and potassium iodide percentages do not add up to a hundred shows that the crystals were not perfectly dry. This was recognized by Johnson.

Our results agree with Johnson's theory even better than his own do and much better than they should considering the peculiar properties of the crystals. There was no conceivable reason why Johnson or those who followed him should have questioned the existence of a solid potassium tri-iodide.

On the other hand Parsons and Whittemore found that no potassium tri-iodide crystallized along the whole isotherm and our experiments, already cited, showed that there is no stable tri-iodide. Consequently, Johnson's crystals either represented a metastable phase or there is something wrong

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

TABLE III

Analyses of Crystals (KI_3)

	grams sample	% KI	grams sample	% I_2	Ratio KI/I_2
Sample 1	0.0393	37.15	0.0695	57.49	
Sample 2	0.1654	37.19	0.0599	57.91	
Sample 3	0.0618	36.89	0.0968	57.70	
Mean		37.08		57.70	1.002
Johnson 1	0.789	37.90	0.66	58.94	
Johnson 2	0.717	36.96	0.762	58.67	
Mean		37.43		58.80	0.973

in the analyses. It does not seem probable that Johnson's crystals were metastable, because he says that "the crystals first deposited were dark-coloured cubes, which proved to be potassium iodide, coloured by a little free iodine; but after some days, lustrous dark-blue prismatic crystals, sometimes two inches long, were deposited, which had the composition required by the formula KI_3." One would hardly expect a metastable form to come out in presence of potassium iodide crystals.

As these crystals came out of solution in long needles in much the same way that potassium iodide crystallizes out of a supersaturated solution of potassium iodide under special conditions, this seemed to tie in with the results of Parsons and Whittemore. If the crystals are really potassium iodide colored with iodine, the question comes up why the crystals should analyze as KI_3 if they are essentially potassium iodide. The mother liquor is richer in iodine relatively to potassium iodide, which would bring the iodine content too high. The more serious difficulty is that drying between filter paper removes relatively more potassium iodide than iodine. If this is the case, an analysis of wet crystals should show less iodine than an analysis of dried crystals. The data illustrating this are given in Table IV.

TABLE IV

Analysis of Wet Crystals

% KI	% I_2	Ratio KI/I_2
35.2	44.1	1.92 wet 1.00 dry
31.0	45.2	2.22 wet
From Table III		1.00 dry

We have here the extraordinary phenomenon that the wet crystals contain less iodine than the dried crystals, even though the mother liquor contains much more iodine relatively than the crystals. It is of course an unfortunate coincidence that the analysis of the dried crystals should have come

out so close to KI_3. The odds are almost anything one pleases against this happening; but it did. The discovery of this remarkable and entirely unexpected error means that the only analyses of the solid phases which have any value show the solid phases to be potassium iodide and iodine.

If there is no solid potassium tri-iodide, there must be something wrong with the experiments by Wells, Wheeler and Penfield.[1] They accepted Johnson's analysis and their melting-point of 38° was seven degrees below that which Johnson found and at least 42° below what seems to be the lowest possible melting point for the system. These are natural errors; but it does not seem possible that they could have slipped up on their crystallographic data, and yet they apparently did. It is also possible that people have overestimated in the general discussion the magnitude of the difference between a cubic and a monoclinic crystal. If the potassium iodide from the iodine solution contains a little iodine in solid solution, as it may well do, that might be enough to change one of the axes slightly. It should be kept in mind that all that Wheeler and Wells have done was to show that the crystals that they examined differed slightly from potassium iodide. They accepted Johnson's inaccurate analysis without question and without proof. There is really nothing in their work to show that they were studying potassium tri-iodide and we know that they were not. The crystals come out either as columns, which may be cubes in a row, or as needles. Qualitatively similar types of crystals can be obtained from potassium iodide solutions containing no iodine under suitable conditions and the only possible conclusion is that the crystals are potassium iodide colored by iodine and that Wells, Wheeler and Penfield were misled by the assumed analogy with cesium iodide.

As a matter of fact, Briggs[2] has shown that Wells[3] and his co-workers slipped somewhat in their work on cesium iodide and iodine. "Wells and Penfield stated that cesium tri-iodide melts at 210° and 'whitens' through loss of iodine at 330° when heated in an open tube. It is apparent from the diagram [Fig. 4] that they were right enough about the 'melting' point, although the melting of course was not complete. The 'whitening' temperature, however, was placed too high, since the iodine may be boiled out completely at about 303°.

"Wells and Wheeler, in describing the higher polyiodide which they took to be CsI_5, stated that it melted at 73°; but they also remarked—and this puzzled them greatly—that mixtures of iodine and cesium iodide between CsI_4 and CsI_9 likewise melted at 73°. It is apparent from the diagram that the temperature referred to as a melting point by Wells and Wheeler is actually the eutectic temperature for iodine and polyiodide as solid phases. Accordingly, their mixtures of the two components could not have melted completely in general as they thought—that is to say, these investigators

[1] Am. J. Sci., (3) 43, 475 (1892).
[2] J. Phys. Chem., 34, 2260 (1930).
[3] Wells and Penfield: Am. J. Sci., (3) 43, 17 (1892); Wells and Wheeler: 44, 43 (1892).

made the same mistake that Abegg and Hamburger and Kremann and Schoulz made at a later date in the case of iodine and potassium iodide. They mistook the eutectic for a melting point.

"We can go still farther, in addition, and say with confidence that, since Wells and Wheeler gave 73° as the melting point of the higher polyiodide, they could not have prepared it pure. They really had a mixture of the higher polyiodide and iodine, and for this reason the analyses which they made in an attempt to establish the formula of the polyiodide are worthless. They do give the clue to the correct formula, however; but it lies hidden in the statement that mixtures on the iodine side of CsI_3 melt always at 73°. This is precisely what the present investigation has shown to be the upper limit for the first eutectic and is additional evidence to prove that the higher polyiodide is unquestionably CsI_4. It is most interesting to find this bit of evidence tucked away in the original paper of Wells and Wheeler."

We have still to consider the X-ray determinations by Clark and Duane.[1] "With the new method of crystal structure analysis established in its fundamental features by the study of KI, its extension to the more complex structures of secondary valence compounds followed. It seemed logical to select potassium tri-iodide, not only because of its close relationship as a polyiodide to KI, but also because of its great chemical interest and importance in such matters as iodometric analysis, etc.

"Splendid crystals of convenient size and thickness for transmission experiments separated after very slow spontaneous evaporation *in vacuo* from a strong aqueous solution containing theoretical quantities[2] of KI and iodine. Without a very careful control of the evaporation, a mud of indefinite composition[3] precipitated. Since the vapor pressure of iodine from the compound reaches 760 mm in an enclosed space at 146°C, it became necessary during the analysis to protect the crystal against rapid loss of iodine by enclosing it in a very thin glass bulb mounted on the crystal table.

"The analysis proceeded in exactly the same way as outlined for KI. In the determination of the angles between planes, peak reflections occurred at angles of almost 90° and 45° from the peak for the 100 reflections. The angular reading for the 100 peak was 45°48′, and for the 100 peak 0°30′. This slight departure of about 18′ from perfect cubic symmetry verifies the discovery by Wells and Penfield in goniometric measurements that one of the axes is slightly inclined to the plane containing the other two at right angles. The experiments indicate, therefore, a cube slightly distorted into a monoclinic prism. The critical voltage for the 100 peak produced by transmission through the crystal approximated 11,300 volts at an angle, θ, of 6°45′, corresponding to the wave-length 1.09Å. Substituting this value in the equation $\lambda = 2\,d \sin\theta$, gives $d_{100} = 4.68 \times 10^{-8}$ cm. The number of molecules per unit, calculated from $m = \rho d^3/Ww$, where ρ, the density, is 3.398, W, the

[1] J. Opt. Soc. America, 7, 472 (1923).

[2] [Nobody, not even Johnson, has ever claimed that KI_3 crystallizes first from such a solution.]

[3] [This cannot be true if KI_3 is a definite chemical compound.]

molecular weight is 419.86 and w, the weight of the hydrogen atom, is 1.663×10^{-24}, comes out 0.51 or 1/2 molecule. Hence the original unit cube of KI with d = 3.532 has expanded to a very slightly distorted cube with an edge length of 4.68×10^{-8} cm and with an extra atom of iodine at or near the center.

"Again, as in the case of KI, the spectrum of the reflection furnished striking configurations and additions. The KI_3 spectrum duplicates that of KI in that it is characteristic of iodine. The spectra of the former for the 100 and 010 planes show the iodine peaks at almost the same angles. A well-defined first-order peak at the top of the sharp absorption drop appears at 2°21′ and another, less prominent and incompletely separated, at 2°39′. As in the case of KI, the center of the absorption drop, the higher and the lower peaks have wave-lengths corresponding, respectively, to the critical absorption, the Kβ and Kα lines of iodine. The same reflections repeat themselves through 4 orders. Calculating d from $0.388 = 2\ d \sin (2°21')$ and $0.437 = 2\ d \sin (2°39')$ gives the value 470×10^{-8} cm. Considering that the calculation from a wave-length in the continuous spectrum involved an unusually long wave-length, 1.09Å, the value of d agrees remarkably well with that calculated from the characteristic iodine wave-lengths."

It is purely a grand-stand play to speak about studying solid potassium tri-iodide because of its importance in iodometric analysis. Solid potassium tri-iodide is not used in iodometry. It is important that iodine is soluble in a potassium iodide solution; but it is quite immaterial whether this is because of the formation of polyhalides or for some other reason.

There is nothing in this work of Clark and Duane to show that they had potassium tri-iodide at all. It all goes back to the now discredited analysis published by Johnson in 1877. Their own statements show that their material was impure. Pure iodine has a vapor pressure of 760 mm at 184.35° according to Ramsay and Young[1] and the dissociation pressure of a stable polyiodide cannot be higher than the vapor pressure of pure iodine. Clark and Duane claim that the dissociation pressure of the alleged compound is 760 mm at 146°, which is absurd, quite apart from the fact that we now know that there is no stable compound[2] between iodine and potassium iodide in contact with the melt. Clark and Duane's material must have contained water for it to have had the vapor pressure which they give. This is not surprising because we know from the melting-points that Johnson's preparations and those of Wells and Wheeler contained water. There does not seem to be any justification for mentioning a vapor pressure of 760 mm at 146° without comment, because Regnault had put the boiling-point of iodine at 175° as far back as 1862.

Clark and Duane did not determine the density of their material themselves but took the value found by Johnson which we know to be wrong because Johnson's material was not pure. Consequently Clark and Duane worked with impure material of unknown composition with a false density,

[1] J. Chem. Soc., 49, 461 (1886).

[2] Briggs: J. Phys. Chem., 34, 2250 (1930).

and they calculated their results by means of a formula which did not apply. They resemble the billiard sharp in the Mikado, who played on a cloth untrue, with a twisted cue and elliptical billiard balls.

We may seem to be a little harsh on Mr. Clark; but he has had over two years in which to correct the erroneous statement, made at Swampscott, that he had proved the existence of solid KI_3; and he has not taken advantage of the days of grace.

We are not the only people to criticize Mr. Clark's conclusions. R. W. G. Wyckoff[1] says that "both the data and their treatment are, however, incapable of proving anything definite about the manner of atomic arrangements in crystals with such low symmetry." Ewald and Hermann[2] say that "in these three papers [by Clark and Duane] they have worked with the selective reflection of the iodine radiation in KI_3 crystals. *The results are probably wrong.*"

Mr. H. M. Southworth of the Department of Physics at Cornell University was good enough to make some X-ray measurements by the powder method on potassium iodide and so-called potassium tri-iodide. The latter crystals were drained, ground, and put into tubes along with some adhering mother liquor.

Four spectrographs were made: two each from two tubes. The first pair were over-exposed; but the second, using exposures of 10 and 7 minutes respectively, were fairly good. In Table V are given the data read from the latter two films, with the lines for KI as computed for unit cell = 7.052Å[3] for a face-centered cube.[4]

TABLE V

		I 10 min.		II 7 min.	
n	KI comp. 7.052 Å/$n^{1/2}$	KI	KI_3	KI	KI_3
3	4.07	4.07	4.07	4.05	4.05
4	3.53	3.49	3.49	3.49	3.49
8	2.49	2.50	2.50	2.48	2.48
11	2.12	2.12	2.12	2.12	2.12
12	2.04	2.04	2.04	2.03	2.03
16	1.76	1.76	1.76	1.76	1.76
19	1.62	1.62	1.62		
20	1.58	1.58	1.58		
24	1.440	1.443	1.443	1.44	1.44
27	1.358	1.358	1.358	1.355	
32	1.247	1.250			

"As is seen from the data, the lines observed check closely with the computed values, in the case of KI_3, as well as in that of KI. Except for the last line (n = 32), which was very faint for KI, lines were observed for KI_3

[1] "The Structure of Crystals," 339 (1924).
[2] Strukturbericht, 287 (1913-1926).
[3] "International Critical Tables," 1, 345.
[4] Clark: "Applied X-rays," 134.

corresponding to each of the lines for KI, and no other lines for KI_3 were observed. The lines for KI_3 were in general fainter than those for KI."

We are not qualified to interpret X-ray data; but we are told that Table V is not an argument for the separate existence of KI_3. We express our sincerest thanks to Mr. Southworth.

The belief in the existence of a solid potassium tri-iodide, stable at 25°, rests on the analysis made by Johnson in 1877—which has since been shown to be wrong—and on the fact that a solid potassium tri-iodide was a natural thing to expect. In the paper already cited, Grinnell Jones says that he "gives greater weight to the definite, circumstantial, positive evidence of the existence of solid KI_3 than to the negative evidence of the investigators who failed to find it." As a general principle this is perfectly sound; but it happens to be an unfortunate position to take in this particular case.

We have duplicated Johnson's results and anybody can duplicate Johnson's results. In fact Wells and Wheeler did and Clark and Duane did. All three sets of people had material which was obviously impure from its properties, and Johnson was the only one who made an analysis. His analysis was made by a method which could not possibly give accurate results with such a substance as the hypothetical potassium tri-iodide. We have duplicated his analysis and have shown that the error was in the method and not in his manipulation. We have confirmed the experiments of Abegg and Hamburger and of Parsons and Whittemore that potassium tri-iodide does not crystallize from these solutions. A better statement by Grinnell Jones would have been that Johnson obtained KI_3 by an obviously inaccurate method of analysis, whereas Abegg and Hamburger and Parsons and Whittemore found no such compound, when using phase rule methods which are known to be more accurate. The analyses by Scherer confirm those by Parsons and Whittemore. As these last had been made before Grinnell Jones wrote his article, and as he had been told about them, one can hardly praise him for his calm, impartial attitude.

While the experiments with benzene by Abegg and Hamburger are puzzling and should be repeated, Parsons and Corliss[1] have obtained results with aqueous alcohol which agree absolutely with the later work by Parsons and Whittemore with water alone. From the view-point of phase-rule work, it is immaterial whether one uses pure water, pure alcohol, or any mixture of them as the solvent, provided the ratio of water to alcohol is kept constant throughout. If neither water nor alcohol forms part of the solid phases under the conditions of the experiment, the nature of the solid phases must be independent of the composition of the aqueous alcohol used.

"In order to obtain the solubility curves and corresponding solid phases for the system, various mixtures were prepared and placed in 100 cc. hard-glass bottles, the glass stoppers of which had been carefully ground. The bottles were then rotated in a large thermostat carefully regulated at 25°. The rotating was started December 1, 1909, and the bottles were removed from

[1] J. Am. Chem. Soc., 33, 1367 (1910).

time to time for analysis and for the addition of more potassium iodide or of iodine as the case might require, should examination show that the solid phase had all disappeared. Equilibrium was reached most quickly in the more concentrated solutions, which was directly contrary to previous experience in pure alcohol. Many of the bottles had not reached equilibrium on March 1 after three months rotation. Practically all were in equilibrium by April 1; but the two where pure iodine alone was present in solution still showed slight gains on June 1 over analyses made some two weeks previously. They were, however, very near to saturation."

TABLE VI

Solubility of Iodine and Potassium Iodide in Forty Percent Alcohol at 25°

Analysis of liquid phase			Analysis of solid phase with adhering mother liquor		
% KI	% I_2	% H_2O	% KI	% I_2	% H_2O
		(a) In equilibrium with potassium iodide			
42.10	0.0	57.90	100.00	0.0	0.0
40.83	3.76	55.41	89.21	0.70	9.09
38.94	10.09	50.97	88.80	1.90	9.30
37.41	15.71	46.89	88.19	3.02	8.79
36.25	20.52	43.23	87.04	4.21	8.75
35.38	24.44	40.15	86.08	5.11	8.81
33.26	33.62	33.12	83.61	8.41	7.99
31.71	39.99	28.30	82.06	10.76	7.18
30.59	44.76	24.65	80.80	12.35	6.85
28.56	55.30	16.14	75.90	18.63	5.87
26.95	60.27	12.78	74.77	20.86	4.37
24.52	65.93	9.55	72.98	23.61	3.41
23.04	69.93	7.03	72.35	25.04	2.51
		(b) In equilibrium with iodine			
0.0	2.97[1]	97.03	0.0	100.00	0.0
8.45	28.70	62.85	1.85	84.51	13.64
12.56	40.63	46.81	3.41	84.02	12.57
15.20	49.95	34.85	4.98	83.81	11.21
16.02	52.95	31.03	5.60	82.96	11.44
17.18	57.37	25.45	6.61	83.60	9.79
19.20	66.89	13.91	8.45	85.16	6.39
20.12	69.10	10.78	7.08	88.81	4.11
20.12	69.10	10.78	7.08	88.81	4.11
		(c) Quadruple point			
22.50	70.79	6.71	19.48	76.24	4.28
22.43[2]	70.88	6.69	69.37	26.14	4.49

[1] Final analysis June 1. Saturation may not have been quite reached.
[2] After addition of KI and further rotation.

The data for 40 percent alcohol are given in Table VI and Fig. 5; and those for 60 percent alcohol in Table VII and Fig. 6. In regard to Table VI Parsons and Corliss say: "The analyses given are the final ones after equilibrium had been proven. Their accuracy may be judged from seven analyses given of the most concentrated liquid at the invariant [quadruple] point No. 20. At this point the liquid was shown to be in equilibrium with iodine, with potassium iodide; and with two mixtures of iodine and potassium iodide. It

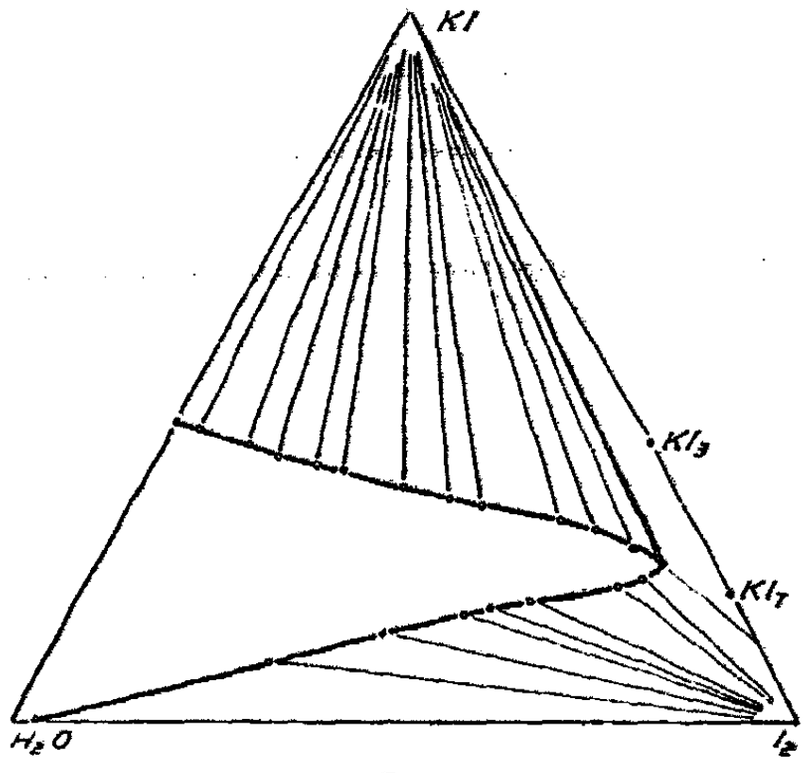

FIG. 5
Forty Percent Alcohol Isotherm at 25 degrees.

was first found to be in equilibrium with two solid phases, which could from the nature of the curve be only iodine and potassium iodide. For the sake of further demonstration the liquid was separated from the solid, pure iodine added, and further rotated in the thermostat without change in composition. Potassium iodide was now added and it [the solution] was later found to be in equilibrium with this new mixture. It was again separated from the solid and rotated in contact with pure potassium iodide but no change in composition took place. As only two solid phases can co-exist at the invariant [quadruple] point, no polyiodide can be present. It might also be well to call attention to the highest concentration and the interesting fact that a mixture of twenty grams of potassium iodide and 72.5 grams of iodine can be kept in solution by 7.5 grams of 60 percent alcohol at 25°."

It is rather interesting to note what Parsons and Corliss[1] say about their predecessors in this field. "As usually happens, the literature contains claims for the existence of solid polyiodides of potassium and also evidence of the non-existence at least of the tri-iodide. Johnson[2] states that he succeeded in

[1] J. Am. Chem. Soc., 33, 1368 (1910).
[2] J. Chem. Soc., 31, 249 (1877).

TABLE VII

Solubility of Iodine and Potassium Iodide in Sixty Percent Alcohol at 25°

Analysis of liquid phase			Analysis of solid phase with adhering mother liquor		
% KI	% I_2	% H_2O	% KI	% I_2	% H_2O
(a) In equilibrium with potassium iodide					
30.93	0.0	69.07	100.00	0.0	0.0
29.87	4.51	65.69	89.13	0.71	10.16
28.39	12.48	59.13	86.60	2.27	11.13
28.00	18.60	53.40	87.30	3.21	9.49
27.60	21.80	50.60	85.75	4.25	10.00
27.00	28.00	45.00	84.39	6.05	9.56
25.90	40.52	33.58	81.05	10.30	8.65
24.90	52.42	22.68	76.21	16.73	7.06
24.40	58.93	17.67	73.20	21.04	5.76
22.49	65.75	11.76	71.66	24.15	4.19
21.50	68.95	9.55	70.04	26.42	3.54
(b) In equilibrium with iodine					
0.0	23.04[1]	76.96	0.0	100.00	0.0
7.36	43.05	49.59	1.40	88.76	9.84
10.60	49.38	40.02	2.50	88.21	9.29
12.44	55.33	32.23	3.72	87.10	9.18
13.74	59.26	27.00	4.41	86.60	8.99
15.20	62.66	22.14	5.80	85.20	9.00
17.72	69.10	13.18	7.15	85.49	7.36
19.30	71.90	8.80	7.45	88.96	4.59
(c) Quadruple point					
20.11[2]	72.51	7.38	——	——	——
20.03	72.46	7.51	21.84	74.64	3.52
20.05	72.54	7.41	——	——	——
19.98	72.44	7.58	7.40	89.81	2.79
20.08	72.51	7.41	20.61	74.09	5.30
20.06	72.44	7.50	——	——	——
20.05	72.48	7.47	33.46	63.19	3.35

obtaining lustrous, dark-blue crystals by evaporating concentrated solutions of iodine in both aqueous and alcoholic potassium iodide, which analysis showed him to be the tri-iodide. As all the mixed crystals obtained from these strong solutions have much the same appearance and can not be separated from the mother liquor, his conclusions are not to be relied upon, especially as analysis is no criterion whatever of the formula of a substance unless its identity as a single compound is proven by other means. The more recent

[1] Final analysis June 1, saturation point may not have been quite reached.

[2] Analysis April 12.

work of Abegg and Hamburger[1] upon solutions of iodine in aqueous potassium iodide is extensive, and they conclude that no polyiodide of potassium exists of less complexity than KI_7. A difference of opinion may be held as to whether the solid phase they analyzed as near to KI_7 was in reality homogeneous. Foote and Chalker[2] give results which, if correct, prove the existence of KI_3 and KI_7. They are in direct opposition to our own and both cannot be right. We must leave the judgment to others. We can only suggest that possibly

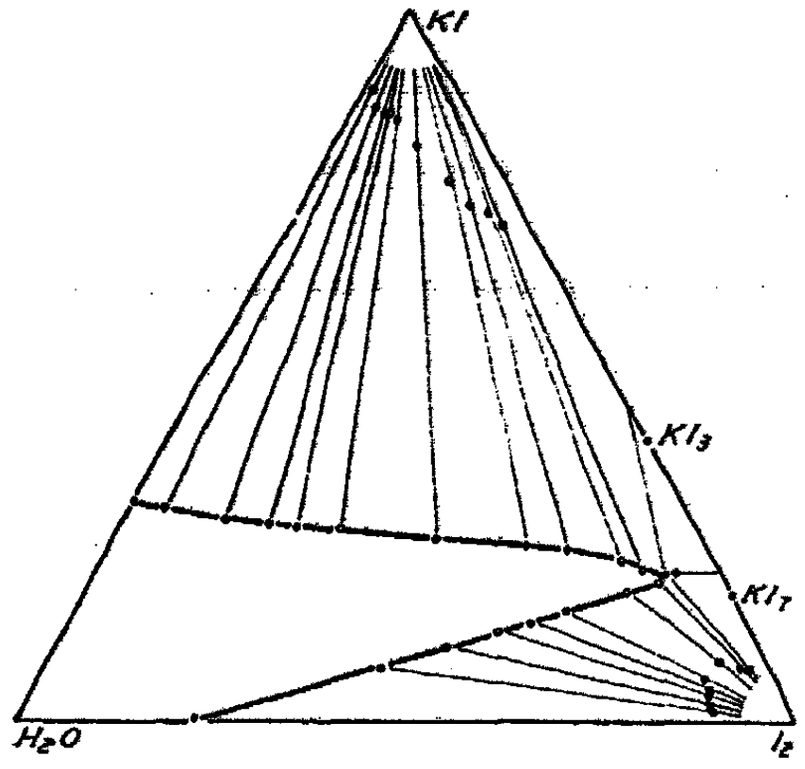

FIG. 6
Sixty Percent Alcohol Isotherm at 25 degrees.

equilibrium was not attained, that the analyses of the solutions supposed to be constant are not in sufficient agreement to prove constancy of composition and that in these concentrated solutions the potassium iodide content of the solid phase, after pressing between filter paper, is alone no real criterion of its true composition. Furthermore, we are unable to plot their results on any semblance to a solubility curve."

It is difficult to believe that Grinnell Jones read the papers by Parsons and Corliss, and Parsons and Whittemore either sympathetically or understandingly. He has quite overlooked what everybody knows, that the man who challenges the work of his predecessors has usually taken some pains to satisfy himself that his work is right. He should receive at least as much consideration as the man who never knew that anybody was going to question his data. It is quite certain that Foote and Chalker would have taken more pains if it had occurred to them that their data would be challenged. Most people would also have noted that nobody has attempted to controvert the data published by Parsons more than twenty years ago.

[1] Z. anorg. Chem., 31, 249 (1906).
[2] Am. Chem. J., 39, 561 (1908).

The fact is that the only evidence for the existence of solid potassium tri-iodide is the analysis by Johnson in 1877 of an admittedly impure product by an admittedly inaccurate method. The experiments of Wells and Wheeler were made with an impure product—as shown by the melting-point—which they did not analyze. There is nothing in their results inconsistent with the assumption that their product was essentially potassium iodide which had taken up enough iodine to change one of the axes slightly. Clark and Duane worked with an impure product—as shown by the boiling-point—which they did not analyze. There is nothing in their results inconsistent with the assumption that their product was essentially potassium iodide which had taken up enough iodine to change one of the axes slightly. The phase rule studies by Abegg and Hamburger, Foote and Chalker, Parsons and Whittemore, and Scherer show no signs of potassium tri-iodide as a solid phase at 25°, while Briggs has shown that no polyiodide exists in stable equilibrium with the melt. The evidence against the existence of potassium tri-iodide as a solid phase stable at 25° is overwhelming. On the other side there is one inaccurate set of analyses, made before any doubt had been cast on the existence of solid potassium tri-iodide. The work of Parsons and Corliss with aqueous alcohol confirms the results of Parsons and Whittemore. The work of Abegg and Hamburger with benzene appears to prove the existence of solid KI_7.

The general results of this paper are as follows:—

1. In 1877 Johnson analyzed impure crystals from a potassium iodide-iodine solution and seemed to prove that the solid phase was KI_3. Johnson's experiments have been duplicated by Scherer who got the same results as Johnson; but who showed that these results were wrong.

2. Wells and Wheeler did not analyze their product but relied on Johnson's analysis which has now been discredited. The melting point of their product shows it to have been impure.

3. Clark and Duane did not analyze their product but relied on Johnson's analysis which has now been discredited. The boiling-point of their product shows it to have been impure.

4. Abegg and Hamburger, Foote and Chalker, and Parsons and Whittemore found no evidence of the existence of solid potassium tri-iodide at 25°. Their line of attack was sound theoretically, while Johnson's was not. It must be remembered that Johnson's method was the only one known at the time he did his experiments.

5. The experiments of Wells and Wheeler show nothing for or against the existence of solid potassium tri-iodide. Their results are consistent with the assumption that their product was potassium iodide which had taken up enough iodine to change one crystal axis slightly.

6. The experiments of Clark and Duane show nothing for or against the existence of solid potassium tri-iodide. Their results are consistent with the assumption that their product was potassium iodide which had taken up enough iodine to change one crystal axis slightly.

7. The X-ray measurements by Mr. H. M. Southworth of the Department of Physics show no signs of the presence of potassium tri-iodide.

8. The experiments of Briggs prove that no polyiodide of potassium can exist in stable equilibrium with the melt.

9. Our experiments prove that those of Parsons and Whittemore are not vitiated by presence of a metastable phase.

10. Solid potassium tri-iodide does not occur as a stable phase at 25°.

11. Parsons and Whittemore are right in saying that potassium iodide and iodine are the only solid phases which can be stable at 25°.

12. The experiments of Parsons and Corliss with aqueous alcohol confirm those of Parsons and Whittemore.

13. The experiments of Abegg and Hamburger appear to prove the existence of solid KI_7. Since this does not exist, there is something wrong about the experiments, possibly the assumption that iodine crystallizes pure from benzene.

14. Professor Grinnell Jones is right in saying that the non-existence of potassium tri-iodide as a solid phase stable at 25° proves nothing either way as to the existence or non-existence of potassium tri-iodide in solution. It is interesting, however, to note the lengths to which people have gone in trying to foster the belief that solid potassium tri-iodide does occur as a solid phase stable at 25°.

Cornell University.

THE REDUCTIVITY OF HYDROGEN AT CERTAIN METAL SURFACES IN RELATION TO THE OVERVOLTAGE*

BY G. RAYMOND HOOD** AND FRANCIS C. KRAUSKOPF

A study of the reduction effected by metallic couples such as Mg-Cu, Zn-Cu, in aqueous potassium chlorate solution and a comparison of the "reduction efficiency" of the hydrogen evolved in the several cases investigated[1] led us to inquire if some relation exists between the cathodic overvoltage and the efficiency of electrolytic reduction.

The correct method of determination of overvoltage is a disputed question. The proponents of the theory of transfer resistance uphold the commutator method of Newbery, which yields values independent of the density of the polarizing current.[2] Other investigators deny the existence of transfer resistance and support the direct method of measurement, which relates the overvoltage as a logarithmic function of the applied current.[3] From thermodynamical considerations, it is generally conceded that the latter method yields the more nearly correct results.[4]

Apparatus

An apparatus was constructed by which cathode potentials could be determined by the direct method during electrolytic reduction. This consisted essentially of (1) the electrolytic cell, (2) apparatus for the control and measurement of the electrolyzing current, (3) a reference electrode and potentiometer for the measurement of the cathode potential.

The electrolytic cell was a 400 c.c. beaker (Pyrex) equipped with motor-driven glass stirrer. The anode was a sheet of platinum foil, 2.5 × 1.25 × 0.02 cm., with a platinum lead sealed into a supporting glass tube containing mercury for electrical contact. The cathodes were in the form of rectangular plates, usually 2.0 × 4.0 cm., with an extension at one end, about 8.0 × 0.4 cm., which served as a support in fixing the cathode in position. In general, the back and edges of the cathode and the supporting strip were insulated so as to leave an area of 8.0 sq. cm. exposed, either with a coating of de Khotinsky

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* Contribution from the laboratory of general chemistry of the University of Wisconsin.

** The material here presented is a portion of that used by G. Raymond Hood in his dissertation presented in partial fulfilment of the requirements for the degree of Doctor of Philosophy at the University of Wisconsin.

[1] W. Caldwell: Unpublished thesis, this laboratory (1928).

[2] Newbery: J. Chem. Soc., 105, 2419 (1914); 109, 1051, 1066, 1107, 1359 (1916); Sand, Weeks, and Worrell: 123, 456, 1745 (1923).

[3] MacInnes: J. Am. Chem. Soc., 42, 2233 (1920); Dunnill: J. Chem. Soc., 119, 1081 (1921); Tartar and Keyes: J. Am. Chem. Soc., 44, 557 (1922); Knobel, Caplan, and Eiseman: Trans. Am. Electrochem. Soc., 43, 55 (1923); Glasstone: J. Chem. Soc., 123, 2926 (1923); 125, 2414 (1924); Knobel: J. Am. Chem. Soc., 46, 2613 (1924).

[4] Jahn and Schoenrock: Z. physik. Chem., 16, 53 (1895); Jahn: 26, 422 (1898); Tafel: 50, 641 (1905); Lewis and Jackson: 56, 193 (1906).

cement covered with a film of paraffin wax, or with Vinylite 80.[1] In a few experiments where the cathode was uninsulated, the surface exposed to the electrolyte was 17 sq. cm. The electrodes were arranged with their plane faces parallel and opposite at a distance of 4 cm. and symmetrically with reference to the walls of the beaker.

The reference electrode was a saturated calomel half-cell of "Absolute" potential 0.472 volt at 20°C.; where the "Absolute" potential of the standard N/10 potassium chloride calomel cell is taken as 0.560 volt. The important feature of this part consisted of a double salt-bridge, where the liquid junction between the electrolyte and the saturated potassium chloride solution was made in a vessel outside the electrolytic cell, in order to prevent contamination of the cell contents, (Fig. 1.)

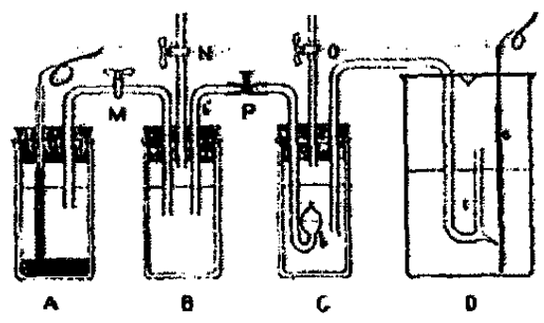

FIG. 1

A is the simple calomel half-cell, B a small jar of saturated KCl solution dyed with methylene blue, C is a similar jar containing the electrolyte used in the electrolytic vessel D. The construction of the tip t, which presses against the cathode face c, permits hydrogen entering it to pass freely to the surface. In setting up the apparatus, B was filled to a predetermined depth with fresh KCl solution, the clean dry jar C and the connecting tubing assembled, the part t dipping into the liquid in the beaker D. The cock M being closed, gentle air pressure at N forced KCl solution over until the bulb b was nearly but not quite filled. Closing N, and tightening the pinch-clamp P, the bulb could be filled until the KCl just entered the capillary. The open vertical tube of t was then closed with the tip of a finger and suction at O drew electrolyte into C until the level of the liquid in the jar was just below that of the electrolyte remaining in D; the final adjustment of the levels by siphonage proceeded until equilibrium was established. The cock O was then closed, the tip t was pressed against the face of the electrode, and all else made ready for the experiment. Then gentle pressure with the fingers forced out the small bubble of air trapped in the capillary of b, and opening the clamp P slowly drew electrolyte into b until the liquid junction rested at the widest portion of the bulb. Upon opening M the junction remained stationary at this desired position provided that pains were taken to insure the tightness of the rubber stoppers and the fit of the cocks M, N, O. The junction KCl—electrolyte obtained was beautifully sharp, and as the arrangement was not subjected to any movement after the junction was made it remained distinct for an hour or more. After the sharp definition of the junction became blurred, the rubber tube at P was compressed with the fingers until the bulb b was filled with KCl and overflowing—as could be seen by the streaky ap-

[1] A lacquer manufactured by the Carbide and Carbon Chemical Corporation, 30 East 42nd Street, New York City.

pearance of the heavier liquid falling through the electrolyte to the bottom of the jar C—careful release of the pressure drew back fresh electrolyte into b and a new distinct junction was formed. A slight closure of the clamp P brought the junction to the widest portion of the bulb.

The drift in junction potential with this arrangement did not exceed 0.5 millivolt per hour; and potentials after renewal of the junction rarely varied by as much as 2 or 3 millivolts from those immediately preceding the renewal, and commonly agreed within a millivolt if the test electrode itself was in a consistently steady state. There is doubtless some fall in potential involved between the cathode and the half-cell element through the intervening double bridge, but this drop must be practically uniform among the several experiments. This apparatus effectually prevented contamination of the electrolyte; chloride neither diffused nor siphoned back into the electrolytic cell.

A variable resistance to adjust the applied current and an ammeter for its measurement—of 1.5 amperes range divided into 150 scale divisions—with a potentiometer for the determination of the E. M. F. of the cell: test electrode—calomel electrode, and the accessory wiring, completed the apparatus.

Experimental

Preliminary experiments with N/10 sulfuric acid as electrolyte showed that our overvoltage measurements exhibited marked imperfection from the quantitative standpoint. The observations were continued and the technique and experimental conditions checked by control tests until it was established to our satisfaction that the shortcomings in our data constituted a difficulty inherent in the problem and were not due primarily to faults in the apparatus or in manipulation.

The chief source of error, from the experimental side, lay in the variation in potential arising from slight differences in the position of the junction tip t with reference to the face of the test electrode and in the pressure with which it opposed the slight spring tension of the supporting strip, from one experiment to another. Our findings were quite in accord with those of other investigators;[1] the error attributable to these differences in the adjustment of the tip was not less than 5 millivolts, and at times may have amounted to 2 or 3 hundredths of a volt.

However, our results showed that the potential exhibited by a metal was influenced much more by its surface condition than by this or other factors (e.g., temperature, rate of stirring, etc.) which might affect it. The electrodes were polished uniformly with fine emery; but the surfaces could not be initially reproduced from one experiment to another.[2] Further, the process

[1] Knobel, Caplan, and Eiseman: Trans. Am. Electrochem. Soc., 43, 55 (1923).

[2] Dunnill: J. Chem. Soc., 119, 108 (1921); and others.

of electrolysis effected an alteration in the surface, so that the overvoltage varied markedly with time.[1] Thus in studying the relation between current density and overvoltage with nickel and copper cathodes, it was found that the order in which the observations were taken materially altered the results obtained. The theoretical relation

$$\pi = a + b.\log I$$

(where π is the overvoltage, I the polarizing current density, and a and b are constants)

which has been experimentally established in the case of mercury[2] and other metals, was not obtained when the current density was changed in a random manner; instead the relation was more nearly

$$\pi = a + b.I$$

contrary to the recent finding of Sand[3] with nickel and silver electrodes. The theoretical relation was approached if the observations were made methodically at continuously increasing current and at consistently longer time intervals. These discrepant results could only be attributed to alteration in the cathode surface resulting from electrolysis.

The cathode potentials of Cu, Al, Ni, Ag, Cd, and Fe in N/10 sulfuric acid as affected by time were studied in detail. In each experiment, the acid was electrolyzed at uniform current, usually for 5 hours—rarely for shorter intervals and occasionally for 10 hours—and the cathode potentials measured at intervals of from 3 to 30 minutes throughout this time. Individual points "off the curve" located by all the points seldom were in error by more than 3 to 5 millivolts at current density 0.0125 amp./sq. cm. The deviation increased slightly when the current was doubled.

The relation appeared to be specific for each metal, but for a given cathode the potential-time curves were fairly reproducible. Typical examples are given in Fig. 2, representing the potentials of iron and copper in N/10 sulfuric acid, at 0.0125 amp./sq. cm. The form of the curves for nickel at the same current density imitated those for copper, and the average maximum potential was identical with that attained by copper; i.e., 0.927 volt. The agreement among individual curves was however less satisfactory. The curves for silver started at a potential of 1.00 volt, and fell to a minimum of 0.84 volt in about 100 minutes, thereafter rising slowly; with closer agreement among the individual curves than was obtained with any other metal. Aluminum exhibited a sharp maximum potential; with wide variation among the several experiments. The average maximum potential was about 1.25 volt.

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[1] Beetz: Wied. Ann., 10, 348 (1880); Roszkowski: Z. physik. Chem., 15, 287 (1894); Förster and Piguet: Z. Elektrochemie, 10, 718 (1904); Tafel (which see); and others.

[2] Bowden: Trans. Faraday Soc., 24, 473 (1928); and others.

[3] Sand: Trans. Faraday Soc. 26, 19 (1930).

The potential of copper was also measured at a number of current densities, determining a potential-time curve for each. The form of the curve at 0.0125 amp./sq. cm. was copied very exactly at higher currents to 0.0272 amp./sq. cm. but the individual error involved in failure to reproduce exactly the initial cathode surface obscured any quantitative relation between cur-

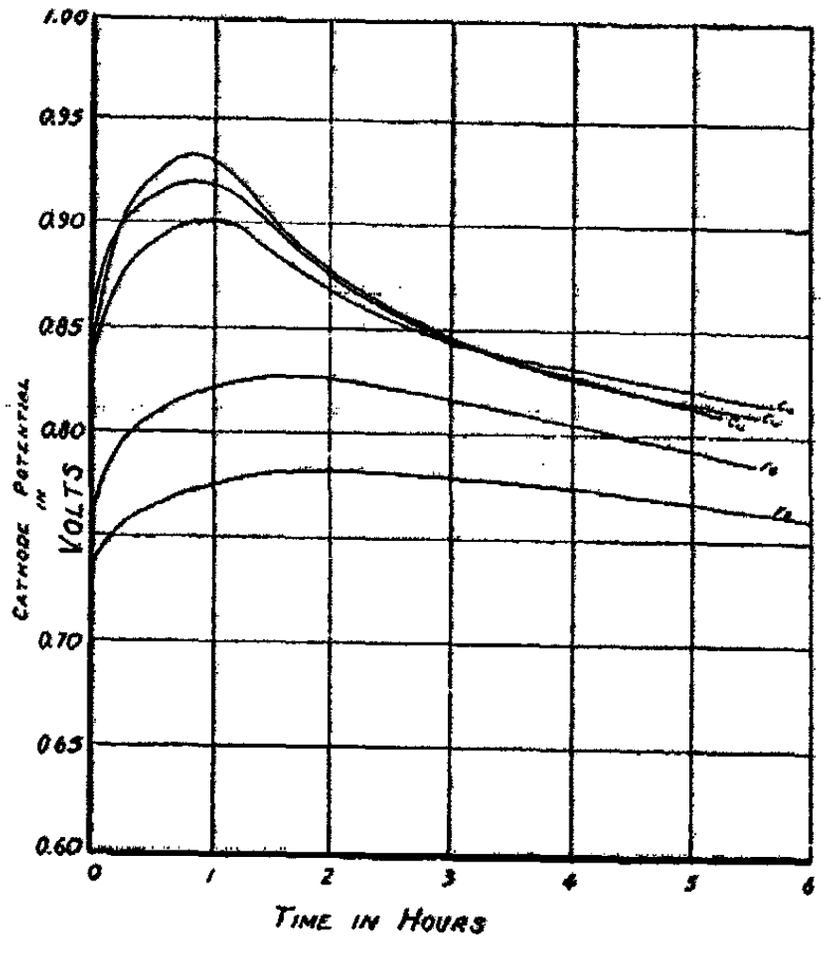

FIG. 2

rent density and the maximum potential. Certainly, the maximum π increased as I increased, but neither the relation

$$\pi = a + b. \log I$$

nor

$$\pi = a + b. I$$

could be preferentially established from the observed values.

The apparent impossibility of obtaining closely reproducible potentials from one experiment to another and the variation in potential during the course of the electrolysis made it clear that in seeking a relation between overvoltage and reduction efficiency, the potential and the reduction must be concurrently determined.

Potassium chlorate was chosen as the reducible substance for this study: (1) because it affords an easy, accurate determination of the reduction accomplished (by gravimetric analysis for chloride) and (2) because the diffi-

culty of the reduction would preclude marked changes in concentration which might obscure an existent relationship between the cathode potential and the current efficiency.

The chlorate was of technical quality (Merck), recrystallized 5 times. It then showed no trace of chloride. A solution was made up with redistilled water, approximately half-molar; the exact concentration was 0.493 Molal.

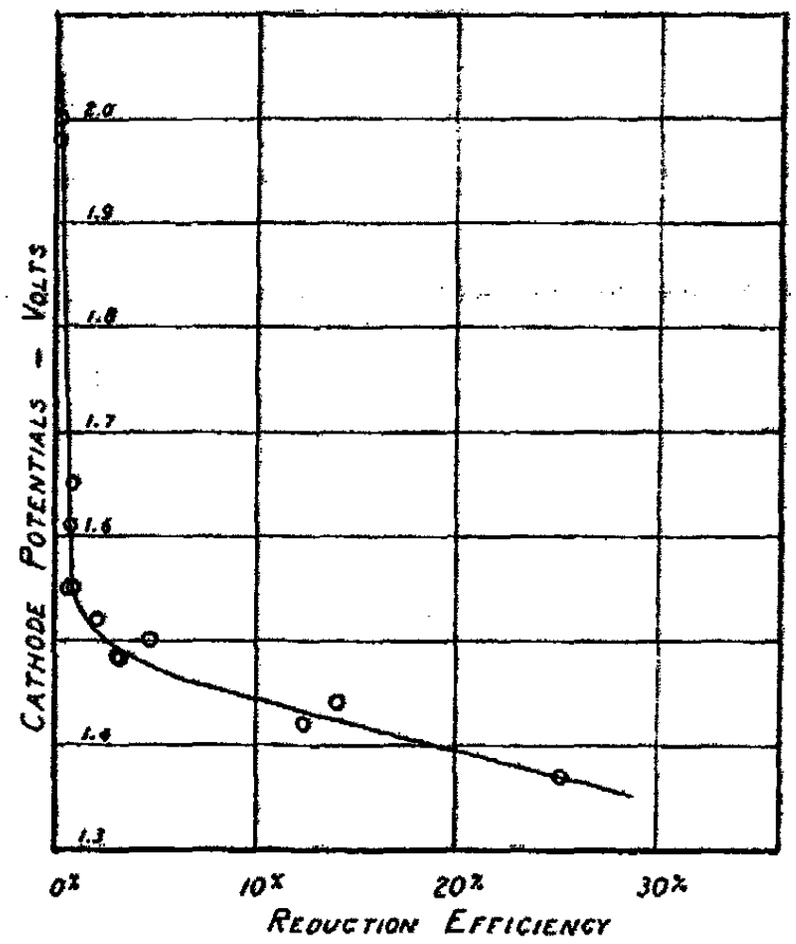

FIG. 3

Potential-time curves for Ag, Cu, Ni, Fe, Al, Sn, Zn, Cd, and Pt were observed over 5-hour periods during the electrolysis of (approximately) 200 c.c. portions of this solution under a uniform current of 0.30 amp. and the efficiency of the concurrent reduction was determined. In general, the potentials exhibited less variation with time in chlorate solution than in acid. The current efficiency was calculated on the basis of the equations

$$KClO_3 = KCl + 3\,O$$
$$Cl^{+++++} + 6\,e = Cl^-$$

One ampere-hour is then equivalent to 0.2204 g. of chloride. The chloride found, divided by 0.2204 g., equals the efficiency.

The results of these experiments are summarized in Table I and also presented graphically in Fig. 3. The cathode potentials are averages over 5 hours, and the reduction efficiencies found experimentally with cathodes of

different areas are for easy comparison calculated to the corresponding efficiencies with a uniform area of 10 sq. cm.[1]

TABLE I

Cathode Metal	Current Density Amp./sq. cm.	Cathode Potential	Current Efficiency
Fe	0.0125	1.37	25.35%
Cu	0.025	1.42	12.55%
Fe	0.025	1.44	14.20%
Ag	0.0118	1.48	3.36%
Ag	0.025	1.485	3.23%
Cu*	0.0125*	1.50*	4.85%*
Ni	0.025	1.52	2.66%
Cu	0.0118	1.55	1.02%
Ni	0.0118	1.55	0.67%
Pt	0.032	1.61	0.78%
Cd	0.25	1.65	0.89%
Sn	0.0125	1.98	0.16%
Zn	0.0118	2.00	0.21%

* The polarizing current was 0.10 Amp. and 1/2 ampere-hour passed in this experiment.

The data show that when the potential of the cell: test electrode-calomel electrode exceeds 1.5 volt the electrolytic reduction is negligible, and that reduction occurs the more readily, the more the potential falls below this value.

Two other studies were carried out in an endeavor to throw some light upon the mechanism by which overvoltage occurs, and to correlate this mechanism with the process of reduction. The first of these consisted of a series of experiments on the catalytic reduction of potassium chlorate solution at room temperature by means of hydrogen in the presence of finely divided platinum.

Portions of platinum black were uniformly prepared by reduction of 1.0 gram samples of platinic chloride with magnesium powder and hydrochloric acid. Hydrogen gas, passing through a purification train of alkaline permanganate, alkaline pyrogallol, saturated mercuric chloride, and twice through redistilled water, was bubbled through measured volumes of well-stirred 0.493 M. $KClO_3$ in the presence of the catalyst for definite periods of from 4 to 28 hours, and the resulting chloride determined.

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[1] The data for aluminum are omitted from the table as a secondary phenomenon, i.e., solution of the cathode, intervened. In two experiments, apparent efficiencies of 53.78% and 77.21% were obtained at about 1.34 volt and 1.32 volt respectively. Corrected for the aluminum dissolved from the electrode, on the supposition that

$$2\,Al \rightleftharpoons Cl^-$$

these values were reduced to 21.42% and 26.25% resp. Cf. Lloyd: Trans. Faraday Soc., 26 .15 (1930).

The reduction appeared to follow the law for unimolecular reaction processes.[1]

Another approach to the problem consisted of a study of decomposition potentials. These were measured by determining the break in the curve obtained by plotting the applied E. M. F. against the current.[2]

The anode was a square of bright platinum foil, 1 × 1 × 0.02 cm. with a platinum lead sealed into a supporting glass tube containing mercury for electrical contact. The platinum cathode was made identically; cathodes of other metals were formed from polished strips 1 cm. wide and of convenient length, insulated so as to leave 1 sq. cm. exposed. The decomposition potential curves for N/10 H_2SO_4, 0.493 M. KCl, and 0.493 M. $KClO_3$ were determined, using this platinum anode and cathodes of Pt, Cu, Fe, Ni, Al, Ag, and Sn arranged parallel and opposite at a distance of 4 mm. The observations were made according to a methodical, timed procedure, so that errors introduced by polarization phenomena at potentials above the decomposition potential were comparable among the several experiments.

The curves for platinum and iron given in Fig. 4 are typical of the results.

It was observed that the breaks in the decomposition curves for sulfuric acid occurred at increasing potential in the order of the metals: Pt, Fe, Ag, Cu (and Ni the same as Cu), and Al; in accord with the order of arrangement of increasing cathode potential in the same electrolyte. Likewise, the breaks in potassium chlorate agreed with the magnitude of the overvoltage: Fe, Cu and Ni, Ag, Pt, Sn—with Al in doubt.[3]

When the curves for potassium chloride were compared with those for chlorate for each cathode, another parallelism appeared. With a platinum

[1] Saturation of the solution with hydrogen gas must have been accomplished in a relatively negligible time. The rate of formation of active hydrogen capable of effecting reduction from the ordinary inactive molecular form would therefore depend upon the superficial area of the platinum. The rate of reaction should depend upon the probability of collision between a molecule of the reducible body and the catalytic surface, and therefore upon *its* concentration alone.

The reductions obtained with different samples of catalyst were rather variable, and the reaction constant K obtained in a series of experiments with the same catalyst likewise varied to a considerable extent. The value of K increased quite irrespectively of the value of t in the formula

$$K = 1/t \cdot \log \frac{a}{a - x}$$

but fairly steadily with the length of its use. Thus K at first increased about 1% per hour and later less rapidly for perhaps 60 hours, and then decreased, falling to about 2/3 of its initial value in another 40 hours.

This behavior was attributed to two causes: (1) that mechanical agitation in the course of a series of reduction experiments increased the area of the catalyst by breaking down clots of platinum black into smaller aggregates, enhancing the activity; and (2) that traces of impurity failing of removal from the hydrogen stream or introduced by successive additions of chlorate solution were adsorbed, depressing the activity. The initially preponderant dispersion phenomenon must approach a limit and the cumulative nature of the poisoning eventually decrease the reaction rate.

[2] Allmand: "Principles of Applied Electrochemistry," 112 (1920).

[3] The curve with aluminum really consisted of three parts: an initial portion of slop about 1.8 ma./volt; an intermediate slope of about 3.5 ma./volt beginning about 0.5 vol below the sharp break in the curve; and a final slope of about 230 ma./volt. The formation of $Al(OH)_3$ was observed over the intermediate portion of the curve, and solution of the electrode was rapid at higher E.M.Fs. If the second break marks the decomposition potential aluminum probably belongs between platinum and tin.

cathode, the curve for KCl broke at a lower potential than that for $KClO_3$, and so generally with the other metals. Iron proved an exception; and iron appeared to be the only metal capable of the reduction of chlorate with any marked degree of efficiency.

What appeared to be of more importance was that the difference in *E. M. F.s* between the decomposition potentials of H_2SO_4 and $KClO_3$ with

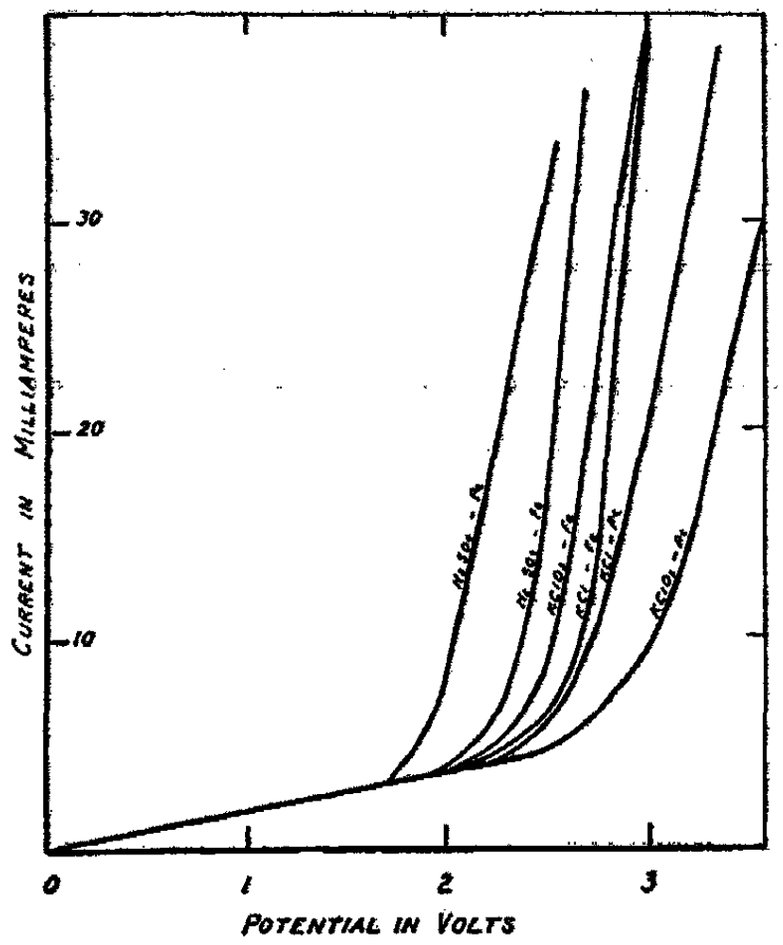

FIG. 4

the same cathode became progressively greater in the order of the metals: Fe, Cu and Ni, Pt, Sn. It was questionable whether silver should precede or follow platinum; and the position of aluminum was doubtful, but the order of magnitude of the increment of E. M. F. certainly placed this metal as more nearly allied to iron than to tin in its behavior.

Discussion

Of the various hypotheses which have been devised to explain what is taking place when an overvoltage occurs, the conception that the effect is due to the slowness with which monatomic hydrogen is converted into molecules seems most reasonable.[1] The theory supposes that metals of high overvoltage, possessing in a large degree the property of rendering difficult the escape of hydrogen gas from the cathode, will as a rule be capable of electrolytic reductions which are not produced by cathodes of lesser overvoltage.[2]

[1] Tafel: Z. physik. Chem., 50, 641 (1905); Lewis and Jackson: Proc. Am. Acad., 41, 399 (1906); Bennett and Thompson: Trans. Am. Electrochem. Soc., 29, 269 (1916).

[2] Tafel and Neumann: Z. physik. Chem., 50, 713 (1905); Böhringer: Z. Elektrochemie, 12, 745 (1906); Chilesotti: 12, 146, 173, 197 (1906).

To explain anomalies, it has been suggested that other factors involved may mask the relation between hydrogen overvoltage and reducing power, e.g.: that one substance may be adsorbed at one cathode more easily than at another, so that the effective concentrations are changed, and conversely; that the electrode may act as a catalytic agent on the reaction; or that apparently inert substances in the electrolyte may modify the overvoltage.[1]

It does not appear to follow necessarily that a high concentration of monatomic hydrogen associated with large overvoltage implies a high reduction efficiency, save that it is the usual case. It was long since pointed out[2] that the activity of nascent hydrogen is intimately related to the nature of the reaction whence it originates, and it may be supposed that hydrogen *in statu nascendi* is monatomic hydrogen associated with a certain energy content varying with its mode of formation. That nascent hydrogen is the active agent in the reduction of chlorate seems evident from the experiments on catalytic reduction[3] while it appears from the decomposition potential measurements that the energy associated with the hydrogen atoms set free at the several electrodes must be greater in the order of the metals Fe, Cu and Ni, Ag?, Pt, Sn; i.e., in the order of the cathodes producing increasingly greater overvoltages and effecting less and less reduction in potassium chlorate solution.

The relative stability of hydrogen atoms in the gaseous phase lends weight to the hypothesis that their recombination into molecules involves a three-body collision.[4] If it is supposed that evolution of gas involves a comparable collision between hydrogen and hydrogen; and reduction a collision between hydrogen and chlorate at the cathode surface; the experimental facts appear to indicate that only *slow* or *cold* atoms can act as reductors. It has been noticed that close resonance is of importance for the transfer of energy among atoms and molecules involved in collision[5] in another field of study, and it is suggested that the application of the resonance principle is equally applicable in this connection.

Summary

An apparatus is described by which cathode potentials can be determined during electrolytic reduction without contamination of the electrolyte.

The efficiency of electrolytic reduction of aqueous potassium chlorate is negligible when the cathode potential exceeds 1.5 volt, and increases rapidly as the potential falls below this value.

Electrolytic reduction, catalytic reduction by hydrogen gas in the presence of platinum black, and decomposition potential measurements all point to the same conclusion as to the reaction mechanism.

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[1] Müller: Z. anorg. Chem., 26, 1 (1901); Müller and Weber: Z. Elektrochemie, 9, 955 (1903); Taiel and Emmert: Z. physik. Chem., 52, 349 (1905).

[2] Tommasi: Chem. News, 40, 245 (1879); 41, 1, 176 (1880); J. Phys. Chem., 1, 555 (1897).

[3] Hoitsema: Z. physik. Chem., 17, 1 (1895).

[4] Wood: Proc. Roy. Soc., 102A, 1 (1922); Herzfeld: Z. Physik, 8, 132 (1922).

[5] Cario and Franck: Z. Physik, 11, 161 (1922); Beutler and Josephy: Naturwissenschaft, 15, 540 (1927).

THE MECHANISM OF PLASTIC FLOW

BY G. E. CUNNINGHAM

The investigation discussed in this paper is an effort to arrive at some conclusion as to the fundamental difference or differences between the mechanisms of plastic and viscous flow, with particular reference to the plastic flow of clay pastes.

Most of the previous studies on the subject of plastic flow have been made by means of measurements of the rate of flow of the plastic material through capillaries of different dimensions and under different pressures. According to one theory,[1] the relation between the velocity of flow and the pressure is parabolic and may be expressed by the equation

$$V = k \cdot P^n$$

where k and n are constants for the given material. The Bingham theory[2] states that the velocity of flow is a linear function of the pressure and may be expressed by the equation

$$V = k(P - p)$$

where k and p are constants, p being the pressure required to start the flow, or the yield value. Unfortunately, neither of these theories is directly applicable unless the experimental data are obtained under "ideal" conditions.

The Bingham theory has proved useful in the study of slips and thin pastes, but it is well known that the deviation from the linear relationship not only is apparently much greater with some substances than others, but increases with the concentration of the solid phase in the mixture,[3] as one approaches the concentrations of the plastic state. Where experimental results have deviated but little from the ideal, corrections have been suggested to account for plug flow,[4] seepage and slippage,[5] proximity of a solid wall[6] and elastic deformation.[7] *The deviation has also been attributed to a change* in the consistency of the slip at high velocities of shear.

Schofield and Scott Blair[8] forced a clay paste through a metal tube which had a very small opening in the side for collecting a sample of material from

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[1] cf. Ostwald et al: Kolloid-Z., 36, 99, 157 (1925); 38, 261 (1926); 43, 190 (1927); 47, 176 (1929).

[2] Bingham: "Fluidity and Plasticity," 217 (1922); Wilson: "Ceramics,—Clay Technology," 56 (1927).

[3] Cf. Green: Proc. Am. Soc. Testing Materials, 20 II, 451 (1920).

[4] Buckingham: Proc. Am. Soc. Testing Materials, 21, 1154 (1921); Reiner: Kolloid-Z., 39, 80 (1926); Scott Blair and Crowther: J. Phys. Chem., 33, 321 (1929).

[5] Bingham: "Fluidity and Plasticity," 231 (1922).

[6] Scott Blair: J. Phys. Chem., 34, 248, 1505 (1930).

[7] Bingham and Robertson: Kolloid-Z., 47, 1 (1929).

[8] J. Phys. Chem., 34, 259 (1930).

the layer next the wall. No difference in the concentration of the paste was found, although quite an appreciable difference would have been required to account for the deviation from the linear relationship at low rates of shear.

H. E. Phipps[1] determined the viscosity of cellulose acetate by both the capillary and the falling sphere types of viscosimeter, in the latter case using a series of spheres of the same size but different densities. Notwithstanding the marked difference between the methods, the curves were found to coincide over the curved portion at low shearing stresses.

Bingham[2] states that "polar" colloids exhibit the curvilinear relationship at low rates of shear, but "non-polar" colloids do not. However, clay was classed as a non-polar colloid and numerous examples may be cited (cf. Fig. 1) in which clay has exhibited the non-linear relationship. In another paper,[3] the same author states the theory, credited to F. Williamson, that the "apparent fluidity" of polar colloids is a linear function of the shearing stress.

It has been frequently recommended[4] that workers avoid difficulty by choosing the conditions of slip concentration, capillary dimensions and shearing force to ensure the linear relationship. This procedure, however, avoids the region of the curve which is different in shape from the curve for ideal liquids and the data fit the equation best when the measurements are made on the material when it is not in the plastic condition. Since the mobility (slope of the straight line) supposedly depends upon both the inherent plasticity and the dilution, which are independent of each other, it is difficult to know just what dilutions to use in order to compare the plasticities of two different substances.

Hall[5] attempted to solve this difficulty by making up the slips to the concentrations required to give equal mobilities, i. e., equal slopes of the pressure-velocity curves in the region of the linear relationship. He found that the more plastic of the two clays showed much the greater yield value. In each case, the relationship between velocity and pressure is far from linear and smooth curves may be drawn through the origin which include more of the experimental points than do the straight lines. In fact, the logarithm curves are better straight lines than the pressure-velocity curves, indicating the applicability in this case of the parabolic equation. For the purpose of the present discussion, however, it is sufficient to point out that the relation is not entirely linear. (See Fig. 1). The curves are approximately parallel in the upper portion, however, and Hall was perhaps justified in assuming that he had equal mobilities.

If we consider that the rate of flow is an actual measure of the fluidity (or mobility) at all pressures and that there is a change in the mobility with increasing pressure, we see that in the case of these two slips, of which the

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[1] Colloid Symposium Monograph, 5, 259 (1927).

[2] J. Phys. Chem., 29, 1201 (1925); Colloid Symposium Annual, 7, 207 (1930).

[3] Colloid Symposium Monograph, 5, 222 (1928).

[4] Bingham: Proc. Am. Soc. Testing Materials, 21, 1158, 1169 (1921); "Fluidity and Plasticity," 222 (1922).

[5] J. Am. Ceramic Soc., 5, 352 (1922).

maximum mobilities are equal, the less plastic has the greater mobility at zero pressure and therefore the more plastic one undergoes the greater change in mobility before reaching the maximum.

Bleininger and Ross,[1] working with clay in the plastic condition, studied the relation between pressure and rate of flow through an orifice and found a curvilinear relationship. In apparent contradiction to the findings of Hall with thin slips, these workers found that, when each of the clays studied was made up to its maximum plasticity as judged by the working test, the pressure

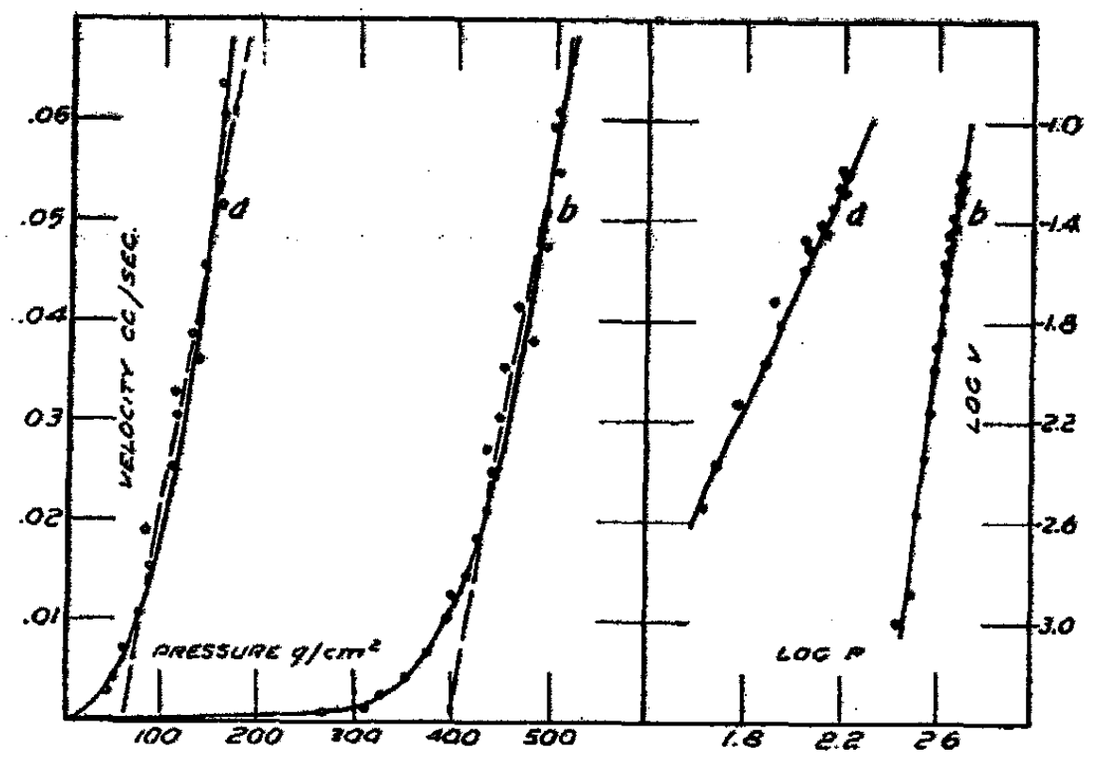

FIG. 1

Velocity of flow through a capillary.
(a) English China Clay, (b) English Ball Clay.
After Hall (loc. cit.)

required to produce a given rate of flow was least with the most plastic clay and the others came in exact order of decreasing plasticity. These results seem to indicate that the more plastic the clay the less the pressure required to reduce its resistance to flow at a given value. Their investigation is considered of importance in this connection because their method duplicated the flow of clay through a die; and approximated the conditions of the potter's wheel more closely than does the flow of a slip through a capillary.

If consideration be given to the possibility that plasticity is related to a change in viscosity with pressure, further consideration must be given to the possibility of, and reasons for, such a change.

It is common knowledge that pastes of clays and also of other materials "break down", or become fluid, with repeated working.[2] It is also well known among clay workers that a column of clay exuded through a die

[1] *Trans. Am. Ceramic Soc.*, **16**, 392 (1914).
[2] Cf. Hatschek: Kolloid-Z., 13, 88; Bergquist: J. Phys. Chem., 29, 1264 (1925).

appears to be wetter than the same clay before pressing. J. W. Mellor[1] has shown that the amount of water required to wet a clay to maximum stickiness decreases with increasing pressure. For an earthenware body, the amount of water required was 26.4 per cent at atmospheric pressure and only 5.6 per cent at 200 kilograms per square centimeter. Hind[2] states that Mellor's data may be expressed by the equation

$$A = 2.78 + 0.00437\ P^{3/2},$$

where A is the ratio of clay to water and P is the pressure in the above units.

On a basis of the above discussion, it does not seem unreasonable to assume that plasticity of a clay paste may be associated with a decrease in resistance to flow under the influence of pressure, caused by an increase in the actual liquid phase at the expense of adsorbed liquid or by a redistribution of the water in the gelatinous phase. If there were a coagulation of part of the gelatinous material in a clay paste under the influence of pressure, the water liberated would either remain between the particles of clay as free, lubricating, liquid or be taken up by the uncoagulated colloid, thereby producing a thinner gel.

Experimental

I. Relation of the Water Content of a Clay Paste to the Precipitating Centrifugal Force.

The water given up by the coagulated material is to be considered as at least momentarily free, as there is no other way to account for the phenomenon of seepage. In order to measure the quantity of water set free, seepage was purposely induced under varying pressures and the concentrations of the resulting pastes were determined. The following method of procedure was employed:

Approximately ten-gram samples of dry, pulverized clay were placed in weighed 30-cc. test tubes, the tubes then being filled to about two-thirds their depth with distilled water and shaken vigorously. After standing over night, the suspensions were shaken again and then centrifuged for thirty minutes at different speeds. The supernatant liquid was then poured off and the tubes were wiped dry, inside and out, and weighed. They were then dried to constant weight[3] at 125° C., and the ratio by weight of water to clay was calculated for each paste.

The rheostat by which the speed of the centrifuge was regulated was so designed that the setting of the dial was proportional to the centrifugal force, i. e., to the square of the angular velocity. The manufacturer's calibration was checked for the dial settings used and found to be correct. The

[1] Trans. Ceramic Soc. (England), 21, 91 (1921-22).

[2] Trans. Ceramic Soc. (England), 29, 177 (1930).

[3] In order to prevent the steam generated at the beginning of the heating from forcing the plug of clay out of the test tube, a weighed wick of rolled filter paper was forced to the bottom of the tube by means of a stiff wire. All weighings were made on a trip balance to the nearest 0.05 g.

diameter of the centrifuge at the tips of the tubes was 39 cm. and the maximum speed was about 3,000 r. p. m., giving a relative centrifugal force of about 2,000 times gravity.

The data obtained for the variation of the water content of several different clays with centrifugal force are given in Table I and plotted in Fig. 2.

TABLE I

Relation of the Water Content of Clay Pastes to Centrifugal Force

Rheostat setting	Ratio of water to clay: Experimental values				Average
Florida kaolin					
5	1.250	1.226	1.231		1.24
10	0.900	0.830			0.87
15	0.735	0.770			0.75
20	0.715	0.740			0.73
Kentucky ball clay					
5	0.974	1.000			0.99
10	0.815	0.785			0.80
15	0.645	0.715			0.68
20	0.654	0.644	0.667		0.65
Scranton, Iowa, clay					
5	0.604	0.600			0.60
10	0.615	0.596			0.60
15	0.594	0.562			0.58
20	0.564	0.534			0.55
North Carolina kaolin					
5	0.548	0.575	0.590	0.566	0.57
10	0.524	0.520	0.552	0.560	0.54
15	0.526	0.528	0.512	0.515	0.52
20	0.512	0.540	0.532	0.514	0.52
Pulverized grog					
5	0.429	0.451			0.44
10	0.452	0.430			0.44
15	0.453	0.447			0.45
20	0.452	0.438			0.44
Scranton, Iowa, clay + grog, 1:1					
5	0.568	0.590	0.606	0.597	0.59
10	0.531	0.544	0.569		0.55
15	0.438	0.465	0.491		0.46
20	0.421	0.444	0.504		0.45

It is interesting to observe that curve (e), Fig. 2, was obtained with a mixture of equal parts by weight of the materials used for curves (c) and (f), respectively. The curve for the mixture lies between the other two, but approaches the curve for the more plastic ingredient at low speeds and the other at high speeds.

The method was found to be inapplicable for clays of high colloid content (extremely "fat" clays) because the high centrifugal force necessary for complete precipitation did not leave a sufficient working range.

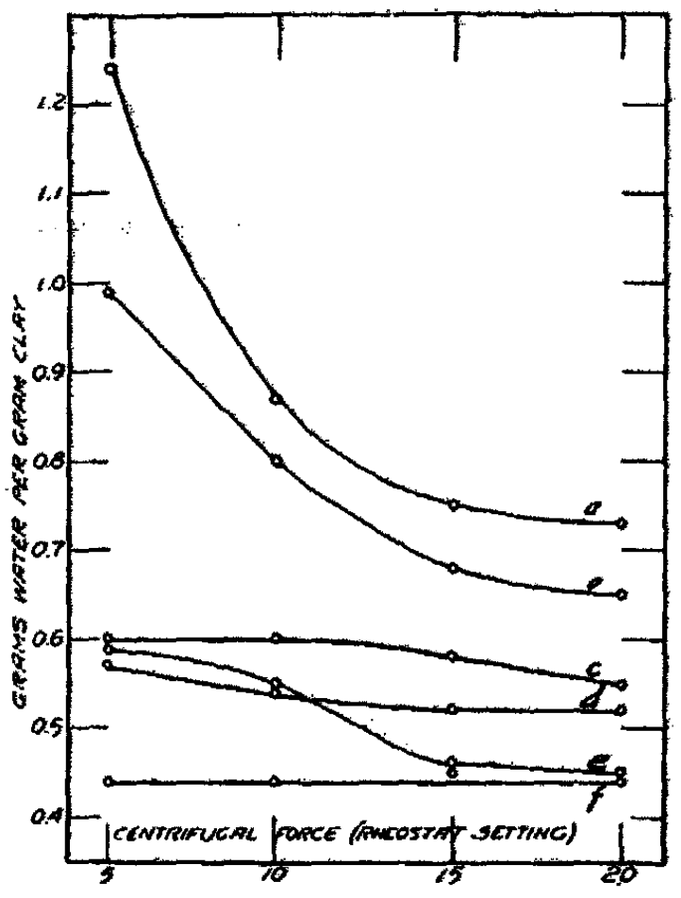

FIG. 2

Centrifugal force (rheostat setting)

Relation of water content of clay pastes to centrifugal force. (a) Florida kaolin; (b) Kentucky ball clay; (c) Scranton, Iowa, clay; (d) North Carolina kaolin; (e) Scranton, Iowa, clay + pulverized grog, 1:1; (f) pulverized grog.

It will be noted that some of the curves are concave upwards and others concave downwards, while one is an inflected curve showing bends in both directions and the non-plastic material, powdered grog, shows a constant water content. It is probable that, if one could work over a sufficient range of centrifugal forces, all the curves for the plastic materials would show the inflection. It is to be expected that if the pressure influences the extent of gelation at all, the effect occurs between two limiting pressure values.

II. Effect of External Pressure upon the Rate of Flow through a Funnel.

As a preliminary experiment, in order to ascertain whether pressure, independent of shearing force, exerted any effect upon the consistency of clay

slip, a thick slip was poured into a Gooch funnel having a stem bore of about 7 mm. and the funnel was entirely enclosed in a vacuum desiccator. The lid was clamped on the desiccator and the time between drops of slip flowing through the funnel under its own head was determined in vacuo, at atmospheric pressure and at about three pounds per square inch above atmospheric pressure.

A marked decrease in the rate of flow was observed as the pressure decreased. During the first trial, however, bubbles of entrapped air expanded to considerable size in the stem of the funnel at low pressures and it was feared that they might be contributing to the retardation in the rate of flow. The experiment was therefore repeated with a slip which had been boiled to expel entrapped air, and the effect of a change in pressure was found to be even greater than before. As an extreme case, the time between drops was $4\frac{1}{2}$ minutes in vacuo (water pump), 25 seconds at atmospheric pressure and 15 seconds at three pounds per square inch above atmospheric pressure.

III. Effect of External Pressure on the Mobility of Clay Pastes as determined in the Torsion Viscometer.

In order to make more accurate measurements of the effect of applied pressure on the mobility of clay pastes, the following apparatus was constructed:

A rectangular[1] box was made of sheet steel, of the correct dimensions to conveniently enclose a MacMichael torsion viscometer of the standard type. The viscometer was set permanently on the bottom, and the remainder of the box could be lifted away for filling and adjusting the viscometer, by means of a rope and pulley. When in place, the box was fastened to the bottom piece by means of bolts placed $1\frac{1}{2}$ inches apart, the joint being sealed with a rubber gasket. The box was provided with an accurate pressure gauge and with stopcocks for the inlet and outlet of air. Electrical contacts for the viscometer motor and a 10-watt light were made through the bottom by means of brass screws passing through fibre washers. The speed-regulating screw on the gearing mechanism was turned to give the highest possible speed, and the speed of the motor was then regulated by means of a rheostat placed outside the box. A plate glass window in one side of the box facilitated observations of the angular velocity of the cup, and another in the top made it possible to read the angle of twist imparted to the wire.

The cup used had an inside diameter of 7 cm. and the plunger was a brass cylinder 1 cm. in diameter.

With stiff pastes, particularly of lean clays, it was not possible to center the plunger of the viscometer with sufficient accuracy to prevent some sideway as the cup was rotated. This did not cause rotational oscillation in the torsion wire, but it caused the clay to work away from the plunger and the effect was increased at higher pressures. The difficulty was practically

[1] For work at very high pressures, it would be desirable to have the box cylindrical in shape. This was not done in the present case because of the additional weight and volume entailed.

obviated by wrapping a single layer of sixteen-mesh copper gauze around the plunger. In order to prevent the paste from drying out during a series of observations, a beaker of water was placed inside the box to keep the air saturated with moisture.

It will be seen that, with this method of procedure, the applied pressure is independent of the shearing force. Readings being made at a constant velocity of rotation, the rate of shear is kept constant; and the shearing force, measured by the twist in the wire, actually diminishes with decreasing resistance to shear.

Preliminary trials were made with moderately thick pastes, running the motor continuously and varying the pressure in steps of ten pounds per square inch. A marked decrease in the resistance to flow with increasing pressure was indicated but it was found impossible to obtain checks with a given sample. This difficulty was attributed to the probability that the effects of both the shearing force (local pressure) and the external pressure were not completely, or at least immediately, reversible.

Accordingly, the published data were obtained by making only one run with a given sample, checks being obtained by using another sample of the same composition. The pressure was increased in steps and readings were taken at a constant rate of shear at five-minute intervals until two consecutive equal readings were obtained, the motor being stopped between readings. The velocity of rotation was 10 to 20 r.p.m., depending upon the stiffness of the paste. The time for equilibrium was 45 minutes to 1 hour at $2\frac{1}{2}$ pounds pressure, for the thickest pastes, decreasing to about 10 minutes at 40 pounds. The greater part of the change always took place within the first 5 to 10 minutes and equilibrium was reached much more quickly with thin pastes than with thick ones.

The thinnest of the pastes used were sufficiently thick to retain an unevenness in the surface over a period of several hours but were thin enough to pour, very slowly. The majority of them were thick enough to retain their shape indefinitely and the stiffest ones were not diluted much beyond the range of optimum workability, from the potter's point of view.

Each of the thinner pastes was made up by adding water to a previously unused portion of the thickest one. Each paste stood in a vacuum desiccator, which contained water instead of desiccating agent, for several hours before being used, for the purpose of removing entrapped air. There is, of course, the possibility that at high pressures air would redissolve in the paste and change the viscosity, but water so readily displaces adsorbed air from clay particles, and with the evolution of so much heat, that it is not likely that this source of error was very great. At most, it could account for only a small per cent of the observed effect of the pressure.

For the purpose of plotting, each of the mobilities at higher pressures was reduced to the fraction of the mobility at atmospheric pressure. In other words, the points plotted are reciprocals of the twist in the wire, the reading at atmospheric pressure being taken as unity. It is to be remembered that, while the initial readings are all given a value of one, the actual mobilities

of the pastes increased with increasing dilution at all pressures. No effort was made to compare the mobilities of the different pastes quantitatively for the reasons that different wires, whose relative constants were not known, had to be used for different pastes, and it was not convenient to fill the cup to the same depth for each run, particularly with the stickier pastes. The wires used ranged from No. 17 Brown and Sharpe gauge piano wire to the No. 30 wire supplied by the manufacturers of the viscometer.

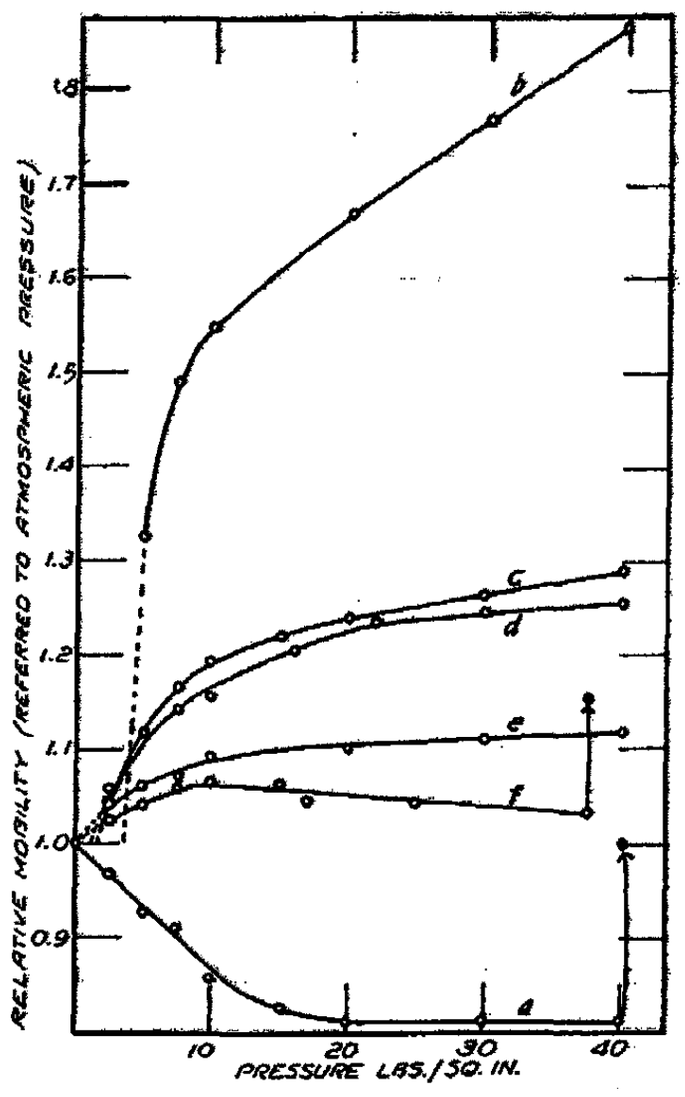

FIG. 3

Effect of pressure on the mobility of pastes of Kentucky ball clay; ratios of water to clay as follows: (a) 0.63; (b) 0.84; (c) 0.99; (d) 1.01; (e) 1.31; (f) 1.67. Solid circles: readings taken at atmospheric pressure immediately after pressures plotted.

Figs. 3 and 4 give the data obtained with pastes of Kentucky ball clay and North Carolina kaolin, respectively, pressures being plotted as abscissae and relative mobilities as ordinates. The ball clay is fat and plastic, while the kaolin is quite lean and possesses very little plasticity from the potter's point of view.

IV. Differential Effect of Pressure on Internal Friction.

The increase in the resistance to flow at low, and again at high, pressures may be attributed to a differential friction effect due to pressure before the

increase in the liquid phase begins and again after it is complete. In Fig. 3, the points indicated by the solid circles are for readings taken at atmospheric pressure immediately following the reading at the pressure plotted. The inference was made that, while the differential friction effect is immediately

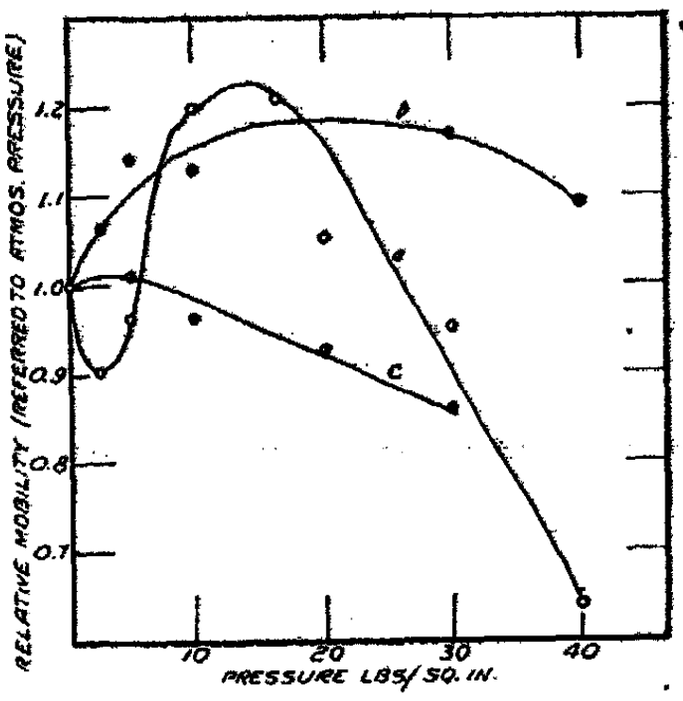

FIG. 4
Effect of pressures on the mobility of pastes of North Carolina kaolin; ratios of water to clay as follows: (a) 0.44; (b) 0.52; (c) 0.60.

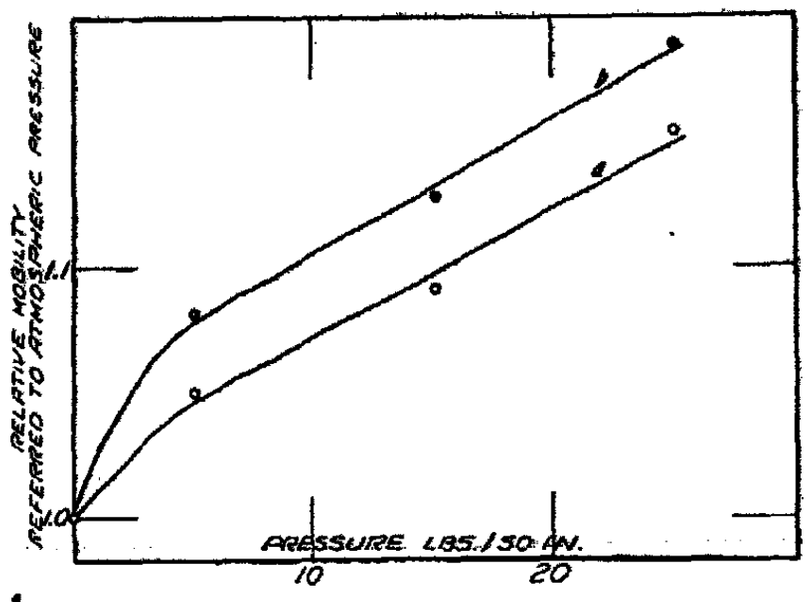

FIG. 5
Kentucky ball clay. (a) Values at pressures plotted; (b) values at atmospheric pressure immediately following pressures plotted.

reversed upon the removal of the applied pressure, the coagulation effect is not. Accordingly, runs were made in which the procedure was modified by following each differential pressure reading with a reading at atmospheric pressure, it being hoped in this way to trace the magnitude of each effect throughout the range of pressures studied. Fig. 5 shows the results of one

such attempt with a very thin paste. The curve for the readings at atmospheric pressure falls above the curve for the readings at the increasing pressures. With thicker pastes, the experiment was unsuccessful, the atmospheric pressure curve coinciding with or even falling below the other. This is not to be interpreted as meaning that the differential friction effect was negative, which would be absurd, but rather that the reversibility of the liquid-gel change more than offset the decrease in internal friction when the pressure was released. The values at atmospheric pressure invariably decreased with time, and the readings therefore had to be taken as quickly as possible. Even in Fig. 5, the points on the upper curve probably are too low to give an exact indication of the magnitude of the friction effect.

Discussion of Results

It might, of course, be argued that the results of the experiments with the centrifuge do not prove the theory that water would be liberated under the influence of pressure in the absence of conditions which permitted seepage and consequent shrinkage in volume. However, they are exactly what one would expect if the theory were true. Moreover, there is no other obvious way to explain the decrease in the resistance to flow of the clay pastes when pressure was the only variable condition and seepage and breakdown of the gel structure due to shear were eliminated. (It will be recalled that the cup of the viscometer was not in motion except while readings were actually being made, and the recorded increases in the mobility took place between readings.) If there were simply a breakdown of gel structure due to contraction under pressure, the viscosity at a given pressure would be expected to increase with time as the gel had a chance to reset in its new position. There was no indication of the latter phenomenon.

Let it be assumed, therefore, that a symmetrical inflected curve is the ideal for the relation of free water content to pressure, any water which has been liberated being regarded as free water whether it has been taken up by other portions of the colloid or not, for the sake of convenience in the discussion. The P-W curve then takes the shape indicated in Fig. 6 (a), where P is the pressure and W is the content of free water. Plotting dW/dP against P then gives a curve of the shape of the theoretical probability curve as indicated in Fig. 6 (b). This is probably related to the quantity distribution of the increments of gel-forming material with regard to their swelling power. Conversely, of course, the amount of liquid phase present at any pressure is given by the area of the probability curve up to that pressure. Fig. 6 (b) was plotted by letting $c = 1$ in the theoretical equation[1]

$$dW/dP = \frac{c}{\sqrt{\pi}} e^{-c^2P^2},$$

and then translating the origin to avoid negative values of P.

If the mobility at any pressure p, as measured in the torsion viscometer, is to be compared with the mobility at atmospheric pressure, it must be re-

[1] E. B. Wilson: "Advanced Calculus," 388 (1912).

membered that the internal friction is greater when there is a high contact pressure between the particles than it would be for the same liquid content at atmospheric pressure. The rate of change of internal friction with pressure, dF/dP, will be constant as long as there is no appreciable change in the amount of free water present, i.e., at pressures less than p_1 and greater than p_2 in Fig. 6, and would be expected to have a smaller value in the latter pressure range than in the former on account of the higher content of free

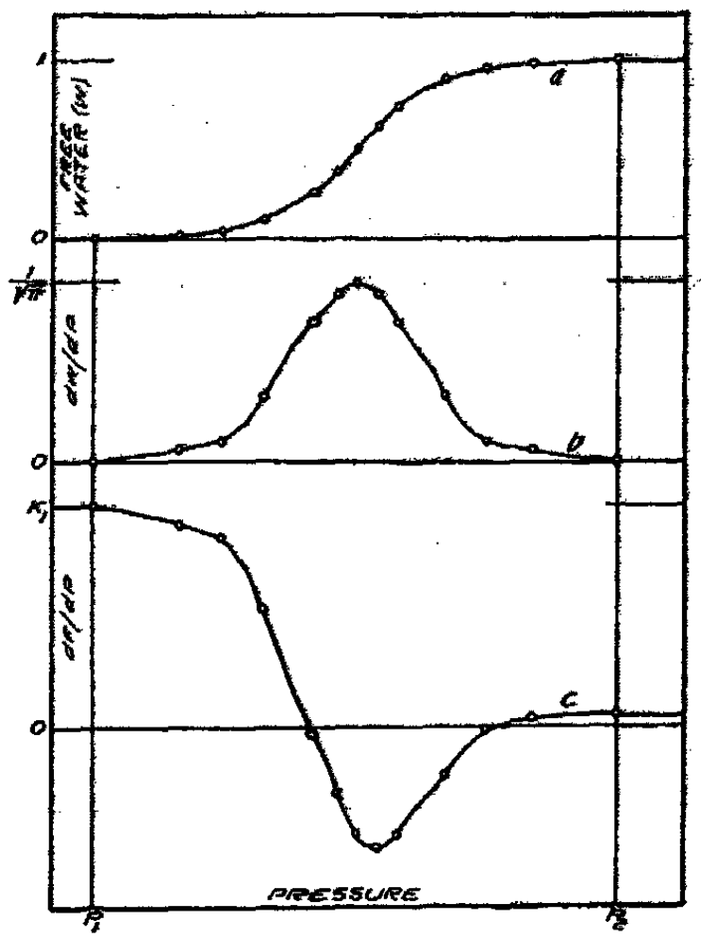

Fig. 6
Typical theoretical curves: (a) pressure-free water (P-W) curve; (b) P-dW/dP curve; (c) P-dF/dP curve (where F = internal friction).

liquid in the paste. At pressures between p_1 and p_2, the value of dF/dP will be dependent upon the values of both W and dW/dP. Let W be the water content at pressure p, and ΔF and ΔW be the changes in friction and in free water, respectively, between the pressures of p and $(p + \Delta p)$. ΔF will be smaller the greater the value of W, and also will decrease with increasing values of ΔW. The value of ΔW might even become so great as to give ΔF a negative value. However, the total effect of the pressure on the friction must be positive at all points, so that the negative area between the P-dF/dP curve and the pressure axis, Fig. 6 (c), must never exceed the positive area.

These conditions are satisfied by the equation

$$dF/dP = k + f(dW/dP) + \Phi(W),$$

and for the purpose of plotting the theoretical curve it has been assumed that

$$dF/dP = k_1 - k_2 \cdot dW/dP - k_3 \cdot W.$$

Curve (c), Fig. 6, was plotted by assigning to the constants the relative values $k_1:k_2:k_3 = 1:1:\frac{1}{2}$. Corresponding values of dW/dP and W were determined by estimating the area under the P-dW/dP curve, Fig. 6 (b).

It seems reasonable to assume that, neglecting the differential effect of pressure on the internal friction, the increase in mobility will be proportional to the increase in the amount of the lubricating liquid phase. On a basis of this assumption, the curve (M), Fig. 7, is obtained, in which the relative

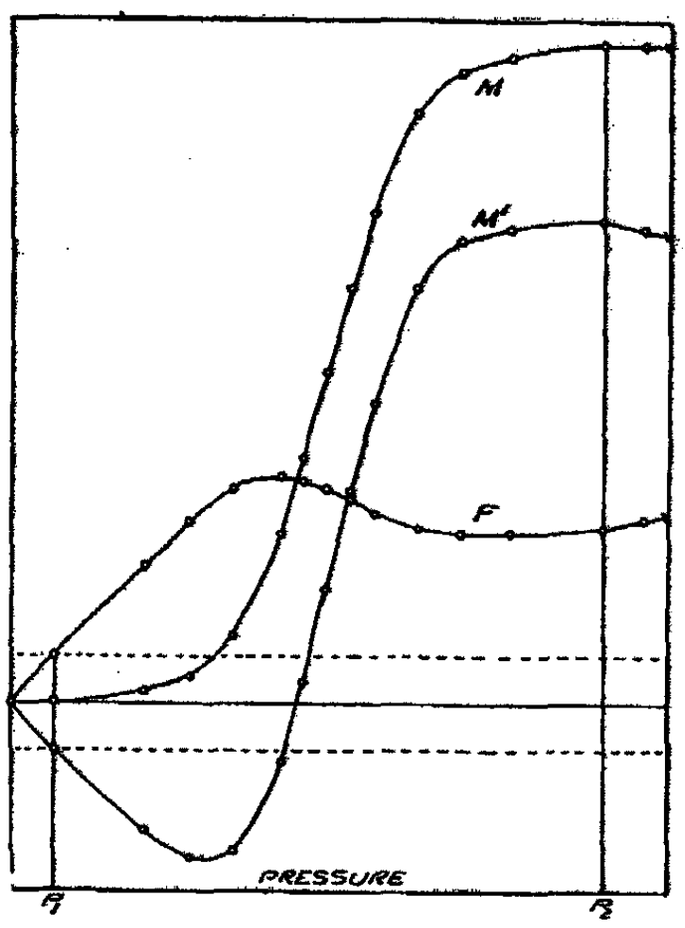

Fig. 7

Typical theoretical curves. (F) differential effect of pressure on internal friction; (M) effect of pressure on mobility, neglecting friction effect; (M') effect of pressure on mobility, allowing for friction effect. ($M' = M - F$).

mobility referred to atmospheric pressure (neglecting friction) is plotted against pressure. The total increase in the mobility at any pressure is proportional to the corresponding area in Fig. 6 (b). The same curve could, of course, be obtained by direct reasoning from the P-W curve, Fig. 6 (a).

The curve (F) in Fig. 7 shows the relation of the friction effect to the pressure. The value of the friction, F, at any pressure is given by the corresponding area under the P-dF/dP curve, Fig. 6 (c). A curve of the same general type could also be obtained by more direct reasoning: The relation between pressure and friction is linear in the regions where there is no change in the amount of liquid phase present, and the friction is less after the formation of free liquid has reached its limit than before it started. The two linear portions of the curve are joined by a smooth non-linear portion.

The net effect of the pressure upon the measured mobility is the difference between the two above mentioned effects, and gives a curve of the type M′, which is the difference between curves M and F.

The complete curve would be exhibited by a paste which contained no free water at the beginning, and in which the change was completed in the range of pressures studied. Curve (a), Fig. 4, is of this type. Curve (a), Fig. 3, is for a paste which contained no, or very little, free water at the beginning, but which did not give the complete change within the available increase of pressure.

Applying pressure has the same outward effect as increasing the water content of the paste, namely, that the degree of wetness is increased. It would be expected that those particles of clay, or better, perhaps, those incremental portions of gel which swell the least at atmospheric pressure would be the first to become saturated under the influence of increasing pressure. Therefore, regardless of whether the wetness is increased by adding water or by increasing the pressure, free water appears first in the same increments of gel. Therefore, if the paste contains free water at atmospheric pressure, the left-hand portion of the curves in Fig. 7 will disappear, the extent of the effect depending upon the amount of free water present. The effect of the free water formed as the result of the pressure will be relatively less, the greater the amount of free water already present. In other words, the integral effect of adding water to a clay paste is to cut off the left-hand portion of the P-M′ curve, and at the same time to expand the remaining portion of the curve in the direction of the pressure axis.

Curves (b), (c), (d), (e) and (f), Fig. 3, and (b) and (c), Fig. 4, give experimental justification of this portion of the theory. These curves, of course, approach the curve for pure water as the water content of the slip increases.[1]

The phenomena of flow through a capillary may also be explained on a basis of this theory. In a capillary viscometer, the bulk of the material is subjected to pressure within the bulb before entering the capillary. The material at the entrance to the capillary is under the applied pressure, but atmospheric pressure prevails at the exit. In other words, the flow is in the same direction as the application of pressure, so that the differential effect of the pressure on internal friction within the capillary itself is zero. For flow through a capillary, therefore, the mobility curve corresponds to the curve M in Fig. 7. It is seen that in its middle portion the curve is approximately linear, agreeing in this region with the theory of Williamson.[2] The velocity of flow, V, is proportional to both the mobility, M, and the pressure, P. Therefore,

$$V = C.M.P$$

where C is the proportionality constant arising from the constant factors in the Poiseuille equation. Since the effect of pressure is not instantaneous, there

[1] The viscosity of water also decreases under pressure, but at room temperature the decrease is only about one per cent for a pressure of 600 atmospheres. Cf. Bingham: "Fluidity and Plasticity," 139 (1922).

[2] loc. cit.

may be a time effect which would slightly alter the equation but would not influence the general shape of the curve. The greater portion of the material remains in the bulb under pressure for considerable time, and the pressure effect reaches its limit much more quickly with the thin pastes and slips such as have been almost universally used in the capillary type of viscometer than with the thicker pastes.

Fig. 8 shows two theoretical pressure-flow curves. Curve (a) was plotted by determining the value of P·M from the curve (M) in Fig. 7 and curve (b) was plotted from a similar P-M curve, not reproduced in this paper, obtained by substituting $c = \frac{1}{2}$ in the probability equation for the relation of dW/dP

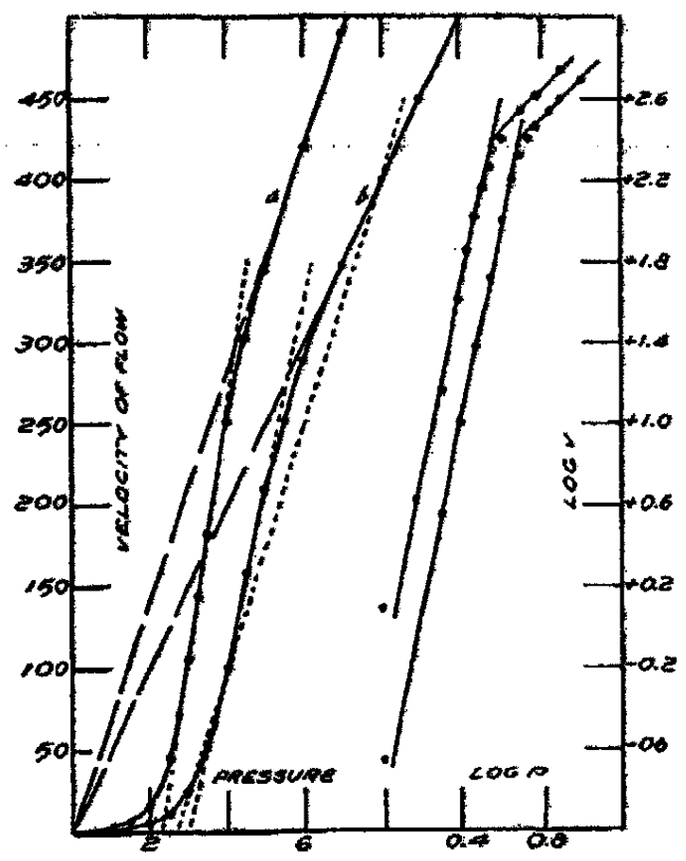

FIG. 8

Typical theoretical curves for flow through a capillary.

to P. It is seen that in each case a curve is obtained which approximates the letter S in the lower portion, but which terminates at the upper end in a straight line (where M becomes constant) which may be extrapolated through the origin. The logarithm curves show that, neglecting the very lowest points, one parabolic relationship holds for the portion of the curve which is concave to the left and another for the portion which is concave to the right.

The dotted lines indicate other portions of the curve which might easily be taken as linear in an experimental determination of points provided the points were taken within too limited a range or too far apart. Particularly in the middle portion of the S is the approach to linearity quite close and this fact, together with the fact the relation is parabolic through this region as well as through the curved portion preceding it, makes it seem likely that

it is the lower half of the S which has been the subject of controversy between the respective supporters of the parabolic and linear theories.

Two examples of data of other workers may be cited to illustrate the applicability of the theory. Curve (a), Fig. 9, was plotted from data obtained by Ostwald and Auerbach[1] using a one per cent gelatine solution and a burette type viscometer. The curve is exactly as those authors plotted it, except that approximately three-fourths of their points, all of which fall upon the curve within the limits of observation, are omitted. The curve has the exact shape of the theoretical curve except that in the extreme upper region there is a

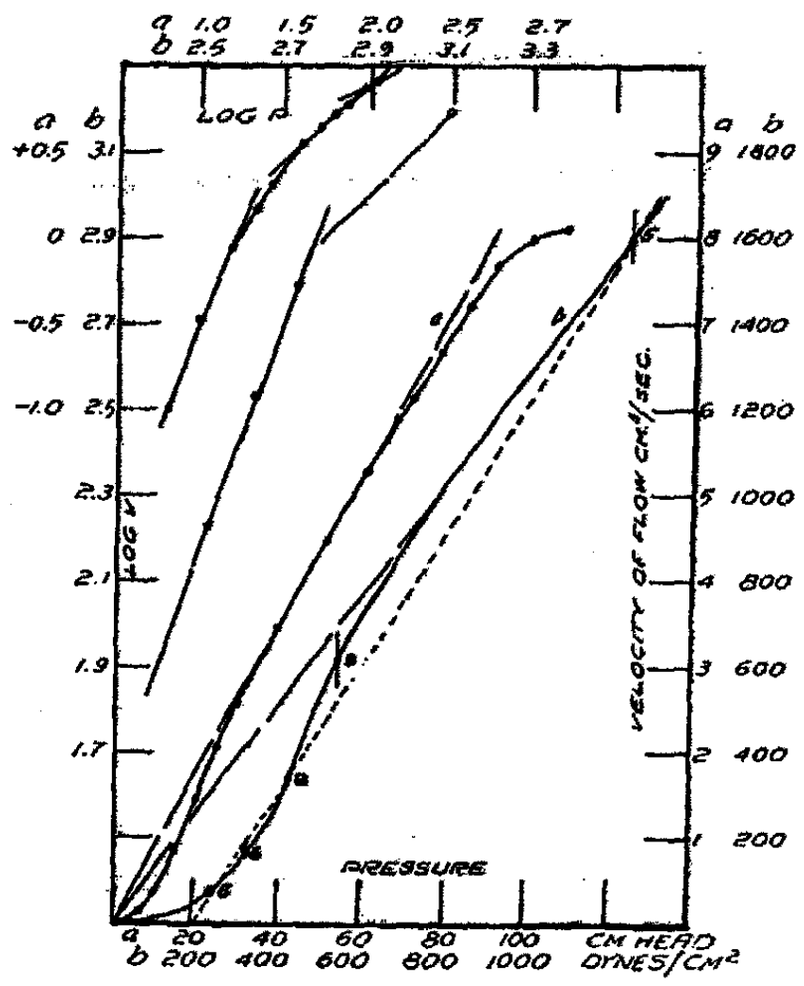

FIG. 9

Experimental curves for velocity of flow through a capillary. (a) One per cent gelatine solution, after Ostwald and Auerbach (loc. cit.); (b) 43 per cent ammonium oleate solution, from data of Bingham and Robertson (loc. cit.).

final curvature to the right. Ostwald assumes that the linear portion is the region of ideal flow, in which the material behaves as a true liquid. The S-curve is attributed by him to "structural" flow, that is, to the formation of clumps which are broken up by the consumption of energy from the shearing stress.[2] The curvature at the upper end of the straight line was attributed to turbulence in the liquid at high velocities of flow. Turbulence might well be given consideration, particularly with slips and thin pastes, but it is also

[1] Kolloid-Z., 38, 261 (1926).

[2] cf. Bingham: Colloid Symposium Monograph, 2, 111 (1925).

true that the same effect would be produced if the rate at which the material could enter the capillary were retarded by the increase in the internal friction of the material in the bulb under high pressures, similar to the way in which sand may be held in a box which has relatively wide cracks in the bottom.

Curve (b), Fig. 9, was plotted from the data of Bingham and Robertson[1] obtained with a 43 per cent ammonium oleate solution. The short, vertical lines through the small circles include all the experimental values for the velocity of flow determined at the respective pressures, of which the points at the centers of the circles are the averages. The numbers beside the circles indicate the total number of accepted experimental determinations at each pressure. The dotted line is the line drawn by Bingham and Robertson in accordance with the Bingham theory. It passes through the averages of the third and fifth (counting upward) sets of points and entirely misses three sets of six, six and nine values, respectively. Moreover, neglecting the average values entirely, it is not possible to draw any straight line which even touches more than three of the five sets of points, except by taking the very lowest values in the fifth set, and that throws the fourth set still farther out of alignment. It seems that the nine values included in the fourth set of points are worthy of consideration for several reasons: The set contains more determinations than any other set of values; these values were determined at a higher rate of shear than the values in the three preceding sets and therefore, on a basis of the Bingham theory, should fall closer to the straight line than the preceding ones. It has been stated that a precision of 0.1 per cent is possible in fluidity determinations with the capillary viscometer,[2] and as the values under discussion have been further corrected for elastic deformation they should be at least moderately accurate.

It is seen that if a straight line be drawn which includes both the fourth and fifth groups of points, it leaves the other three groups on its right instead of on its left as would be expected on a basis of the Bingham theory. The logical conclusion in the absence of data for intermediate pressures therefore is that the curve is S shaped and, using the average values, would fall approximately as indicated by the solid line. This is borne out by the logarithm curve. It is not possible to determine from the data available whether or not there is a curvature to the right at the upper end of the straight line. With the thicker paste used in these experiments, turbulence would be less likely but the differential effect of the friction within the bulb would be more pronounced.

Time has not permitted a thorough search of the literature for additional data in agreement with the theory in the upper region of the curve, but it is believed to be safe to say that in the majority of cases where the supposedly linear relation has been followed through a considerable pressure range the upper points tend to veer either to the right or to the left of the straight line. They could shift either way, depending upon which portion of the theoretical curve was taken as linear.

[1] Kolloid-Z., 47, 1 (1929).
[2] Bingham: Colloid Symposium Monograph, 2, 112 (1925).

It has been suggested to the author by Dr. E. E. Porter that probably the swelling process is a composite, rather than a simple, phenomenon; and that, while swelling as a whole is accompanied by a decrease in volume, there might be a particular contributory stage which causes or is related to the actual setting of the gel and which is accompanied by an increase in volume. If such were true, a reversal of the setting process would be favored by an increase in pressure.

If various stages of the composite effect took place simultaneously in different incremental portions of the gel, it would not be possible to detect an increase in volume due to one of the stages. It is not unlikely that an increase in pressure would increase the adsorptive power of certain portions of the colloid relative to other portions, with a consequent shifting of water from the latter portions to the former. This process might well be accompanied by a decrease in volume if there were a closer packing of molecules in the new arrangement.

The experiments seem to justify the conclusion that the property of plasticity is related to the ability of the plastic material to undergo a change in viscosity under the influence of pressure. The proposed theory precludes the possibility of a single substance's exhibiting the property of plasticity, but plasticity as outlined in this theory is not to be confused with the property of ductility, which may be regarded as the slippage of structural units, e.g., atomic planes in a crystal lattice or granules of solid held together by a fluid bonding agent. A plastic material is to be regarded as one of the latter type in which the bonding agent becomes more fluid under the influence of pressure.

A paste of clay which is quite lean, i.e., deficient of colloidal matter, does not afford conditions essential to a high degree of fluidity under any pressure. The flow of such a paste is to be regarded as more ductile than plastic in nature. On the other hand, a clay which is too fat, i.e., too rich in colloidal matter for optimum workability, produces a paste in which the bonding medium is quite fluid and causes trouble due to its stickiness. In such a paste the colloidal bonding phase is probably so uniform in structure that all portions of it are practically equally affected by a change in the pressure so that there is very little accompanying change in the mobility. Any possible change in the mobility is minimized in working the paste, due to the fact that the bonding medium flows so readily (when sufficiently wetted) that the shearing pressure is only momentarily applied to any portion of it. The addition of non-colloidal matter, such as grog, which frequently improves the plasticity of a fat clay, would be expected to influence the ability of colloidal matter clinging to its surface to adsorb water and thereby afford the proper conditions for a change in mobility under the influence of pressure.

A general outline of the above theory was drawn up after the data for curves (a) and (b) of Fig. 3 only had been obtained, and on a basis of the theory the general shape of each of the other curves was predicted accurately. In view of this, and of the fact that the existing data for flow through a capil-

lary are also explained, it seems that, whether or not the theory gives a true picture of the mechanism of plastic flow, it is at least workable.

The theory of a change in the viscosity of gels caused by pressure should give a new turn to the problems of lubrication, since lubricating oils and greases are used under pressure. A study of the influence of pressure on the mobility of lubricating greases is now in progress.

The application of the theory to the comparison of various clays and other substances with regard to their plasticity is reserved for a later paper.

Acknowledgment

The original data published in this paper were secured by the author in the laboratories of Iowa State College.

Summary

On centrifuging clay suspensions at different velocities, a curvilinear relationship was found between water retained and centrifugal force, or pressure exerted on the gelatinous material. Plotting pressure against rate of change with respect to pressure of the amount of water retained gave a curve which corresponds to the theoretical probability curve.

In a viscometer, the free liquid which forms as the result of pressure on the gel remains between the particles and acts as a lubricant or forms a thinner gel.

Preliminary experiments showed that a clay slip flows through a funnel under its own head much more slowly in a partial vacuum than at higher pressures.

The effect of external pressure upon the mobility of clay pastes was studied quantitatively by means of a torsion viscometer entirely enclosed in a steel jacket in which the air pressure could be varied.

With thick pastes, the mobility was found to decrease at low pressures, increase far beyond its original value at intermediate pressures and decrease again at higher pressures. The net change at any given pressure was shown to be the difference between (1) the increase in mobility due to the increase of liquid water phase at the expense of adsorbed water and (2) the decrease due to the effect of increased pressure on the internal friction. Increasing the water content of the pastes tends to diminish both effects.

The theory has been shown to agree with existing data for flow through a capillary, and to correlate the Ostwald and Bingham theories.

The experiments seem to justify the conclusion that the property of plasticity is due to the ability of the plastic material to undergo a change in mobility under the influence of an applied pressure which may be entirely independent of the shearing force.

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DIELECTRIC CONSTANT AND STRUCTURE OF THIXOTROPIC SOLS*

BY S. S. KISTLER

Introduction

It has been found in recent years, particularly by Freundlich and co-workers,[1] that rather a large variety of colloidal solutions may under suitable circumstances display the property of thixotropy. This phenomenon has been subject to rather careful investigation. The conditions under which it may be caused to appear are fairly well known, accompanying optical phenomena have been subject to careful scrutiny, the relations between time of setting, temperature, size of vessel, and concentrations of sol and electrolyte are thoroughly cataloged (at least in the case of Fe_2O_3), and empirical rules devised; yet not very much positive evidence has been accumulated supporting any one theory of the cause of the phenomenon. Even well-formed theories are scarce. It was with the idea in mind that any light whatever shed on the subject would eventually contribute to the solution of the problem that the present work was undertaken.

That thixotropy in hydrophobic sols, such as those of Fe_2O_3, Al_2O_3, or V_2O_5, is closely connected with coagulation cannot be doubted. The same agencies which produce coagulation produce thixotropy. It seems that when the repelling forces between the colloidal particles are reduced to a certain point, reversible gelation may occur. If these forces are still further reduced, coagulation occurs.[2] The assembling of the particles into a semi-rigid framework, which, when disturbed, automatically reforms, has been explained by Haber[3] as being due to the "ionic cloud" surrounding the particles. Under suitable conditions of charge on the micelles and ionic concentration in the dispersing medium, the electrical forces are such that the micelles tend to assume fixed positions with respect to each other. If the gel is agitated, they assume the randomness of a sol; but, immediately upon the restoration of quiet, the orientating tendency exhibits itself again and gelation occurs. This conversion from sol to gel and vice-versa may be repeated an optional number of times without affect upon the cycle itself, unless the sol is sensitive to agitation and some disturbing effect arises such as coagulation.

On the other hand, numerous workers[4] have found the assumption of the existence of a hydration layer of considerable thickness surrounding the micelles, to be more satisfying. Upon approaching the conditions for thixo-

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* Contribution from the Kaiser Wilhelm Institut für physikalische Chemie und Elektrochemie, Berlin.

[1] H. Freundlich: Kolloid-Z., 46, 289 (1928).

[2] W. Heller: Kolloid-Z., 50, 125 (1930).

[3] F. Haber: J. Franklin Inst., 199, 437 (1925).

[4] See for example E. A. Hauser: Kolloid-Z. 48, 57 (1929); A. Paris: Sitzungsber. Naturforsch. Ges. Univ. Tartu, 35, 135 (1929).

tropy, the amount of water held more or less firmly by each particle in suspension increases until a point is reached where the particle no longer is free to move independently but becomes limited by its neighbors in such a way that the aggregate displays elastic resistance to deformation.

Evidence for the electrical hypothesis is to be found in the conditions necessary to bring about solidification in the hydrophobic sols. When electrolyte is added to the sol a little at a time, a point is finally reached where the solidification will occur if given enough time and if the sol is in a small enough vessel. Since one of the chief causes of precipitation in these sols is assumed to be electrical and since thixotropy has been shown to be so closely connected with precipitation, it is a small step to the assumption that the forces producing the gel are electrical in origin. The addition of non-electrolytes, such as alcohol, produces thixotropy.[5] This is attributed, however, to the increased "efficiency" of the electrolyte present, produced by the non-electrolyte. None of the hydrophobic sols are stable without the presence of some electrolyte.

In the case of Bentonite the transition from the thixotropic to non-thixotropic condition can readily be brought about by dialysis, and the thixotropic condition again induced by addition of electrolyte.

The affect of the individual ions also is such as would support the electrical hypothesis. The larger the charge of the anion the smaller the amount necessary to produce thixotropy. For example, Freundlich[1] lists the concentrations of various salts that have been found to have equal effects in inducing thixotropy in Fe_2O_3 sols as shown in Table I. The charge on the cation does not have so large an effect.

TABLE I

Electrolyte	Conc. Millimols/liter	Electrolyte	Conc. Millimols/liter
NaCl	45	Na_2SO_4	12
KCl	45	Na_2CrO_4	9.5
KBr	62	K_3Citrate	7
NaOH	18		

Heat is also effective, at least in the case of Fe_2O_3 sols, but here also it is not excluded that the primary effect is not on the concentration of the electrolyte or on the amount of electrolyte adsorbed.

On the other hand it has been assumed that the changes in electrolyte concentration effect changes in the amount of water held in the hydration shell surrounding the particles, and that the phenomenon of thixotropy is directly dependent upon hydration, which itself is dependent upon electrolyte concentration.

Very strong evidence limiting the applicability of the purely electrical hypothesis is to be found in the existence of thixotropy in hydrophilic sols such as gelatin[6] that are very insensitive to changes in electrolyte concentra-

[5] E. Schalek and A. Szigvari: Kolloid-Z., 33, 326 (1923).

[6] Freundlich and Abramson: Z. physik. Chem., 121, 278 (1927).

tion, and in other sols where the presence of foreign electrolyte is entirely unnecessary, such as those of barium malonate and dibenzoyleystine.[7]

That aggregation of the particles of a sol does not accompany the production of thixotropy was well shown by Hauser in the case of Bentonite sols.[8] He observed dialyzed Bentonite sols under the ultramicroscope while the electrolyte concentration was gradually increased. A small addition stops the translatory Brownian movement, while a little more stops also the rotatory movement. An excess of the salt produces coagulation, but with the concentrations to be found in the thixotropic gels the evidence is that the particles are no closer together than in the sols. Hauser considers that an increased hydration layer due to the presence of the salt accounts for the observed phenomena.

General Considerations

According to the Debye theory of the origin of dielectric constant in polar substances, it can readily be shown that an adsorbed layer should have a different and in general a lower dielectric constant than the free substance. It is well known that the measurements of dielectric constants in vapors and gases of large molecular weight are attended with difficulties on account of the adsorption on the electrodes with the consequent uncertainty in both the actual mass of gas between the electrodes and the dielectric constant of the adsorbed part. Palmer[9] finds that it is necessary to assume a dielectric constant of approximately 3.5 for adsorbed water vapor on fine tungsten wire in order to explain his experiments on contact resistance.

Kallmann and Dorsch[10] carried out some very fine measurements on the dielectric constants of thin films of liquids in an attempt to find an effect due to the adsorption or orientation of molecules on the electrodes, but in spite of the accuracy attained were not able to demonstrate any effect. Unfortunately, the number of molecules whose dielectric constants must be changed by proximity to the electrodes in order to give a measurable effect by this method is so large that a negative result is rather to be expected than to be surprising. Indeed, it would be astonishing if the sought effect were large enough to be so measured.

Marinesco[11] has been active in determining the degree of hydration of hydrophilic colloids by measurement of their dielectric constants at 6.5 meters wave-length. He has assumed that surrounding every particle of the disperse phase there is a layer of water that has been "dielectrically saturated." For example, he calculates the thickness of the water envelope surrounding a methemoglobin particle of radius 27×10^{-8} cm. to be 70×10^{-8} cm. He arrives at the conclusion that crystalline hemoglobin "fixes" 15 grams of water per gram of hemoglobin, gelatin 8-10 grams and egg albumin 11-13

[7] H. Zocher and W. Albu: Kolloid-Z., 46, 27 (1928).
[8] E. A. Hauser: Kolloid-Z., 48, 57 (1929).
[9] W. G. Palmer: Proc. Roy. Soc., 106A, 55 (1924).
[10] H. Kallmann and K. E. Dorsch: Z. physik. Chem., 126, 305 (1927).
[11] N. Marinesco: Compt. rend., 189, 1274 (1929).

grams. By introducing degree of hydration he is able to calculate the dielectric constants of levulose solutions with fair agreement with the measurements.

Although such calculations are undoubtedly of high value in indicating the direction in which to look in a search for a measure of the amount of hydration of colloidal particles, the assumptions made are perhaps a little too simple. If a shell of water is "fixed" around each particle so that it displays only the dielectric constant of ice, the mechanism of this fixation should at least be placed on a plausible basis. Electrical saturation effects undoubtedly occur in solutions of electrolytes, where the field strength surrounding an ion is large. Sack[12] has calculated the sphere of influence of an ion and arrived at the conclusion that the influence of the ion is practically independent of its radius and may be expressed by the equation

$$\epsilon^* = \epsilon\,(1-\gamma C)$$

where ϵ^* is the observed dielectric constant of a solution, ϵ is the actual dielectric constant, C is the concentration in moles per liter and γ is a constant for any one salt and varies from salt to salt directly with the number of ions produced and as the $3/2$ power of the valences of the ions. In the case of a colloidal solution, the concentration C is so small that even though there are numerous charges per micelle and the effect of the radius is included, the total measurable effect of the electric saturation on the dielectric constant is negligible unless γ is of an entirely different order of magnitude than that found for electrolytes. The existence of a field of 70 Å thickness surrounding a hemoglobin particle so strong as to greatly change the apparent dielectric constant of the water molecules within it through electric saturation is certainly not to be expected.

On the other hand, it seems reasonable to assume that while the field does produce electrical saturation in a few molecules closest to the micelle it also has an effect upon the freedom of rotation of the molecules much farther removed, due to the orientation produced and their tendency to link up into chains.[13] This linking tendency with its consequent interference with the freedom of rotation would presumably be most intense near the micelle and decrease with distance from it. It would be observed as an increased relaxation time for the molecules affected. This predicted increased relaxation time would tend to give abnormally low dielectric constants, just as has been found to be the case with the solutions studied by Marinesco.

The amount of this reduction of the measured dielectric constant will depend upon the frequency used in making the measurements, and it no longer is possible to make a simple calculation of the degree of hydration from measurements at one wave-length without the introduction of an arbitrary definition.

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[12] H. Sack: Physik. Z., 27, 206 (1926).

[13] J. W. McBain, [Nature, 120, 362 (1927)], considers the tendency of molecules to orientate at a surface and for transient chains to form extending from the orientated layer considerable distances, to be a very general tendency in liquids.

The fact that values of the dielectric constant of non-conducting solutions may vary with wave-length has often been neglected. It is well illustrated by measurements on sucrose.

Table II and Fig. 1 show the measured values obtained by Harrington[14] with a wave-length of approximately 300 meters, the author at 140 meters, Keller[15] at 76 cm. and the author at 32.7 cm.

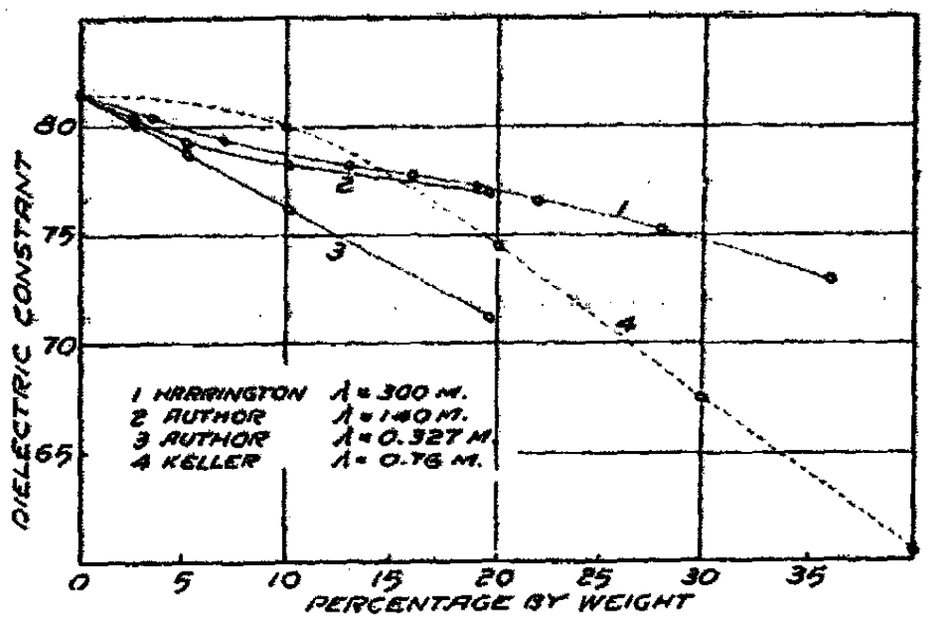

FIG. 1
Sucrose Solutions

TABLE II
Dielectric Constants of Sucrose Solutions

Harrington* 300 m.		Author 140 m.		32.7 cm.	Keller* 76 cm.	
% wt.	D. C.	% wt.	D. C.	D. C.	%wt.	D. C.
0.0	81.5	0.0	81.5	81.5	0.0	81.5
3.5	80.4	2.6	80.5	80.2	10.	80.0
7.	79.4	5.15	79.3	78.7	20.	74.5
13.	78.2	10.10	78.3	76.2	30.	67.5
16.	77.7	19.45	77.0	71.1	40.	60.4
19.	77.2				50.	49.3
22.	76.5					
28.	75.1					
36.	72.9					
41.	71.1					

* Recalculated to a fiducial value for water of 81.5.

The figure illustrates well the necessity of taking the wave-length into consideration in any theory devised to explain the slope of the solute concentration-dielectric constant curve. (It seems evident that the data of Keller's are not to be relied upon.)

[14] E. A. Harrington: Phys. Rev., (2) 8, 581 (1916).
[15] R. Keller: Kolloid-Z., 29, 193 (1921).

One might adopt as the degree of hydration that which is measured with such low frequency oscillations that only molecules very strongly bound will fail to rotate freely, but from the work of Kitchen and Mueller[16] on rosin and that of Errera[17] on ice, it appears that even molecules that might be thought of as being solidified on a surface, will have measurable relaxation times, and therefore a constant value for hydration at long wave-lengths is not to be looked for.

The function connecting the increase in the relaxation time of the solvent molecules with distance from the particle surface is entirely unknown; but one can safely assume that the effect decreases rapidly with distance, so that only molecules lying comparatively close are greatly affected. The nature of the function can be found by a study of the variation with varying frequency attributable to the solute of the dielectric constant. The nearer the frequency used lies to the frequency at which the uninfluenced solvent molecules no longer can freely follow the alternations in polarity of the field, the greater will be the influence of the solute on the measured dielectric constant. The greatest influence will occur where the curve connecting dielectric constant with frequency has a maximum slope. The lower limit of frequency available for studying solvation is probably in the region where the large molecule or particle, if polar, begins to follow the changes in the field and thus exhibits its own polarity. If the calculation of the degree of solvation is based upon measurements at one frequency only, one automatically introduces an arbitrariness into the results. Such results may have good value for comparison between several substances if the same wave-length is used throughout.

The earlier objection to the electric field surrounding a hemoglobin particle extending for 70 Å from the surface with such intensity as to produce electrical saturation applies also to some extent to the present argument. Rather than think of a hydrophile micelle as being surrounded by such a mass of strongly influenced water molecules, it is perhaps better to think of the particle as containing much water within its structure in such a way that very many molecules of water can come within a strong field of influence. In fact, that can well explain the fact that it has been difficult to demonstrate any hydration of hydrophobe colloids. The particles are compact and therefore a relatively much smaller mass of water is influenced.

If there is a sufficiently large sphere of influenced water surrounding the hydrophobe particles in a thixotropic gel, such as that of Fe_2O_3, to account for the solid condition, it should have a measurably smaller dielectric constant at very high frequencies than that of pure water. The present work is an attempt to measure this change in dielectric constant as a sol is brought to the thixotropic condition and then as it is allowed to solidify.

Kallmann and Kreidl[18] investigated the dielectric constant of V_2O_5 sols and thixotropic gels at a wave-length of 50 m. and found that while that of

[16] D. W. Kitchen and Hans Mueller: Phys. Rev., (2) 32, 979 (1928).
[17] J. Errera: J. Phys., (6) 5, 304 (1925).
[18] Not yet published.

the gel was the same as that of water the sol had a dielectric constant of about 6% higher. No conclusions can be drawn from these results concerning the hydration of the particles or the condition of the water between the micelles in the gel except that the water is not solidified. The larger dielectric constant of the sol was undoubtedly due to some orientation of the smaller particles in the oscillating field, while this was prevented in the gel. In radio parlance a wave-length of 50 m. is considered very short, but it is still so far from the anomalous dispersion region for water that only very large changes in relaxation time of the molecules could be detected.

In addition to the necessity for working at very high frequency, it has the very real advantage of eliminating the disturbing influence of small quantities of electrolyte. On the other hand, accurate measurement of dielectric constant with wave-lengths less than a meter becomes difficult due to the necessity of using one of the Drude methods[19] involving standing waves on parallel wires or an optical method such as that of Nichols and Tear.[20] Of greatest difficulty is the generation of undamped oscillations sufficiently rapid, intense and constant.[21]

The most ideal wave-length with which to work with these sols would be less than 10 cm. but due to the difficulties involved it was decided to work with somewhat longer wave-lengths at first and eventually carry the measurements to this frequency. Owing to the constancy of wave-length and the satisfactory intensity obtained, it was decided to use the special high frequency tube modeled after the directions of Kohl[22] made by the Telefon-, Apparat-, Kabel-, und Drahtwerke A. G., Nuernberg, Germany. The wave-length obtained was 32.7 cm. and remained very satisfactorily constant during any one day although over a long period it showed some drift, probably due to reduction of the diameter of the filament due to evaporation.

Measurements were made by the second Drude method as modified by Coolidge[23] and yielded an accuracy well within one per cent. The reproducibility of results depended largely on the character of the solution investigated, being excellent for sucrose solutions and rather disappointing for V_2O_5 sols, probably due to precipitation on the electrodes. With sucrose the deviations of single values from the average were within 0.2%. Although the method adopted is probably the best, it has the serious disadvantage for very sensitive colloidal solutions that any modification of the solution in the immediate neighborhood of the electrodes is much magnified in the results.

When the frequency of alternation of the field becomes so great that the polar molecules lag behind, dielectric absorption occurs. In the study of the thixotropic solutions, it is evident that at frequencies where absorption oc-

[19] P. Drude: Z. physik. Chem., 23, 297 (1897).

[20] Nichols and Tear: Phys. Rev., (2) 21, 587 (1923).

[21] For a good summary of methods for generating high frequencies see W. H. Moore: J. Franklin Inst., 209, 473 (1930).

[22] K. Kohl: Ann. Physik, (4) 85, 1 (1928).

[23] W. D. Coolidge: Ann. Physik, (3) 69, 125 (1899); see also G. Potopenko: Z. Physik, 20, 21 (1923), who has discussed the method and given equations. He has paid particular attention to absorption.

curs the greater relaxation time of molecules within the sphere of influence of the particles will produce enhanced absorption, unless the frequency used is greater than the frequency of the maximum absorption. Measurement of absorption has the advantage that a small change in relaxation time can be detected at a greater wave-length than by measurement of dielectric constant if the percentage accuracy in the two cases is the same. Absorption measurements were accordingly made on all the solutions investigated. Unfortunately, the logarithmic damping decrement did not prove to be constant over the whole resonance curve with the particular set-up used and consequently the absorption measurements do not carry the weight that they should otherwise have. Also there occurs an anomalous absorption band for water at the wave-length produced by the tube, and that reduced the accuracy of the measurement of the small effect sought.

Temperature as a factor was ruled out by making all of the measurements in a constant temperature room where the daily fluctuation amounts to 0.2°

Three measuring condensers of different sizes were used, each calibrated against solutions of acetone in water which Drude[24] found to have practically a linear relationship between per cent by weight and dielectric constant.

As fiducial value for the dielectric constant of water at 17.5°, the room temperature, that of Coolidge[25] was taken, viz., 81.5. The value of 21.3 for acetone was taken from the measurements of Colley.[26]

Experimental Results

Al_2O_3. Aluminum oxide sols made by Gann's method (the hydrolysis of aluminum acetate) are quite stable and are readily made thixotropic by the addition of electrolyte.[27] Upon shaking the gel it becomes a fluid of low viscosity which resets to a gel again on standing. A well dialyzed sol was divided among eight well cleaned test-tubes with ground glass stoppers and solutions of K_2SO_4 added drop by drop with shaking until the concentration of the Al_2O_3 was reduced to 0.97%, while that of K_2SO_4 varied from tube to tube from 0.16 to 1.64 millimols per liter. The solutions containing 1.34 millimols per liter K_2SO_4 or more were thixotropic.

TABLE III

Millimolar conc. K_2SO_4	Dielectric Constant	Millimolar conc. K_2SO_4	Dielectric Constant
0.00	81.1*	0.89	80.4
0.16	80.55	1.34	80.1*
0.45	80.55*	1.64	79.8*

* Ave. of several measurements.

[24] P. Drude: Z. physik. Chem., 23, 288 (1897).
[25] W. D. Coolidge: Ann. Physik, (3) 69, 134 (1899).
[26] A. R. Colley: Physik. Z., 11, 324 (1910).
[27] H. Freundlich and L. L. Bircumshaw: Kolloid-Z. 40, 19 (1926).

Fig. 2 and Table III represent the results of the measurements of dielectric constants. It will be noted that the first small addition of electrolyte produces a much larger depression of the dielectric constant in proportion than additions thereafter.

Although numerous measurements were made with the greatest possible care on the thixotropic sols before and after gelling, they showed the same dielectric constant within the experimental error.

Absorption measurements indicated only that the absorptions in the sols and gels in water are the same within 2-3%.

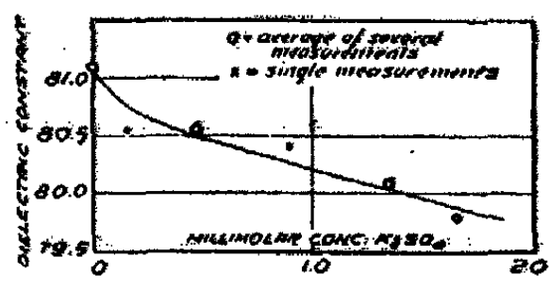

Fig. 2
Aluminum Oxide

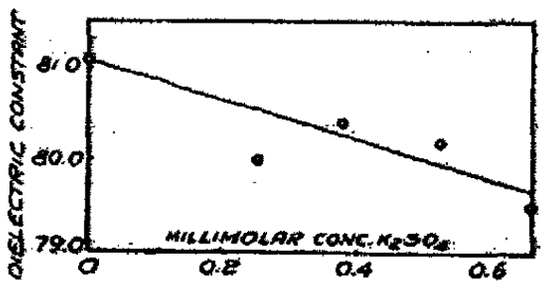

Fig. 3
Ferric Oxide

To make sure that the above effects were not due to the K_2SO_4 in solution, a 1.64 millimolar solution of K_2SO_4 in pure water was measured, and showed a dielectric constant of 80.9 and an absorption of 6% higher than water. The probabilities are that most of the K_2SO_4 in the Al_2O_3 sols is adsorbed so that the disturbance due to that in solution is negligible.

Fe_2O_3. The most completely studied of the thixotropic gels are those of Fe_2O_3[5,7]. A commercial sample made by the hydrolysis of $FeCl_3$ was dialyzed through cellophane for 20 days and then made up into portions with different K_2SO_4 concentrations and an Fe_2O_3 content of 3%. The longer dialysis of such a sol is pursued, the less electrolyte is required to give it thixotropic properties, and also the more readily it is precipitated. The ease of precipitation probably accounts for the relatively low accuracy of the results.

Table IV and Fig. 3 show the results of measurements on one series of sols. The general decrease in dielectric constant with increasing quantities of K_2SO_4 is quite plain. Sols with 0.5 millimols per liter of K_2SO_4 or more were thixotropic.

TABLE IV

Conc. K_2SO_4 millimols/l	Dielectric constant	Conc. K_2SO_4 millimols/l	Dielectric constant
0.00	81.1	0.53	80.2
0.25	80.0	0.67	79.5
0.38	80.4		

Again numerous measurements were made on the same sols both before and after gelling. The results indicate that the gels may have constants 0.2 higher than the sols, but that is a smaller difference than the probable experimental error so cannot be relied upon.

The absorption was found to be the same as in water.

Bentonite. Natural Bentonite forms a thixotropic gel when above 7-8% concentration.* By dialysis it loses this thixotropy which can be revived by the addition of electrolyte. In this case the most effective salts are those with polyvalent cations.

The dielectric constant of a 7.1% sol remained constant at 72.6 with increasing concentrations of $CaCl_2$ up to 1.7 millimolar.

The absorption in the dialyzed sol was 10% greater than in water and increased steadily with increasing $CaCl_2$ concentration to 20% greater than water at 1.7 millimolar.

Although the Bentonite had been dialyzed for two weeks in 0.03 mm. thick cellophane, the removal of electrolyte was not complete enough to completely destroy thixotropic properties, so no figure can be given on the minimum concentration of $CaCl_2$ necessary to bring it about.

V_2O_5. The V_2O_5 sol was made according to the Biltz method[28] (the treatment of ammonium vanadate with HCl, washing and peptizing with water). The sol was over 3 years old so that all ageing effects should have already occurred. It was dialyzed 11 days before using.

As stated earlier, it was very difficult to obtain concordant results due, no doubt, to precipitation on the electrodes. A film of V_2O_5 was readily detectable over the electrodes after a measurement. The average of numerous measurements on a 0.9% dialyzed sol gave a dielectric constant of 81.0, while the dielectric constant for a sol of equal concentration made 2.2 millimolar in KCl was 82.2.

This is the only sol showing high absorption. Both the 0.9% dialyzed sol and sol containing the KCl showed 100% greater absorption than water.

Gelatin. Since gelatin is a representative of the hydrophile colloids and represented by Keller[15] as having a very large affect upon the dielectric constant at a wave length of 76 cm., two solutions of Agfa color filter gelatin of 0.55 and 1.10% concentration respectively were measured. The results are compared with those of Keller in dilute solution in Table V.

TABLE V

Keller		Author	
Conc.	D.K.	Conc.	D.K.
1.9%	74.9	0.55	80.7
4.8	68.3	1.10	79.9

Such a large difference in values is hard to explain. It is to be noted that Keller, using the same apparatus, obtained the objectionable results for sucrose recorded earlier.

Marinesco's[29] figures at 6.5 m. on the other hand show a maximum in the dielectric constant-concentration curve at 0.6% gelatin, which he ascribes to

[28] H. Freundlich: Colloid Symposium Monograph, 2, 46 (1925).

[29] N. Marinesco: Compt. rend., 188, 1163 (1929).

a large dipole moment in the single gelatin molecules. That a molecule of 10,000 molecular weight[30] could display its dipole in a field of such rapid oscillations seems possible since the relaxation time varies directly as the volume of the molecule.[31] If as a rough approximation it is assumed that the ratio of the relaxation times of gelatin and water is that of the molecular weights, gelatin should display anomalous dispersion at a wave length 500 times as great as for water. The region for water practically lies between 0.1-10 cm. which would place it roughly between 50-5000 cm. for gelatin. Due to the highly hydrated character of the gelatin molecule, one would not expect its density to be large and 6.5 meters should be on the high frequency side of its anomalous dispersion range.

Sucrose. Although a study of sucrose does not properly belong with that of thixotropic gels, it seemed to be of sufficient interest to make measurements on its solutions since much attention has been given to its hydration.[32]

Table II and Fig. 1 give the results at two very different wave-lengths.

The absorption increases with concentration of sugar and is 6% greater than water in the 19.45% solution.

Discussion

The very definite slope to the curves for Al_2O_3 and Fe_2O_3 indicate that the previous assumption of increased hydration due to the addition of electrolyte to these sols is correct. The dielectric constants of the dialyzed sols are surprisingly near that of water. Little can be inferred fron this fact except that in the absence of all but a trace of electrolyte the fraction of the water molecules seriously hindered in their adaptation to the impressed field is too small to be measured in the present experiments.

The first small addition of electrolyte affects a larger relative change in hydration than subsequent additions, which might be expected from a consideration of the probable connection with adsorption of the ions on the micelles. One would also expect the curves to flatten out with larger quantities of electrolyte. In the cases of Al_2O_3 and Fe_2O_3 this expectation would probably be realized if a suitable correction were introduced for the electrolyte effect on the dielectric constant at the higher concentrations. With Bentonite where one can reasonably assume some electrolyte already present, the curve is found flat.

Whether the increase in hydration and the decrease in stability of these sols are intimately connected or merely independent results of the same cause is uncertain but one is inclined to feel that the latter is more nearly correct. If the sol is considered to have two sources of stability affected by the addition of electrolyte, viz., the electrostatic repulsion between the charged particles and the cushioning effect of the hydration layer, the addition of electrolyte will serve on the one hand to decrease the stability due to the reduction of

[30] E. J. Cohn: J. Biol. Chem., 63, 721 (1925).
[31] P. Debye: "Polar Molecules," pp. 84-85 (1929).
[32] J. W. McBain and S. S. Kistler: J. Phys. Chem., 33, 1806-12 (1929).

charge on the particle and on the other hand to increase the stability by increasing the hydration layer. What the sum total effect will be with very small additions of electrolyte cannot at present be predicted. With large additions it is to destroy the stability. The course of the stability curve might very well go through a maximum.

If the stability of the sol is reduced by some other means than the addition of electrolyte, the decrease will probably be, in part at least, due to the reduction of charge.[33] The increase in hydration, if any, does not completely compensate for the decrease in charge. Now when electrolyte is added the sol is found very much more sensitive to it because of the already diminished charge. One must assume that hydration alone cannot maintain the dispersion of hydrophobe particles. This prediction is very well confirmed by the behavior of Fe_2O_3 sols. A sol that has been dialyzed a long time is several times as sensitive to the addition of electrolyte and the thixotropic gel formed is coagulated by much shaking, whereas a gel made from not too long dialyzed sol stands a great deal of shaking without effect. The hypothesis that the degree of hydration increases with the decreasing total stability is borne out by the fact that the longer an Fe_2O_3 sol is dialyzed before the addition of electrolyte, the smaller is the concentration of the Fe_2O_3 necessary to produce a thixotropic gel.

(Dialysis and addition of electrolyte seem to be antagonistic treatments, but it must be borne in mind that the Fe_2O_3 sols made by the hydrolysis of $FeCl_3$ are really colloidal basic chloride with a certain tendency to decompose irreversibly. Colloidal solutions of pure Fe_2O_3 of the concentrations used cannot be produced.)

One would look immediately to the absorption measurements for confirmation of the conclusion that addition of electrolyte to Al_2O_3 and Fe_2O_3 sols increases hydration. A lack of an increase in absorption would not disprove the above findings since if the water molecules affected are altogether prevented from following the field, no absorption will occur; however, one would expect many of the molecules to be only partially hindered and consequently act as absorbers. It is unfortunate that the most convenient method of producing high frequency should have produced a wave-length lying in an absorption band of water, and also that the logarithmic damping decrement could not be exactly determined with the given set-up.

Probably the most important conclusion to be drawn from the measurements is that there is no measurable change in the degree of hydration as represented by dielectric constant and absorption measurements when a sol sets to a gel. This means that the internal viscosity of the gels is very little, if any, higher than that of the sols, since the measure of what we have chosen

[33] B. N. Ghosh (J. Chem. Soc., 1929, 2693) finds that whether precipitation of an Fe_2O_3 sol is produced by the addition of univalent or divalent salts or by the addition of AmOH, at the point where rapid precipitation occurs the zeta potential has been reduced to practically the same value.

to call the degree of hydration has been nothing more nor less than a measure of the change in the viscosity of the medium experienced by the water molecules themselves.[31]

Measurements on the 1.1% gelatin sol before and after gelling lead to the same conclusion. The fluidity of the solution in the interstices of the gelatin gel is very nearly the same as that between the micelles before setting, and not widely different from that of pure water.

The behavior of V_2O_5 sols was to be expected. Errera[34] has found them extraordinarily polar at long wave-lengths, the polarity extending down to such short wave-lengths as to exclude any possibility of its arising from a fixed dipole in each colloidal particle.

Szegvari and Wigner[35] have probably rightly placed this polarity as arising from surface conductivity of the elongated particles greater than that of the surrounding medium so that ions can migrate along their lengths and produce charges on their ends. The calculations of Szegvari and Wigner have been given a more acceptable mathematical foundation by Bikerman.[36] If one uses the assumptions of Bikerman's as to possible size of the particles and introduces surface conductivity of the order of magnitude of that found by McBain and Peaker[37] for glass and fused silica in 0.001 N KCl, he can qualitatively duplicate the curve of dielectric constant against frequency found by Errera.

The increase in dielectric constant of the V_2O_5 sols with addition of electrolyte is readily explained on the ground of increased surface conductivity, while the large absorption is to be expected, both due to the surface conductivity of the particles and to the fact that the V_2O_5 is precipitated by the alternating charges and forms a film on the electrodes. Any hydration effects are completely obscured.

In order to see how great a change of relaxation time the above figures would represent, two calculations were carried out using the equations of Debye relating dielectric constant, absorption and relaxation time.[38] In the first calculation an increased absorption of 10% was assumed, and it was further assumed that all of this increase in absorption is due to change of relaxation time. In view of the fact that at the wave-length of 32 cm. there is more absorption than would be predicted from the Debye calculations, a large element of uncertainty enters since there is no way of predicting whether or not a change in relaxation time will be accompanied by a change in the other properties producing absorption. If, as above, the 10% increase in total absorption is ascribed solely to a change of relaxation time, it would represent an increase in this time of 70%.

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[31] J. Errera: Kolloid-Z., 32, 157 (1923).
[35] A. Szegvari and E. Wigner: Kolloid-Z., 33, 218 (1923).
[36] J. J. Bikerman: Physik. Z., 27, 769 (1926).
[37] McBain and Peaker: J. Am. Chem. Soc., 51, 3294 (1929).
[38] P. Debye: loc. cit., p. 92.

The second calculation showed that a five-fold increase in the relaxation time would decrease the dielectric constant measured at 32.7 cm. wave-length by approximately one unit. From the measurements on the Al_2O_3 and Fe_2O_3 sols it is safe to say that the reduction of dielectric constant ascribable to hydration is less than one unit so that the maximum effect that the sol particles can have upon the relaxation time of the bulk of the water is a five-fold increase. Probably half that value is more nearly correct. In other words, the viscosity of the water between the micelles in one of these thixotropic gels is of the order of three times that of pure water. Any change that may occur upon gelation must be a small one.

Even though it has been shown that when a hydrophobic sol is brought to the thixotropic condition an increase in hydration occurs, it can be reasonably questioned whether this hydration is sufficient to account for gelation. If, however, chains of water molecules tend to extend out from the surfaces of the micelles, it is reasonable to suppose that when sufficient of these chains exist and a solid support, such as the walls of the containing vessel, is sufficiently close, the mass of micelles would tend to be linked into a complicated network that would possess some resistance to deformation.

The network of chains of water molecules between the micelles would tend to draw them together, while electrical charge would resist this tendency and a state of equilibrium would be attained. Upon too large reduction of charge by addition of electrolyte, the repulsion could no longer balance the pull and coagulation would occur.

When one considers that the tensile strength of water is of the order of thousands of kilograms per square centimeter, it is obvious that only a very small fraction of the total water present need be connected in chains at any one instant. The observed phenomena in thixotropic gels are quite in harmony with this assumption of connecting chains.

That some sort of anisotropy exists in ordinary liquids is very strongly indicated by recent X-ray investigations. For example, Stewart[39] finds that if one assumes that the molecules group themselves into evanescent associations resembling crystallites the observed phenomena are most readily explained. Even in such a liquid as mercury where association is ordinarily assumed to be very small or absent Debye[40] finds definite maxima in the molecularly scattered X-rays and is of the opinion that "the clarity of these maxima must be connected with a certain regularity of the arrangement of the molecules themselves in the liquid, a regularity which perhaps reminds one of the grating arrangement of atoms in solid crystals".

Whether the phenomena observed are due merely to rythmical density variations in the liquid with orientation of the molecules or possibly to linkage of molecules into chains, it is perhaps too early to state, but the important fact for consideration here is that in all probability this anisotropy would

[39] G. W. Stewart: Phys. Rev., 32, 558 (1928).
[40] P. Debye: Paper before the Deutsche Gesellschaft für technische Roentgenkunde, Heidelberg, June 2-3, 1930.

tend to extend from an orientating surface, and under suitable circumstances could give rise to the phenomenon of thixotropy observed in gels.

In this place I should like to express my gratitude to Professor H. Freundlich for permission to work in his laboratories and for kind advice and interest in the progress of the work, and also to H. Kallmann for the use of apparatus and for much friendly assistance. I am also indebted to the American-German Student Exchange for funds which greatly aided in the pursuit of the problem.

Summary

Hypotheses of the origin of thixotropy in gels are reviewed, and the assumption that hydration is at least a contributory cause is favored.

Calculation of degree of hydration from dielectric constant measurements is discussed and it is emphasized that the results obtained depend directly upon the frequency of oscillations in the measuring circuit. The influence of hydration on the dielectric constant is shown to be probably due to a direct influence on the relaxation time of the water molecules near a hydrated molecule or micelle due to their orientation and their tendency to link together. Electrical saturation effects are probably minor. No quantitative values for the degree of hydration can be given without the introduction of some arbitrary definition or the arbitrary selection of conditions of measurement.

The influence of hydration on dielectric constant will be greater the greater the frequency of the measuring circuit, reaching a maximum where the slope of the dielectric constant-frequency curve is a maximum.

Measurements on dialyzed Fe_2O_3 and Al_2O_3 sols at 32.7 cm. wave-length show little, if any, hydration but give quite definite indications of hydration in the presence of small concentrations of electrolyte.

In none of the cases studied is the viscosity of the intermicellar solution measurably higher in the gel than in the sol before gelling, nor is this viscosity widely different from that of water.

Thixotropy is most readily explained by the assumption that some form of orientated anisotropy of the water, probably chains of water molecules, extends out from the surface of each colloidal particle and tends to link it with the neighboring particles.

Kaiser Wilhelm Institut für physikalische Chemie und Elektrochemie, Berlin.
June 30, 1930.

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NEPHELOMETRIC TITRATIONS. II

The Standard-Solution End-Point*

BY CLYDE R. JOHNSON**

A previous paper[1] from this laboratory has called attention to a possible source of error in the equal-opalescence end-point used in nephelometric atomic weight titrations. It is the purpose in the present article to suggest an alternative end-point for such titrations, free from this source of error, and possessing certain other advantageous features. To distinguish the proposed end-point from the other, it may be termed the standard solution end-point.

The proposed standard solution method differs from the equal-opalescence method only in the determination of the end-point of the reaction under investigation. That is, one precipitates an acid solution containing the chloride (or bromide) ions from a weighed quantity of a pure compound in the usual manner, using within a few tenths of a milligram of the theoretical amount of pure silver, weighed, and dissolved in nitric acid. At this stage, without necessarily making further additions to the system, one determines the end-point by measuring the *absolute* amounts of silver and halide ions in the supernatant liquid. This is done by comparing test portions of the supernatant liquid with standard solutions having practically the same composition as the supernatant liquid itself, with the aid of the nephelometer.

In each individual titration, two sets of standard solutions are required, for the determination of the silver and the halide, respectively, in the test portions of the analytical solution. The details of the preparation of these standards must, of course, vary with the particular "atomic weight" ratio under investigation. The general procedure in the use of the proposed end-point may be inferred from the tests described below. It may be noted that all of the water and nitric acid used in these experiments was purified by the methods usually employed in atomic weight determinations.

Experimental

A number of 18 gm. portions of pure silver nitrate were dissolved in 1100 cc. volumes of water in glass-stoppered 3-liter Pyrex Erlenmeyer flasks and precipitated at the rate of about 4 cc. a minute with equal volumes of hydrochloric acid containing a slight excess of HCl. The precipitates, after stand-

* Contribution from the Chemistry Department of The Rice Institute.
** National Research Fellow in Chemistry.
[1] Johnson: J. Phys. Chem., 35, 540 (1931).

ing, were washed about 20 times with 300 to 500 cc. portions of water, with intermittent soaking and shaking during a period of a week. After this time, varying calculated amounts of nitric acid were added to the flasks, and the volume was in each case made up to 1500 cc. with water. The solutions were then saturated with silver chloride by intermittent shaking over a period of several days.

The silver and chloride content of each solution at approximately 0°C. was determined as follows. The flask containing the solution was partially immersed in an ice-salt bath until the contents had completely frozen. It was then removed, carefully washed, and allowed to stand in air until about three-fourths of the contents had melted, whereupon it was placed in a bath of cracked ice and allowed to stand, usually for at least eight hours, with occasional gentle but thorough shaking. About two hours after the final shaking, 400 cc. of the clear supernatant liquid were withdrawn with a pipette and placed in a Pyrex bottle, which had been cleaned, dried, and rinsed with a small amount of the liquid. In other cases the solution was not frozen, but was withdrawn after cooling in an ice bath for several hours, with frequent shaking. Some preliminary experiments showed the inadvisability of removing the flask from the ice bath until after the sample had been withdrawn, even for the purpose of shaking the solution. The sample was allowed to stand overnight before making the nephelometric tests, as it was also found important that it should be at exactly the same temperature as the standard solutions used in its analysis.

The acid concentration of each sample was next determined by titration of 25 cc. to 100 cc. portions with 0.505 M sodium hydroxide, using methyl orange as an indicator. The chloride and silver content of each of the samples was determined by nephelometric tests, which consisted in comparing 22.00 cc. portions of the samples with standard solutions of equal volume. These standards were prepared from pure water, 5.16 M nitric acid, and solutions made by diluting measured volumes of primary standard solutions of silver nitrate or sodium chloride containing 1.000 mg. of silver or its equivalent per cc. In all of the volumetric measurements calibrated apparatus was used, of dimensions intended to give the measurements, without exception, a precision of 1 part in 500 or better.

In analyzing for chloride, the standard and test solution were precipitated with two equal 1.00 cc. portions of the primary standard solution of silver nitrate; in analyzing for silver, the standard and test solution were precipitated with two equal 1.00 cc. portions of the primary sodium chloride standard. In the precipitation of the solutions, and in reading the nephelometer, the precautions given by Richards and Wells[1], and Wells,[2] were observed. The procedure employed was adapted from that described by Scott and Johnson,[3]

[1] Richards and Wells: Am. Chem. J., 31, 235 (1904); J. Am. Chem. Soc., 27, 484 (1905).
[2] Wells: Am. Chem. J., 35, 99 (1906).
[3] Scott and Johnson: J. Am. Chem. Soc., 52, 2644 (1930).

with slight modifications to make it suitable for the present experiments. The silver chloride used in this work, except the minute amounts employed in nephelometric tests, was illuminated only by red light.

The typical data of a single analysis is given below in condensed form:

Analysis of Sample from Flask No. 1

Sample: 400 cc. of solution; frozen; melted; cooled for 9 hours; withdrawn at 1.0° C.; warmed to 30° C. Found to be 0.485 M in nitric acid at 30° C.

Test Solution: 22.00 cc. of above sample.

Standard Solution: Made from 2.07 cc. of 5.16 M nitric acid and 19.93 cc. of sodium chloride solution containing the equivalent of 0.001124 gm. of AgCl per liter. It thus contained sodium chloride equivalent to 0.00102 gm. of AgCl per liter, in 0.485 M nitric acid, at 30° C.

One hour after precipitation of the two solutions with excess silver nitrate, the mean of 20 settings gave a value of 1.01 for the nephelometric ratio, with an average deviation of 0.025 unit. The standard tube had the weaker opalescence.

Therefore the test solution contained 0.00103 gm. of AgCl per liter.

The results of other similar analyses are given in Table I. Each result recorded in the table corresponds to a set of 20 nephelometric readings, made with an independently-prepared standard and a fresh portion of the sample.

Analysis of Silver Chloride Solutions

TABLE I

Molarity of sample in HNO_3	Time of cooling Hours	Temp. at removal Corr °C.	Nephelometer Ratios and Grams of AgCl per liter: Ratio	Found as NaCl	Ratio	Found as $AgNO_3$
			Part 1			
0.000	10	0.5	1.40	0.00106	1.00	0.00104
	10	0.4	1.34	0.00101	1.07	0.00111
0.111	6	0.4	1.68	0.00172	1.68	0.00173
	14	0.4	1.10	0.00093	1.35	(0.00138)
0.241	3	1.4	1.55	0.00197	1.31	0.00238
	3	1.4	1.14	0.00217		
0.485	6	0.5	1.54	0.00186	1.16	0.00148
	6	0.5	1.08	0.00166		

TABLE I (Continued)

Molarity of sample in HNO_3	Time of cooling Hours	Temp. at removal Corr °C.	Ratio	Nephelometer Ratios and Grams of AgCl per liter: Found as NaCl	Ratio	Found as $AgNO_3$
			Part 2			
0.000	9	0.4	1.35	0.00077	1.63	0.00064
	9	0.4	1.33	0.00078	1.53	0.00068
			Average	0.00078		0.00066
0.111	8	0.6	1.00	0.00091	1.18	(0.00077)
	8	0.6	1.01	0.00092	1.01	0.00092
	8	0.6	1.04	0.00094	1.06	0.00086
			Average	0.00092		0.00089
0.241	6	0.6	1.13	0.00100	1.16	0.00103
	8	0.6	1.10	0.00098	1.15	0.00102
			Average	0.00099		0.00103
0.485	1	0.5			1.45	(0.00100)
	6	1.0	1.08	0.00109	1.14	(0 00089)
	9	1.0	1.01	0.00103	1.02	0.00104
	9	1.0			1.02	0.00100
			Average	0.00106		0.00102
0.988	8	0.4	1.08	0.00100	1.01	0.00107
	8	0.4	1.03	0.00104	1.04	0.00104
	8	0.4	1.04	0.00103	1.02	0.00110
			Average	0.00102		0.00107

Part 1 of the table includes analyses of solutions cooled without freezing; Part 2 includes analyses of solutions frozen and melted before cooling. The nephelometric measurements were made at temperatures varying from 30° to 33° C. For purposes of comparison, both of the constituents determined have been calculated as AgCl. The nephelometric ratios included in the table show only the relative compositions of the standard and test solutions, as the ratios have been calculated so that they are uniformly greater than unity. No analyses have been omitted; the bracketed values I am inclined to reject.

While the tests described above were not intended primarily as solubility measurements, it is interesting to note that the data in Part 2 of Table I form a consistent set of determinations of the solubility of silver chloride in varying

concentrations of nitric acid. Giving each independent analysis equal weight, and reducing all of the values to 0.5° C., the data combine as follows:

Temp.	Molarity of Nitric Acid	Gm. AgCl per liter
0.5	0.000	0.00072
0.5	0.111	0.00090
0.5	0.241	0.00100
0.5	0.485	0.00102
0.5	0.988	0.00105

Discussion of Results

It seems reasonable to conclude that the data in Table I show that the standard solution end-point is suitable for use in nephelometric atomic weight titrations. In solutions at the stoichiometrical point (saturated silver chloride solutions) the method indicates that the silver and chloride ions are equal, with the desired precision. That is, the average silver and chloride, calculated as AgCl, agree within a few hundredths of a milligram, when the tests are made under the proper conditions (Table I, Part 2).

These conditions, as defined by the present experiments, may be summarized: (1) The cooling of the solutions should be preceded by freezing and melting. This treatment hastens the attainment of equilibrium, decreases the amount of dissolved material to be determined, and reduces the measurements to a common basis. The latter feature may prove of value in detecting any abnormality in the end-point of the titration. (2) In general, the measurements become somewhat more dependable as the nephelometric ratio approaches 1.00. It follows that successively-prepared standards should approximate more and more closely to the test solution in composition. In any case, in the determination of each constituent the analyses should be made at least in triplicate, with fresh, independently-prepared standards. (3) In every analysis the standard and test solutions should be at exactly the same temperature. (4) Acid concentrations between 0.3 M and 1.0 M are suitable for use in the analytical solutions. (5) The method used in preparing the standard solutions evidently involves no serious error. Nevertheless, the possibility of introducing improvements and refinements in the method is apparent. The use of solutions of silver chloride as primary standards has been considered.

It is recognized that in some atomic weight determinations the preparation of standard solutions containing suitable amounts of the "extra" ions present in the analytical solutions may involve difficulties. However, in all but exceptional cases it should easily be possible to prepare standards of the necessary purity with an accuracy at least ten times greater than that required. In spite of the great sensitivity of the nephelometer, nephelometric observations are accurate only to about 1 part in 50.

General Discussion

It is not the intention in this paper to imply that the possibility of an error in the equal-opalescence procedure, in certain types of titrations, affects in any way its past or present general usefulness, or that the proposed standard solution procedure is anything more than a possible alternative or supplementary one. Both methods have their characteristic advantages. For the present, attention is confined to two advantages peculiar to the standard solution method: (1) It offers the opportunity of comparing, in the nephelometric tests, systems which are practically identical in composition. The importance of this feature has often been stressed by Richards.[1] The same opportunity does not appear in the equal-opalescence method, in which one compares systems precipitated with *equivalent* rather than with *equal* amounts of the precipitating reagents. (2) In the standard solution method one measures the *absolute* amounts of silver and halide ions in the analytical solutions; in the equal-opalescence method only the *relative* amounts are found. The use of the standard solution procedure gives valuable data regarding the solubility of silver chloride in the analytical solutions, and information concerning the equilibrium between silver and halide ions in the neighborhood of the end-point. This feature is of value if the nephelometric analyses are to be followed by incidental gravimetric analyses, as it permits an exact correction for chloride lost in the nephelometric tests. Reports of such atomic weight determinations, in which it has been customary to employ the equal-opalescence method, give one the impression that this rather important correction has frequently been neglected, although corrections involving smaller quantities of material have been taken into consideration.

In conclusion, it may be said that while the measurements recorded in this paper show the essential validity of the proposed end-point, the usefulness of such an end-point can only be established by actual trial under the conditions arising in atomic weight work. Such a trial is desirable, if only for the reason that it is good policy in atomic weight investigations to gather evidence from many sources.

Summary

An end-point for use in nephelometric atomic weight titrations has been proposed. Experiments show that under a specified set of conditions the end-point corresponds to the stoichiometrical point with the desired accuracy.

Houston, Texas.

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[1] Richards: Am. Chem. J., 35, 511 (1906). See also, Richards and Wells: Am. Chem. J., 31, 242 (1904).

SOME PHYSICAL PROPERTIES OF THE TERNARY SYSTEM PHENOL-BENZENE-WATER*

SAMUEL H. WEIDMAN AND LLOYD E. SWEARINGEN

In this laboratory, a study is being made of the physical properties of certain liquid mixtures. Some of the physical properties of the binary systems, phenol and water[1] and phenol and benzene[2] have previously been reported by one of the authors. During the progress of other work in this

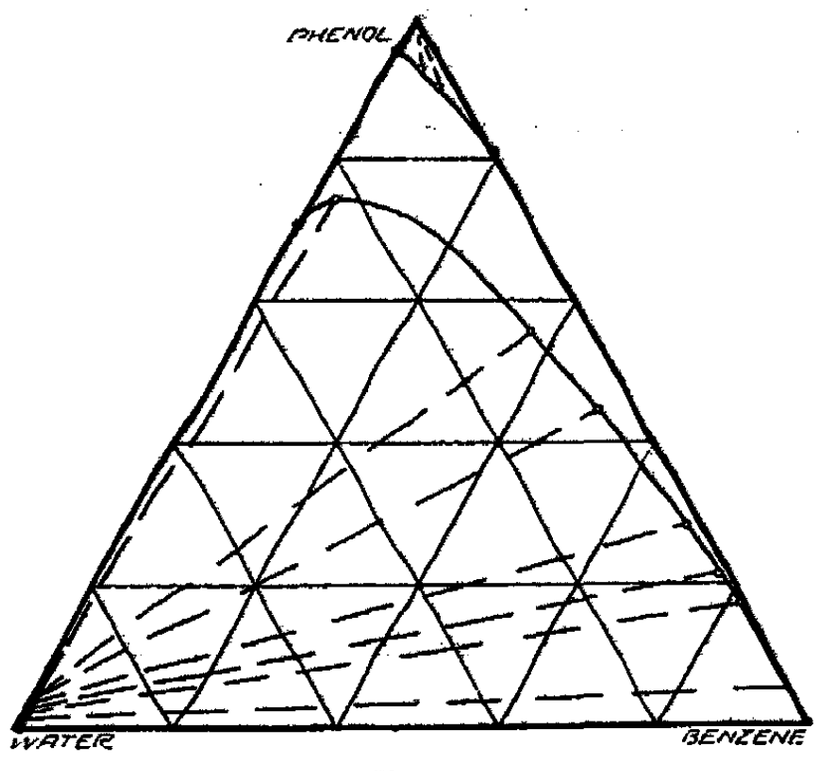

FIG. 1

Phenol-Benzene-Water.
Composition Diagram 25°C in Weight Percent (S. Horiba)

laboratory, a need occurred for some surface tension data on the ternary system phenol, benzene and water. These measurements were made and it was thought desirable to determine a few other physical properties of this system while the materials were at hand.

This ternary system is one for which the phase equilibrium has already been determined.[3] The composition diagram is herewith produced as Fig. 1. Measurements of the surface tension, density, viscosity and index of refraction of various mixtures, whose compositions fall within the completely miscible part of the system, have been investigated.

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* Contribution from the Chemical Laboratory, University of Oklahoma.

[1] Swearingen: J. Phys. Chem., 32, 785 (1928).

[2] Swearingen: J. Phys. Chem., 32, 1346 (1928).

[3] S. Horbia: Mem. Coll. Sci. Kyoto, 1, 49 (1914).

Experimental

Materials. The *benzene* used in these experiments was furnished by the J. T. Baker Co., and was designated as C.P. and thiophene-free. This benzene was further purified by fractional crystallization.

Phenol. The phenol used was Mallinckrodt's C.P. quality and was further purified by fractional cr ystallizatiom.

Water. A good grade of conductivity water was prepared and used in the preparation of the various samples.

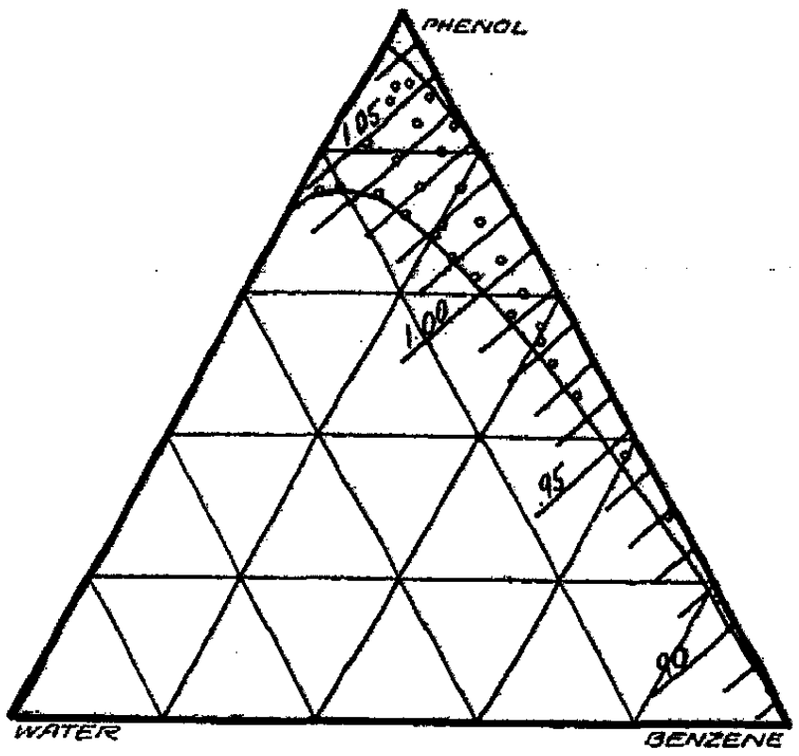

FIG. 2
Phenol-Benzene-Water.
Densities at 25°C

Preparation of Solutions

Representative points throughout the completely miscible portion of the system were selected and solutions corresponding to these compositions were prepared. All compositions are expressed on a weight basis. Thirty-one different samples were prepared. Samples numbered 9 and 13 were lost in preparation and were replaced by samples numbered 32 and 33. The compositions of the various samples are shown in Table I.

The densities were obtained by calculation from the specific gravities, measured at 25°C. with a Mohr-Westphal balance. The balance was adjusted so that water had a specific gravity of unity at 25°C. The densities calculated are those at 25°C. referred to water at 4°C. The temperature was controlled by a water thermostat, equipped with a thermo-regulator and stirrer. The temperature could be kept at 25° ± 0.1°C. with no difficulty. The specific gravity and density data are given in Table II and Fig. 2.

The viscosity measurements were made at 25°C ± 0.1°C. with a modified Ostwald-Poiseuille viscosimeter. The time of flow was determined with a stop watch which recorded time to two-fifths seconds. The data in all cases

TABLE I

Composition in Weight Percent of the Phenol-Benzene-Water Solutions

Sample No.	Percent Phenol	Percent Benzene	Percent Water
1	74.50	3.00	22.50
2	75.00	5.00	20.00
3	81.00	5.00	14.00
4	87.00	5.00	8.00
5	89.05	4.78	6.17
6	74.00	10.00	16.00
7	79.00	10.00	11.00
8	84.00	10.00	6.00
9*			
10	71.00	15.00	14.00
11	75.00	15.00	10.00
12	80.00	15.00	5.00
13*			
14	68.10	20.05	11.85
15	69.94	20.07	9.99
16	75.00	20.00	5.00
17	64.66	24.36	10.98
18	70.02	25.02	4.96
19	62.11	28.85	9.04
20	64.87	30.16	4.97
21	57.03	35.20	7.77
22	59.99	35.09	4.92
23	53.64	40.38	5.98
24	55.40	39.68	4.92
25	50.36	43.84	5.80
26	46.08	49.26	4.66
27	37.76	59.79	2.45
28	29.24	69.78	0.98
29	17.60	81.68	0.72
30	4.74	95.03	0.23
31	89.72	6.27	4.01
32	87.67	9.84	2.49
33	83.94	15.06	1.00

were reproducible to within 0.4%. Absolute viscosities were calculated from the viscosities relative to water and the absolute viscosity of water. The value 8.949×10^{-3} (in C.G.S. units) given by the International Critical Tables for water at 25°C. was used in calculating the absolute viscosities of the different samples. The viscosity data are given in Table II and Fig. 3.

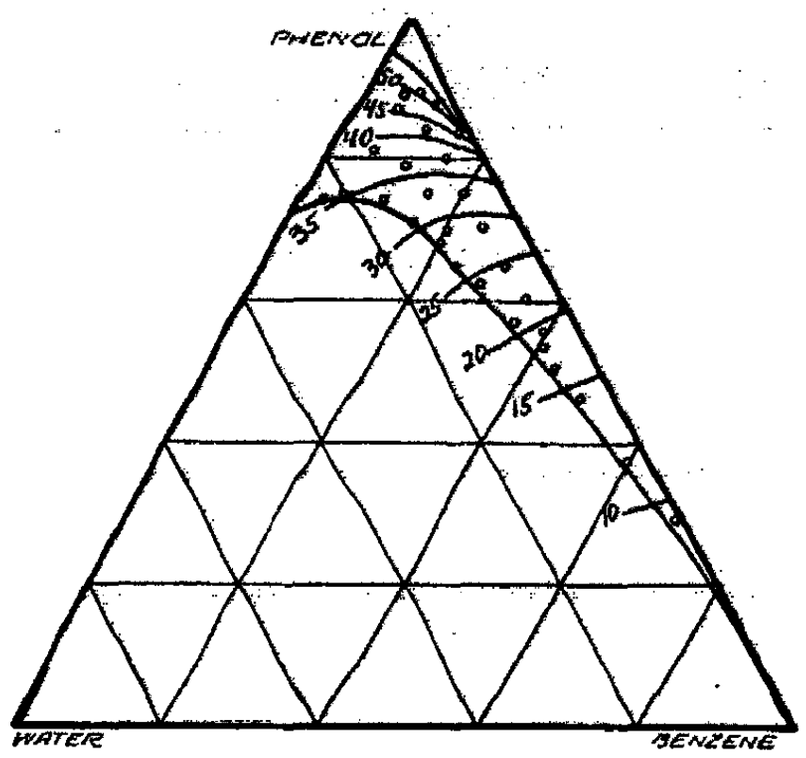

FIG. 3
Phenol-Benzene-Water. Viscosities $\times 10^{-3}$ at 25°C.

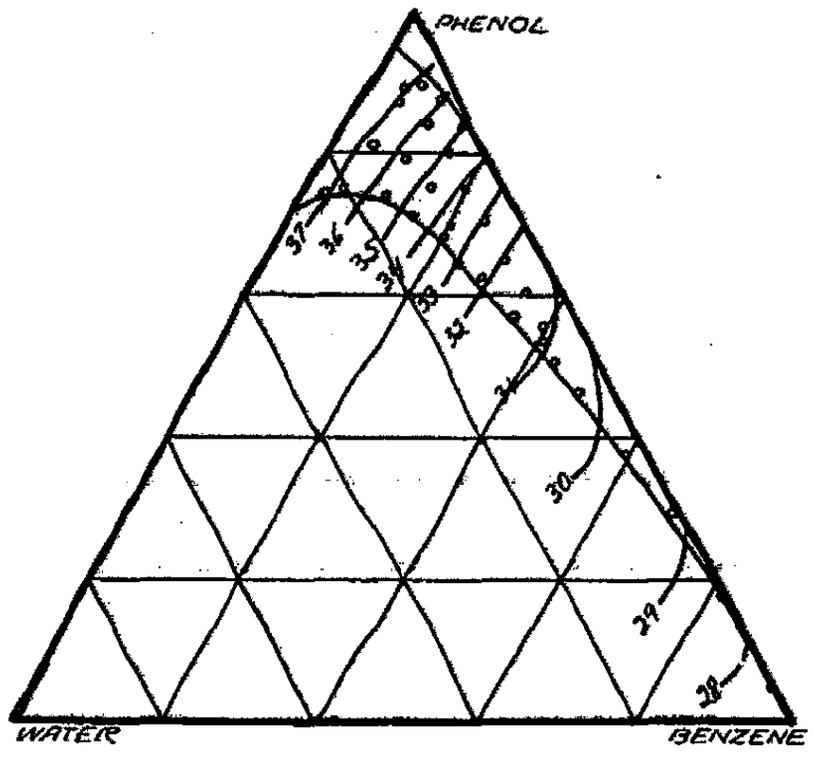

FIG. 4
Phenol-Benzene-Water. Surface Tension at 25°C.

TABLE II

The Specific Gravity, Density and Viscosity of Phenol, Benzene and Water Solutions at 25°C

Sample No.	Specific Gravity D_{25}^{25}	Density D_4^{25}	Relative Viscosity	Absolute Viscosity $\times 10^{-3}$
1	1.0481	1.0450	3.955	35.39
2	1.0452	1.0422	3.919	35.07
3	1.0497	1.0467	4.315	38.61
4	1.0542	1.0511	5.040	45.10
5	1.0574	1.0543	5.583	49.96
6	1.0381	1.0351	3.742	33.49
7	1.0418	1.0388	4.071	36.44
8	1.0459	1.0429	4.616	41.31
10	1.0290	1.0260	3.453	30.90
11	1.0312	1.0282	3.653	32.69
12	1.0354	1.0324	4.184	37.44
14	1.0212	1.0183	3.228	28.88
15	1.0224	1.0195	3.233	28.99
16	1.0248	1.0218	3.597	32.19
17	1.0116	1.0087	2.927	26.20
18	1.0161	1.0131	3.210	28.73
19	1.0047	1.0017	2.637	23.60
20	1.0048	1.0019	2.768	24.77
21	0.9923	0.9894	2.349	21.02
22	0.9945	0.9916	2.435	21.80
23	0.9830	0.9802	2.122	18.99
24	0.9855	0.9827	2.170	19.42
25	0.9765	0.9737	1.943	17.32
26	0.9657	0.9629	1.711	15.31
27	0.9463	0.9436	1.338	11.98
28	0.9287	0.9260	1.096	9.80
29	0.9075	0.9049	0.876	7.40
30	0.8841	0.8815	0.706	6.31
31	1.0562	1.0531	5.852	52.37
32	1.0470	1.0501	5.645	50.52
33	1.0400	1.0370	5.030	45.01
Water	1.0000	0.99707*	1.000	8.949*
Benzene		0.8734*	0.6668	5.967
Phenol		1.071*	9.952†	89.06

* Data from International Critical Tables.
† Experimental value obtained on supercooled phenol.

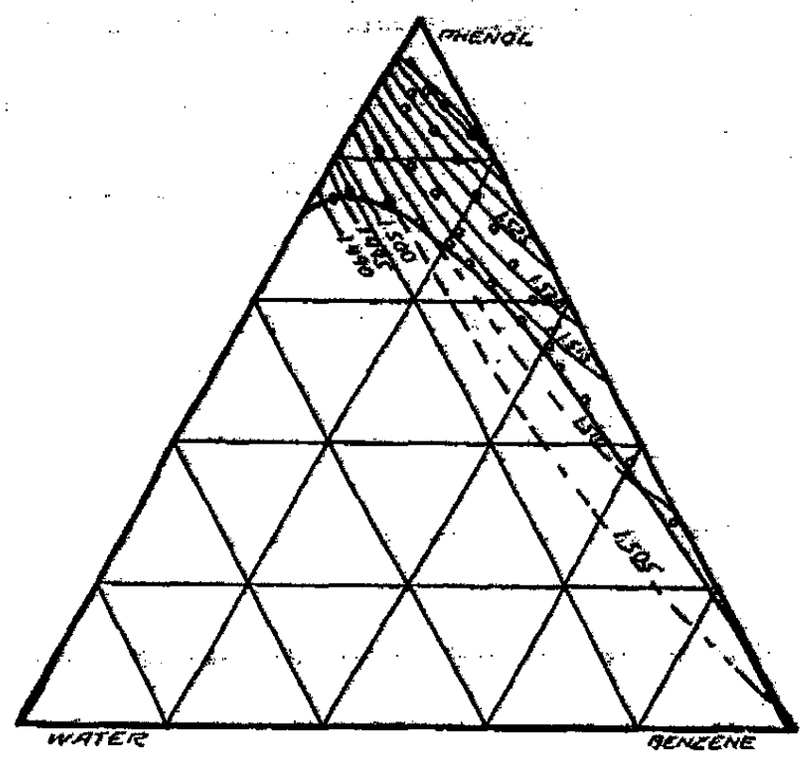

FIG. 5
Phenol-Benzene-Water. Indices of Refraction at 25°C.

TABLE III

The Surface Tension and Index of Refraction of Phenol, Benzene and Water Solutions at 25°C

Sample No.	Surface Tension dynes/cm.	Index of Refraction	Sample No.	Surface Tension dynes/cm.	Index of Refraction
1	37.15	1.4934	19	32.29	1.5132
2	36.59	1.4975	20	31.77	1.5219
3	36.87	1.5114	21	31.25	1.5121
4	36.98	1.5251	22	31.68	1.5193
5	37.26	1.5301	23	31.17	1.5116
6	35.48	1.5046	24	31.29	1.5159
7	35.87	1.5162	25	30.84	1.5134
8	35.75	1.5271	26	30.34	1.5121
10	34.36	1.5075	27	29.55	1.5116
11	34.63	1.5185	28	29.27	1.5097
12	34.92	1.5296	29	28.32	1.5047
14	33.52	1.5114	30	27.60	1.5001
15	32.72	1.5156	31	37.04	1.5372
16	33.88	1.5269	32	36.48	1.5402
17	32.96	1.5120	33	35.36	1.5412
18	33.41	1.5243	Water	71.97*	1.3325*
			Benzene	27.263**	1.4997
			Phenol	38.38†	1.5425††

* Data from the International Critical Tables.
** Fischler: Z. Elektrochemie, 19, 128 (1913).
† Experimental data on supercooled phenol.
†† at 41°C.

The surface tension measurements were made at 25° C ± 0.5°C. with a du Nouy tensimeter. Since most of the surface tension values to be measured were nearer the surface tension of benzene than water, the instrument was calibrated with benzene. With care and proper technique, the results were easily reproducible. The surface tension data are given in Table III and Fig. 4.

The indices of refraction were measured at 25°C. ± 0.2°C. with an Abbe Refractometer. These data are given in Table III and Fig. 5.

Discussion of Results

In the graphical representation of data, curves have been drawn through points having the same value of the property under consideration. Points on the phenol-benzene axis were obtained by interpolation of Swearingen's data for this binary system.

The density-concentration relation is a linear one for both of the binary systems phenol-benzene and phenol-water. This same relation also is found to hold in the ternary system. The densities of the ternary systems studied were found to be additive functions of the concentration.

The viscosities of the binary systems involved are not additive functions of the concentration and as might be expected, the data for the ternary system shows this to be the case also. The ternary system shows viscosity characteristics which partake of the characteristics of the three classes of systems into which Dunstan and Thole[1] classifies solutions. The characteristic which predominates depends upon the relative mol fractions of the components present. In the binary system phenol-benzene, the phenol exists to a large extent as associated molecules[2] thus forming a solution of the third class, in which the viscosity is less than that required for an additive effect. As water is added, there is not only a tendency to form unassociated phenol molecules, but also a tendency to form a hydrate.[3] This favors the formation of a solution partaking to some extent of the characteristics of Dunstan's second class, where the observed viscosity is greater than that required for

TABLE IV

Calculated and Measured Viscosities of Phenol, Benzene and Water at 25°C

Sample No.	Mol Fraction Phenol	Mol Fraction Benzene	Mol Fraction Water	Calculated Viscosity $\times 10^{-2}$	Measured Viscosity $\times 10^{-2}$
25	.3773	.3958	.2269	18.16	17.39
16	.5988	.1924	.2088	32.80	32.19
6	.5162	.1244	.3594	27.90	32.69
3	.5058	.0376	.4566	28.20	38.61
2	.4044	.0325	.5631	22.38	35.07

[1] "The Viscosity of Liquids" (1914).

[2] Kwantaro Endo: Bull. Chem. Soc. Japan, 1, 25 (1926).

[3] Smits and Maarse: Proc. Roy. Soc. Amsterdam, 14, 192 (1922).

additive effects. In solutions rich in benzene and poor in water, the observed viscosity of the ternary system should be less and for those solutions rich in water and poor in benzene the observed viscosity should be greater than the values required for additive effects. At some intermediate composition, the two effects should be compensating and the viscosity for the ternary mixtures should become an additive function of the composition over a short range. That such a prediction is justified is shown by Table IV, where the measured viscosity is compared with the viscosity calculated on the basis of an additive effect.

Summary

The densities, viscosities, surface tensions and indices of refraction for the ternary system phenol, benzene and water have been measured at 25°C., over a wide range of concentrations within the completely miscible portion of the system.

13-43-

CARBORUNDUM FRACTIONATING COLUMNS

BY ESTHER C. FARNHAM

In the spring of 1929 Thomas Midgley, Jr.,[1] published a very interesting paper entitled "Coated Spiral Fractionating Columns". "Some time ago it was observed that a Hempel column filled with a material which would behave as a 'boiling stone' in the liquid being distilled gave better results than did the customary glass beads. It was believed that varying degrees of efficiency might exist among different materials which behave as 'boiling stones'. To determine this, the following experiment was conducted: A 2-liter round-bottom flask was mounted beneath a reflux condenser and half filled with a mixture of equal parts of benzene and toluene. A thermometer, reading in tenths of a degree, was placed in the liquid and constant heat applied to the flask. After refluxing started, the temperature was observed until it became constant. This procedure was repeated with various materials as 'boiling stones' with the following results:—

Material	Temp.	Material	Temp.
No boiling stones	94.0°C	Glass beads	94.0°C
Crushed antimony	93.8	Steel strips	94.0
Crushed porcelain	92.6	Etched brass	94.0
Carborundum cloth	88.7	Etched steel	94.0
Brass strips	94.0		

"A Hempel column was then filled with small scrolls of carborundum cloth and the fractionation of benzene and toluene attempted. The results were quite unsatisfactory. It is believed that this was due to the absorption and holding of a large quantity of liquid by the cloth".

A special metal column was made containing a spiral metal strip coated with carborundum. "To measure the efficiency of this column 150 cc of pure benzene and 150 cc of pure toluene were mixed and distilled. The over-all rate of delivery was 1 cc per minute. Ninety-four percent of the benzene and eighty-six percent of the toluene were recovered, of practically the same purities as were the original materials".

The following investigation was undertaken to develop a theory concerning the high efficiency of this carborundum-coated fractionating column. The presence of a coating of carborundum seems in some way to catalyze the equilibrium between liquid and vapor so that such a column gives a very much better separation of the two liquids which are being fractioned than do ordinary columns filled with glass beads.

There are several possible explanations of this action of carborundum:—

1. There may be some correlation between the efficiency of a substance as a "boiling stone" and its efficiency as a column filling. With the "boiling

[1] Ind. Eng. Chem., Anal. Ed., 1, 86 (1929).

stone" the important thing is the ease of formation of the vapor. Since condensation and not boiling takes place in the column, this did not seem very probable. On the other hand, it was the superior behavior of carborundum as a "boiling stone" which led Midgley to try it in the column.

2. There may be an increased rate of condensation or evaporation or both, due to the presence of sharp points. This seems plausible because reactions between vapor and solid have been shown to take place most rapidly

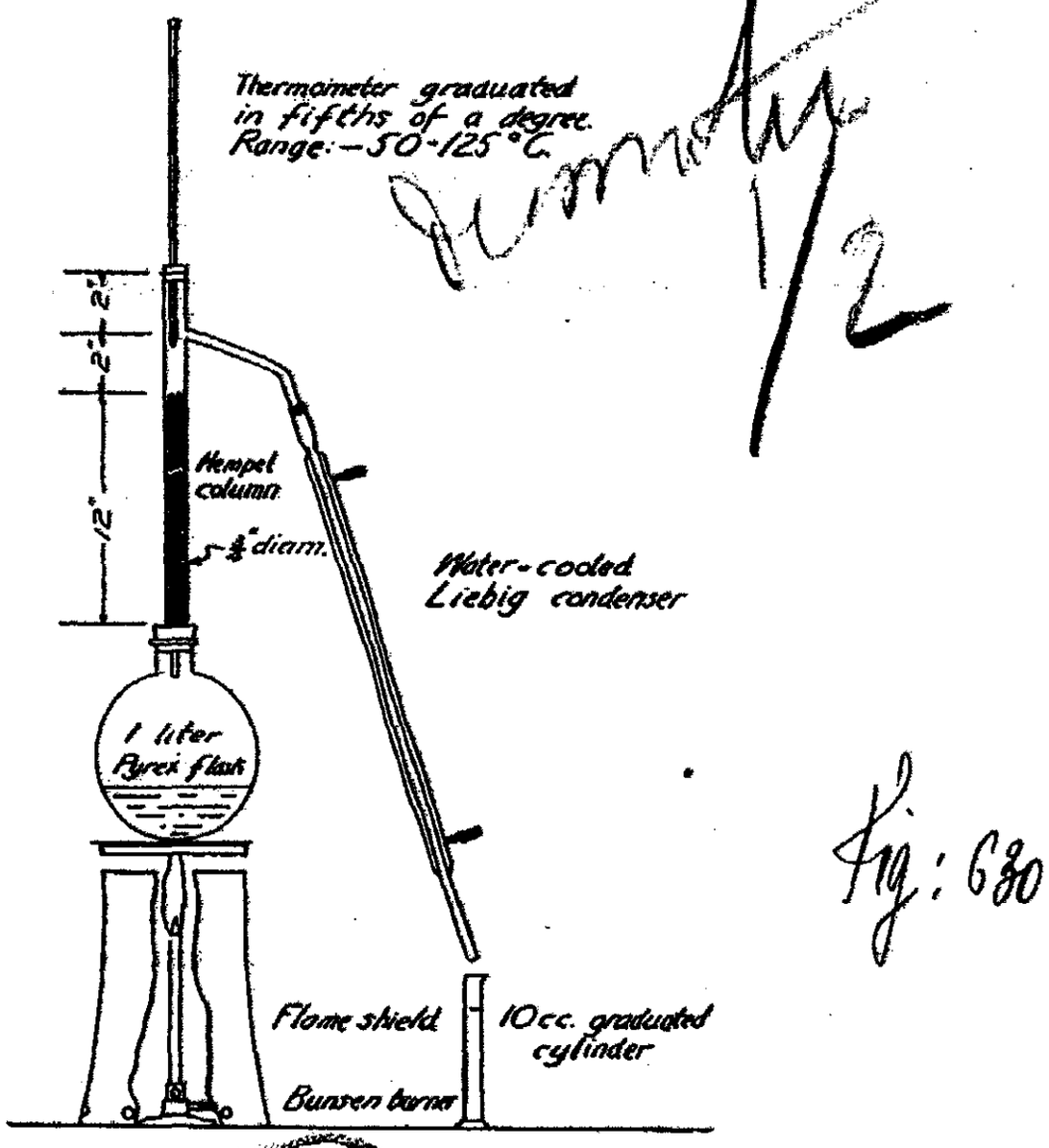

FIG. 1

at sharp points. Reboul[1] states that "there exists at the surfaces of separation between a system, solid and gas, adhesion forces analogous to those of capillary attraction. These forces produce at points of small radius of curvature a concentration of the gas which favors attack on the solid".

It will be shown later that this factor is not the essential one in the action of carborundum, though it has some minor effect.

3. There may be a selective adsorption of vapor in the column, due to the specific adsorbing power of the material, to its crystalline structure, or to the arrangement of its surfaces.

[1] Compt. rend., 158, 1228.

Tests were made of the efficiencies of various substances first as boiling stone and later as column filling. The results of the first of these tests were as follows:—

Material	B. Pt.	Material	B. Pt.
Glass beads	90.8°	Micaceous haematite	90.7°
Tourmaline	90.8	Carborundum chips	90.9

There was almost no effect on the boiling point of the solution even when micaceous haematite was used, though this substance was later shown to be one of the best column fillings. This is not surprising, because, as has been mentioned, we are dealing with the system vapor in liquid in the case of boiling stones, while we have the system liquid in vapor in the distilling column and are primarily concerned with increasing condensation.

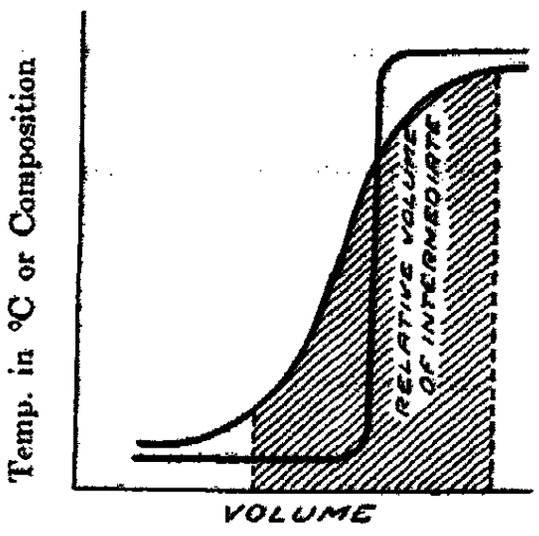

FIG. 2

In making test distillations no attempt was made to construct a very excellent fractionating apparatus. The simple set-up, Fig. 1, was used in all runs. The only precautions taken were to use the same height of column filling and to maintain a constant rate of distillation. Benzene and toluene, benzene and pyridine, pyridine and water, and, in a few cases, 95% alcohol and water were the liquid pairs used. Benzene and pyridine seemed most satisfactory because of the ease with which the distillates could be analyzed. Five cubic centimeters of the mixture were shaken in a graduated test-tube with ten cubic centimeters of dilute hydrochloric acid. The pyridine was completely soluble in the acid, and practically pure benzene separated as a second liquid layer. A number of trials with known mixtures showed this method to be accurate to within 2-4%.

In each run the distillate was collected in ten-cubic centimeter cuts; the temperature of the condensing vapor was recorded at the end of each cut; and the composition of the distillate was determined by the method described above. The curves plotted from the data thus obtained show temperature versus volume of distillate, which can be translated, if desired, into composition versus volume of distillate. In all cases where two or more curves were compared, the rates of distillation were kept as nearly alike as possible. In most cases a rate of 1.6-1.7 cc per minute was used.

In the discussions, the term "efficiency of a column" is often used. The writer understands fully that it is not used in the orthodox sense. The industrial chemist uses this term to mean the reciprocal of the height equivalent to a theoretically perfect plate.[1] I have used it in reference to distillation

[1] Peters: J. Ind. Eng. Chem., 14, 476 (1922).

curves as illustrated in Fig. 2. Curve A represents almost complete separation of the two components being distilled. It may be considered an ideal case, since the volume of intermediate is practically zero. Curve B shows a poor separation with a relatively much larger volume of intermediate. A column may be called more efficient as the curve obtained approaches the form of curve A.

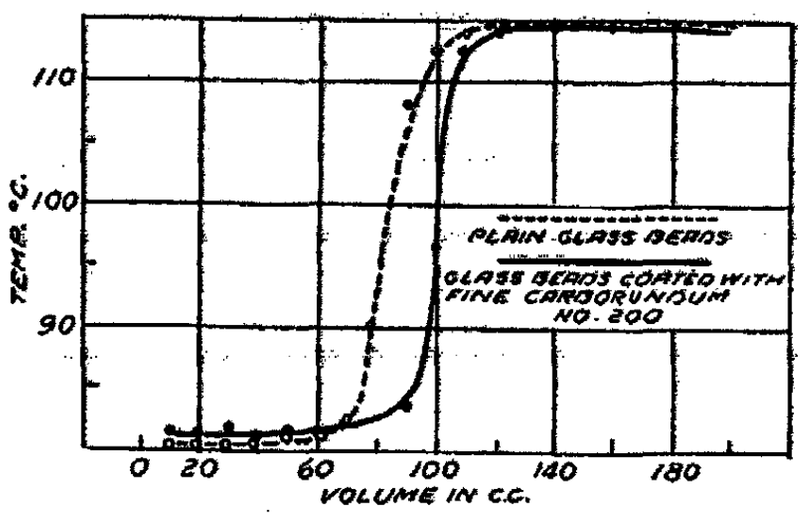

FIG. 3
Benzene and Pyridine

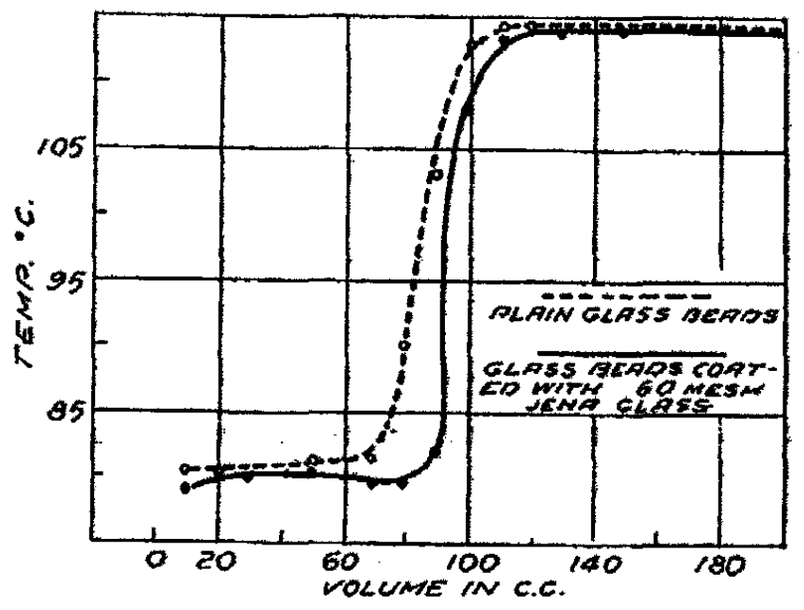

FIG. 4
Benzene and Pyridine

Carborundum occurs in flat plates with sharp edges. Micaceous haematite was picked out as coming somewhere near carborundum in structure. Needle ore is a haematite which crystallizes in needles and therefore has sharp points. A comparison of these two should show whether it was essentially a question of the chemical nature or of the shape of the crystals. A fine carborundum powder has, presumably the same composition as the coarse forms and has more edges but is less plate-like. Mica splits into thin plates and thin sheets of glass can be studied either plain or after being silvered. Alundum and tourmaline differ essentially in crystal form from carborundum and micaceous haematite. Ferrous sulphide was an after-thought.

The first set of distillation curves for benzene and pyridine, Figs. 3-6, is a study of the efficiencies of columns filled with ordinary glass beads coated with different substances. These coatings were applied by shaking the beads with 40% sodium silicate solution, draining them partially, and then shaking them with the dry material to be applied. They were then dried in an oven at 110° for several hours. After a little practice one obtains a very satisfactory

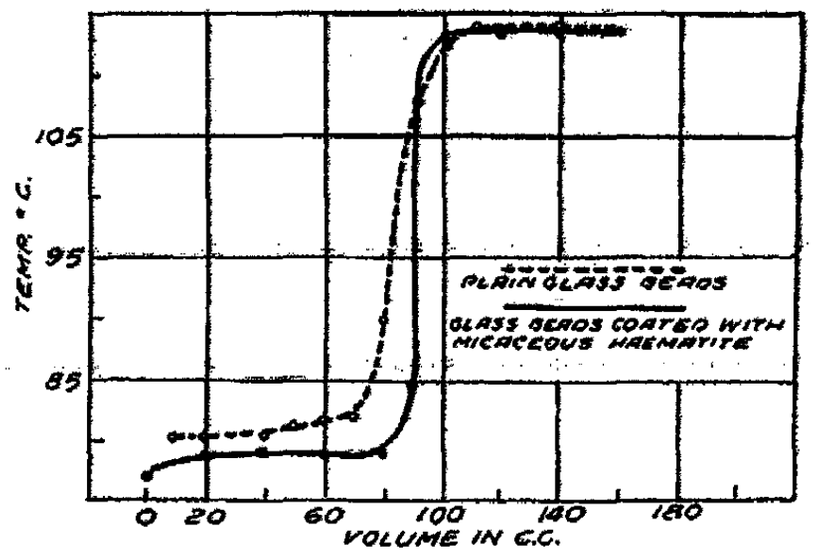

FIG. 5
Benzene and Pyridine

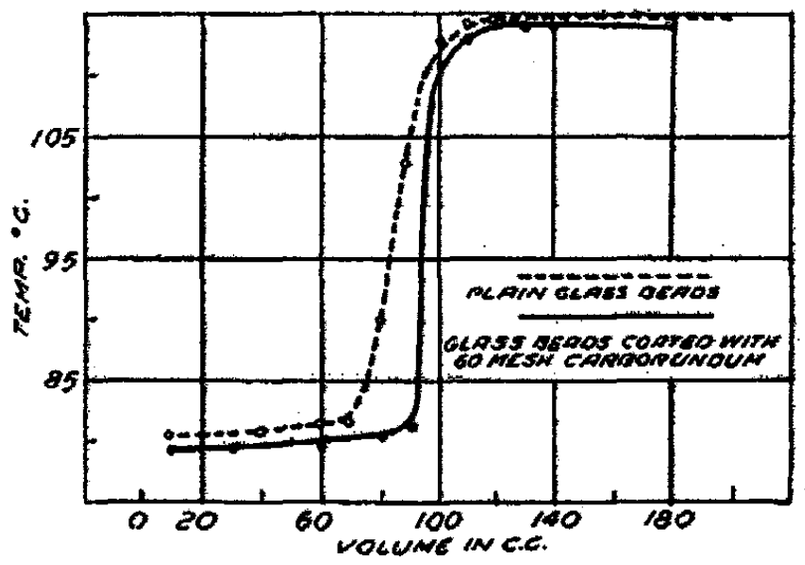

FIG. 6
Benzene and Pyridine

coating which does not chip off easily. Shellac was also tried as a binder; but sodium silicate seems much superior. Both shellac and sodium silicate were used by Midgley. In the first run plain glass beads were used and the curve obtained was used as a standard of reference for the others.

From the curves Figs. 3-6, it appears that:—

1. In general, a coating of rough particles on the beads gives a better fractionation than smooth beads give. This is to be expected, because there is a large increase in surface and increased friction, which tends to prolong the contact between liquid and vapor in the column, giving a better opportun-

ity for equilibrium to be reached. In connection with this it was noted that it is much easier to distill slowly at a uniform rate in a column filled with coated beads.

2. The substances vary greatly among themselves. Alundum (not shown) is not good and neither is the fine carborundum, No. 200 of the Carborundum Co. The 60-mesh Jena glass is better than the fine carborun-

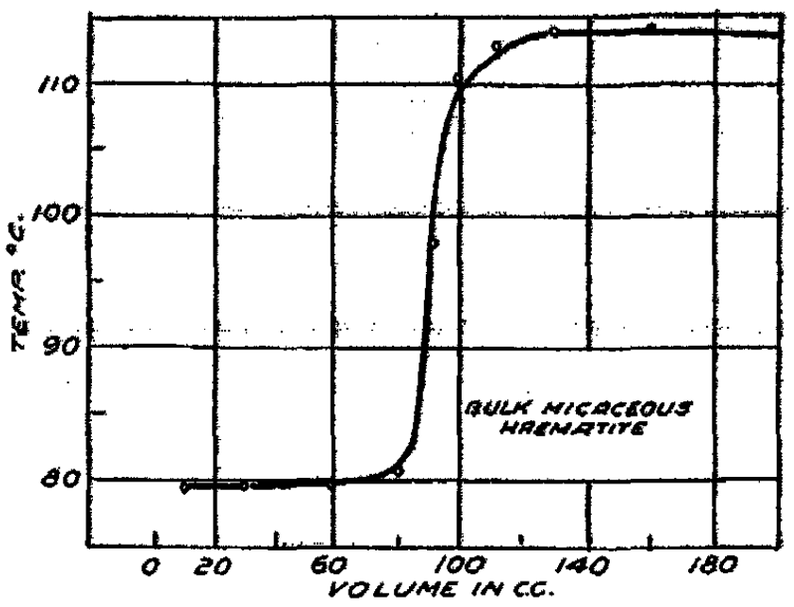

FIG. 7
Benzene and Pyridine

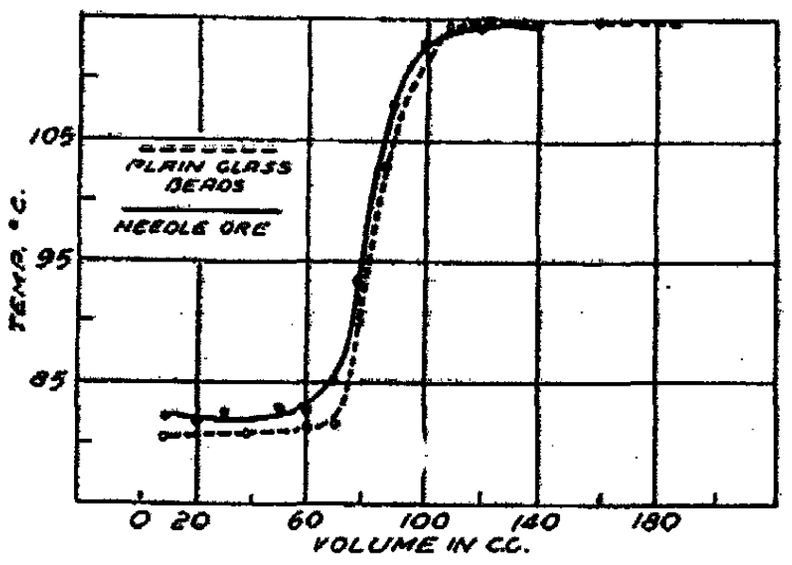

FIG. 8
Benzene and Pyridine

dum. On the other hand the 60-mesh carborundum is better than any of these, which confirms what Midgley found. For this particular pair of liquids, the micaceous haematite, Fig. 5, is better than the 60-mesh carborundum.

Since there were these marked differences between different materials, it seemed wise to eliminate the coated beads and to make another set of runs, using various substances in a crushed condition as a column filling. The materials were crushed to a convenient size with a hammer. The curves obtained from this set of runs are shown in Figs. 7-10.

Under these new conditions the carborundum and the micaceous haematite are practically equally efficient. The two curves are very close to duplicates. Both substances have the same general form, thin rhombic plates having very definite edges. Both belong to the same crystal system. Neither carborundum nor micaceous haematite (in the forms used) has especially sharp points.

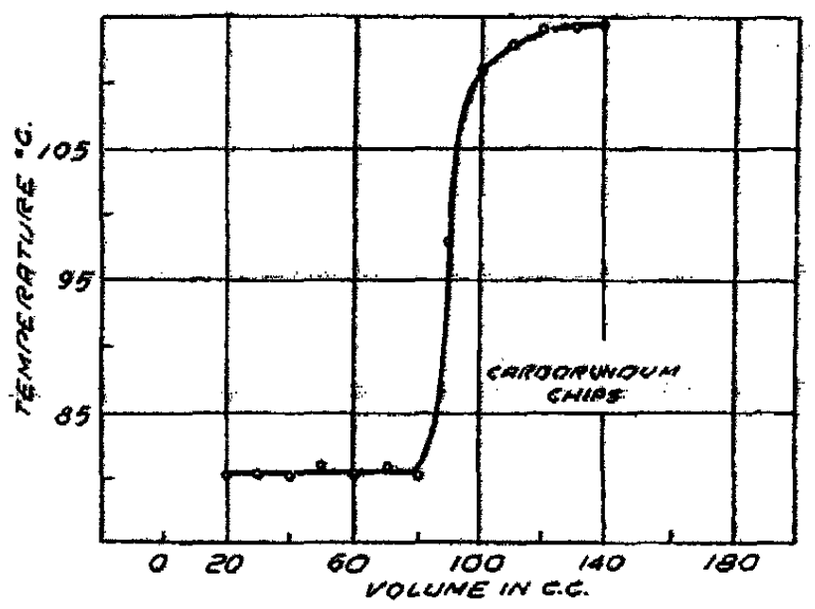

FIG. 9
Benzene and Pyridine

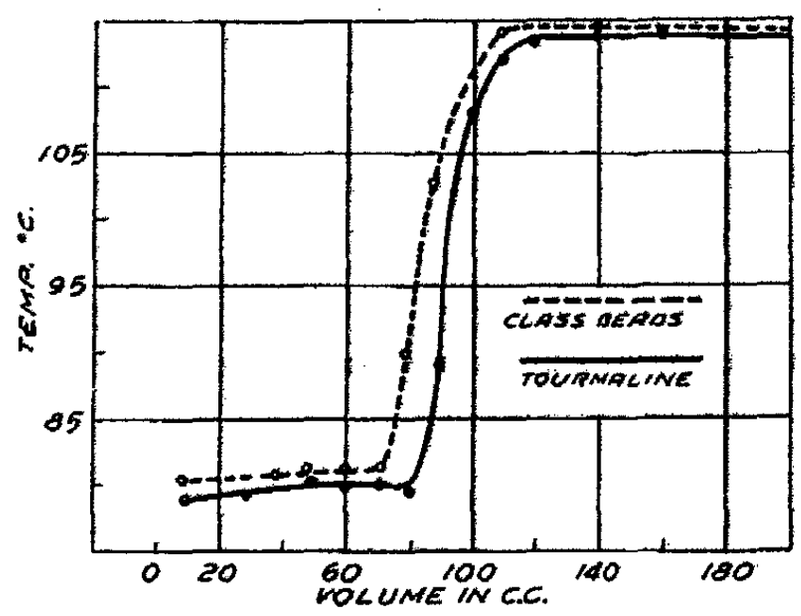

FIG. 10
Benzene and Pyridine

Needle ore, on the other hand, has extremely sharp points. It is evident, however, from Fig. 8 that needle ore is not quite so good as plain glass beads.

The evidence so far is that the form of the crystals is more important than the chemical nature. To test the possibility that thin plates make a better filling, a third set of runs was made using the following films:—

(a) Sheets of mica.

(b) Very thin glass plates made by blowing out glass bulbs almost to the breaking point and smashing the bulbs into suitably sized fragments.

(c) Glass films plated with silver.

The results of these runs are given in Figs. 11-13, using benzene and pyridine and alcohol and water.

Mica was not a success with benzene and pyridine; silver-plated glass films were better than the plain glass ones. On the other hand plain glass films were better than micaceous haematite with alcohol and water. There is,

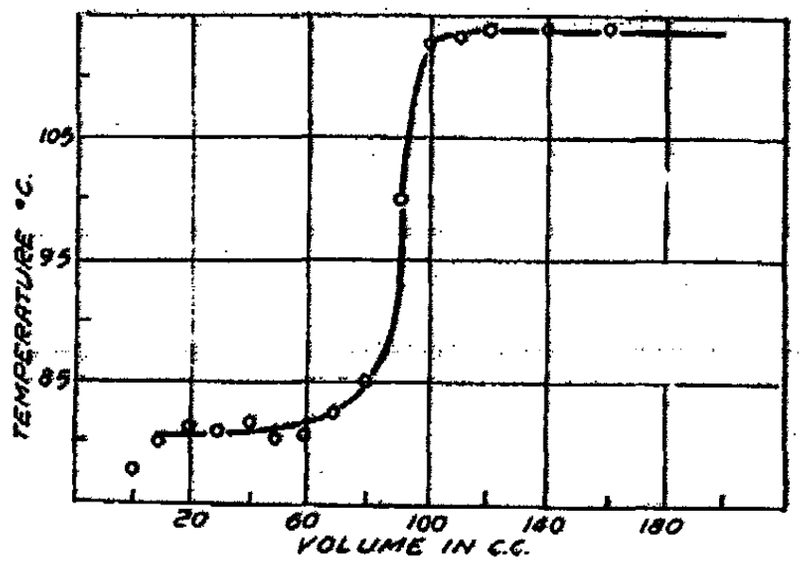

FIG. 11
Benzene and Pyridine (*Mica*)

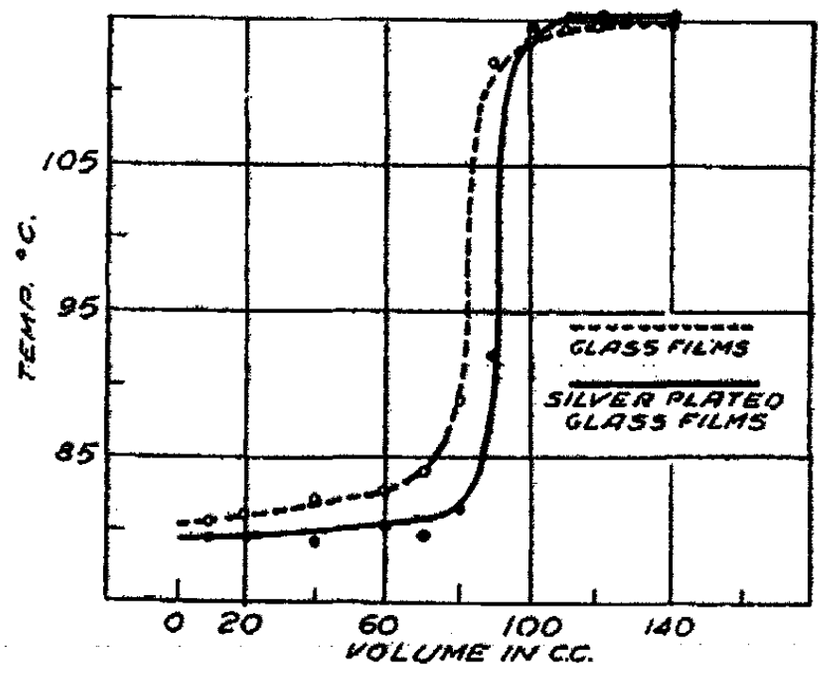

FIG. 12
Benzene and Pyridine

therefore, some specificity of action between the column filling and the substances being distilled. Peters[1] has shown that a given column gives different efficiencies with different pairs of liquids; but that might be a question of the form of the vapor and liquidus curves. It does not follow at all from his work that the efficiencies would vary with the packing material apart from the arrangement.

[1] J. Ind. Eng. Chem., 14, 477 (1922).

No hint of anything of this sort appears in the book by Robinson,[1] also from the Massachusetts Institute of Technology. "It will be recalled that a fractionating column consists of a system up through which vapors are passing, and down through which a liquid is running, countercurrent to the vapor, the liquid and vapor being in more or less intimate contact with each other. Furthermore, the vapor and liquid should be in equilibrium with each other at

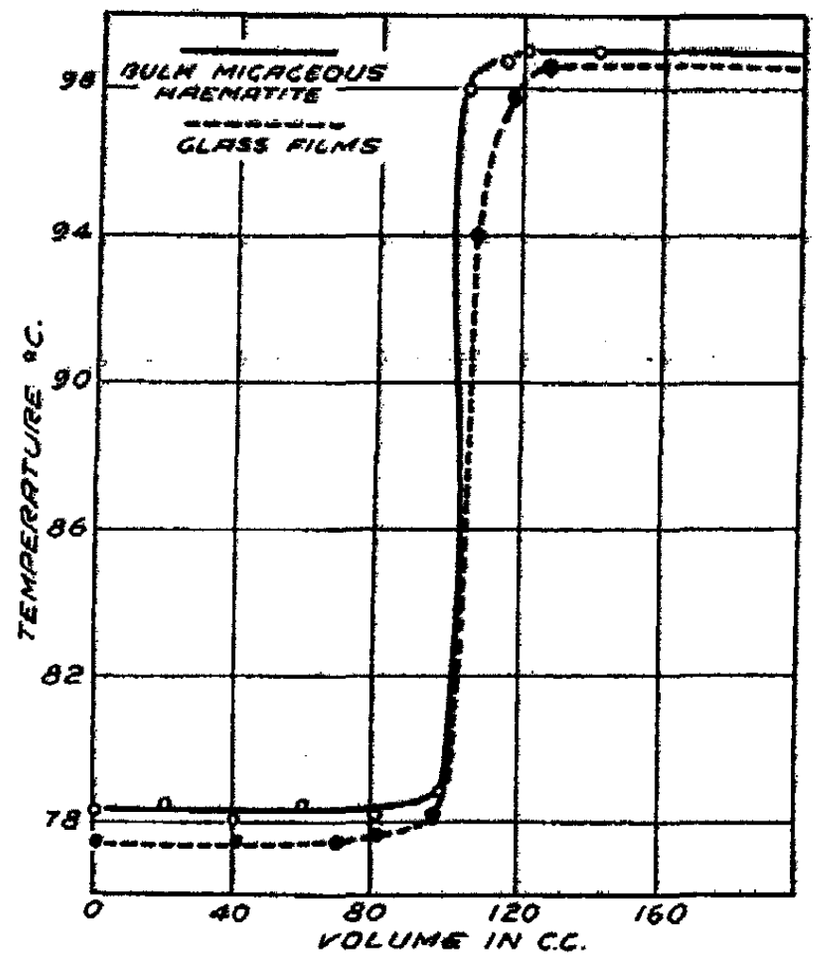

FIG. 13
Alcohol and Water

any point in the column, the liquid and vapor at the bottom of the column being richer in the less volatile component than at the top. It is evident therefore that the action of such a column is similar to that of a scrubbing or washing column, where a vapor is removed from a gas which is passing up through the column, by bringing into contact with it, countercurrent, a liquid in which the vapor is soluble, and which will remove it from the gas."

"In general, fractionating columns may be said to consist of cylindrical shells filled with distributing material which breaks the descending current of liquid up into thin streams and brings the ascending current of vapor into intimate contact with these streams. The earliest type of column, and one which is still used to a large extent, consists of a cylindrical shell filled with pieces of inert solids, usually small irregular pieces of stone, porcelain, coke, and other similar materials. This type of column is similar to the fractiona-

[1] "The Elements of Fractional Distillation", 58, 83 (1930).

ting device which is used in the chemical laboratory, which consists of a glass cylinder filled with a large number of small glass beads. This type of column is inexpensive to construct and, for many purposes, will furnish sufficiently good fractionation. It, however, tends to form channels; that is, the vapor will tend to pass up through one portion of the cross-section of the column while the liquid may tend to descend through another portion of the cross-section, thus defeating the purpose of bringing the liquid and vapor into intimate contact with each other.

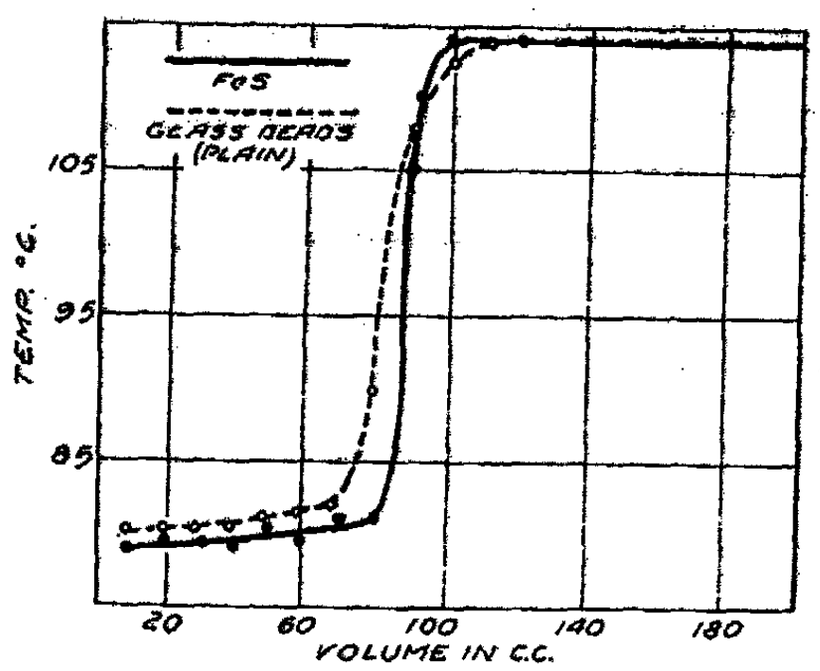

FIG. 14

Benzene and Pyridine

"In filled columns of this sort, channelling is, to a certain extent, overcome by using filling material of a uniform nature, such as specially-made stoneware shapes which, when carefully packed into the column by hand, insure even distribution of vapor and liquid. Such filled types of columns are frequently used in the distillation of acids such as nitric and sulphuric acid and are very successful for such purposes. It must be remembered, however, that even under the best circumstances, the contact between vapor and liquid in such columns is poor, and therefore they should be used only where it is a relatively simple matter to separate the more volatile from the less volatile component."

"Another variety of fractionating column of the filled type has for the filling material, small cylindrical rings or tubes, the length of each ring being equal to its diameter. These rings, which are known as Raschig rings from their inventor, are not packed carefully into the columns, but are dumped in, and owing to their dimensions and shape, form a fairly uniform packing with very little opportunity for liquids and gases to channel. They have the further advantage of offering a very large surface wet with liquid and exposed to the action of the vapor and there are no pockets where liquid may be caught and held from running down."

It seems probable that selective adsorption accounts for glass films being worse than carborundum or micaceous haematite with mixtures of benzene and pyridine, and better than micaceous haematite (and presumably carborundum) with mixtures of alcohol and water. It is known that water wets glass more readily than it does carborundum and that benzene and pyridine wet carborundum and micaceous haematite more readily than they wet glass. On this basis the better behavior of silver-plated glass films over plain glass

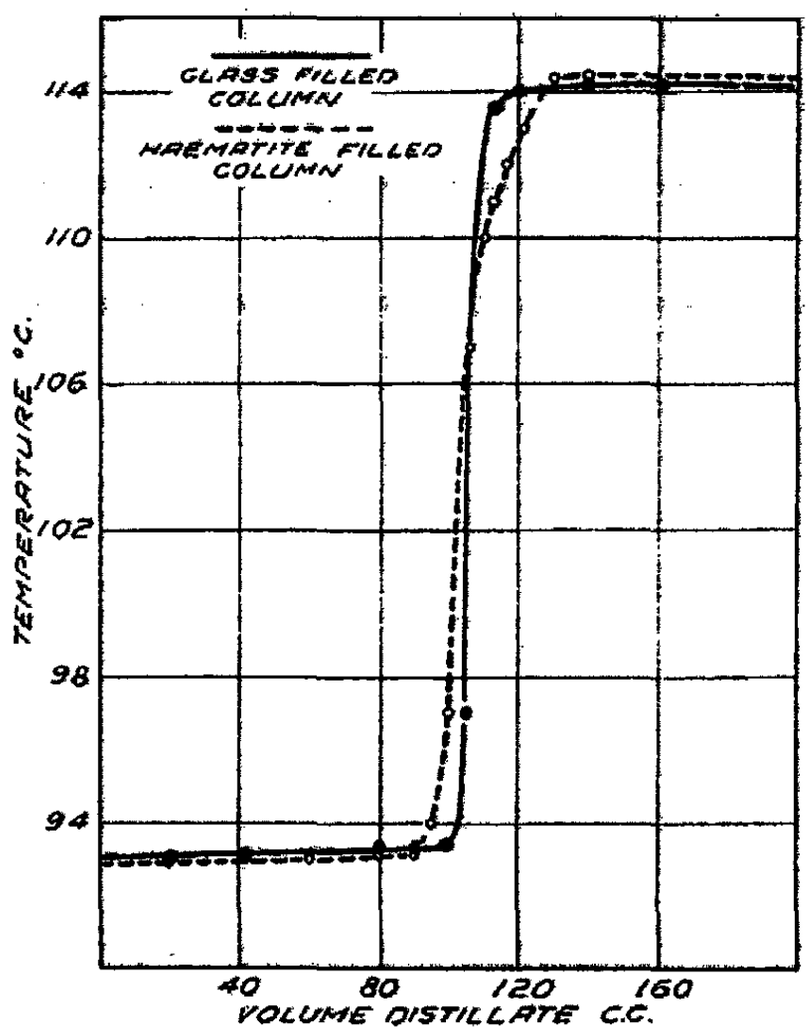

FIG. 15

Water and Pyridine
Excess of pyridine over the constant-boiling-mixture

films with benzene and pyridine would be due to the fact that the hydrocarbons wet metal more readily than they do glass. If this is a good working hypothesis, we should expect ferrous sulphide to make a good column filling for benzene and pyridine, even though it does not form flat plates or have sharp edges. The bubble flotation process for ores depends on the fact that the sulphide ores are adsorbed strongly by "oil" while the siliceous gangues are not.

Bulk ferrous sulphide was crushed to particles of somewhat larger size than the glass beads used in the check run. The results are shown in Fig. 14 and indicate that ferrous sulphide is much more satisfactory as a column filling than glass beads when one is fractionating benzene and pyridine.

The question of specific action is brought out even more clearly by some experiments with pyridine and water. There is a constant-boiling-mixture, which we will call CBM. It contains fifty-nine percent pyridine and boils at 93.2°. Experiments were made on the separation of the constant-boiling-mixture from pyridine and from water with glass beads and with micaceous haematite. The results are given in Figs. 15 and 16. When separating the constant-boiling-mixture from pyridine, glass Raschig rings are distinctly better than micaceous haematite. When separating the constant-boiling-mixture from water, micaceous haematite is distinctly better than glass rings.

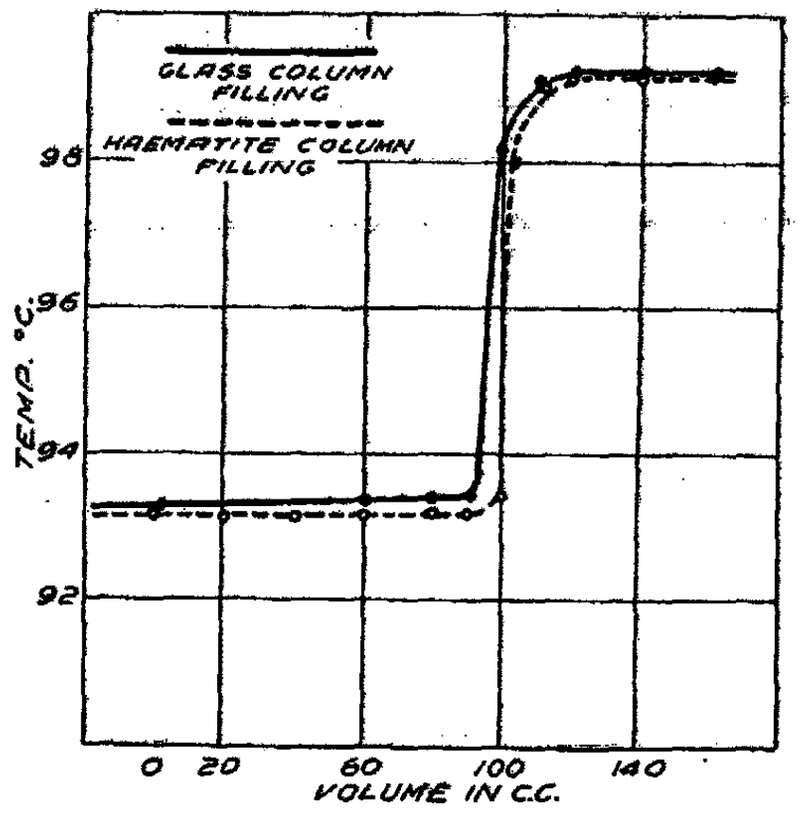

FIG. 16
Water and Pyridine
Excess of water over the constant-boiling-mixture

It seems, therefore, to be established that selective adsorption must be a factor in determining the efficiency of a fractionating column. The next question is how it probably acts. It is obvious that a column filling must adsorb the liquids, at least to the extent of being readily wetted by them. If they did not, the column filling would simply be so much dead space in the column and we would in effect be distilling through a narrow tube. One such experiment was tried using chloroform and alcohol, and distilling them through a column containing activated cocoanut charcoal. Chloroform vapor is only adsorbed very slightly by this charcoal but is readily adsorbed by glass. At the beginning of the distillation the charcoal remained perfectly dry and the liquid meniscus could be observed to climb up the glass wall of the distilling column.

Of course if the filling were of some porous adsorbing material, the liquid would be adsorbed so strongly that it could not pass down through the column

as reflux or re-vaporise, and flooding would result. This happens if we try to use pumice or charcoal. If, however, the adsorption takes place only on the surface, the time of contact is increased, all of the surface is utilized, and the column therefore works well.

We have not yet considered the reflux or down-flowing portion of liquid rich in the volatile component. This is one of the most important factors in column operation. It is better distillation practice to obtain this reflux by condensing all of the vapor at the top of the column and returning a portion from this point, so that the reflux passing down the column is a maximum throughout the entire length of the column.[1] This practice is almost universal in the operation of large commercial stills; but is not ordinarily used in small laboratory columns. The latter depend upon condensation within the column to furnish the reflux. While this is not the best practice, it is less bad in a column which condenses the vapor readily by adsorbing it without making it necessary to distill very slowly.

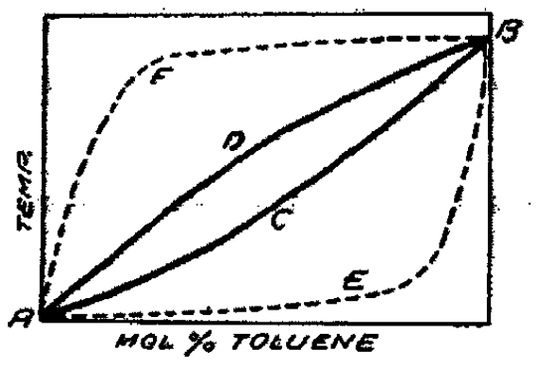

FIG. 17
Boiling-point Curves for Benzene and Toluene.

There are evidently two limiting possibilities in regard to selective adsorption by the column filling. There may be almost exclusive adsorption of the lower-boiling component or almost exclusive adsorption of the higher-boiling component. It is obvious that the first would be bad because that would lower the vapor pressure of the lower-boiling component and would therefore make fractional separation by distillation more difficult. At first sight it seems as though very strong adsorption of the higher-boiling component would be desirable and that view was held in this laboratory for a while. A more careful study of the situation showed the fallacy in the reasoning. If we could get practically exclusive adsorption of the higher-boiling component, there would be no need to do fractional distillation. We should then filter the solution through a sufficient mass of the adsorbent and draw off the lower-boiling component practically pure. If we did do fractional distillation, we should get a very effective separation at first, but after that, we should get no beneficial effect from the column filling.

It is thus evident that a good column filling should adsorb both components of the distilling mixture quite definitely and the problem is to define the ideal way in which the adsorption with varying composition of the distilling mixture. In Fig. 17 are shown the boiling-point curves for benzene and toluene as taken from Robinson.[2] The abscissas are molecular concentrations of the two liquids and the ordinates are temperatures when the pressure is one atmosphere. ACB is the liquidus curve and ADB the vapor composition curve. I have added two dotted lines showing hypothetical

[1] Robinson: "The Elements of Fractional Distillation," 83 (1930).
[2] "The Elements of Fractional Distillation," 41 (1930).

compositions of the adsorbed liquid films for the two limiting cases. AEB is the curve when the lower-boiling component is adsorbed almost exclusively and AFB is the curve when the higher-boiling component is adsorbed almost exclusively. The actual curves and also the ideal curve will lie somewhere between these limiting curves AEB and AFB. The moment the facts are presented in this way, it seems certain that the ideal adsorption curve would coincide with the liquid ACB, because the adsorption forces would be tending to produce a liquid film having exactly the same composition as the liquid in equilibrium with the vapor. In other words, an ideal column filling would adsorb the two components of any binary liquid mixture as is, without producing positive or negative adsorption.

It would take a good while to prove this point and the time at my disposal was unfortunately too short, so the study of the selective adsorption by solids from binary liquid mixtures has had to be postponed. Until that has been done, it does not seem profitable to discuss the question of plates versus needles in much detail. With thin plates there is more surface in proportion to the edges than in prismatic needles. Bancroft[1] has pointed out that "a plane will adsorb a certain amount of gas under standard conditions; but that two plane surfaces placed close together will adsorb a good deal more gas than the same surfaces would if each did not re-enforce the other and modify the concentration gradient". If, as seems probable, the condensation and evaporation take place at the edges, the liquid then spreading over the surface or being drawn from it, this might account for the phenomena observed.

The general results of this paper are as follows:—

1. Mr. Midgley's observations on fractional distillation have been confirmed and extended.

2. Other things being equal, thin plates are better as a column filling than needles.

3. The chemical nature, as well as the physical structure, of the column filling affects the curve for fractional distillation, the effect being specific.

4. With benzene and pyridine, carborundum and micaceous haematite are better than glass beads or silver-plated glass films.

5. Ferrous sulphide is better than glass with benzene and pyridine.

6. Needle ore (a form of haematite) is not good with benzene and pyridine; nor is a very fine carborundum.

7. With alcohol and water, glass is better than micaceous haematite.

8. Glass Raschig rings are better than micaceous haematite when separating the constant-boiling mixture of pyridine and water from excess of pyridine, and worse when separating this constant-boiling mixture from excess of water.

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[1] "Applied Colloid Chemistry", 7 (1926).

9. It is probable, though not yet proved, that the ideal adsorption curve for a column filling would coincide with the liquidus curve in the boiling-point diagram for that pair of liquids.

This problem was suggested by Mr. Thomas Midgley, Jr. and I thank him for his assistance in connection with it. The work has been done under the direction of Professor Bancroft who formulated the present theory of the phenomenon. I am indebted to the Carborundum Company and to the Norton Company for samples of carborundum and crystolon respectively. The two products behaved alike in the fractional distillation. I also wish to express my thanks to Miss Anna S. Nestmann for work done on the drawings.

Cornell University.

THE DESORPTION OF GASES FROM MOLECULARLY PLANE GLASS SURFACES[1]

BY JAMES ROWLAND CURRY[2]

Previous investigators[3] have shown that when non-aqueous vapors were adsorbed on molecularly plane glass surfaces the layer of adsorbed molecules was not more than of mono-molecular thickness. However, as Latham pointed out, the method used did not permit them to determine to just what extent the surface was covered and indeed did not prove definitely that under the conditions used the adsorption of a mono-molecular layer of vapor really did take place. Obviously it would be of interest to determine if there were adsorption and if so, to investigate how much and at what temperature desorption from the glass surface occurred.

In order to measure small amounts of adsorption or desorption it is necessary to measure the change in the pressure in a system that has a large ratio of surface to volume. Past investigators have achieved this experimental condition by using a very large surface, usually powdered glass, glass wool or cover glasses, and measuring the pressure change by means of a sensitive gauge. In all such methods the results are influenced by capillarity and besides there is some doubt as to the exact extent of the surface since in no case is the surface molecularly smooth. It was thought that a very simple apparatus could be designed in which there would be no doubt as to the condition and extent of the surface. It was believed that the best way to achieve this was to obtain a large ratio of surface to volume by using an adsorption bulb in which the volume was very small. In order to obtain this small volume, it was thought that the use of a fine capillary tube afforded the best way, but the use of such a tube would preclude the method used by the above investigators for the production of a molecularly plane surface, i.e., by blowing the bulb in a thoroughly melted piece of glass taking particular pains to exclude all moisture. However, the belief was held that if glass were kept for some time at a temperature somewhat below the temperature of definite softening the surface would become molecularly plane due to the action of the surface tension. Consequently preliminary work was done to find out whether or not this idea was correct.

Preliminary Work

The method used to determine if the surface was molecularly smooth was that of the above mentioned workers so it will not be described in detail. In principle it consists in measuring the pressure-temperature relationship of

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[1] From the dissertation submitted to the Johns Hopkins University in partial fulfillment of requirements for the degree of Philosophy.

[2] Du Pont fellow in Chemistry.

[3] Frazer, Patrick and Smith: J. Phys. Chem., 31, 897 (1927); Latham: J. Am. Chem. Soc., 50, 2987 (1928).

a vapor at its dew-point. If the intersection of the vapor pressure curve and the Charles law curve is a sharp angle, it indicates that there is no adsorption greater than a mono-molecular layer so the surface is assumed to be molecularly plane.

The apparatus used was essentially like that of McHaffie and Lenher[1] so will not be described. The only difference was in the treatment of the bulb in which the measurements were made. In this case a piece of soda lime glass was obtained from the stock room and the dust carefully wiped out of it by means of cotton. Then it was washed with alcohol and one end sealed shut so as to form a cylinder. Care was taken not to heat any more of the glass than was absolutely necessary. This bulb was immersed in a Kjeldahl flask partially full of boiling sulfur so that its bottom was just above the surface of the sulfur. The bulb was connected to a trap and this latter to an oil pump. The trap was kept surrounded with solid carbon dioxide in order to keep oil vapors out of the bulb. The sulfur was kept boiling vigorously so that its vapors surrounded the bulb and a vacuum maintained for slightly over four hours. Then after cooling the pump was shut off and air let into the bulb through a tube containing P_2O_5. The bulb was then sealed to the rest of the apparatus and immediately pumped out.

The vapor used in the measurements was toluene which had been well deaerated. The pressure-temperature relationship was measured when the temperature was both rising and falling. A slight hysteresis was found but in both cases the intersections of the vapor pressure—Charles law curves were very sharp. From this it can be concluded that the surface of a fresh, unwashed, soft-glass tube is rendered molecularly plane by long heating at a temperature somewhat below its melting point.

Description of the Apparatus

The principle, upon which the determination of the amount of desorption was based, consisted in measuring the gas pressure, as the temperature was raised, in a fine capillary tube by means of an adjustable mercury manometer one side of which formed part of the capillary tube.

A diagram of the adsorption apparatus is given in Fig. 1. It consisted essentially of a 0.10 mm lead-glass capillary tube joined to a 1.0 mm capillary tube by means of a very square joint. Care was taken in making this joint to keep the larger capillary tube very uniform and the result was that mercury could move in it very uniformly and regularly up to 1.0 mm from the square joint. This uniformity also did away with capillary depression, so consequently the mercury stood at the same height in tube A and on the fine capillary side when the pressures above the two columns were the same. The tube leading from the cut-off connected to a leveling arrangement in which all rubber was eliminated. The mercury level in these two vertical tubes was adjusted by the movement of a solid glass rod dipping into the open end of the mercury reservoir. The height of the adsorption apparatus in

[1] McHaffie and Lenher: J. Chem. Soc., 127, 1559 (1925).

relation to the leveling arrangement was such that when a vacuum existed in the apparatus the mercury meniscus was slightly below the cut-off.

The tube A was connected by a soft glass to pyrex seal to traps and a pumping system consisting of a mercury diffusion pump backed up by a Hyvac oil pump. Between the mercury pump and the rest of the system there was a trap which was kept surrounded by solid carbon dioxide, principally to keep oil vapor out of the apparatus. The rest of the system consisted of a McLeod gauge and several bulbs and mercury traps which were used to de-aerate liquids. Between the two pumps there was a stop-cock for the purpose of introducing gases.

The furnace used to heat the apparatus consisted of an iron pipe covered with a layer of asbestos upon which nichrome wire was evenly wound and finally a thick layer of asbestos on the outside. It was arranged so that it could be readily slipped over and removed from the capillary tube and was also adjustable vertically above the zero point. The temperature of the furnace was measured by a chromel-alumel thermocouple connected to a portable potentiometer. The movement of the mercury meniscus was followed by means of a carefully leveled cathetometer capable of reading to 0.03 mm.

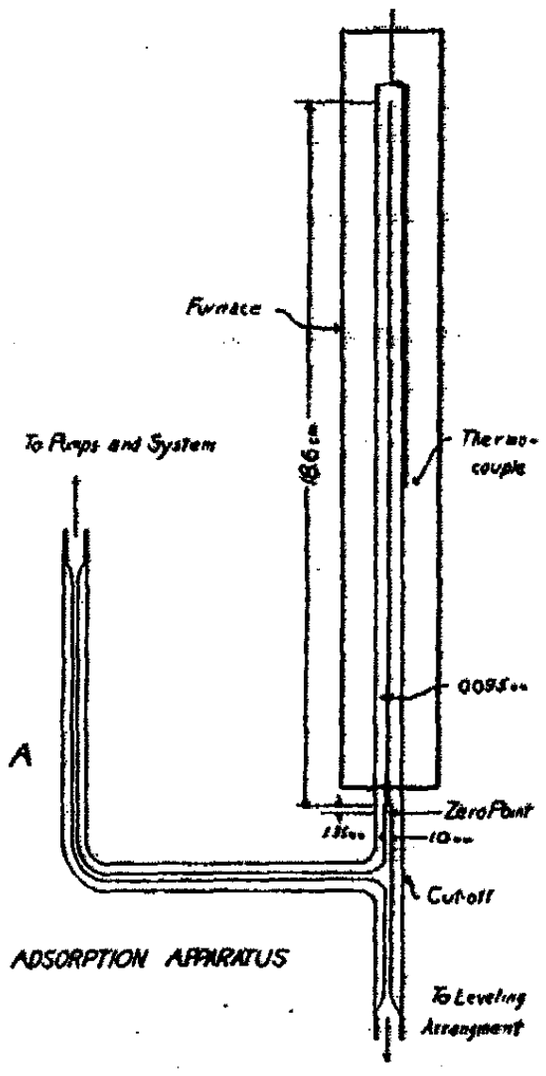

FIG. 1

From the dimensions of the apparatus it is seen that if the mercury is kept at the zero point the ratio of surface to volume in the fine capillary is about 200 and a rough calculation shows that if a mono-molecular layer of a gas is desorbed at 300°C while the volume is kept constant the pressure increase will be about 8 mm and this would be shown by a rise of this height in the mercury in tube A. Thus it is seen that the apparatus is quite sensitive to desorption.

The ratio could have been increased greatly by bringing the mercury up into the fine capillary tube; but preliminary work had shown that experimental difficulties prevented this procedure. In practice the bottom of the furnace was about 1.0 cm above the mercury meniscus at the zero point and under such conditions the vapor pressure of the mercury did not interfere seriously.

After the apparatus was completed it was sealed to the system and the furnace lowered as far as possible. It was then pumped out to a pressure of less than 10^{-6} mm and heated for two hours while the temperature rose

gradually to 300°C, then during the next two hours the temperature was allowed to rise to 400°C. At this point the pumps were turned off and air allowed to enter the system through a tube containing P_2O_5. The temperature was kept between 400°C and 425°C for six hours and then the system allowed to cool slowly. The preliminary work had been with soda-lime glass and since the capillary tube was of lower melting lead glass it was thought that the above treatment was ample for the production of a molecularly plane surface and the results obtained later verified this. After this treatment great care was taken not to allow any moisture to get into the system.

The gases used, their source and method of drying are given below:

Carbon dioxide, hydrogen, ethylene and ammonia were obtained from iron tanks. The first three were dried by passing them through a tube filled with P_2O_5; the ammonia was passed through a tube of calcium oxide.

Carbon monoxide was made by dehydrating formic acid by means of concentrated sulfuric acid. It was passed through soda-lime and stored over water. Before it was allowed to enter the apparatus it was passed through a tube of P_2O_5.

The toluene was some that had been dried over P_2O_5 and was de-aerated until the partial pressure of air in it was less than 10^{-4} mm.

Experimental Procedure

The procedure followed in an experiment was the following. The adsorption apparatus was pumped out for several hours at 340°C by means of the diffusion pump and then allowed to cool with the pumps still in operation. When the temperature had fallen to about 75°C the pumps were shut off and in a short time the gas to be studied was allowed to enter the apparatus by means of the previously mentioned stop-cock until the pressure was about one atmosphere. Then the gas was pumped out until the pressure was less than 0.01 mm; this flushing-out process was repeated three times and the gas finally allowed to remain in the system at a pressure of 760 mm. The apparatus was allowed to stand in this condition for varying lengths of time and then pumped out for three-quarters of an hour by means of the oil pump alone. Sometimes the capillary tube was surrounded by solid carbon dioxide during the pumping-out period; when this procedure was used, the pump was not started until the cooling agent had been in position for twenty minutes and in addition the cooling mixture was adjusted so that a reading could be made while it was in place.

The manipulation of the apparatus was quite simple. After the pumping period was over, the mercury was raised above the cut-off (see Fig. 1) so that the meniscus came exactly to the zero point. From the dimensions of the apparatus it was calculated that due to compression the pressure in the capillary was 5.8 times what it was at the end of the pumping-out period. Under experimental conditions this pressure was about 0.10 mm when the meniscus was at the zero point. With the meniscus at the zero point the height of the meniscus in tube A, was read; then the mercury was lowered

about one mm while the capillary tube was heated; then at various temperatures, after standing half an hour or longer, the meniscus was brought up to the zero point and the increase in height noted on the other side. Three readings were made at each temperature and the mean recorded; they checked within 0.10 mm.

The temperature was never raised much above 325°C due to the possibility of the capillary tube collapsing. In some cases after the last reading at the highest temperature the furnace was turned off but the mercury not lowered. Then a reading was taken in the morning and recorded.

Since part of the volume (that just above the mercury meniscus) was not in the furnace it was necessary to find its temperature for different furnace temperatures. This was done by putting a thermocouple in contact with the exposed portion and finding its temperature as that of the furnace was raised. These values were plotted to assist in the calculations. When the furnace temperature was 330°C the temperature of the exposed portion was 120°C.

Since the mercury at the zero point did not remain at room temperature it was necessary to run a blank in order to obtain the necessary corrections to apply to the readings observed when a gas was being desorbed. To do this the apparatus was given the usual preliminary pumping-out at 340°C and in addition was pumped out by means of the diffusion pump for two hours at room temperature before a reading was made. Then the usual readings were taken as the temperature was raised. When the temperature had reached 330°C the mercury was lowered and the apparatus thoroughly pumped out by means of the diffusion pump for an hour and a half and then the mercury raised and another reading taken. The two readings checked within 0.10 mm indicating that the slight pressure increase noticed had not been due to desorption of a gas. At 330°C the value of the blank was 0.45 mm. This blank experiment was made several times and the average values at the different temperatures plotted against the corresponding furnace temperatures.

Results

When the above procedure was followed the data given below were obtained.

TABLE I

No. 1: Air, 10 hrs. P.P. 0.011 mm.

Temp.	T. S.	O. R.	C. P.	m*
25°C	.5	0.06mm.	0.0mm.	0×10^{13}
100	.5	1.0	.85	6
235	.5	1.5	1.10	7
315	.5	1.8	1.25	7
315	1.0	1.9	1.35	7

TABLE I (Continued)

Temp.	T. S.	O. R.	C. P.	m*
No. 2: Carbon dioxide, 14 hrs. P.P. 0.011 mm.				
25°C	.5	0.07mm.	0.0mm.	0×10^{13}
120	.5	0.7	0.50	4
205	.75	1.7	1.35	9
290	.75	2.6	2.10	12
298	1.0	2.55	2.05	11
No. 3: Carbon dioxide, 35 hrs. P.P. 0.018 mm.				
25°C	.5	0.1mm.	0.0mm.	0×10^{13}
100	.5	0.9	0.7	5
190	.5	1.5	1.15	8
315	.75	2.25	1.65	9
315	2.75	2.90	2.30	12
310	4.0	2.90	2.30	12
No. 4: Toluene, at 27 mm. for 13 hrs. P.P. (0.017)				
25°C	.5	0.1mm	0.0mm.	0×10^{13}
105	.5	0.55	0.35	3
210	.75	1.35	0.95	6
315	.5	1.85	1.25	7
315	2.0	1.80	1.20	7
305	4.0	1.90	1.30	7
Morning		0.60	0.50	4
No. 5: Ammonia, 10 hrs. P.P. 0.02mm.				
25°C	.5	0.12mm.	0.0mm.	0×10^{13}
120	.75	1.6	1.35	10
212	1.5	1.95	1.55	10
325	1.5	2.45	1.80	10
No. 6: Ammonia, 17 hrs. P.P. 0.04 mm.				
25°C	.5	0.22mm.	0.0mm.	0×10^{13}
105	.5	1.5	1.15	9
220	.75	2.75	2.20	14
320	.75	2.95	2.15	12
No. 7: Hydrogen, 18 hrs. P.P. 0.008 mm.				
25°C	.5	0.05mm.	0.0mm.	0×10^{13}
120	.5	1.0	0.85	6
220	.75	1.45	1.1	7
320	.75	1.40	0.90	5
320	1.25	1.40	0.90	5

TABLE I (Continued)

Temp.	T. S.	O. R.	C. P.	m^*
No. 8: Hydrogen, 16 hrs. P.P. 0.02 mm.				
−78°C	.5	0.09mm.	0.0mm.	0×10^{13}
25	1.0	3.30	3.2	27
120	.5	5.8	5.55	40
215	.5	6.0	5.40	36
310	.75	6.15	5.55	32
Morning		2.20	2.10	18
No. 9: Hydrogen, 16 hrs. P.P. 0.036 mm.				
−78°C	.5 hrs	0.15mm.	0.0mm.	0×10^{13}
25	1.5	2.9	2.7	23
200	.5	6.2	5.7	39
300	.5	6.3	5.6	33
340	1.0	5.7	4.9	27
Morning		1.9	1.7	14
No. 10: Hydrogen, 111 hrs. P.P. 0.007 mm.				
−78°C	.5 hrs.	0.03mm.	0.0mm.	0×10^{13}
25	1.0	1.85	1.8	15
120	1.0	4.15	4.00	29
220	.5	5.4	5.1	33
325	.5	5.5	5.0	28
325	1.0	5.2	4.7	26
330	2.0	4.9	4.4	24
330	3.0	4.75	4.25	24
Morning		2.6	2.55	22
No. 11: Carbon Monoxide, 12 hrs. P.P. 0.006 mm.				
−78°C	.5 hrs.	0.03mm.	0.0mm.	0×10^{13}
25	1.0	2.3	2.25	20
120	.5	3.4	3.25	24
200	.5	3.85	3.55	24
330	1.0	3.6	3.1	18
Morning		1.2	1.15	10
No. 12: Carbon Monoxide, 16 hrs. P.P. 0.007 mm.				
−78°C	.5 hrs.	0.03mm.	0.0mm.	0×10^{13}
25	1.0	1.6	1.55	13
105	.5	3.15	3.00	23
200	.5	3.65	3.35	22
325	.1	4.35	3.85	22
325	.5	4.05	3.55	20
325	1.5	2.9	2.4	14

TABLE I (Continued)

No. 13: Carbon Monoxide, 68 hrs. P.P. 0.008 mm.

Temp.	T. S.	O. R.	C. P.	m*
−78°C	.5 hrs.	0.04mm.	0.0mm.	0×10^{13}
25	1.0	1.7	1.65	14
115	.5	3.7	3.55	25
200	.5	5.1	4.8	32
315	.5	5.6	5.1	29
315	1.5	4.4	3.9	23
315	2.0	3.5	2.15	18
Morning		2.2	2.15	18

No. 14: Ethylene, 15 hrs. P.P. 0.015 mm.

25°C	.5 hrs.	0.09mm.	0.0mm.	0×10^{13}
120	.5	0.9	0.7	5
205	.5	1.2	0.85	6
325	.75	1.35	0.75	4
325	1.5	1.3	0.7	4
Morning		0.3	0.3	2

No. 15: Ethylene, 15 hrs. P.P. 0.01 mm.

−78°C	.5 hrs.	0.06mm.	0.0mm.	0×10^{13}
25	1.0	1.45	1.4	12
130	1.0	2.6	2.4	17
200	1.0	3.2	2.9	19
320	.5	3.4	2.85	16
325	1.25	3.0	2.45	14
340	1.5	3.1	2.5	14
Morning	0.8	.75		6

The number of hours following the name of the gas in Table I gives the length of time that the gas was allowed to stand in the apparatus before it was pumped out. The value following P.P. indicates the pressure at the end of the pumping-out period, i.e. just before the mercury was raised above the cut-off. The temperature is that of the furnace. Where the initial temperature is −78°C it means that the capillary tube was surrounded by solid carbon dioxide while it was being pumped out and then a reading taken under those conditions. The figures under T.S. give the length of time in fractions of an hour that the furnace was kept at the temperature in question before a reading was taken. The values listed under the heading O.R. show the height in mm. that the mercury column rose while the temperature rose from the initial value to the value in question. The value for O.R. at the lowest temperature was obtained by multiplying P.P. by 5.8 (ratio of volumes before and after compression).

The rise observed in the mercury column in tube A as the temperature is increased is the result of three influences, (1) the increase in thermal pressure of the molecules present originally in the gas phase, (2) the change due to the increase of the vapor pressure of the mercury, (3) desorption of molecules and the increase in thermal pressure of molecules desorbed at lower temperatures.

The magnitude of (1) is small since the original pressure was always about 0.10 mm. and it can be calculated from the original pressure and the temperature of the exposed and covered parts of the adsorption apparatus. (2) is found from the results of the blank experiment. Applying these corrections the values listed under C.P. (corrected pressure) show the increase in pressure that is due to desorbed molecules. The next column, m*, gives the number of molecules which correspond to the pressures listed under C.P. and of course these figures give the total number of molecules that had been desorbed up to and including the temperature in question. The way m* increases shows the amount of desorption that takes place as the temperature is raised.

In order to calculate m* it was assumed that all the volume in the furnace was at the furnace temperature and all the exposed portion was at the temperature as determined by the thermocouple put in contact with it. This latter assumption is undoubtedly not quite correct but since this exposed volume occupied such a short length it is quite justifiable. Using these temperatures and the respective volumes as calculated from the dimensions of the capillary tube and the corrected pressures, m* was calculated for each temperature.

From the observed pressures and the size of the capillary tube a calculation shows that in some cases the mean free paths of the molecules are larger than the diameter of the tube and one might think that the phenomenon of thermal transpiration would cause a complication in the calculations. However, when this was calculated it was found that it would change m* by much less than the experimental error so it is not of any importance.

In order to calculate the precision of m* it is necessary to take into account the magnitude of the error in O.R., the blank, the temperature, the pressure of the molecules originally present and the volume of the adsorption apparatus. Estimating all these as fairly as possible it comes out that the percentage error in m* is 25% when C.P. is 1.0 mm., and 15% when C.P. is 2.0 mm. and for higher pressures it is 10%.

Discussion of Data

Since the way desorption took place for the individual gases is plainly shown by the way m* changed with temperature it will not be necessary to go into a detailed discussion of the results for each experiment. Consequently only the more important things will be mentioned for each gas and finally a summarizing table will be given.

Air.—Desorption was practically complete by 100°C and further heating at higher temperatures caused no more change. Of course from this experi-

ment alone it is impossible to tell if nitrogen or oxygen was the desorbed gas. In the work presented here it was not planned to study mixtures and this experiment was made essentially for orienting purposes.

Carbon dioxide.—Desorption seemed to be continuous up to 300°C so there is nothing to indicate that the glass surface was free of carbon dioxide at that temperature. In the second experiment, where the gas had stood in the apparatus over twice as long, the desorption at the higher temperatures seemed to take place a little more slowly but the total amount desorbed at 300°C was the same in both cases. It should be noted that a final heating of four hours at this temperature caused no further change.

Toluene.—This had been allowed to stand in the apparatus at a pressure of 27 mm. Since P.P. could not be measured it was assumed to be of the magnitude of the other experiment, since the pumping was the same as usual. The desorption seemed to be gradual and even in amount up to 250°C where it was complete. Keeping the temperature at 300°C for six hours caused no change whatever. The morning reading, which of course was at 25°, indicated that not quite half the molecules had been re-adsorbed. This last point will be discussed later.

Ammonia.—For this gas the second experiment, for which the time of standing was slightly longer and the initial pressure slightly higher, showed that the maximum desorption took place at a higher temperature and was a little larger in amount than for the conditions of the first experiment.

Hydrogen.—The data and the summarizing table show the main features of interest. Of course when the capillary tube was surrounded with solid carbon dioxide the amount of desorption was larger. One striking thing, that first became noticeable with this gas, is that at the higher temperatures there was an actual decrease in the number of molecules present. That is, when the temperature was increased the pressure did not increase as much as it should, and indeed in some cases after standing some hours at a high temperature the pressure was actually less than it had been previously. Since this phenomenon was encountered with other gases its explanation will be postponed until later. In some cases the desorption seemed to be reversible but it was not at all clean cut. In this connection it must be remembered that the morning reading was always at 25°. The results obtained when hydrogen was allowed to remain in the apparatus seven times as long as usual showed that, although the maximum desorption was slightly changed, there was no great difference in the behavior.

Carbon monoxide.—There is nothing in particular to be emphasized here. Long standing seemed to raise the minimum temperature and the amount of maximum desorption as well as to decrease the reversibility somewhat.

Ethylene.—The only unusual point to be noted here is that at the higher temperatures there was a decrease in pressure at first but on long standing it came to a constant value.

For purposes of comparison and for recapitulation of the above statements Table II has been compiled.

TABLE II

Temp. of 25°C

Exp.	14	1	7	4	5	6	2	3
Gas	C_2H_4	Air	H_2	C_2H_2	NH_3	NH_3	CO_2	CO_2
S.	15 hrs	10	18	13	10	17	14	35
P. P.	.015mm.	.011	.008	.017	.020	.040	.001	.018
M. T.	205°C	150	150	250	120	220	300*	300*
M. M.	6×10^{13}	7	7	7	10	13	12	12
F.	.32	.20	.20	.48	.24	.31	.36	.36

Temp. of −78°C

Exp.	15	12	11	13	10	9	8
Gas	C_2H_4	CO	CO	CO	H_2	H_2	H_2
S.	15 hrs	16	16	68	111	16	16
P. P.	.010mm.	.007	.006	.008	.007	.036	.020
M. T.	200°C	105	120	200	220	200	120
M. M.	19×10^{13}	23	24	32	33	39	40
F.	1.0	.76	.80	1.0	.94	1.1	1.1

T.S and P.P. have the same meanings as before. M.T. (minimum temperature) refers to the lowest temperature at which desorption was complete. M.M. refers to the maximum number of molecules that have been desorbed up to this temperature. F. refers to the fraction of the surface covered by the molecules desorbed.

In calculating this latter quantity, it was assumed that the desorbed molecules came exclusively from the surface that was entirely in the furnace, this had a magnitude of 0.55 sq. cm. and is 86% of the total possible area. Undoubtedly there was some desorption from the exposed surface but using the above assumption the value calculated will be the maximum possible. The diameter, or sphere of influence, of an adsorbed molecule was calculated from the density of the substances in the liquid state as given in the International Critical Tables. Since the densities are not available for all the substances at 25° and −78° one should not put too much weight on the absolute values listed under F. They only show the order of magnitude and the point to be emphasized is that even taking into account the above mentioned uncertainties there was no evidence that the layer of adsorbed molecules was of polymolecular thickness.

From the table the most striking thing is that for all the gases except carbon dioxide desorption was complete at fairly low temperatures. In some cases this minimum temperature was less than 120° and in only one was it over 220° and this was somewhat doubtful. It should also be added that desorption seemed to take place rather slowly at room temperature but when the temperature was above 150° it took place within about half an hour as a rule.

It appeared that a long saturation period had a slight effect on the subsequent desorption but it varied with the gas. The change was not striking enough to warrant any discussion.

In general, all that can be said as to the reversibility of the desorption is that the apparatus used did not permit careful study. The difficulty is that the conditions under which re-adsorption took place were quite different from the initial conditions of adsorption, particularly in regard to pressure, so one can not really say much about this.

From the data it will be noted that the gases which showed a decrease when kept for some time at the higher pressures were hydrogen, carbon monoxide, and ethylene but this behavior was not noticed with toluene or carbon dioxide. The decrease seemed to be of larger magnitude the higher the temperature and pressure and as mentioned before on very long standing at the higher temperatures it stopped entirely.

There seem to be only two reasonable explanations for this. The first is that at the higher temperatures the glass becomes permeable to some of the gases. This behavior has been well established experimentally but in this case there is no apparent reason why the decrease should finally stop as it did with ethylene. The other suggestion is that at the higher temperatures the mercury becomes permeable to some of the gases. Although this at first seems rather novel there is nothing known either from the standpoint of the properties of mercury or the results obtained with the above gases that is in conflict with this hypothesis. On the other hand there is no positive evidence as yet that mercury does behave in this way.

The above results on the desorption of gases are in accordance with the observations of Sherwood[1] who found that if glass was previously well annealed and then allowed to stand in the atmosphere for some time the gases given off when it was heated again to a temperature slightly below the annealing temperature were true adsorption products and corresponded roughly to a mono-molecular layer. In the above work the temperature never was raised above the preliminary annealing temperature and from the results of the experiments and the blank determinations there was nothing to indicate that there were any gases coming from the decomposition of the glass itself.

Experiments and Results with Water-treated Surfaces

All the work described above has been done in connection with glass surfaces that were molecularly plane and from which moisture had been carefully excluded. Naturally it would be of interest to obtain data on the desorption of water and also to see to what extent the surface of the glass was changed by contact with water vapor. Accordingly experiments were made to determine these points.

In order to do this the adsorption apparatus was allowed to remain for several days open to a bulb of water that had been sealed into the system.

[1] Sherwood: Phys. Rev., 12, 448 (1918); J. Am. Chem. Soc., 40, 1645 (1918).

The vapor pressure was that of water at the temperature of the room and was about 25 mm. After this period the adsorption apparatus was pumped out for an hour and a half at room temperature by means of the oil pump and during this time the rest of the system was thoroughly out-gassed by means of a hand-torch. Then an experiment was made in the usual manner and the following data obtained.

No. 16	Water, 62 hours		P.P. (0.017mm)	
Temp.	T. S.	O. R.	C. P.	m*
25°C	.5 hrs	0.10mm	0.00mm	0×10^{13}
110	.4	9.75	9.55	72
210	.15	23.65	23.65	159

It is evident from these figures that water vapor is adsorbed strongly compared to the other gases and vapors used; undoubtedly a change in surface and mechanism of adsorption played an important role in this case.

After the last reading at 210° the apparatus was opened to the diffusion pump for ten minutes; then the furnace was turned off but the pump kept in operation. In an hour when the temperature had fallen to 65° the mercury was raised and a reading taken. Then the furnace was heated to 210° and in fifteen minutes another reading taken. The increase amounted only to 0.40 mm and indicated that practically all the water vapor desorbable at this temperature had been desorbed. The adsorption apparatus was then opened to the diffusion pump and the furnace turned off. When it had cooled to 65° it was opened to the bulb of toluene and flushed out in the usual way. The following results were then obtained.

No. 17	Toluene, 16 hours		P.P. (0.017mm)	
Temp.	T. S.	O. R.	C. P.	m*
25°C	.5 hrs	0.10mm	0.0mm	0×10^{13}
90	.15	0.90	0.75	7
135	.25	1.10	0.85	6
200	.33	5.15	4.80	33

This experiment was identical in all respects to that made before with toluene (No. 4) when the surface was molecularly plane. It will be seen that in this case the desorption up to 120° was slightly higher than that obtained before with toluene, in magnitude it was about the same as that of the previous maximum desorption. From this point on the desorption was very large so the value at 200° was over four times that of the other toluene experiment. It should be noted that the maximum temperature here was slightly lower than the maximum used in the water experiment. This, together with the check made after the previous experiment and the exhaustive pumping would indicate that this large desorption was due to toluene and not to additional water.

After this experiment the system was pumped out and a blank made and then dry hydrogen introduced as usual and the following results obtained.

No. 18	Hydrogen, 17 hours		P.P. 0.007 mm	
Temp.	T. S.	O. R.	C. P.	m*
25°C	.5 hrs	0.13mm	0.0mm	0×10^{13}
110	.15	0.45	0.30	2
200	.33	2.7	2.4	14
300	.33	12.7	11.55	69

This experiment was identical with the first one made on hydrogen (No. 7) except for the intervening water treatment. In this case the desorption at 200° was three times greater than it had been in the previous hydrogen experiment and from the considerations mentioned it is believed that this desorption corresponded to hydrogen and not to water vapor or toluene. In order to see what would happen when the temperature was raised above the maximum attained up to this point it was increased to 300°. The desorption occurring in this interval was very large, in all probability it was mostly water, but perhaps some toluene and hydrogen.

After the last reading at 300° the apparatus was pumped out for half an hour by means of the diffusion pump and then allowed to cool with pumping and again filled with hydrogen.

No. 19	Hydrogen, 17 hrs		P.P. 0.007 mm	
Temp.	T. S.	O. R.	C. P.	m*
25°C	.5 hrs	0.03mm	0.0mm	0×10^{13}
125	.15	0.35	0.15	1
190	.25	0.65	0.40	3
290	.25	1.65	1.20	10
325	.25	4.5	3.60	22

From this experiment it is seen that the desorption up to 200° is much smaller than in the preceding experiment; this is the interval in which the desorbed gas is in all probability hydrogen. In the last three experiments the temperature had never been raised higher than 300° and it is interesting to note that raising it in this experiment to 325° brought about quite a noticeable amount of desorption considering the small temperature interval, this was undoubtedly mostly due to the desorption of water.

By a comparison of the data obtained before and after the surface had come in contact with water vapor the following conclusions seem legitimate.

The water vapor itself is strongly adsorbed and comes off continuously while the temperature is being increased. A second heating through the same temperature range causes no further desorption but heating above the previous maximum temperature brings about more desorption.

After standing in contact with water vapor the glass showed a distinct but not enormous change in surface. Both toluene and hydrogen were adsorbed to about three times the amount on such a surface as on a molecularly plane surface and the desorption did not take place so readily. However,

after additional experiments the amount of desorption diminished, which indicated that the surface was tending to become more and more molecularly plane. This points toward the action of water vapor alone as not being very drastic. It was consideration of this last point that led to the procedure of keeping the apparatus at a high temperature for only a short time. It is not to be expected that water vapor alone would dissolve out part of the glass and change the surface as much as treatment with cleaning solution and subsequent washing with water.

The author wishes to express his appreciation to Professor J. C. W. Frazer and Professor W. A. Patrick for suggesting the problem to him and also for advice during the pursuance of the work.

Summary

A simple apparatus has been designed for measuring the desorption of gases from glass surfaces. Its unique features are a very large ratio of surface to volume and the possibility of rendering its surface molecularly plane.

With the surface molecularly plane desorption measurements were made at −78°C and 25°C with the following gases, air, carbon dioxide, toluene vapor, ammonia, hydrogen, carbon monoxide and ethylene.

Measurements were also made after the glass surface had come in contact with water vapor.

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SOME PHYSICO-CHEMICAL PROPERTIES OF GUM ARABIC-WATER SYSTEMS AND THEIR INTERPRETATION

BY ROBERT TAFT AND LLOYD E. MALM

Water and gum arabic form systems which are generally regarded as colloidal systems, forming typical hydrophilic sols; or, at least, they are cited as examples of this class of systems in a number of text books of colloid chemistry.[1] Kruyt and Tendeloo[2] have in particular emphasized the lyophilic character of gum arabic and from viscosity studies upon gum arabic-water systems in the presence of electrolytes conclude that "gum arabic sols show the typical properties of a lyophilic colloid."

On the other hand, Thomas and Murray[3] have recently submitted evidence that these systems have some properties which resemble those of electrolytic solutions. These investigators showed that the metal-free material obtained from the electrodialysis of the commercial gum was an acid, possessing definite titration value with bases, and that the water solution of this material possessed a high osmotic pressure. This substance was therefore called arabic acid. The preparation of this material involved treatment with acids and precipitation by alcohol from water solutions of the original material. Carefully selected gum arabic without the acid treatment yields approximately 3% ash which O'Sullivan[4] showed to be chiefly calcium and magnesium carbonates. O'Sullivan considers this ash to be present in the original gum either as these metals in combination or as adsorbed salts. Apparently from the results of Thomas and Murray this mineral matter can be accounted for by assuming gum arabic to be a mixture of calcium and magnesium arabates.

We have determined a number of the physical properties of gum arabic-water systems in the hope that additional evidence for one or the other point of view as stated above could be found. The determinations were made upon purified gum; but the purification did not involve electrodialysis or precipitation with acid and hence the substance was not arabic acid but a supposed mixture of the calcium and magnesium salts of this acid. The properties determined were viscosities and densities over a considerable range of temperatures and concentrations, and in the presence of added electrolytes; freezing points up to a weight concentration of forty-five per cent; electrical conductance as a function of concentration at 30°C; and the hydrogen ion concentration of such systems.

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[1] A few examples are given herewith: Hatschek: "Physics and Chemistry of Colloids," 82 (1926); Zsigmondy, Spear: "Chemistry of Colloids," 24 (1917); Freundlich, Hatfield: "Colloid and Capillary Chemistry," 596 (1922).

[2] Kolloidchem. Beihefte, 29, 396 (1929).

[3] J. Phys. Chem., 32, 677 (1928).

[4] J. Chem. Soc., 42, 1322 (1882).

Purification of Material

The gum arabic used was a commercial product described as "first grade tears." It was composed of small tear-like pieces, some of which were nearly colorless, while others were yellow. A small number of dark red to brown particles were distributed throughout the gum. In order to obtain a uniform product for examination a large quantity of the gum was dissolved in as little water as possible. This amounted to about twice as many cubic centimeters of water as there were grams of gum employed. This viscous solution was filtered under pressure and a clear colorless filtrate obtained. The acacia was then precipitated by the addition of ethyl alcohol. A sticky, white precipitate was obtained which was repeatedly washed with alcohol. It was then drained, pressed as free from alcohol as possible, and dried at room temperature. The product was then ground to a powder, placed in a long tube and a stream of dry air passed over it until it no longer had the slightest odor of alcohol. It was kept in this dry condition in desiccators containing calcium chloride and concentrated sulfuric acid. The dried product was a pure white powder, more dilute solutions of which were colorless. The more concentrated ones possessed a slight yellow color.

According to O'Sullivan, purification by this process in not too dilute solutions gives a product which is unaltered from its original state; i.e. no hydrolysis or other chemical changes have taken place.

Purification of two samples by this method gave specimens, 5% solutions of which, possessed identical densities and viscosities. A third sample purified by another observer gave a 5% solution possessing a viscosity approximately 2% lower than the above pair. This deviation was traced to insufficient drying and the sample was found to contain about 10% moisture. The supply of material used contained 0.87% moisture as determined by heating to 85° until constant weight was obtained. The original gum contained 10.5% moisture by this same procedure. When ignited and the ash content determined, two samples gave (dry basis)

I 3.05% Ash
II 3.07% Ash

Melting point determinations were attempted but the material charred between 190° and 200°C.

Viscosity and Density Determinations

A. Viscosity as a Function of Concentration.

There is very little published data upon the viscosity of gum arabic solutions, especially in the more concentrated systems. Much of the data that is given is stated without specifications of the method of purification, of the temperature at which the determinations were made or of the pH of the solutions. Went[1] has determined the viscosity of gum arabic solutions up to concentrations of 6% at different temperatures and pH values but in most

[1] Am. J. Physiol., 85, 458 (1928).

cases takes no account of the effect of electrolytes which were added. H. Walter[1] has investigated the viscosities of such systems up to 12% at various temperatures, but the concentrations of many of her solutions were not determined directly.

Our determinations of viscosity were made with two Ostwald pipettes. One of these viscosimeters required approximately 85 seconds for the flow of 5.32 cc of water through its capillary at 30°. The radius and the length of this capillary were determined by a measuring engine and found to be 0.087 cm. and 7.64 cm. respectively. The second viscosimeter had a volume of 1.84 cc, a capillary length of 7.91 cm. It is referred to below as the 20-second viscosimeter. The liquids were allowed to flow through these viscosimeters under their own hydrostatic head and consequently the kinetic energy correction was negligible and not applied.

The viscosimeters were calibrated by means of twenty, forty, and sixty weight per cent sucrose solutions as these solutions had viscosities which covered nearly the whole range of viscosities obtained for the gum arabic-water systems. The data for the absolute viscosities and densities of the sugar solutions were obtained from the International Critical Tables and Landolt-Börnstein Tabellen (1929) respectively.

Determination of the density and time of outflow were then made for the gum solutions and for the time of outflow of the sugar solutions. The absolute viscosities of the gum solutions were then computed from the usual relation

$$\eta_{gum} = \eta_s \times \frac{D_g \times t_g}{D_s \times t_s}$$

where the subscripts g and s refer to the gum and sugar solutions respectively.

A stop-watch reading to 0.1 second was used for determining the times of outflow. The time in most cases could be checked to within 0.1 seconds but in the most concentrated ones deviations as high as 0.5 seconds were encountered.

The densities were determined in a 25 cc narrow necked flask fitted with a glass stopper. The flask was calibrated with water, using ICT data for the densities of water at the various temperatures. The volume could be adjusted to within 0.02 cc and consequently results are expressed with four significant figures.

Two automatically-regulated constant-temperature baths were employed for the determinations at 30° and 45°. Maximum temperature variations on these baths were ±0.01°C and ±0.03°C respectively. The measurements at 0°C were made in a clear three-liter Dewar flask filled with chipped ice and water, the top being carefully insulated. The temperature was checked with a certified thermometer and lay between 0.00° and 0.03°C during the determinations. To secure constant temperature at 15°C a four-liter beaker was filled with water at approximately 15° and the temperature was held to within 0.05° by hand regulation of the flow of cold tap water through a coil placed along the walls of the beaker.

[1] Sitzungsber. Akad. Wiss. Wien., 129 IIa, 709 (1920).

The pH determinations in this and subsequent series of measurements, were made by the use of a quinhydrone electrode and a saturated calomel electrode at 25°. The potentials of the cells were measured by Leeds and Northup student potentiometer balanced by means of a certified standard cell. The pH values were computed from the expression

$$pH = \frac{0.6992 - 0.2458 - E_o}{.0591}$$

where E_o is the measured cell potential, 0.6992 the electrode potential of the quinhydrone electrode at unit hydrogen ion concentration, 0.2458 the value assigned to the saturated calomel electrode and 0.0591 the value of the thermodynamic function 2.30 log RT/F at 25°C.

The data obtained at 30°C for various concentrations of gum arabic up to approximately 35 weight per cent are tabulated in Table I and the relative viscosities are shown graphically in Fig. 1.

TABLE I

The Viscosities of Gum Arabic Solutions at 30°C
pH of all solutions = 7.14 ± .02

	Wt. %	Density	Effective Density	Time	η_s/η_{sug}	η_s	η_s/η_{H_2O}
1.	1.22	1.000	1.610	37.0	0.985	.0132	1.65
2.	2.10	1.003	1.593	47.8	1.06	.0160	2.00
3.	2.70	1.006	1.607	51.4	1.22	.0184	2.30
4.	3.85	1.010	1.600	238.9	1.55	.0234	2.92
5.	3.95	1.011	1.599	65.2	1.56	.0235	2.93
6.	4.77	1.014	1.606	263.4	1.71	.0259	3.23
7.	5.54	1.017	1.608	79.2	.653	.0287	3.59
8.	7.33	1.024	1.595	106.8	.887	.0390	4.87
9.	8.55	1.029	1.604	120.0	1.00	.0440	5.50
10.	11.73	1.042	1.601	190.4	1.60	.0707	8.84
11.	15.68	1.050	1.604	256.1	2.18	.0959	11.9
12.	16.48	1.062	1.599	370.1	3.18	.140	17.5
13.	18.69	1.071	1.597	498.3	4.33	.190	23.7
14.	34.92	1.141	1.568	6070.0	7.08	2.41	300.

η_s is the absolute viscosity of the gum arabic solution. η_{sug} that of the sucrose solution used in the calibration of the pipette. η_s/η_{H_2O} is the relative viscosity of the gum arabic solution compared to that of water at 30°C. The effective density tabulated is a quantity which will be referred to later. Trials 4 and 6 were run with the 80 second viscosimeter. The 20% sucrose solution was used as the standard for trials 1 to 6 inclusive; the 40% sucrose solution for No. 7 to 13 and the 60% sucrose solution for No. 14.

The small diagram on the right of Fig. 1 is drawn with larger units of ordinates and abscissae in order to show the relative viscosity for the highest concentration of gum arabic used.

B. Viscosity as a Function of Temperature.

Determinations on the viscosities of two gum-arabic solutions were made at the temperatures of 0°, 15°, 30°, and 45°C. The concentrations of these two solutions were 3.84 weight per cent and 9.09 weight per cent respectively. Data for the first solution are given in Table II and that for the more concentrated one in Table III.

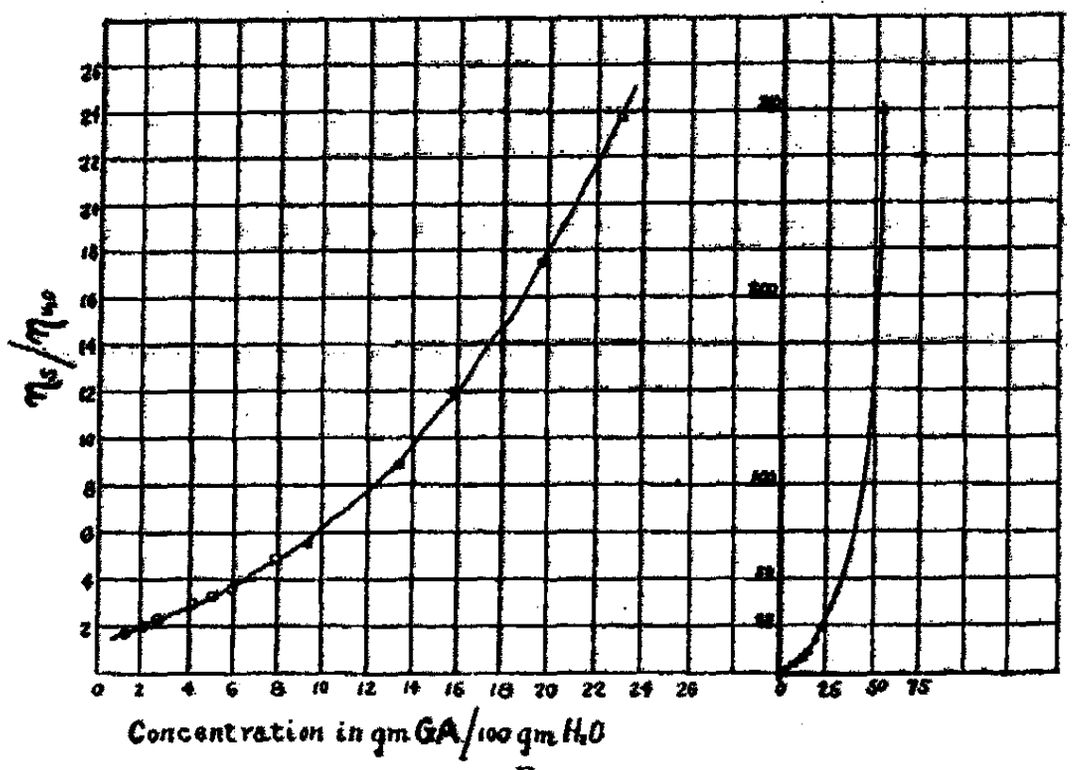

FIG. 1

Relative viscosity as a function of concentration at 30°C.

TABLE II

Concentration Gum Arabic, 3.84%

Temp.	D_s	Time	η_s/η_{w0}	η_s	Temp. Coeff.
0°	1.019	573	3.38	.0605	
15°	1.018	348	3.13	.0357	3.44
30°	1.101	239	2.93	.0234	2.76
45°	1.009	175	2.74	.0170	2.14

TABLE III

Concentration Gum Arabic, 9.09%

Temp.	D_s	Time	η_s/η_{w0}	η_s	Temp. Coeff.
0	1.197	1197	7.17	.128	
15	1.034	719	6.57	.0749	3.52
30	1.031	480	5.97	.0478	2.94
45	1.025	344	5.48	.0327	2.55

The relative viscosities as functions of temperature are shown graphically in Fig. 2, Curve 1, being that of the more dilute solution. The temperature

coefficients tabulated in Tables II and III are in reality the average percentage decreases of viscosity per degree for each 15° interval and were computed from the relation

$$\text{Temp. Coeff.} = \frac{\eta t_1 - \eta t_2}{15} \times \frac{200}{\eta_2 + \eta_1}$$

C. Viscosity as Functions of Heat Treatment, Mechanical Treatment and Age.

Table IV shows the effect of heat treatment upon the viscosity of a gum arabic solution containing 5 grams of gum arabic in 100 grams of water. The solution was prepared at 25°, then placed in the constant temperature

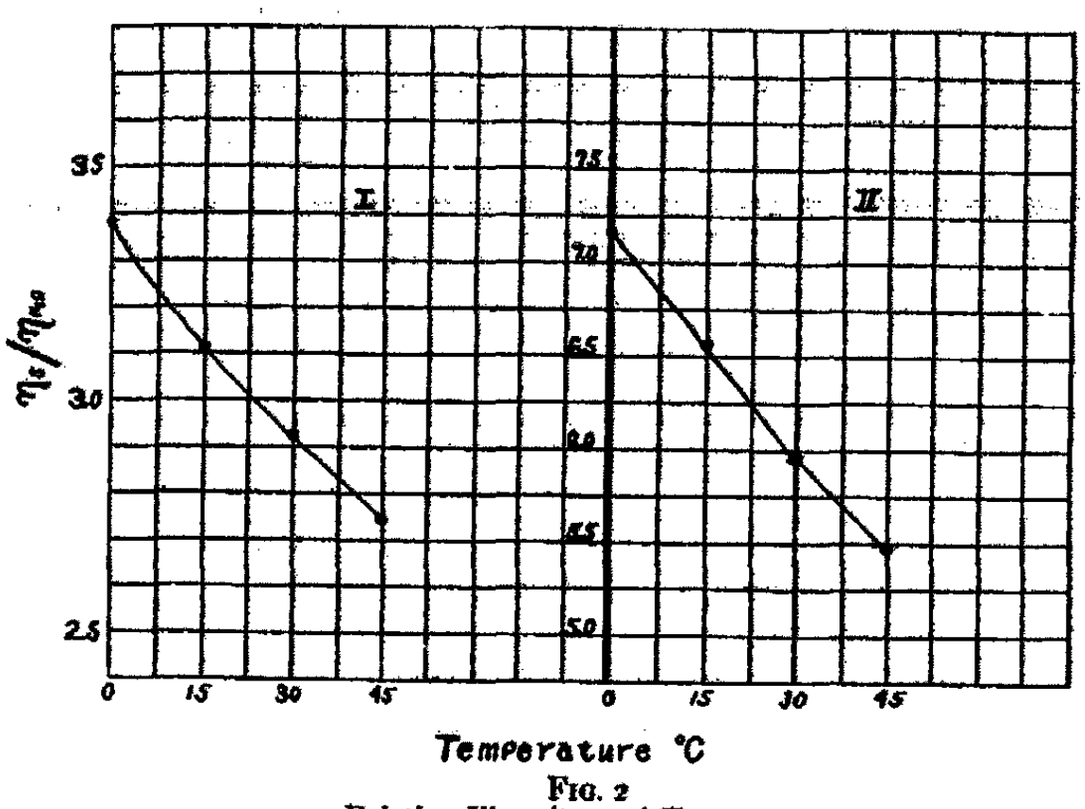

FIG. 2
Relative Viscosity and Temperature
Curve I–3.84% gum arabic; Curve II–9.09% gum arabic.

bath and its viscosity determined. Another portion of the solution was heated in a closed container on a water bath at 60° for one hour and then recooled to 30° and its viscosity determined. Similar treatment was given the solution at 80° and 95° for different lengths of time.

TABLE IV

5 grams Gum Arabic in 100 gms. of Water, 30°C

	D	T	η_s/η_{H_2O}	η_s
Orig. Sample	1.014	72	3.23	.0259
60°—1 hour	1.014	71	3.20	.0257
80°—4 hours	1.014	67.5	3.05	.0244
95°—6 hours	1.014	52.2	2.36	.0189

To determine the effect of mechanical treatment a solution of gum arabic similar to that described above was drawn thru the capillary of the viscometer and rapidly expelled some twenty times. The time of outflow was then determined and found to be unchanged as compared to that of the untreated sample.

Measurements of the variation of viscosity with age are limited as to length of time because bacterial action sets in from 36 to 48 hours after the solutions are made up. After several weeks the growth produced as a result of this action was present as large slimy lumps and the solutions had a sour smell. The more concentrated solutions did not show this phenomena until a much longer period had elapsed. The pH value of a 5% solution decreased by approximately six per cent in a period of several months. Keeping the solutions on ice very much retarded the formation of the growth.

Viscosity measurements on solution for different periods of time up to the appearance of the growth gave the same viscosities for solutions of the same concentration and temperature.

D. Viscosity as Function of Neutral Salt Content.

The viscosities of a solution of 5 grams of gum arabic in 100 grams of water were determined in the presence of a number of neutral salts, the concentration of the salt being made equal to 0.1 molal. The data is recorded in Table V, the temperature of measurement being 30°C. η_e and η_w represent the absolute viscosities of electrolyte solutions and of water respectively.

TABLE V

Effect of Various Sodium Salts upon the Viscosity of a Solution containing 5 grams of Gum Arabic in 100 grams of water at 30°C

Salt	Density	Time of Outflow	η_e/η_w	$\frac{\eta_{s+e}}{\eta_{sugar}}$	$\frac{\eta_{s+e}}{\eta_{water}}$	$\frac{\eta_{s+e}}{\eta_{elec.}}$	η_{s+e}
NaF	1.016	180.0	1.014*	1.17_2	2.21_2	2.18	.0177
Na_2SO_4	1.026	48.8_7	1.041_3	1.20_7	2.27_8	2.18_8	.0182
NaCl	1.017	180.5	1.009_5	1.17_6	2.21_9	2.19_8	.0178
NaBr	1.023	181.0	1.005_3	1.18_7	2.23_9	2.22_7	.0179
$NaNO_3$	1.018	181.7	1.005_3	1.18_5	2.23_7	2.22_5	.0179
NaI	1.024	179.4	$.997_5$	1.17_7	2.22_2	2.22_7	.0178
NaSCN	1.017	181	.9976*	1.17_9	2.22_5	2.23	.0178
Orig. Solution	1.014		1	1.71_2	3.230		

* The data for the relative viscosity of sodium fluoride and of sodium thiocyanate were determined in this laboratory, but the remaining data were obtained from the International Critical Tables, Volume V, page 15. The determination using sodium sulphate was run with the 20 second viscosimeter.

E. Viscosity as a Function of Calcium Chloride Content.

The effect of progressive additions of calcium chloride up to four gram equivalents per 1,000 grams of water upon the viscosity of a solution of gum arabic containing 5 grams of gum arabic to 100 grams of water was also determined. The observations were carried out at 30° and are tabulated below and shown graphically in Fig. 3, the abscissae representing the concentration of the electrolyte.

TABLE VI

Effect of Addition of Calcium Chloride on Viscosity of a Solution containing 5 gm. Gum Arabic in 100 gms. of Water. Temperature 30°C. pH of all solutions lie between 7.33 and 7.36

Equiv. per 1000 gms. of water	Density	Time	η_s/η_w	$\frac{\eta_s+c}{\eta_{sugar}}$	$\frac{\eta_s+c}{\eta_{water}}$	η_s+c/η_c	η_s+c
0.000	1.014	263.4	1.00	1.71	3.23		.0259
0.002	1.013	239.5	1.00	1.55	2.93	2.93	.0235
0.02	1.014	190.4	1.00	1.24	2.33	2.32	.0187
0.10	1.018	170.0	1.01	1.11	2.09	2.06	.0167
0.20	1.022	168.7	1.03	1.10	2.09	2.02	.0167
0.50	1.034	173.0	1.08	1.15	2.16	2.01	.0173
1.00	1.056	180.0	1.16	1.22	2.30	1.98	.0184
2.00	1.096	198.2	1.35	1.39	2.63	1.95	.0210
3.00	1.113	216.5	1.57	1.57	2.96	1.88	.0237
4.00	1.167	242.6	1.80	1.81	3.42	1.91	.0274

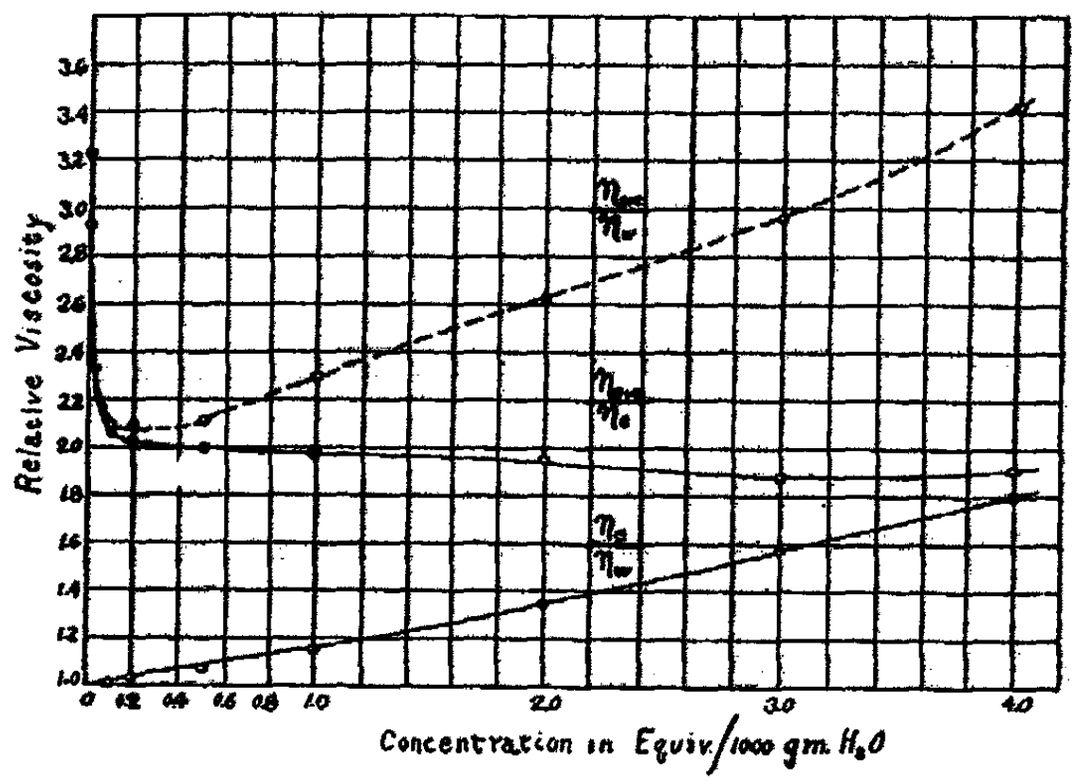

FIG. 3

Relative Viscosity as a function of calcium chloride content, $\frac{\eta_s+c}{\eta_0}$. There is also shown the ratio of the viscosity of the system to that of water, $\frac{\eta_s+c}{\eta_w}$, and the relative viscosity of calcium, $\frac{\eta_c}{\eta_w}$

The symbols have the same meaning as given previously. The data for η_0/η_w was obtained from the International Critical Tables (Vol. 5, p. 15), interpolation being made for those values not stated directly. The pH of all solutions containing the gum arabic was practically constant, lying between the limits of 7.33 and 7.36.

Freezing Point Determinations

The freezing points were determined in the ordinary way by the aid of a Beckmann thermometer up to weight concentration of 17%. Relatively sharp freezing points could be obtained from these solutions which were reproducible to 0.005 of a degree. For the more concentrated solutions a thermometer graduated in 0.1° was used. Here the precision of measurement was considerably less due to the very high viscosity of the solutions. The data obtained are given in Table VII and graphically in Fig. 4.

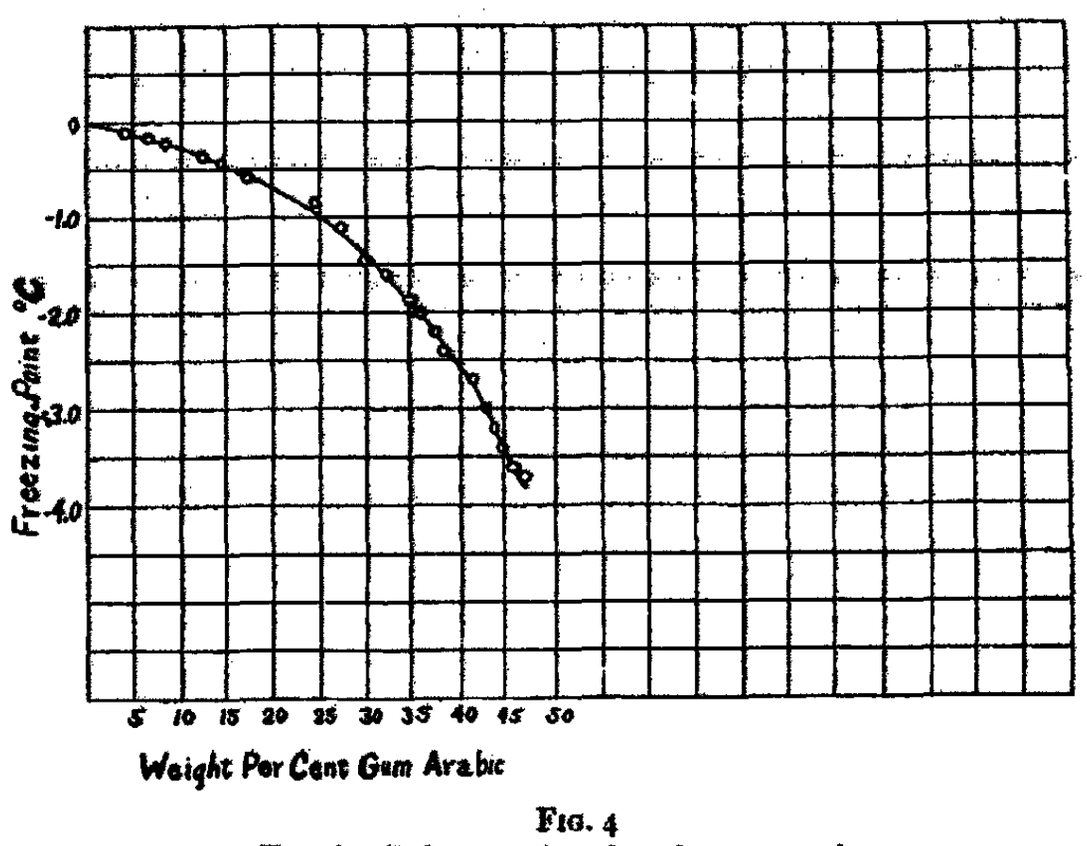

FIG. 4
Freezing Point as a function of concentration.

TABLE VII
Freezing Points of Gum Arabic Water Solutions

No.	Wt. % G.A.	F.P.	No.	Wt. % G.A.	F.P.
1	4.38	−.100	13	30.0	−1.4
2	5.83	−.136	14	32.5	−1.6
3	6.51	−.148	15	35.0	−1.8
4	7.55	−.165	16	36.0	−2.0
5	8.41	−.198	17	37.5	−2.2
6	12.45	−.356	18	38.5	−2.4
7	14.52	−.430	19	41.2	−2.7
8	15.13	−.456	20	42.8	−3.0
9	17.55	−.563	21	43.8	−3.2
10	24.5	−.85	22	44.8	−3.4
11	27.5	−1.1	23	45.9	−3.6
12	29.0	−1.2	24	46.9	−3.7

Newton and Gortner[1] have determined the freezing point of gum arabic solutions up to a weight concentration of nine per cent. Their results show freezing points somewhat higher than those here recorded. These investigators do not state the method of purification or the water content of the material used in their determination as they were interested in relative data only. We have determined the freezing point of our starting material (i.e. crude gum containing approximately 10% water) and have found results practically identical with those of Newton and Gortner. The freezing points of the crude gum were determined over the same range as that of the purified gum and were found to be considerably higher. The solution containing forty-five weight per cent of crude gum has a freezing point depression of about one-half that of the purified gum. These differences are not explainable upon differences of water content alone but point to differences in the hydration of the two samples.

Conductance Data for Gum-Arabic-Water Systems

The conductance of five concentrations of gum arabic at 30° was determined by the aid of the usual conductivity cells using a Leeds and Northup slide wire bridge. Two cells were used, one having a cell constant of 0.448 and the second of 0.103. The constants were obtained by calibration of the cells with solutions of potassium chloride, the data of the International Critical Tables for the conductances of these solutions being used as the basis of the computation. The two most dilute solutions and the conductance water were determined in the cell having the smallest cell constant. The data obtained are given in Table VIII.

TABLE VIII

The Conductances of Gum Arabic Solutions.

Conc. gms/1,000 gms H_2O	N	R (Ohms)	k	Λ_v
215.8	0.180	84	0.00534	26.69
21.58	0.0180	530	0.000847	47.10
2.158	0.0018	4760	0.0000942	52.38
0.2158	0.00018	9000	0.0000097*	53.94
0.02158	0.000018	38000	0.00000099*	55.09
Cond. Water	0	60000	0.00000172	

* Corrected for the specific conductance of water.

N represents the normality of the solution on the basis that 1200 is the equivalent weight[2] of gum arabic and Λ_v is the equivalent conductance, i.e. the specific conductance, k, times the volume in cc containing one gram equivalent.

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[1] Bot. Gaz., 74, 442 (1922).

[2] Thomas and Murray: two values were obtained by these investigators but this value seems the more reliable one. It should be remembered that their value was for arabic acid. Here, as will be pointed out, we are probably dealing with a salt of somewhat higher equivalent weight. The uncertainty in the equivalent weight of the acid, however, does not warrant any correction for the replacement of hydrogen by calcium or magnesium.

Discussion of Results

The viscosity of a true lyophilic sol, presents the following generally recognized characteristics:

a. At constant temperature the viscosity increases more rapidly than concentration of dispersed phase. In some instances the addition of relatively small amounts of dispersed phase (a few weight per cent) will produce a viscosity many times greater than that of the dispersion medium at the same temperature.

b. The temperature coefficient of viscosity is considerably larger than that of the dispersion medium. This is especially marked for sols which set to gels in the neighborhood of their gelation temperatures. In this connection the relative viscosity usually shows a considerable decrease with rising temperature.

c. The viscosity is a function not only of concentration and temperature, but also of the history of the system under examination. Such factors as the mechanical and thermal treatment to which the system has been subjected may influence the viscosity to a marked extent. Very likely the majority of these influences may be traced to their effects upon the degree of dispersion or upon the volume of the colloidal phase.

d. The electrical charge of the particle is also a determining factor in the viscosity of these systems. A reduction of the charge upon the particle presumably has the effect of reducing its size and thereby the viscosity of the system. This phenomenon has been termed by Kruyt[1] "the electroviscous effect". The reduction of charge may be secured by the addition of electrolyte, the ion having a charge opposite to that of the colloidal particle is supposedly the effective one.

An examination of the viscosity data obtained for gum arabic shows that to some extent it resembles those of lyophilic sols. The viscosity increases more rapidly than concentration, the temperature coefficient is greater than that of water, the relative viscosity diminishes with rising temperature and the addition of calcium chloride reduces the viscosity of these systems as compared to that of the dispersion medium.

On the other hand, the viscous behavior of true solutions must be considered. In the case of quite soluble organic substances the viscosity increases more rapidly than does concentration, the behavior being most marked at high concentrations. To be specific, the viscosity data for three substances at 30°C are plotted as functions of their concentration in aqueous solution in Fig. 5. Curve I represents the data of gelatin, a true lyophilic colloid, Curve II that of gum arabic taken from Table I and Curve III that of cane sugar, a non-electrolytic solute. Values for calcium chloride solution, an electrolytic solute, up to thirty weight per cent are nearly identical with those of Curve III.[2]

[1] "Colloids" (trans. by van Klooster), 172 (1927).

[2] The data for calcium chloride solutions is that of the International Critical Tables. Thirty per cent does not mark the limit of solubility at this temperature but is the extent of tabulated data. Without doubt the curve would show an upward trend if data were available to its saturation value of approximately fifty weight per cent.

As will be seen gum arabic occupies an intermediate position with respect to the other two substances.

The temperature coefficients of true solutions are as a rule greater than that of water and become quite large at high concentration of solute. Thus the temperature coefficient of a sixty per cent cane sugar solution between 25°C to 40°C is 4.9; that of water over the same temperature range is 2.07.[1]

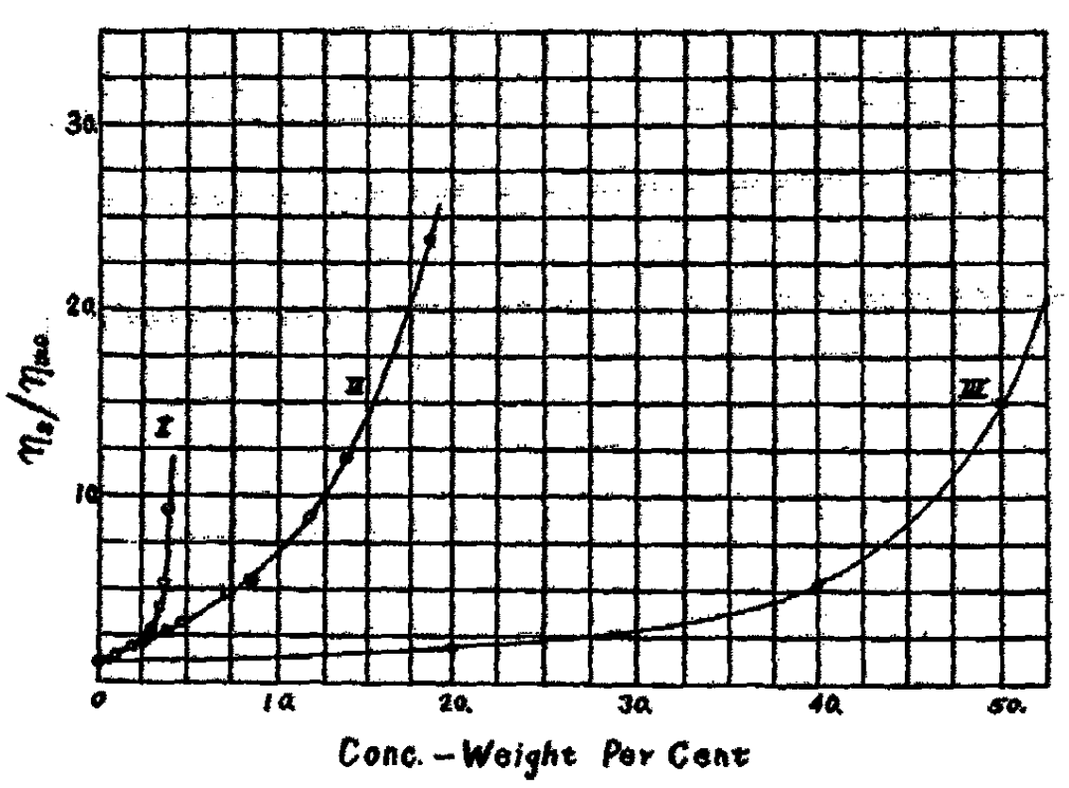

FIG. 5

Viscosity as a function of concentration.
Curve I-gelatin sols (extrapolated from data of Bogue: J. Am. Chem. Soc., 43, 1764 (1921); Curve II-gum arabic solutions (data from Table I); Curve III-Cane sugar solutions (data of Bingham and Jackson: Sci. Paper B. of Stds. 298, 1917).

That of the gum arabic solution of approximately 10 weight per cent is 2.55. If the temperature coefficient had been determined for the more concentrated solutions of gum arabic it would undoubtedly have been large. An examination of Tables II and III will show that an approximate doubling of the weight concentration produces nearly a twenty per cent increase in the temperature coefficient in the interval 30° to 45°.

Greater attention has been paid to the changes in the relative viscosity with temperature than to the variation of the temperature coefficient, especially so since Ranken and Taylor[2] pointed out that in general the relative viscosity of electrolyte solutions increased with rising temperature, while the reverse holds true for solutions of non-electrolytes. Lyophilic sols show the same behavior as organic solutes, i.e. there is a decrease in the relative viscosity with rising temperature.

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[1] Computed from ICT data.

[2] Trans. Roy. Soc. Edin., 45, 397 (1906).

In the case of the gum arabic systems the relative viscosity decreases with rising temperature as has been shown in Fig. 2. If the gum is a mixture of the salts of arabic acid it would be both an organic solute and an electrolyte. If this view is correct the organic character of the material plays a greater part in the determination of the relative viscosity than does its electrolytic behavior. Moreover, the distinction of Ranken and Taylor given above is not an absolute one. There are a considerable number of exceptions to the rule, the most noticeable of which are certain salts of magnesium.

Still another viscosity function of some significance is one having the form $\frac{\eta_s/\eta_o - 1}{F}$ where η_s/η_o is the relative viscosity and F the concentration of solute in gram equvialents. Gruneisen[1] pointed out that this function had a minimum value when plotted against the concentration for solution of electrolytes, but no minimum was apparent for non-electrolytes. Since the quantity F is not determinable for hydrophilic sols, a prediction of the behavior of this function with concentration cannot be made. Gruneisen ascribes the minimum value as being due to electrolytic dissociation. The increase of the relative viscosity per gram equivalent at the smallest concentration being explained by the assumption that increasing dissociation produces an increase in viscosity. It is interesting to note that if the concentrations of Table I are recomputed to gram equivalents and Gruneisen's function is calculated for the gum arabic solutions, that a minimum does occur as is shown in Table IX.

TABLE IX

Concentration of Gum Arabic

No.	Gm. Equiv. per liter*	$\frac{\frac{\eta_s}{\eta_o} - 1}{F}$	No.	Gm. Equiv. per liter*	$\frac{\frac{\eta_s}{\eta_o} - 1}{F}$
1	0.010	64.	8	0.063	62.
2	0.018	57.	9	0.073	62.
3	0.023	57.	10	0.10	77.
4	0.032	59.	11	0.12	91.
5	0.033	58.	12	0.15	127.
6	0.040	56.	13	0.17	136.
7	0.047	55.	14	0.33	900.

* The equivalent weight assumed for gum arabic is 1200 as taken from data of Thomas and Murray. See page 883.

Although the function $(\eta_s/\eta_o - 1)/F$ is somewhat irregular at first, it passes through a well defined minimum at a concentration of 0.047 N. This is of significance when taken into consideration with the other arguments to be developed.

In this same connection should be noted the effect of additions of calcium chloride upon the viscosity of the gum arabic solutions. The reduction to a

[1] Wiss. Abh. phys.-techn. Reichsanstalt, 4, 239 (1905).

minimum value of viscosity occurs at far larger concentrations of electrolyte than do the minimum values which Kruyt finds in the cases of true hydrophilic sols. In these cases the reduction to a minimum value occur at concentration of a few milli-equivalents of electrolytes. In the case of gum arabic, reduction to the minimum value occurs at approximately two hundred milli-equivalents, many times that of Kruyt's values. We are inclined to believe that *the reduction of viscosity here is due to repression of ionization of the calcium and magnesium arabates* and to the influence of the added electrolyte upon the hydration of the gum arabic, rather than to the reduction of the electrokinetic potential upon particles of gum arabic.

The last consideration to be made of the viscosity determination is the effect of neutral salts upon the systems under consideration. An inspection of Table V shows that while the effect of the salts differ to some extent among themselves, and the order is that in general of the lyotropic series, the effect of the iodides and thiocyanides are not as marked as is usually the case for lyotropic effects.

Kruyt[1] ascribes the lyotropic effect to two factors: (1) hydration of ions (2) disturbance of the water equilibria (i.e. those involving dihydrol, monohydrol, etc.).

If this be so, the slight variations which occur in the cases of gum arabic solutions could be ascribed to the first factor; the considerable reduction of all solutions containing electrolyte to the second. Gum arabic in the presence of water is itself without doubt heavily hydrated as judged by its high solubility and high effective density. The addition of ions would result in removal therefore of some of the solvent. If this effect were large an increase of viscosity would result due to the reduction in the mass of the solvent. Actually a decrease occurs, the decrease being approximately the same for all salts.

Density

Wintgen[2] has pointed out that the specific volume of a number of colloidal solutions is a linear function of the weight per cent of the disperse phase, the density being a linear function of the number of grams of disperse phase present in a volume of 100 cc of solution. From the density data given in Table I, it has been found that the specific volume, V, can be computed with considerable accuracy (the variations are considerably less than 1% between calculated and observed values up to 20 weight per cent) by means of the equation:

$$V = 1.004 - .00374P$$

where P represents the weight per cent of gum arabic in solution. The value of V at P = 100% is 0.627. The density of the gum computed from this specific volume is 1.59 as compared to that found directly of 1.48.[3] The

[1] "Colloids," 184 (1927).
[2] Kolloidchem. Beihefte, 7, 251 (1915).
[3] This was found by using mixtures of toluene and carbon tetrachloride and determining the density of the mixture which just floated the purified gum. The original crude gum had a density of 1.51 by this method. The determinations were made at 15°C.

effective densities given in Table I are the equivalent of this quantity and were computed by deducting the volume of water present in a given mass of solution from the volume of the solution and dividing this quantity by the mass of gum present.

Wintgen likewise found large effective densities for the systems examined by him and ascribes the large values to a film of condensed water about each particle. The fact that systems of gum arabic and water show analogous density relations to the colloidal systems investigated by Wintgen should not be taken as evidence for their colloidity. Wintgen himself points out that similar relations hold true for solutions. In the case of cane sugar an equation of the form

$$V = 1.0043 - 0.003860P$$

holds with precision at 30° up to 10 weight per cent. This concentration is approximately of the same molar concentration, as the most concentrated gum arabic solution used if its molar weight is assumed to be 2400. The extrapolated density of solid cane sugar from the above equation is 1.62 which again is higher than the density of solid cane sugar alone (1.59).

Freezing Point Determinations

The important facts to be noted about the data of Table VII and Fig. 4 are (a) the considerable magnitude of the freezing point depression and (b) the increasing magnitude of freezing point depression per unit of mass of solute as indicated by the convexity of the curve toward the concentration axis. If the molecular weight of 2400[1] for gum arabic be assumed, the molar freezing point depression over a range of concentration can be computed. About one-half of the values given in Table IV have been recomputed to a molal basis and the ratio of freezing point depression to molal concentration likewise computed. These are given in the following table, where No. refers to the observations of Table IV, F the molal concentration and ΔT the observed depression.

The striking features about the values of $\Delta T/F$ so calculated are (1) the fact that these values are of the correct order of magnitude for di-monovalent salts;[2] (2) the variations of $\Delta T/F$ with concentration are characteristic of a

TABLE X

No.	F	$\Delta T/F$	No.	F	$\Delta T/F$
1	.019	5.3	11	.16	6.9
2	.029	5.1	13	.18	7.8
5	.038	5.2	16	.23	8.7
6	.059	6.0	19	.29	9.3
7	.071	6.1	22	.34	.10
9	.089	6.3	24	.36	9.7

[1] The titration curves of Thomas and Murray show plainly that arabic acid is a monobasic acid. Calcium arabate would therefore be $Ca(Arabate)_2$. We have used the approximate value of 2400 as the molecular weight. See also page References 883, footnote 2.

[2] For example the value of $\Delta T/F$ for magnesium chloride at 0.025 M is 5.03; compare this value with that of the gum arabic at 0.029 M.

large number of salts, i.e. it starts with a given value, decreases in value with increasing concentration to a minimum and finally increases to a much larger final value. It is true that the increase to high final values for most electrolytes takes place at much greater molal concentration than that found in this case, but it must be remembered that a molal concentration of 0.36 in this case corresponds to a weight concentration of nearly fifty per cent. The evidence from the freezing point data is therefore added proof, to our minds, of the salt-like character of gum arabic.

Conductance Data

If the equivalent conductances of the gum arabic solutions are plotted against the logarithms of their dilutions there is obtained the curve shown in Fig. 6. This is the typical curve obtained for a large number of electro-

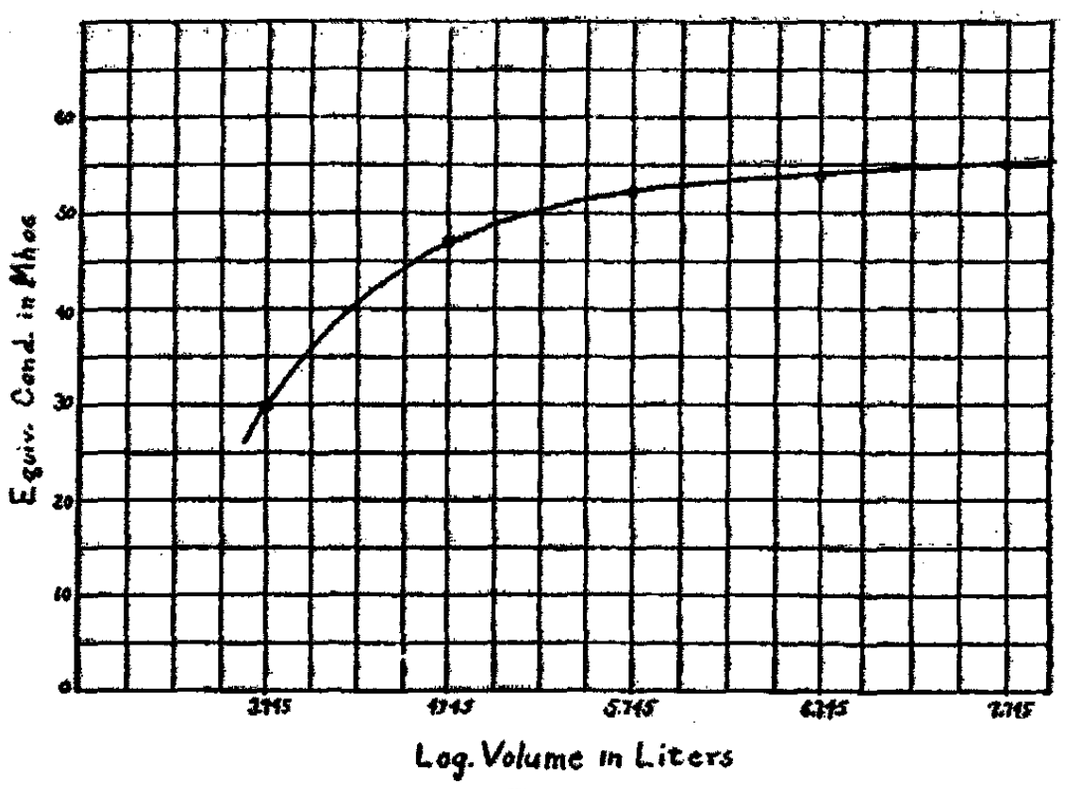

FIG. 6
The Equivalent Conductances of Gum Arabic Solutions.

lytes and when added to the evidence previously adduced leaves little doubt in our minds that gum arabic solutions are actually solutions of calcium and magnesium arabates. Further the equivalent conductance as above computed is a linear function of the square root of the concentration as is shown in Fig. 7. This extrapolated to the value of $c = 0$ gives the equivalent conductance of the gum at infinite dilution, the numerical value of this quantity being 55.5 mhos. At this temperature the value for the equivalent conductance at infinite dilution of the calcium ion singly is 66.1 mhos; that for magnesium ion is 58.8 mhos.[1] *The equivalent conductance of the gum is of the same order of magnitude as that of its positive ions*, i.e. the positive ions are the chief carriers of the current in these solutions. The fact that the equivalent

[1] ICT, 6, 230 (1929).

conductance of the salt is somewhat less than that of either of the positive ions has possible explanation in that the value found for conductances at infinite dilution will depend upon the method of extrapolation (which is different for Ca^{++} and Mg^{++}) and in the second place the conductance of the calcium (or magnesium) ion would doubtless be affected by the presence of the tremendously larger arabate ions. The fact that the equivalent conductance of the gum is practically that of its positive ions would naturally be expected if gum arabic is a mixture of calcium and magnesum arabates. The very large and heavily hydrated anion of low charge (monovalent) could not be expected to transport any great fraction of the current.

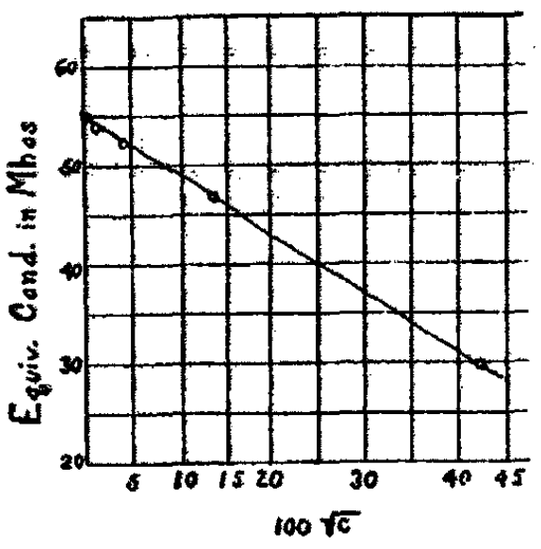

FIG. 7

The Equivalent Conductance as a function of the Square Root of the Concentration (actually 100 $\sqrt{c}$)

Again it should be noted that the data obtained for gum arabic solutions is not explainable upon the basis of McBain's theory of colloidal electrolytes,[1] for in this case the osmotic activity is the same as that of di-monovalent salt, but the equivalent conductance is about one-half that of many electrolytes. Further there is no evidence of the formation of ionic micellae with increasing concentration as the value of $\Delta T/F$ for the gum arabic solutions increases at higher concentrations of the gum and at no time is less than that corresponding to salts of the type MX_2. The contrary is true for soap solutions upon which McBain's theory is based. It should also be pointed out that the lack of gel formation in the case of gum arabic solution is considerable evidence that the aggregation tendency of this material is not great. We have kept systems containing over fifty per cent by weight of gum arabic at zero degrees or lower for many hours with absolutely no evidence of gel formation, the system remaining as a highly viscous one, which upon further cooling separated solid solvent.

pH Measurements

Thomas and Murray (l. c.) have called attention to the fact that arabic acid is a strong monobasic acid as evidenced by the sharpness of the single break of its titration curve. The pH measurements which we have made would tend to confirm this conclusion. The pH of these solutions (determined at 25°) are only slightly greater than that of neutrality and vary but little with concentration (Table I). The presence of neutral salts increases these pH values slightly (Table V).

[1] Bogue: "Colloidal Behavior," 1, 410 (1924).

Conclusion

From the physico-chemical data here found and those furnished by Thomas and Murray, it would appear that the majority of properties of gum arabic solutions can best be interpreted on the basis of the so-called classical theory of solutions.

The protective action of gum arabic solutions which has been known for many years[1] could be explained as due to the high viscosity of these solutions and to the probable high adsorption of the gum arabic molecules. It is well known that many organic molecules show a high adsorbability. The high viscosity, preventing rapid attainment of hydration equilibrium, could also be used to account for the variability of certain properties with time or method of preparation.[2] In the next place certain properties such as the osmotic pressure of gum arabic solutions will be modified by the presence of a large non-diffusible ion. The application of the Donnan theory of membrane equilibria has been successfully applied by Thomas and Murray to such cases.[3]

Still further evidence for our views is found in the lack of solubility of gum arabic in organic solvents as we have previously pointed out.[4] Gum arabic will not dissolve appreciably in any other common solvent than water with the possible exception of ethylene glycol and glycerol. Walden[5] has pointed out that a given electrolyte will show the greatest solubility in a solvent of high dissociating power (i.e. high dielectric constant). The problem is complicated in the case of this solute by the undoubted fact that considerable solvation must accompany solution. The combined ability of water to both solvate and ionize this substance may account for its high solubility in this medium.

Lastly, water solutions of our purified gum arabic give the precipitation reactions of calcium and magnesium salts. If ammonium oxalate is added to a gum arabic solution a precipitate is formed immediately. If this precipitate is filtered off, and the filtrate made alkaline with ammonium hydroxide, a precipitate can be produced by the addition of sodium phosphate. These are the qualitative reactions of calcium and magnesium salts. It should be remarked that the precipitation of calcium oxalate is considerably more abundant from a given mass of gum arabic than is that of magnesium am-

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[1] Lefort and Thibault: J. Chem. Soc., 42, 1322 (1882).

[2] The most noticeable case of such variation is found in the double refraction of gum arabic solutions. Hill (Phil. Mag., 48, 487 (1899)) in measuring double refraction states that the value obtained depends upon the mode of preparation.

[3] We are not in complete accord with these authors, however, upon the application of the Donnan theory to the viscosity effects which result upon the addition of electrolytes. From the results which we have obtained it would appear as if we were dealing with arabate ions and not arabate micellae as Thomas and Murray have assumed. The maximum value of viscosity obtained by these investigators at pH 6.2 is difficult to explain but it must be remembered that similar phenomena occur in other true solutions. Thus the addition o sulfuric acid to nitric acid produces a mixture of lower viscosity than the original nitric acid (Bingham and Stone: J. Phys. Chem., 27, 701 (1923)). Such variations are ascribed to changes in solvation and ionization.

[4] Tran. Kansas Acad. Science, 32, 49 (1929).

[5] Z. physik. Chem., 61, 633 (1908).

monium phosphate. Solutions of our material gave no precipitate in solutions made alkaline with ammonium hydroxide when saturated with hydrogen sulfide, indicating the absence of any heavy metal.

Summary

1. The viscosities, densities, pH values, freezing points, and conductances of gum arabic-water systems have been determined over a considerable range of concentrations. Some viscosity and density measurements have been made through a range of temperatures.

2. These properties are most easily explained by assuming that purified gum arabic is a strong organic electrolyte of high equivalent weight, rather than existing as a colloidal phase when in contact with water.

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THE ROLE OF HYDROCYANIC ACID VAPORS IN THE CORROSION OF IRON

BY J. F. G. HICKS

During the course of the writer's investigation as to the cause of the corrosion of iron, his attention was directed to the disastrous effects of hydrocyanic acid vapors in connection with the internal corrosion of gas-mains. This substance always present in municipal gas, brings about the gradual conversion of metallic iron to dark-blue substances closely approximating the composition of Prussian Blue,[1] which, in the form of dust, ultimately brings about stoppage of service at many points.[2] At this time the question arose as to whether this type of corrosion offered anything new in principle, or whether it merely represented another phase of the general process of corrosion of metals above hydrogen in the electromotive series.[3]

Those investigators who have most carefully studied the principles underlying the process of the corrosion of iron, are, without exception, men not connected with the gas-industry, and they are uniformly silent as to the function of hydrocyanic acid in that process. So far as a study of the literature revealed, this acid is present in all manufactured gas, and the majority of internal-corrosion-products contain the blue substance closely akin to "Prussian blue"; indeed the samples examined contained as high as 91.27% of it.[4] For this reason it is highly important to determine the function of hydrocyanic acid in the process of the corrosion of iron: in other words, is it contributory or causatory?

There is quite a diversity of opinion among the contributors to the literature of gas-technology as to the actual cause of internal corrosion of gas-mains, O_2, CO_2, a mixture of these two (in the presence of moisture) and HCN all being assigned causatory and contributory parts. As the writer views it,[5] this diversity of opinion is due chiefly to the fact that these investigators have failed to distinguish between a causative agent and an accelerator, much as did Howe.[6] Thus, Taplay and Parkinson[7] consider HCN as the *primary corrosion-agent, and note the accelerating-effect of* O_2, while

[1] See footnote to Table I, this article.

[2] The internal corrosion-rate of Portland City gas-mains has been estimated at about an average of 0.001 lb./ft.^{2}/yr., a yearly total of 9500 lbs. Fe = 10 tons Prussian blue.

[3] J. Phys. Chem., 33, 789, 790 (1929).

[4] See this article, Table I.

[5] J. Phys. Chem., 33, 780 (1929).

[6] Howe: Am. Soc. Test. Mat., 8, 278T (1908).

[7] Taplay and Parkinson: Chem. Abs., 13, 1919; Gas J., 146, 622; Gas World, 70, 451 (1919).

Taplay later[1] asserts that "corrosion may be brought about in at least six different ways", citing as the six causatory agents HCN, CO_2, excess O_2, CO, SO_2, and "the products of the reaction between NH_3 and CS_2" (most probably thiocyanates). Coleman[2] definitely states that "HCN initiates corrosion, which is carried on by the normal rusting action of moist carbon dioxide and oxygen"; the occurrence of Prussian blue in the observed frequency and relative quantity, however, would not tend to support this view.[3] Richardson[4] and Williams[5] consider that the action of HCN in the corrosion-process is subsidiary, and that moist O_2 and CO_2 *together* initiate corrosion, and conclude that corrosion need not necessarily cease if HCN be eliminated.

TABLE I

Iron Compounds found in Corrosion-Deposits (in per cent), Dry Basis

Sample No.	1	2	3	4	Averages
Ferric Oxide	2.75	0.87	3.75	4.63	3.00
Ferric Sulfate	0.87	0.62	1.95	2.01	1.36
Ferrous Sulfide	1.12	1.39	0.00	1.95	1.12
Prussian Blue[6]	74.19	85.12	91.27	89.56	85.04
Totals	78.93	88.10	96.97	98.15	90.52

Upon conversion to metallic iron the above data yields:

Sample No.	1	2	3	4	Average	Factor to multiply above percentages
Ferric Oxide	1.93	0.61	2.63	3.24	2.10	$\frac{2Fe}{Fe_2O_3} = 0.70$
Ferric Sulfate	0.35	0.22	0.78	0.80	0.54	$\frac{2Fe}{Fe_2(SO_4)_3} = 0.40$
Ferrous Sulfide	0.72	0.91	0.00	1.15	0.72	$\frac{Fe}{FeS} = 0.64$
Prussian Blue	34.13	39.16	41.98	41.20	39.12	$\frac{7Fe}{Fe_4[Fe(CN)_6]_3} = 0.46$
Totals	37.13	40.90	45.39	47.39	42.48	
% total iron as Prussian Blue	91.92	95.75	92.50	86.94	91.78	$\frac{\%Fe \text{ as Prussian blue}}{\text{Sum of } \%Fe \text{ in each component.}}$

[1] Taplay: Chem. Abs., 14, 2411; Gas J., 150, 583; Gas World, 72, 481 (1921).

[2] Coleman: Gas J., 162, 794 (1923).

[3] This article, Tables I, II, and comments.

[4] Richardson: Chem. Abs., 17, 2493 (1923); 18, 580 (1924); Gas J., 162, 348 (1921); 164, 515 (1923); Gas World, 79, 468 (1924).

[5] Williams: Chem. Abs., 17, 2493, 2749; Gas J., 162, 725 (1923).

[6] When the blue iron-compounds are analyzed, (CN) is determined and calculated to Prussian blue by means of the factor $\frac{Fe_4[Fe(CN)_6]_3}{18\ (CN)} = 1.795$. In reality, however, no analyses made during the course of this investigation ever indicated a compound exactly corresponding to that of Prussian blue: they yielded 53.75 – 54.28% $(CN)^-$. The theoretical value for Prussian blue is 54.42% $(CN)^-$. A sample from Merck (Blue Label) yielded 54.20%, and one prepared in the laboratory 54.10% $(CN)^-$.

Bertelsmann[1] assumes a rather non-committal attitude, holding that moist O_2, CO_2 and sulfur-compounds are the causes of internal corrosion, and at the same time admitting that HCN is highly destructive as a corrosive agent.

Some idea as to the importance of HCN in the process of internal corrosion may be had from Table I.

The fact that the corrosion-deposits averaged a percentage of iron equal to 42.70% of the dry sample, of which iron an average of 91.78% was found to be in the form of Prussian Blue, renders the determination of the function of HCN in the internal corrosion process highly important.

Possible Corrosion Products; Their Susceptibility to Attack by HCN.

Consideration of Table I would suggest that Prussian blue is the final product of internal corrosion, and it therefore follows that there should be some intermediate products. The nature of these will depend upon the composition and relative concentration of the several corroding-agents present. These are as follows:

TABLE II

Corroding Agents

Corroding agent	Present in % by volume	Action in the Corrosion Process
CO	6.80	Forms carbonyls of iron which remove iron by volatilization and mechanical transfer.
CO_2	0.95	Forms H_2CO_3 (with water vapor)[2] and hence increases concentration of H^+.
O_2	0.10	Depolarizes[3]; forms $Fe(OH)_3$, less soluble than $Fe(OH)_2$.
CS_2	0.02	Form HNCS (strong acid) and H_2S[4].
NH_3	0.001	
HCN	0.004	Forms blue compounds like Prussian blue, and thereby removes $Fe(OH)_2$ and $Fe(OH)_3$.

[1] Het Gas, 42, 142 (1922); Gas und Wasserfach, 65, 43, 686 (1922).

[2] J. Phys. Chem., 33, 784 (1929).

[3] J. Phys. Chem., 33, 783-4 (1929).

[4] Perhaps this can be best explained by the following system of equations:

(1) $C\begin{matrix}=S + HNH_2 \\ -S + HNH_2\end{matrix} \rightarrow C\begin{matrix}-NH_2 \\ =S \\ -NH_2\end{matrix} + H_2S$; $H_2S + Fe \rightarrow FeS + H_2$

(2) $C\begin{matrix}-NHH \\ =S \\ -NH_2\end{matrix} \rightarrow H\text{-}N = C = S + NH_3 \rightleftarrows NH_4NCS$

(3) Or, possibly: $C\begin{matrix}=S + H_2NH \\ -S\end{matrix} \rightarrow S=C=N-H + NH_3 \rightleftarrows NH_4NCS$

It will be noted that most of the corroding-agents are present in relatively small quantity; the highest volume-percentage, and in fact, the only one above 1%, that of CO_2, is scarcely sufficient to be considered in the light of a serious corrosion-factor. Yet previous work has shown the high degree of activity of both CO_2[1] and O_2[2] in this respect, and the magnitude of the effect of HCN (next to the lowest concentration of any corroding-agent) has already been referred to (introduction). Altho no H_2S is permitted to escape into the mains, some FeS has been observed, due to the formation of H_2S in the mains.[3] The presence of moist CO_2 (= H_2CO_3) would naturally suggest the "intermediate" $Fe(HCO_3)_2$, rapidly changing to $FeCO_3$. As no carbonate has been found in any corrosion-product in situ, these two substances would be relatively low persistency if formed at all (see Table III). We have therefore, logical ground to consider the following "intermediates" in the process of internal corrosion:

1. Ferrous carbonate
2. Ferrous sulfide
3. Ferrous hydroxide (hydrated, xH_2O).
4. Ferrous ferrite, (hydrated Fe_3O_4), $Fe(Fe_2O_4).xH_2O$ (intermediate between Fe^{++} and Fe^{+++}).
5. Ferric hydroxide (hydrated, xH_2O).
6. Ferric oxide (hydrated, xH_2O) ("rust").
7. Ferric sulfate, basic, $xFe_2(SO_4)_3.yFe(OH)_3$.

The behavior of these "intermediates" with respect to HCN was then studied in detail. All tests were made in sealed Erlenmeyer flasks, filled to the stopper with 0.075 (approximately 2%) HCN solution; all dissolving, precipitating and washing were performed in closed vessels, using boiled distilled water, as per Fig. 1. Should any of these "intermediates" be acted upon by HCN they should be rightly considered as such; if not, as "final" corrosion-products. As has been previously pointed out, the marked excess of Prussian blue very strongly suggests it as a final product of internal corrosion.

Samples to be directly tested were weighed out; precipitated material was prepared from aliquots of standardized stock solutions using such quantities that as nearly as possible the same weight of "from stock" and "freshly precipitated" materials was submitted to the test. The samples were treated with a quantity of 0.075 N.HCN solution containing twice the quantity of HCN necessary to convert each to ferrocyanide, and the whole allowed to

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[1] J. Phys. Chem., 33, 784 (1929).
[2] J. Phys. Chem., 33, 783-4 (1929).
[3] $H_2S + Fe \rightarrow FeS + H_2\uparrow$. See equation (1) footnote preceding page.

stand for 100 days, after which it was analyzed for CN-content. The %(CN⁻) in the residues was taken as a measure of their susceptibility to HCN-action and also as a rough measure of the rate of this action. The value of a test of this character is comparative rather than specific. It is not so much a question of *how much* of a given substance will be altered by HCN solution or *how rapidly* it will be altered, as it is a question of the *order of susceptibility* to HCN-action. The results of these tests simply indicate the course of transition from intermediate to final products and the comparative rate of transition.

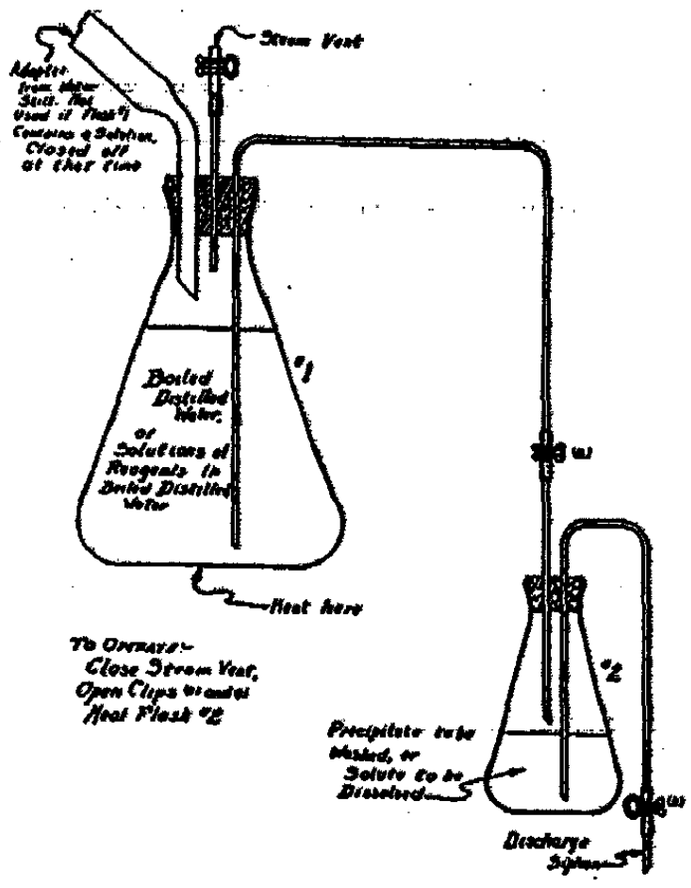

FIG. 1

Due to differences in degree of aggregation, there will be wide differences in physical characteristics (and therefore in susceptibility to solvent or the chemical action at the surface) between a freshly-precipitated substance, and the same substance after having stood for some time or "as purchased". This is due to gradual transition from colloidal to crystalline state, to change in degree of hydration, or both. In a series of tests like these under discussion, it would be essential that a freshly precipitated substance be washed free of dissolved electrolyte, and it would therefore be both colloidal and highly hydrated, all of which means that it would tend to approach maximum particle-surface and therefore maximum susceptibility to solvent or the chemical action at the surface. Crystalline substances would represent the other extreme; any number of intermediate conditions would be possible. Results are summarized on Table III:

TABLE III

Relative Susceptibility to HCN-action of the possible "intermediates" in the internal corrosion-process: 100-day test

No.	Substance tested	Physical Characteristics	% (CN) by wgt. in product, after 100 days	Remarks
1.	Ferrous Carbonate hydrated, precipitated.	Colloidal; washed free of ions other than Fe^{++} and $(CO_3)^{=}$	1.21	Maximum surface, due to highly hydrated colloid particles.
2.	Ferrous Carbonate, anhydrous, J. T. Baker's "C.P."	Microcrystalline.	0.00	Too dense; minimized surface for reaction in small crystals. Requires presence of H_2CO_3 or O_2 before HCN attacks; compare (5).
3.	Ferrous Sulfide, hydrated, precipitated.	Same as (1).	10.52	Same as (1). Seems to be more susceptible to HCN than any of the materials tested. Completion prevented because of closed container, which prevents escape of liberated H_2S.
4.	Ferrous Sulfide, anhydrous, synthetic; P.W.R. Co's. fused sticks.	Perfectly crystalline.	0.31	Readily attacked tho much less so than (3) because of the lessened surface, due to crystals; compare (3).
5.	Ferrous hydroxide, hydrated precipitated,	Same as (1)	0.00	Requires presence of H_2CO_3 or O_2 before HCN attacks. Compare (2).
6.	Ferrous ferrite ("forge-scale") fresh from forge.	Metallic iron coated with "magnetic oxide" (Fe_3O_4).	0.32	Metal and attached scale polar with respect to each other. Iron stained blue.

TABLE III (Continued)

Relative Susceptibility to HCN-action of the possible "intermediates" in the internal corrosion-process: 100-day test

No.	Substance tested	Physical Characteristics	% (CN) by wgt. in product, after 100 days	Remarks
7.	Ferrous ferrite, "Magnetic Oxide", J.T. Baker's "C.P."	Same as (4).	0.00	Same as (2) and (5).
8.	Rusted scrap-iron; "rust" means hydrated ferric oxide	Rust adhering to metal. Red, apparently lost some water.	1.53	Same as (6).[a]
9.	Ferric hydroxide, hydrated, precipitated	Same as (1).	1.33	Same as (1).
10.	Ferric Oxide, hydrated.	Same kind of "rust" as (8), *shaken, not scraped* from rusted metal.	0.92	Same as (6). Absence of metal lessens susceptibility to HCN, because no E.M.F. is possible.[a]
11.	Ferric Oxide, anhydrous J. T. Baker's "C.P."	Crypto- to micro-crystalline.	0.00	Same as (2). Compare (6) and (10).
12.	Ferric Sulfate, basic prepared in laboratory.	Colloidal, washed as in (1).	0.86	$2Fe(OH)_3.xH_2O$ (washed, colloidal) dissolved in solution of $Fe_2(SO_4)_3$, evaporated to dryness, ignited and washed until suspended.

Conclusions: (1) Prussian blue and hydrated ferric oxide are the end-products of the internal corrosion process.
(2) Ferrous compounds would be oxidized to ferric and then changed to Prussian blue.
(3) HCN cannot be a causatory agent, but only contributory.

[a] Aston: Trans. Am. Electrochem. Soc., 29, 449 (1916).

The accelerating effect of O_2 and CO_2 upon HCN-attack upon Fe:

In a previous article[1] the writer has shown that the presence of moist O_2 and CO_2 materially increased the velocity of corrosion of iron; it would therefore seem logical to determine whether the same accelerative effect was noticeable in the system Fe(metal)-HCN(vapor).

The apparatus used was the same as that used for the previous investigation (See Fig. 2) with the exception of the HCN-bottles, shown in detail

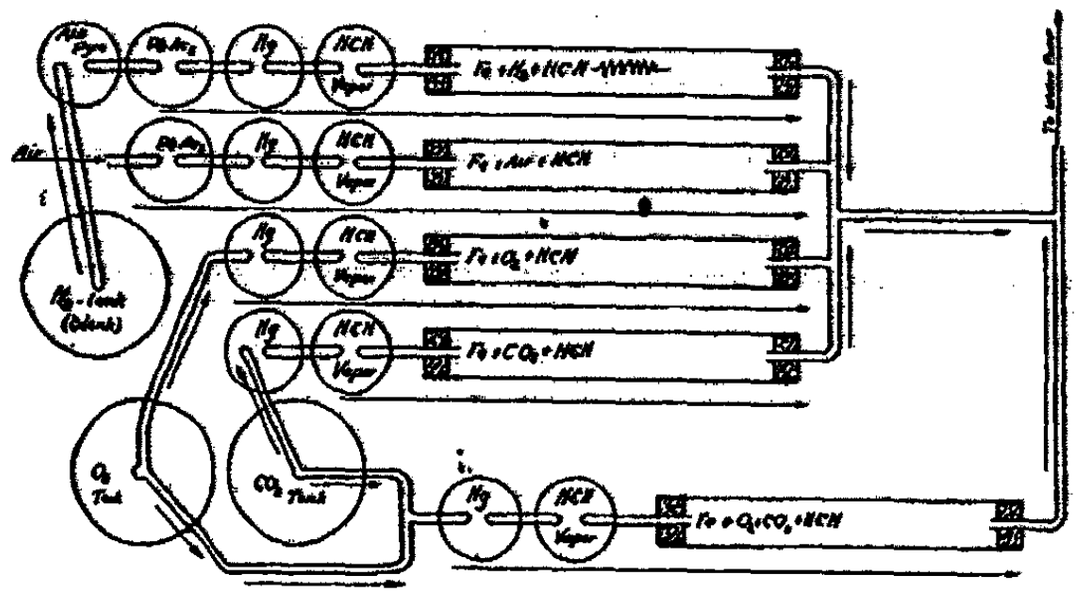

FIG. 2

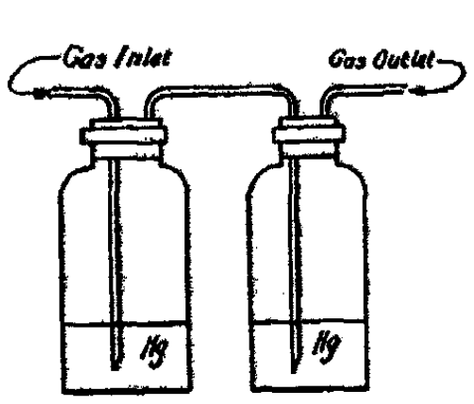

FIG. 2a

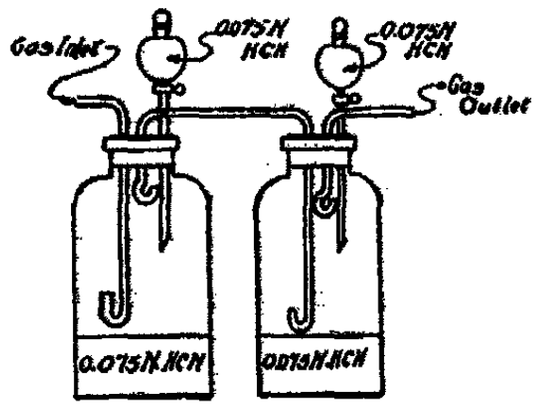

FIG. 2b

in Fig. 2b. Test-pieces consisted of spirals of Malin's No. 10 gauge "music wire", and the duration of the test was fifteen days, as in the case of the similar series of tests[1] where HCN was not used. Interdiffusion of gases was prevented by keeping the gases flowing constantly in the same direction; this was accomplished by the actual pressure of the gases issuing from the containers, and by attaching a suction-pump to the other end of the system. The mercury bubbling-bottle (Fig. 2a) served the purpose of estimating and regulating gas-flow rates by bubble-counting; the HCN (Fig. 2b) bottles insured continuous entrainment of HCN-vapors by the streams of moving gases, which aspirated these vapors into the system as fast as they arose

[1] J. Phys. Chem., 33, 780 (1929).

from the surface of the 0.075 N. HCN solution. Results are summarized in the graphs below. The graphs from the previous investigation[1] are included for the sake of comparison, as they show the effect of the same corrosive agents in the absence of HCN:

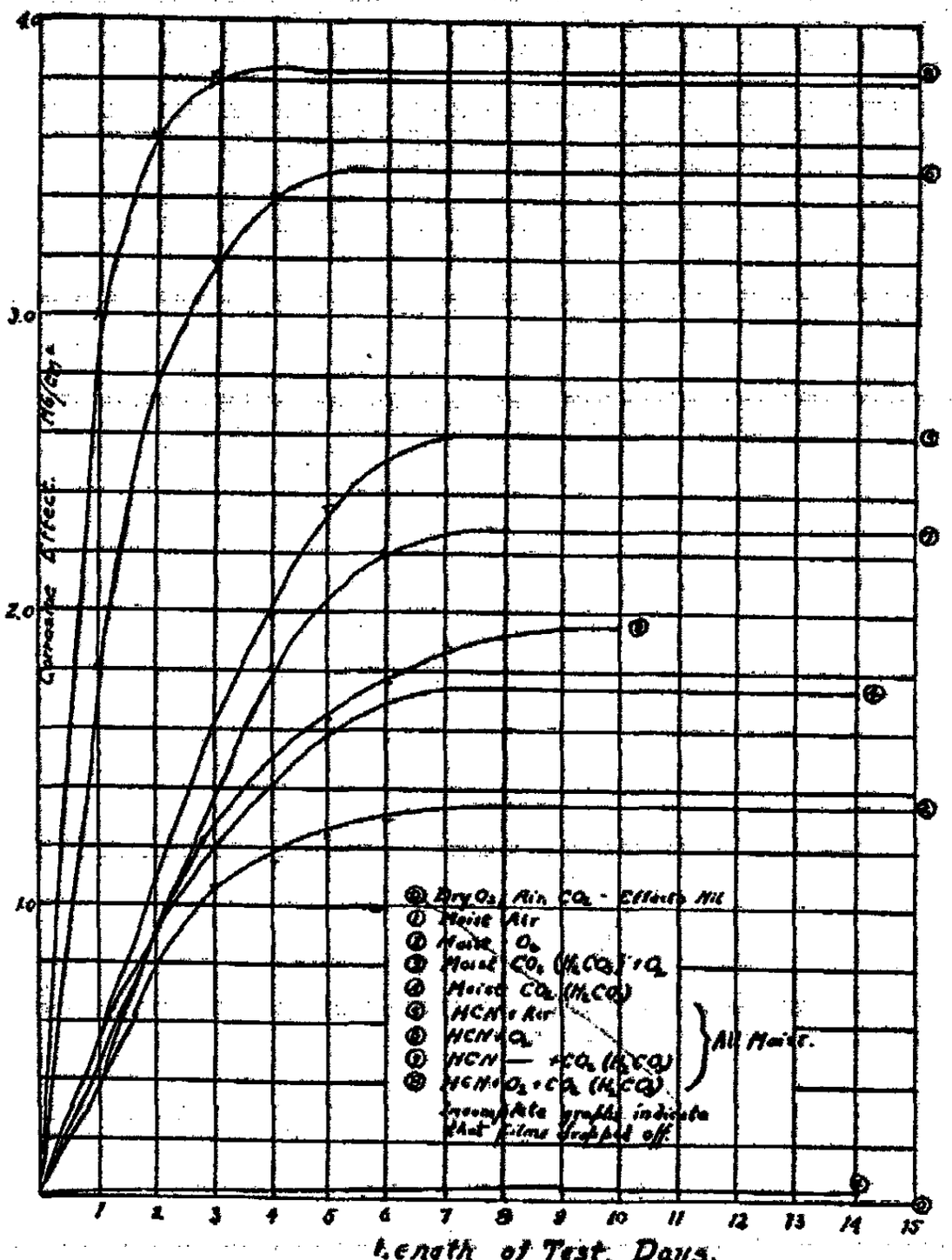

Fig. 3a

Inspection of these graphs will lead to the following conclusions:

1. HCN is the chief contributory factor in the internal corrosion of gas-mains, it being present in all cases whose graphs show high rates of corrosion and high maximum effect. H_2CO_3 and O_2 follow in order.

2. The order of intensity of effect is the order of magnitude of maxima of the graphs.

[1] J. Phys. Chem., 33, 785 (1929).

3. The order of priority of attack is the order of priority of maxima.

4. HCN is not a cause in itself, and is subject to the same accelerative effect as other contributory factors.

Electrochemical Measurements:

The conclusions drawn from the above graphs (i.e., those concerned with HCN) were checked electrochemically, as were those from the other graphs of the previous investigation,[1] and by the same apparatus (See Fig. 4). The

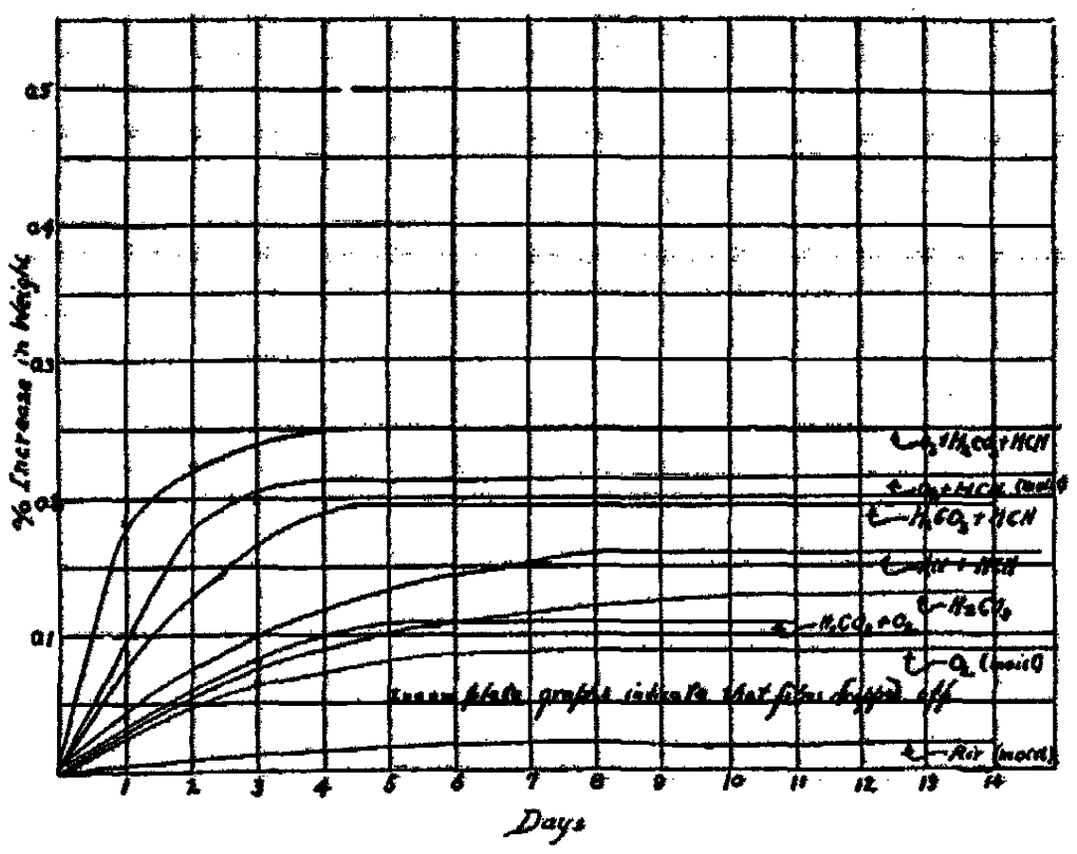

FIG. 3b

cells are essentially the same as those of Evans[2] but adapted to exclusion of air and the bubbling of a gas thru the electrolyte (0.075N.HCN). All electrodes were cut from the same piece of iron; in fact they were those used in the previous investigation. Eight cells, with a total of 370 sq. cm. electrode-area, were used in series for the E.M.F. readings. The cells were allowed to stand until the millivoltmeter registered equilibrium at 25°, after which the gases used were bubbled thru at the rate of 5 cc per minute until equilibrium at 25° was again recorded. The difference between equilibrium-readings (at 25°), one before and during the passage of a given gas thru the cell, represents the E.M.F. developed Results are shown in Table IV(a), which includes parallel results from the previous investigation (b) and the absolute potential difference for the same accelerator due to the presence of HCN (c).

[1] U. R. Evans: "The Corrosion of Metals," 88 (1925). Also Ind. Eng. Chem., 17, 4, 363 (1925).

[2] J. Phys. Chem., 33, 780 (1929).

TABLE IV

E.M.F. Measurements during Corrosion in the presence of HCN

No.	Gas passed thru cells	(a) Electrolyte —0.075N. HCN, millivolts:	(b) Electrolyte —0.01N K_2SO_4, millivolts:	(c) Absolute P.D. due to HCN millivolts:
1.	air	—1.95	0.75	2.70
2.	O_2	—6.20	4.00	10.20
3.	CO_2	—2.65	0.85	3.50
4.	O_2 CO_2, (equal volumes)	—5.00	2.15	7.15

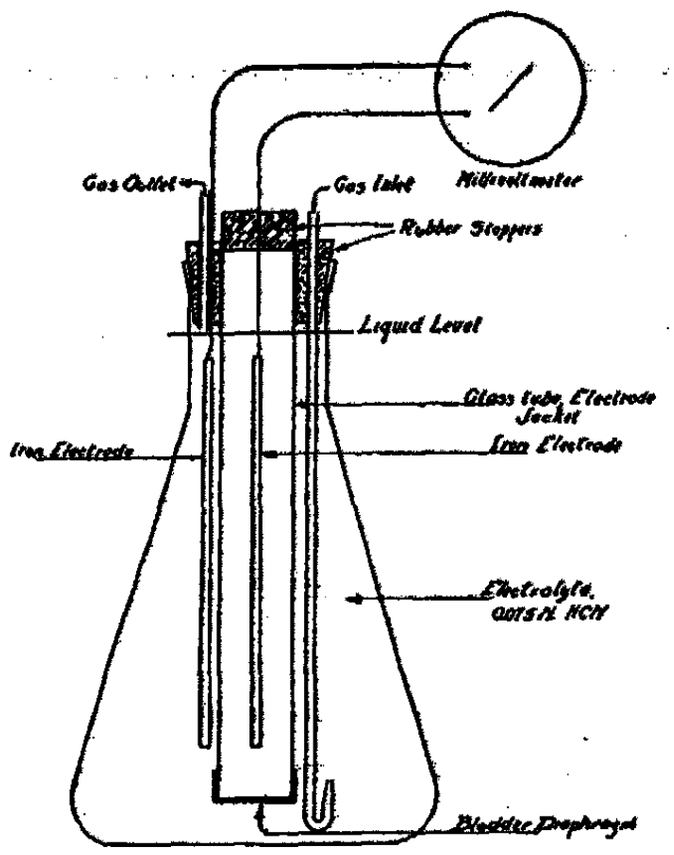

FIG. 4

Eight Cells in Series for E.M.F. readings.

When HCN is one of the concomitants of the corrosion-process, the polarity of the E.M.F. produced is negative with respect to that produced by the same accelerator in the absence of HCN. This is to be expected, since, in the presence of HCN, $Fe^{\circ} \rightarrow [Fe(CN)_6]^{\equiv}$, while in the absence of HCN, $Fe^{\circ} \rightarrow Fe^{++} \rightarrow Fe^{+++}$. The profound effect of HCN is demonstrated by calculating the absolute potential difference for the same accelerator when HCN is present and when it is absent. We are therefore justified in considering HCN as the accelerator of maximum effect in the process of internal corrosion, though not a cause in itself.

Mechanism of the Process of Internal Corrosion in the presence of HCN:

It is thought that this is best represented by the following system of equations:

(1) $Fe + 2\,HOH \rightarrow Fe(OH)_2 + H_2$

(2) $Fe(OH)_2 + 2HCN \rightarrow Fe(CN)_2 + 2H_2O$

(3) $Fe(CN)_2 + 4HCN \rightarrow H_4[Fe(CN)_6]$.

(4) $2Fe(OH)_2 + H_4[Fe(CN)_6] \rightarrow Fe_2Fe[(CN)_6] + 4H_2O$
ferrous ferrocyanide

(5) $6Fe_2[Fe(CN)_6] + 3O_2 + 6H_2O \rightarrow 2Fe_4[Fe(CN)_6]_3 + 4Fe(OH)_3$
Prussian blue.

(6) $4Fe(OH)_3 + 3H_4[Fe(CN)_6] \rightarrow Fe_4[Fe(CN)_6]_3 + 12H_2O$
Prussian blue.

In short, HCN (later aided by O_2) removes $Fe(OH)_2$ from the field of action and displaces the equilibrium[1] shown in (1) to the right, exactly the same as in the cases studied in the previous investigation. Hence the actual process of "cyanide corrosion" is not different in mechanism from the corrosion-process of any other metal above hydrogen in the electromotive series, i.e., HCN is a contributory or maintainence factor.

Summary and Conclusions:

1. The final product of the corrosion of iron in the interior of gas-mains is Prussian blue.

2. HCN produces the corrosive effect of maximum intensity and is first in order of priority of attack.

3. HCN is the most active corrosive agent with respect to moist iron so far studied, but is not a cause of corrosion itself; this cause is the actual dissolving of metallic iron in water, as previously concluded.[2]

4. "Cyanide corrosion" of iron differs from other processes of corrosion of iron with respect to concomitants and end-products only, but not with respect to mechanism.

5. It has been shown that HCN cannot initiate the corrosion process in the cases studied.

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[1] Professor Ulick R. Evans has been kind enough to point out to the writer that, in the 1926 edition of his "Corrosion of Metals," 157 (including footnote 2), there is to be found a similar idea as to the mechanism of the iron-corrosion-process, viz., that, when covered with a *limited* film of moisture, iron will corrode *until* this moisture film is saturated with ferrous hydroxide. In preparing his previous paper, the writer did not have access to this 1926 edition, but only to that of 1924, in which the above statement did not appear. Due acknowledgment is hereby made to Professor Evans for his appropriate and timely suggestion.

[2] J. Phys. Chem., 33, 790 (1929).

THE HEAT OF ADSORPTION OF CERTAIN ORGANIC VAPORS BY CHARCOAL AT 25° AND 50°

J. N. PEARCE AND G. H. REED

Although the thermal effect accompanying the adsorption of gases by charcoal was first noted by Mitscherlich[1] in 1843, it was not until 1874 that Favre[2] first attempted to determine the effect quantitatively by means of a mercury calorimeter. Of the numerous investigations which have been made since that time we shall cite only the more recent. Lamb and Coolidge[3] have measured the heats of adsorption of eleven organic vapors on charcoal. Keyes and Marshall[4] determined the heats of adsorption of oxygen, chlorine, carbon dioxide, ammonia and ether on gas-mask charcoal. Gregg[5] has made similar measurements for eight gases on birchwood charcoal. The ice calorimeter was used in all of these investigations. Gregg also made a few measurements with a phenol calorimeter at 40.35°. Using a potentiometric method Pearce and McKinley[6] have measured the heats of adsorption of nine organic vapors on an acid-washed, ash-free, steam-activated coconut charcoal at 25°. A comprehensive study of the heat of adsorption of oxygen on coals and charcoals at temperatures ranging from 18° to 450° has been made by a number of English investigators.[7] Their data indicate that the heat of adsorption of oxygen increases with rise in temperature. Owing to the ease of combination of oxygen with the adsorbent, and the accompanying heat effect, their results do not suffice for the calculation of the temperature coefficients of the heat of adsorption.

The heat of adsorption of hydrogen on copper catalysts, poisoned and unpoisoned, was determined by Kistiakowski, Flosdorf and Taylor.[8] Patrick and Greider[9] measured the heats of adsorption of ammonia and sulfur dioxide on silica gel. Beebe and Taylor[10] made similar measurements for hydrogen on nickel and copper catalysts, and Beebe[11] has determined the heat effect accompanying the adsorption of carbon monoxide by copper. In all of the experiments with metallic catalysts the catalyst tube itself served as the calorimeter.

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[1] Mitscherlich: Ann. Chim. Phys., (3) 7, 15 (1843).
[2] Favre: Ann. Chim. Phys., (5) 1, 209 (1874).
[3] Lamb and Coolidge: J. Am. Chem. Soc., 42, 1146 (1920).
[4] Keyes and Marshall: J. Am. Chem. Soc., 49, 156 (1927).
[5] Gregg: J. Chem. Soc., 130, 1494 (1927).
[6] Pearce and McKinley: J. Phys. Chem., 32, 360 (1928).
[7] Ward and Rideal: J. Chem. Soc., 130, 3117 (1927); Blench and Garner: 125, 1288 (1924); Garner and McKie: 130, 3451 (1927); McKie: 131, 2870 (1928).
[8] Kistiakowski, Flosdorf and Taylor: J. Am. Chem. Soc., 49, 2200 (1925).
[9] Patrick and Greider: J. Phys. Chem., 29, 1031 (1925).
[10] Beebe and Taylor: J. Am. Chem. Soc., 26, 43 (1924).
[11] Beebe: J. Phys. Chem., 30, 1538 (1926).

In many of the previous investigations heats of adsorption have been measured at the temperature of melting ice. Since most vapors may exist as liquids at 0°, the measured heat effect may consist of at least two heat effects, a heat of adsorption and a heat of condensation. The object of the present work was to study the effect of temperature upon the heat of adsorption. To this end we have worked at 25° and 50°, temperatures which are near, or above, the boiling points of the vapors employed. In this way it is possible to eliminate to a considerable extent at least the heat of condensation. The procedure makes possible also the calculation of the temperature coefficient of the heat of adsorption.

The apparatus used is shown in Fig. 1. It consists entirely of Pyrex tubing and flasks with no stopcocks or rubber tubing above the mercury levels. A detailed

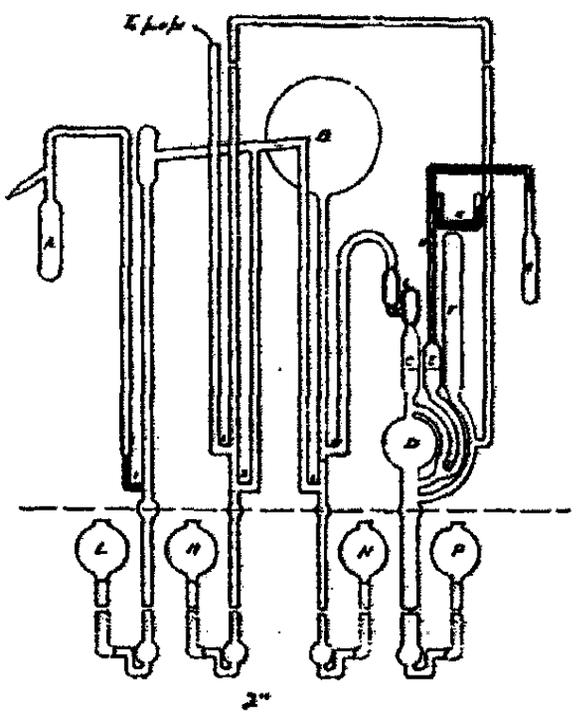

FIG. 1

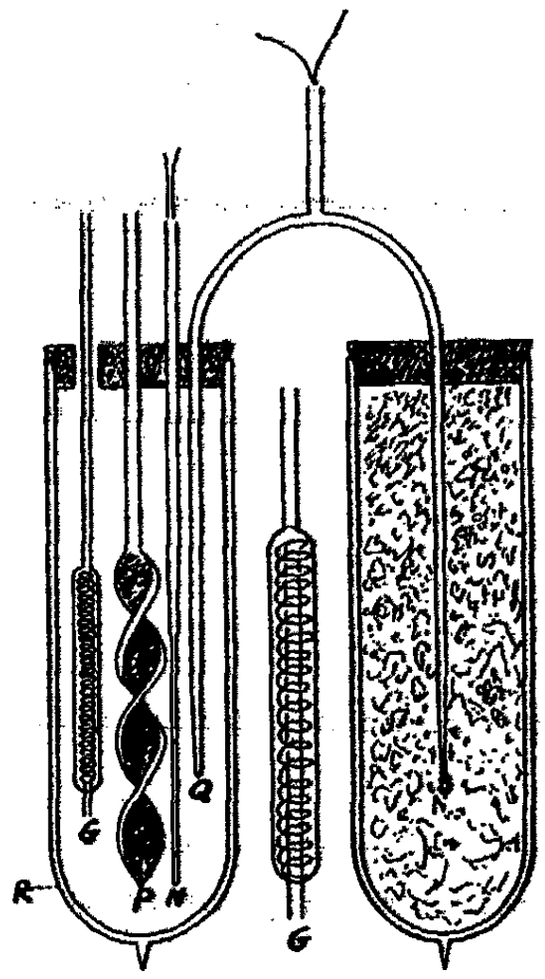

FIG. 2

description of the apparatus is omitted since it is essentially the same as that first used by Coolidge,[12] and later by Pearce and McKinley.[6] The entire apparatus is inclosed in a large, double-walled air-bath provided with adequate means for the rapid circulation of the air. The temperature of the bath is electrically controlled by means of a four-foot mercury thermoregulator and a Bunnell relay to within ±0.05°. The adsorption bulb, shown in Fig. 2, is made of "702P" glass into which is sealed a spiral of tungsten wire. The spiral is so arranged that the ends protrude through the bottom of the bulb, thus facilitating the conduction of heat from the charcoal to the calorimeter liquid. When filled the charcoal is at no point more than three millimeters from the wire.

[12] Coolidge: J. Am. Chem. Soc., 46, 596 (1924).

A diagram of the calorimeter and fixtures is also shown in Fig. 2. The calorimeter is a Dewar flask fitted to accommodate the adsorption bulb, the stirrer and the heater. The water equivalent of the calorimeter and fixtures was accurately determined according to the method described by Pearce and McKinley.[5] A 24-junction copper-constantan thermocouple, made according to the specifications of White,[13] was used in conjunction with a Leeds and Northrup, Type K, potentiometer to measure the heat effects. The thermocouple was previously standardized by Dr. McKinley at the temperatures of liquid air, melting ice and the transition points of $Na_2SO_4.10H_2O$ and $MnCl_2.2H_2O$. The thermal capacity of the calorimeter and fixtures when in use amounts to approximately 170 cals.; the thermocouple is sensitive to 0.001°. Hence, our calorimeter system will respond to a heat transfer of 0.17 cal. The calorimeter liquid is "Finol," a light oil whose specific heats at 25° and 50° were found to be 0.4528 and 0.4674, respectively.

The charcoal used as the adsorbent was taken from a large supply obtained from the National Carbon and Carbide Corporation for an exhaustive study of the adsorption of gases and vapors carried on in this laboratory. It is a coconut charcoal, steam-activated and acid-washed until the ash content is reduced to 0.28 percent. Employing the method of Cude and Hulett,[14] Knudson[15] found the density of the charcoal to be 1.80; its loss in weight on outgassing is 2.5 percent. The liquids whose vapors were studied were purified by the generally accepted methods.[16] Only the constant boiling middle fractions were used. In all cases the purification was done immediately before the liquid was used. Carbon tetrachloride, chloroform, methylene chloride and methyl chloride were chosen with the hope of observing a possible effect of the number of substituted chlorine atoms on the molecular heat of adsorption.

The method of experimentation, as well as the method of calculating the heats of adsorption, was the same as that described in the previous paper.[6]

The data collected in the experimental work are given in Tables I to VIII. In the first column are listed the final equilibrium pressures. The second column gives the number of cc. of vapor adsorbed by one gram of charcoal. In the third column are the observed heat effects, h_{obs}; while the fourth column contains the values of h calculated by means of the formula given below the Table. The deviations between the observed and calculated heat effects are given in the last column. The data given in these Tables has been obtained with various weights of charcoal, some fresh and others previously used, and with variations in the rate of admission of vapor to the charcoal. The agreement between runs, as well as that within individual runs, indicates that the heat of adsorption is definite and reproducible.

Lamb and Coolidge[3] find that chlorine-containing molecules poison charcoal in such a way that the heat of adsorption decreases in subsequent runs on

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[13] White: J. Am. Chem. Soc., 36, 2292 (1914).
[14] Cude and Hulett: J. Am. Chem. Soc., 42, 391 (1920).
[15] Pearce and Knudson: Proc. Iowa Acad. Sci., (1927).
[16] Mathews: J. Am. Chem. Soc., 48, 562 (1926).

the same sample of charcoal. This poisoning effect is not evident from our data; the agreement between runs on new and previously used charcoal is entirely acceptable. The heat of adsorption is independent of the previous use of the charcoal provided that it has been outgassed at 550° to a pressure of 0.0001 mm.

Fig. 3 shows the results obtained when the logarithms of the heats of adsorption are plotted against the number of cc. of vapor adsorbed per gram of charcoal. To avoid overcrowding these curves have been displaced upward by definite increments. The curves are represented mathematically by the expression,

$$\log h = \log m + \log X^n,$$

where X is the number of cc. of vapor adsorbed by one gram of charcoal, n is the slope of the curve and m is the value of h when X is unity. From the slope of the curve and its intercept on the h-axis we obtained the constants for the equations given beneath the Tables. The values of the heat of adsorption calculated from these empirical equations are in good agreement with the observed values as shown in the last column of each Table.

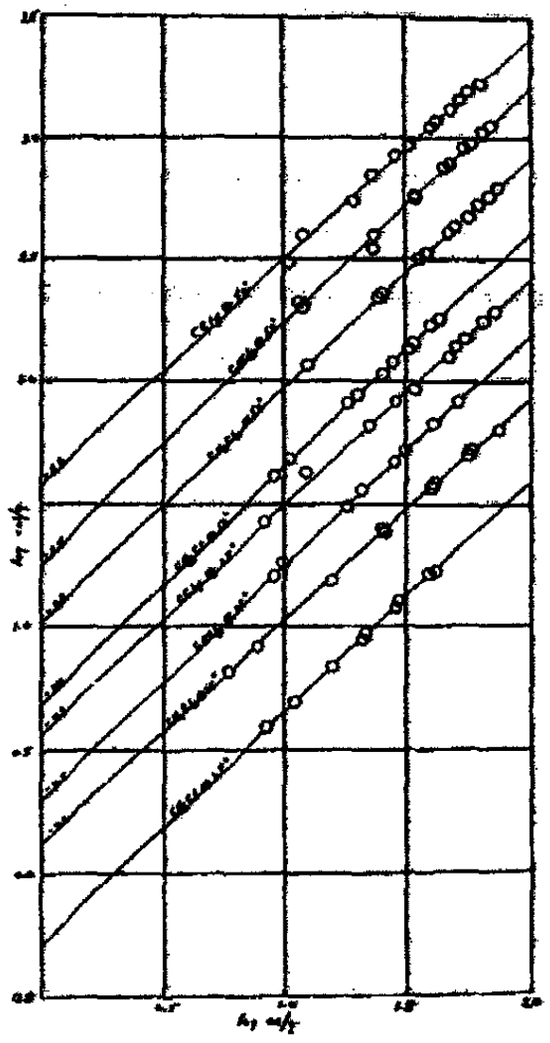

FIG. 3

For the sake of comparison, we have followed the method of Lamb and Coolidge[3] in calculating the molecular heats of adsorption, h_m. Table IX shows the values calculated for the heat of adsorption of a gram molecular weight of the vapor on 500 grams of charcoal. This Table shows also the values of the constants, m and n, of the separate vapors. In all cases the values of n deviate but little from one and are always less than unity. This implies that successive equal increments of a given vapor adsorbed liberate practically the same amount of heat. A comparison of the molecular heats of adsorption of the four vapors at the three temperatures, Table X, indicates that the heat of adsorption is practically constant over the whole range of temperature from 0° to 50°. These results can only lead to the definite conclusion that the temperature coefficient of the heat of adsorption, if there is one, is very, very small.

There is at present no satisfactory explanation for the apparent independence of heat of adsorption and temperature, unless it be that the field forces operative in adsorption processes are too strong to be influenced by the tempera-

ture. Lorentz and Lande[17] believe that temperature should have some influence, while Eucken,[18] on the other hand, holds to the view that the heat of adsorption is independent of the temperature. Lamb and Coolidge[8] consider that the observed heat effect is the sum of two effects,—the heat of vaporization of the substance adsorbed and the net heat of adsorption. If the influence of temperature on these two heat effects were equal and opposite in direction, then no observable effect of temperature should be expected. The net heats of adsorption have been calculated, but, owing to the lack of sufficiently reliable density and heat of vaporization data, they are not included in this paper. In general, the heat of vaporization decreases with increasing temperature while the net heat of adsorption increases.

The slopes of the adsorption isosteres have frequently been used in calculating heats of adsorption. It has been shown that these ($\log p - 1/T$) plots yield, in general, straight and parallel lines for a given vapor. If, therefore, the Clausius-Clapeyron equation is applicable to adsorption, no change in the heat of adsorption with rise in temperature should be expected. However, the values obtained by this method are lower than those obtained experimentally.

In the study of the adsorption of chlorine-containing molecules it has been generally assumed that the molecules are oriented with the chlorine atoms toward the surface of the adsorbent. The chlorine atoms possess seven valence electrons in their outer orbits, and the force fields about them should be large. If we may assume that the heat effect observed in adsorption is a result of the neutralization or saturation of the powerful force fields about the surface atoms of the adsorbent, then carbon tetrachloride with its greater number of chlorine atoms should exhibit the greatest heat of adsorption. This is exactly what we do find. From Table X we see at once that for each temperature the molecular heat of adsorption increases with the number of chlorine atoms in the molecule.

TABLE I

The Heat of Adsorption of Methyl Chloride Vapor at 25°

P cm.	X cc/g.	h(Obs) cal/g.	h(Calc) cal/g.	Dev. cal/g.
0.433	11.17	4.95	4.89	−0.06
1.021	21.01	8.91	8.94	+0.03
1.748	29.11	12.01	12.20	+0.19
3.202	41.34	16.70	17.06	+0.36
1.120	8.57	3.94	3.80	−0.14
2.475	15.79	6.80	6.81	+0.01
3.864	21.79	9.37	9.26	−0.11
5.955	29.66	12.69	12.43	−0.26
9.312	39.08	16.34	16.17	−0.17
				Mean 0.15

$$h = 0.4887\ X^{0.9545}$$

[17] Lorentz and Lande: Z. anorg. Chem., 125, 47 (1922).
[18] Eucken: Ber. deutsch. physik. Ges., 12, 345 (1914).

TABLE II

The Heat of Adsorption of Methyl Chloride Vapor at 50°

P cm.	X cc/g.	h(Obs) cal/g.	h(Calc) cal/g.	Dev. cal/g.
0.322	9.24	4.08	4.07	−0.01
0.932	18.58	8.12	7.95	−0.17
1.695	25.39	10.71	10.75	+0.04
2.612	32.88	13.87	13.78	−0.09
3.781	39.95	16.99	16.61	−0.38
0.401	10.60	4.80	4.65	−0.25
1.254	20.40	8.76	8.71	−0.05
2.111	27.86	11.97	11.76	−0.21
3.102	34.35	14.43	14.37	−0.06
4.960	43.63	18.08	18.08	0.00
			Mean	0.13

$$h = 0.4820\ X^{0.9600}$$

TABLE III

The Heat of Adsorption of Methylene Chloride Vapor at 25°

P cm.	X cc/g.	h(Obs) cal/g.	h(Calc) cal/g.	Dev. cal/g.
0.000	7.89	5.23	5.30	−0.07
0.244	25.41	15.80	15.37	−0.43
0.568	41.30	24.17	23.91	−0.26
1.041	57.83	33.13	32.48	−0.65
0.000	5.83	4.12	4.03	−0.09
0.000	15.68	9.65	9.90	+0.25
0.050	25.97	15.25	15.68	+0.43
0.075	40.37	23.07	23.40	+0.33
0.204	57.35	31.61	32.23	+0.62
0.433	74.19	39.97	40.75	+0.78
			Mean	0.39

$$h = 0.8091\ X^{0.9100}$$

TABLE IV

The Heat of Adsorption of Methylene Chloride Vapor at 50°

P cm.	X cc/g.	h(Obs) cal/g.	h(Calc) cal/g.	Dev. cal/g.
0.124	12.59	7.25	7.36	+0.11
0.302	24.55	13.84	13.79	−0.05
0.610	36.30	20.15	19.92	−0.23
1.070	47.42	25.69	25.61	−0.08
1.660	57.40	29.62	30.65	+1.03
2.602	68.24	36.10	36.05	−0.05
0.000	12.55	7.28	7.34	+0.06
0.074	25.68	14.39	14.39	0.00
0.198	38.78	21.10	21.20	+0.10
0.317	50.44	27.34	27.14	−0.20
0.664	62.29	33.37	33.09	−0.28
1.249	72.75	39.19	38.79	−0.40
			Mean	0.22

$$h = 0.6808\ X^{0.9400}$$

TABLE V

The Heat of Adsorption of Chloroform Vapor at 25°

P cm.	X cc/g.	h(Obs) cal/g.	h(Calc) cal/g.	Dev. cal/g.
0.000	9.22	6.34	6.33	−0.01
0.000	18.48	12.27	12.30	+0.03
0.025	28.42	18.61	18.56	−0.05
0.030	40.93	26.68	26.31	−0.37
0.060	10.07	7.22	6.89	−0.33
0.164	21.15	14.27	14.00	−0.27
0.244	31.63	20.60	20.56	−0.04
0.413	41.39	26.30	26.60	+0.30
0.692	52.10	32.96	33.14	+0.18
			Mean	0.17

$$h = 0.7569\ X^{0.9560}$$

TABLE VI

The Heat of Adsorption of Chloroform Vapor at 50°

P cm.	X cc/g.	h(Obs) cal/g.	h(Calc) cal/g.	Dev. cal/g.
0.000	11.58	8.32	7.82	−0.50
0.000	23.66	15.72	15.65	−0.07
0.035	35.00	22.96	22.88	−0.08
0.074	45.53	30.10	29.53	−0.57
0.154	54.90	36.43	35.41	−1.02
0.302	64.85	42.22	41.62	−0.60
0.000	12.13	7.94	8.18	+0.24
0.000	23.48	13.87	15.52	+1.66
0.040	35.04	22.49	22.90	+0.41
0.069	47.62	30.95	30.84	−0.11
0.119	58.84	37.62	37.69	+0.07
0.421	69.29	44.71	44.38	−0.33
				Mean 0.47

$$h = 0.7261\ X^{0.9704}$$

TABLE VII

The Heat of Adsorption of Carbon Tetrachloride Vapor at 25°

P cm.	X cc/g.	h(Obs) cal/g.	h(Calc) cal/g.	Dev. cal/g.
0.050	12.35	10.53	9.48	−1.05
0.070	29.02	20.78	20.93	+0.15
0.070	47.26	31.59	32.91	+1.42
1.071	61.97	41.72	42.31	+0.59
2.370	64.67	44.41	44.00	−0.41
7.678	71.71	48.05	48.43	+0.38
0.000	8.44	6.68	6.66	−0.02
0.010	22.47	16.51	16.51	0.00
0.086	34.72	22.36	24.72	+1.36
0.494	50.92	34.81	35.26	+0.45
1.915	55.22	38.01	38.01	0.00
				Mean 0.53

$$h = 0.9230\ X^{0.9276}$$

TABLE VIII

The Heat of Adsorption of Carbon Tetrachloride Vapor at 50°

P cm.	X cc/g.	h(Obs) cal/g.	h(Calc) cal/g.	Dev. cal/g.
0.065	10.60	7.68	8.12	+0.44
0.139	18.32	13.76	14.40	+0.64
0.139	28.85	21.11	20.63	−0.48
0.183	40.62	27.85	28.36	+0.51
0.342	48.71	32.77	33.59	+0.82
0.728	63.44	42.00	42.95	+0.95
0.040	12.04	9.92	9.14	−0.78
0.114	23.22	17.59	16.85	−0.74
0.114	33.06	23.34	23.42	+0.08
0.154	42.35	29.31	29.48	−0.17
0.168	52.79	36.00	36.20	+0.20
0.332	57.29	39.18	39.06	−0.12
			Mean	0.49

$$h = 0.9020\ X^{0.9310}$$

TABLE IX

Summary of Calorimetric Data

Substn.	m	n	h_m Cals.
	25°		
CCl_4	0.9230	0.9270	15.6
$CHCl_3$	0.7569	0.9560	14.3
CH_2Cl_2	0.8091	0.9100	12.8
CH_3Cl	0.4887	0.9545	9.2
	50°		
CCl_4	0.9020	0.9310	15.4
$CHCl_3$	0.7261	0.9704	14.5
CH_2Cl_2	0.6808	0.9400	12.1
CH_3Cl	0.4820	0.9600	9.2

TABLE X

Comparison of h_m at 0°, 25°, and 50°

Subs	h_m(0°, L&C) Cals.	h_m(25°, P&McK) Cals.	h_m(25°) Cals.	h_m(50°) Cals.
CCl_4	15.3	15.4	15.6	15.4
$CHCl_3$	14.5	14.5	14.3	14.5
CH_2Cl_2	——	——	12.8	12.1
CH_3Cl	——	——	9.2	9.2

Summary

1. The heats of adsorption of methyl chloride, methylene chloride, chloroform and carbon tetrachloride have been determined at 25° and 50°.

2. The temperature coefficient of the heat of adsorption of the four vapors, if there is one, is very small.

3. The molecular heats of adsorption of the present series increases with increase in the number of chlorine atoms in the molecule.

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THE CATALYTIC DECOMPOSITION OF SODIUM HYPOCHLORITE SOLUTIONS*

III. Promoter Action of Hydrated Magnesium Oxide in the Hydrated Copper Oxide Catalysis of Sodium Hypochlorite*

BY JOHN R. LEWIS

In recent papers,[1] the writer has given the data for the decomposition of sodium hypochlorite solutions in the presence of hydrated copper oxide, used singly, and also in the presence of varying amounts of hydrated ferric oxide. It was shown that the hydrated copper oxide is a fair catalyst for the reaction

$$NaClO \longrightarrow NaCl + 1/2\ O_2$$

It was also shown that small quantities of hydrated ferric oxide, which is not a catalyst for this reaction, greatly increased the activity of the copper catalyst. Such a substance, according to Rideal and Taylor[2] is a promoter.

The investigation has now been extended to include the action of hydrated magnesium oxide. Like ferric oxide, magnesium oxide is not a catalyst for this reaction, but if mixed with the copper catalyst, the activity of the latter is greatly increased.

The particular advantages in studying this problem are:

(1) Catalysts, unpromoted or promoted, can be prepared and used at room temperatures. With many other systems, on the other hand, comparatively high temperatures are required, not only for the preparation of the catalysts, but also for their use in the reactions under investigation.

(2) Duplicate experiments give results which check the original data within experimental error (usually within 2 percent). This places the investigation on a quantitative basis that has not always been realized in other studies in heterogeneous catalysis.

Experimental

Materials and Apparatus.—The sodium hypochlorite and catalysts were prepared according to the methods described in the previous papers. Likewise, the shaker apparatus[3] described in the previous papers was used in following the rate of the reaction.

Experimental Procedure.—The procedure followed in these experiments was essentially the same as that outlined in the second article of this series. The free alkali in the hypochlorite solution was used in precipitating the mixture of copper and magnesium hydroxides. Since, as has been shown by Howell,[4] the hydroxyl ion cuts down the rate of the cobalt peroxide catalysis

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* Contribution No. 35 from the Chemical Laboratory of the University of Utah.
Part of the experimental data given in this paper was obtained while the author was connected with the Department of Chemistry of the University of Wisconsin.

[1] Lewis: J. Phys. Chem., 32, 243-254, 1808-1819 (1928).
[2] Rideal and Taylor: "Catalysis in Theory and Practice" (1926).
[3] Walton: Z. physik. Chem., 47, 185 (1904).
[4] Howell: Proc. Roy. Soc., 104A, 134 (1923).

of sodium hypochlorite solution, it may be argued that the increased catalytic activity of the hydrated copper oxide, in the presence of hydrated magnesium oxide, was due to the removal of hydroxyl ion, by the formation of insoluble magnesium hydroxide. That such is not the case is shown in the following way. Experiments were carried out in which an equivalent quantity of hydrochloric acid was substituted for the magnesium chloride added. This removed the hydroxyl ion by forming water. Typical results are given in Table I.

TABLE I

Effect of Removal of Hydroxyl Ion by Hydrochloric Acid

Number of Experiment	Charge	Time in minutes	cc. oxygen liberated
1	10 cc. NaClO	18	0.63
	.003179 g. Cu	35	1.29
	Water to make	122	3.9
	25 cc.	171	5.1
2	10 cc. NaClO	3	1.8
	.003179 g. Cu	12	10.3
	.001216 g. Mg.	24	19.1
	Water to make	40	29.4
	25 cc.	66	41.0
3	10 cc. NaClO	10	0.43
	.003179 g. Cu	25	1.2
	HCl = .001216 g. Mg.	135	4.4
	Water to make	175	5.6
	25 cc.		

Duplication of Results.—The ease with which results may be duplicated by the experimental method used is illustrated in Table II.

TABLE II

Data for Original and Duplicate Determinations

Original		Duplicate (14 days later)	
Time in minutes	cc. of oxygen	Time in minutes	cc. of oxygen
3	4.1	3	4.4
5	8.5	5	8.8
9	16.8	9	16.7
13	23.9	13	23.7
18	31.4	18	31.2
20	34.2	20	34.0
25	40.4	25	40.2

Results

The results obtained are summarized in Table III and shown graphically in Fig. 1. The value for K_1, the unimolecular constant, is that obtained when the hypochlorite in each determination is 20 percent decomposed.

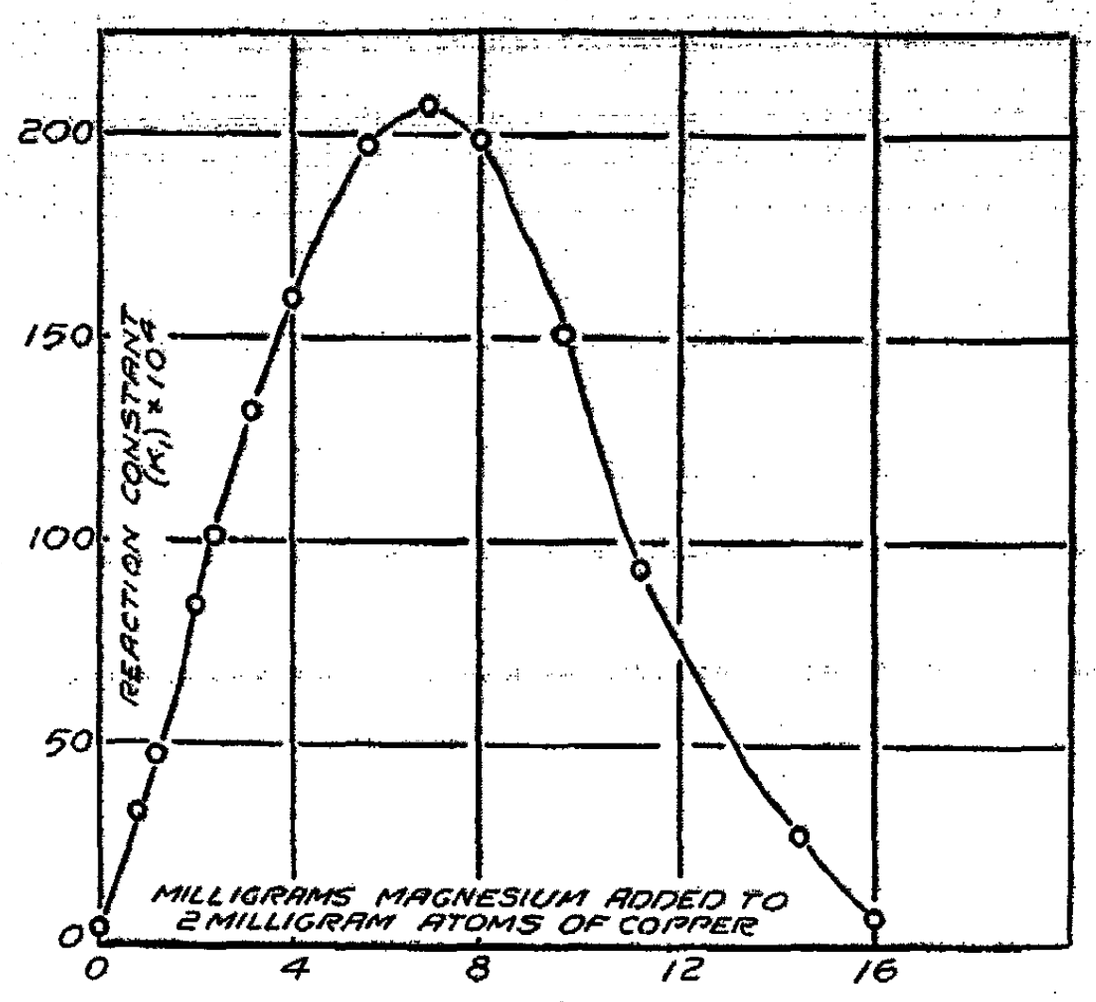

FIG. 1

Curve shows the promoter effect of hydrated magnesium oxide on hydrated copper oxide catalyst.

TABLE III

The Promoter Effect of Hydrated Magnesium Oxide on Hydrated Copper Oxide

Milligrams of copper per liter	Milligrams of magnesium per liter	Percent by weight of magnesium in catalyst mixture	Milligram atoms of magnesium added to two milligram atoms of copper	Unimolecular reaction constant $K_1 \times 10^4$ at 20% decomposition
127.1	0	0	0	3.5
127.1	19.45	13.27	0.8	31.3
127.1	29.2	18.68	1.2	46.8
127.1	38.9	23.2	1.6	72.3
127.1	48.6	27.7	2.0	84.5
127.1	58.3	31.4	2.4	100.5
127.1	77.0	37.7	3.17	132.0
127.1	97.3	43.3	4.0	160.0
127.1	136.0	51.7	5.6	197.0
127.1	165.0	56.5	6.78	207.0
127.1	194.1	60.4	8.0	198.0
127.1	233.5	64.7	9.6	150.0
127.1	272.2	68.3	11.2	93.9
127.1	350.2	73.5	14.4	27.0
127.1	389.0	75.4	16.0	8.34

Discussion of Results

Examination of the data in Table III or the curve in Fig. 1 shows:

1. The maximum promotion of the copper catalyst, under the conditions of these experiments, is reached when the ratio of copper atoms to magnesium atoms is one to three or four.

2. When the ratio of copper to magnesium is one atom to eight atoms, the promoter effect has practically disappeared.

These experimental results may be accounted for by assuming that the promoter aids in the *formation* and *preservation* of active centers on the catalyst particles. It was suggested, in the second article of this series, that the fall in the activity of the unpromoted copper catalyst was due largely to a reduction in the number of active centers, through the agglomeration of the catalyst particles. On the other hand the suitably promoted catalyst maintained its activity due to the *prevention* of *agglomeration* of the particles. Evidence in support of such an assumption is now presented.

The unpromoted hydrated copper oxide catalyst, in these experiments, is blue when first precipitated, but soon changes to a dark brown or black. Weiser[1] states that the blue hydrated copper oxide is more finely divided than the black variety and that the black may be formed from the blue through the coalescence of the particles. The work of Schenck,[2] in Bancroft's laboratory, showed that the blue copper oxide may be ignited without undergoing a change in color if sufficient aluminum hydroxide is present to prevent 'sintering'. In the work in this laboratory, it was observed that in the most actively promoted catalyst, the hydrated copper oxide *remained* blue. In those catalyst-promoter mixtures where the ratio of copper to magnesium atoms was one to ten, twelve or more, the mixture was white, showing that the copper compound was largely covered with the hydrated magnesium oxide. Here, it will be observed, the promoter effect is very slight.

In an important investigation, it has been shown by Frankenberger and Mayrhofer[3] that an iron catalyst for the ammonia synthesis, may be maximally promoted by depositing single iron atoms on a surface in such a way that they cannot coalesce. This was accomplished by spraying a mixture of iron atoms and water molecules, in the ratio of one iron atom to four water molecules, onto a surface cooled with liquid air. It was found that the iron atoms combined with hydrogen molecules in the ratio of one to one. In the experiments described here, the promoter has the same function (at least in part) as in Frankenberger's experiments. In his, the water molecules prevented the coalescence of the iron atoms; in the experiments described here, the magnesium oxide prevented the coalescence of the copper oxide particles. It is not unreasonable to suppose that the ideally promoted hydrated copper oxide catalyst is one in which each molecule is separated from its neighbors by a definite number of molecules of the promoter. It

[1] Weiser: "The Hydrous Oxides" (1926).
[2] Schenck: J. Phys. Chem., 23, 283 (1919).
[3] Frankenberger and Mayrhofer: Z. Elektrochemie, 35, 590 (1929).

seems reasonable to suppose that those oxides or hydroxides whose crystal structures are the same as those of the catalyst oxides should have the property of separating the catalyst molecules from each other in a definite manner, say by forming mixed crystals, and thus becoming the best promoters. It is the intention of the author to make future studies approaching the problem from this point of view.

Summary

1. The promoter effect of hydrated magnesium oxide on the hydrated copper oxide catalysis of sodium hypochlorite has been studied. The data obtained are given in tables and shown graphically.

2. The maximum promoter effect is obtained in those mixtures of catalyst and promoter where the ratio is one atom of copper to about four atoms of magnesium.

3. In the most effective catalyst-promoter mixtures, the color of the hydrated copper oxide remains blue. This shows that the promoter preserves the activity of the catalyst through the prevention of the agglomeration of the particles.

Salt Lake City, Utah.

NEW BOOKS

Crucibles. *By Bernard Jaffe. 9¼ × 17 cm; pp. ix + 377. New York: Simon and Schuster, 1930. Price: $5.00.* This book contains interesting sketches of Bernard Trevisan, Theophrastus Paracelsus, John Joachim Becher, Joseph Priestley, Henry Cavendish, Antoine Laurent Lavoisier, John Dalton, John Jacob Berzelius, Amedeo Avogadro, Friedrich Woehler, Dmitri Ivanovitch Mendeléeff, Svante Arrhenius, Marie Sklodowska Curie, Joseph John Thomson, Henry Gwyn Jeffreys Moseley, and Irving Langmuir.

"Some of the apparatus and utensils which are the tools of the chemist of our scientific laboratories were first introduced by alchemists—cupel, distilling flask, retort, water bath and even the balance in its crude form. The extraction of gold by amalgamation with mercury, the preparation of caustic alkali from the ashes of plants, and other new processes of manipulation and methods of manufacture were developed by the gold cooks in their manifold operations," p. 16.

"The world owes bombastic Paracelsus a great debt. This revolutionist with the imagination of a poet and the fearlessness of a crusader, was much more than the bibulous braggart his enemies had called him. He was a real benefactor of mankind. His great contribution was no one epoch-making discovery, but rather the vital impetus he gave to the study of chemistry for the curing of ills of the body. He swept aside the teachings of the ancient authorities and brought alchemy to the aid of medicine," p. 30.

"Becher introduced the potato into Germany to feed its swine and cattle and to prevent famine among the poor. He patented a method of distilling coal. He started work on a lamp that would burn forever. He invented weaving and spinning machines. Various mining and metallurgical processes were devised by him. They all ended in commercial disaster. But in spite of his many bankruptcies, there was something about Becher that kept the believing world ready to listen to him once more. His fame as an economist had spread. In 1664 he was called to Mannheim to introduce new manufactures. He was to be given a free hand in the development and enrichment of the city. He planned a new era in the industrial life of that city. He outlined projects for the introduction of the manufacture of glass, paper, and even silk. Silk for the looms was to be obtained from a silk-raising industry which he was to inaugurate. It was an ambitious undertaking," p. 45.

Priestley became interested in the gas which bubbles off in the huge vats during the process of beer-making. "Unable to obtain sufficiently large quantities of this gas from the brewery, he learned to prepare it at home. He tried dissolving the gas in water. It was not very soluble, but some of it did mix with water. In this manner in the space of two or three minutes he made, as he related, (a glass of exceedingly pleasant sparkling water which could hardly be distinguished from Seltzer water.) Appearing before the Royal Society he told that learned body of his discovery of what we now know as soda water—a very weak acid solution of carbon dioxide gas in water. The Royal Society was intensely interested, and he was asked to repeat his experiments before the members of the College of Physicians. He jumped at the opportunity, and as he bubbled the gas through water, he asked some of those present to taste the solution. They were very much impressed, and recommended it to the Lords of the Admiralty as a possible cure for sea scurvy. Priestley received the Society's gold medal for this discovery, the first triumph of this amateur chemist in science," p. 56.

"Cavendish obtained six samples of gas by the action of hydrochloric acid and of sulphuric acid on zinc, iron and tin. "The experimenter now brought a lighted taper to his six samples of gas. He watched each specimen of gas burn with the same pale blue flame. Strange that the same gas should be evolved in each case! What else could this inflammable air be, but that elusive phlogiston? For had not Becher taught that metals were compounds of phlogiston and some peculiar earths? Surely Cavendish had proved that the gas came,

not from the acids or water in the bottles, but from the metals themselves! But he must not announce this until he had investigated further—it would not do to startle the world before he had made certain he was right.

"With the crude instruments at his disposal, he passed the gases through drying tubes to free them of all moisture, and then he weighed the pure imprisoned "phlogiston." Though extremely light he found it actually had weight. It was ponderable. He had nailed phlogiston itself! Now, at the age of thirty-five, he published an account of this work on "Factitious Airs" in the Transactions of the Royal Society," p. 76.

"Lavoisier was a careful worker with an idea at the back of his head which grew clearer as he read or repeated the experiments of his predecessors and contemporaries. Slowly he began to weed out the faulty explanations and weak theories that had crept into chemistry. Phlogiston did not fit into his scheme of chemistry. While the rest of Europe clung to it tenaciously he could see through it. To him it was a myth, an idle mischievous theory with neither foundation nor substance. There must be a simpler and more logical explanation of burning than Becher's phlogiston. With the coolness and dexterity of a skilled surgeon, he began to dissect the old idea. The creature was rotten to the core.

"With scientific intuition he rejected this theory before he had thought of a substitute, but he was going to find an alternative. This practical Lavoisier who, at twenty-two received a gold medal from the Academy of Sciences for working out the best method of lighting the streets of Paris; this same Lavoisier who, before submitting his essay, had worked for months on this problem, shutting himself up in a dark room for six weeks to render his eyes more sensitive to different lights; he was going to find the true explanation of burning! Phlogiston would not do," p. 102.

"Suddenly, after deep thought, the whole atomic theory was revealed to him [Dalton]. He did not wait for experimental verification. Like Galileo, he did not feel that experimental proof was always absolutely essential. Like Faraday, he possessed, to an extreme degree, a sense of physical reality. Dalton, cat on his knee, began to draw pictures of his atoms," p. 122.

"Berzelius began to work with his oldest half-brother, Lars Ekmarck, on voltaic electricity. His thesis for his medical degree was on the action of electricity on organic bodies. The following year, with his friend, von Hisinger, he published a paper on the division of compounds by means of the voltaic pile, in which he propounded the theory that metals always went to the negative pole and non-metals to the positive pole of the electrical machine. Benjamin Franklin had introduced this idea of positive and negative electricity. He had called a body positively electrified when it could be repelled by the glass rod rubbed with silk.

"The work of Berzelius, however, hardly caused a ripple in the chemical stream of progress. But four years later a young chemist in England, reading an account of his works and following them up, fired the imagination of the world. Benjamin Franklin had 'disarmed the thunder of terrors and taught the fire of heaven to obey his voice,' but now Humphry Davy, using Volta's electric pile and the research of Berzelius, isolated such new and strange elements as staggered men even more than the discovery of phosphorus a century before," p. 143.

"A firm believer in the atomic theory of Dalton, Berzelius made his new symbols stand for the relative atomic weights of the atoms. The initial letter capitalized represented one atom of the element. These symbols stood for definite quantitative measurements and 'enabled us to indicate without long periphrases the relative number of atoms of the different constituents present in each compound body.' Thus they gave a clew to the chemical composition of substances. This was a tremendous step toward making chemistry a mathematical science," p. 147.

"Not a word of eulogy was pronounced at Avogadro's simple bier. Only brief obituaries appeared in a few scattered scientific journals filled with accounts of the discovery of the first skeleton of a Neanderthal man; of mauve, the first coal tar dye discovered by Perkin in Hofmann's laboratory in London; of a blast furnace for making steel designed by

Bessemer. Not a single word about his monumental memoir of the molecules—a glaring example of the neglect of genius.

"When a bust of Avogadro was unveiled a year after his death, not a chemist was there to utter a word of homage. Even in his own country he was little known. Only two of his pupils, both physicists, recalled his work. His classic theory of the molecules had appeared originally not in Italian but in French. It was later translated into both German and English, and, although most incredible, was not available in his own language until the opening of the twentieth century. So extremely modest and retiring was this Italian professor that, great as were his contributions in the field of science, when the Scientific Congress met in his own native city, he was not even nominated an officer of that body," p. 166.

"When Woehler was sure of his ground, he wrote to Berzelius, 'I must tell you that I can prepare urea without requiring a kidney of an animal, either man or dog.' The Swede enthusiastically spread the news. The world of science was electrified. Chevreul hailed the achievement with joy. Woehler had actually synthesized urea out of inorganic compounds! What was to prevent others from building up the sugars, the proteins, perhaps even protoplasm, the colloidal basis of life itself? A feeble protest still sounded from the vitalists. Urea was perhaps midway between the organic and inorganic world. For to make urea one must use ammonia which originally was of organic origin. The vital force present in organic substances never disappeared and consequently was capable of giving rise to other organic bodies. So they argued. But even that whisper was soon lost in the great tumult of excitement. It was indeed a brilliant new day for chemistry," p. 177.

"Out of Russia came the patriarchal voice of a prophet of chemistry [Mendeléeff]. 'There is an element as yet undiscovered. I have named it eka-aluminum. By properties similar to those of the metal aluminum you shall identify it. Seek it, and it will be found.' Startling as was this prophecy, the sage of Russia was not through. He predicted another element resembling the element boron. He was even bold enough to state its atomic weight. And before that voice was stilled, it foretold the discovery of a third element whose physical and chemical properties were thoroughly described. No man, not even the Russian himself, had beheld these unknown substances," p. 199.

"In the historic chemical laboratory of the University of Leipzig two men, a German born in Riga, and a Swede, met towards the end of the nineteenth century to plan a great battle against an established theory and the scientific inertia which upheld it. Meanwhile, over in Amsterdam, another scientist, a Dutchman, worked in the same campaign. From this triumvirate came a barrage of scientific experiments which made possible a new era in the field of theoretical and applied chemistry. Here, at Leipzig, the Headquarters of the Ionians, the great struggle was directed.

"The three were all young men. Svante Arrhenius was hardly more than a boy. Van't Hoff, the Dutch professor, was thirty-five, and Ostwald, the moving spirit of the revolt, a year younger. The quest for scientic truth had brought these three together, and they vowed to force the venerable authorities of the scientific world to accept the new leaven of the younger generation. The masters, under whom they had cut their scientific eye-teeth, must be shown the folly of ignoring genius among their students," p. 219.

"A strange element had been discovered by a woman. Its salts were self-luminous; they shone in the dark like tiny electric bulbs. They were continuously emitting heat in appreciable quantities. This heat given off was two hundred and fifty thousand times as much as that produced by the burning of an equal weight of coal. It was calculated that a ton of radium would boil one thousand tons of water for a whole year. This new element was the most potent poison known to mankind—even acting from a distance. A tube containing a grain the size of a pinhead and placed over the spinal column of a mouse paralyzed it in three hours; in seven hours the animal was in convulsions and in fifteen hours it was dead. Radium next to the skin produced painful sores. . . . Its presence sterilized seeds, healed surface cancer and killed microbes. It colored diamonds and the glass tubes in which it was kept. It electrified the air around it, and penetrated solids.

"The world marveled at the news. Here was another one of nature's surprises. Chemists were bewildered. A woman had not only pushed back the frontiers of chemical knowledge—she had discovered a new world waiting to be explored. From every laboratory on the face of the earth came inquiries about this magic stone. The imagination of the world was kindled as by no other discovery within the memory of man. Overnight the Curies became world famous," p. 255.

"Three eminent scientists constituted the Board of Electors which was to make the final choice—Lord Kelvin, the Scotchman who in Glasgow worked out the intricate problems of the first Atlantic Cable; Sir George Gabriel Stokes, investigator of fluorescence; and Professor George Howard Darwin, second son of Charles Darwin. They saw inside that massive head of Thomson an imaginative yet crystal-clear mind with powerful penetrating power. The lad from Manchester was chosen. 'Shades of Clerk-Maxwell,' declared one well-known professor. 'Things have come to a pretty pass in the University of Newton when mere boys are made professors.' Michael Pupin, the eminent American scientist, coming from a cracker factory in New York to study physics under Clerk-Maxwell at Cambridge was frightened away when he learned that a young lad, only two years his senior, had been put at the head of the famous Cavendish Laboratory. 'I thought he was too young to be my teacher of physics,' he complained.

"And so it came about that a mere boy filled the chair to two illustrious predecessors, and under his leadership the Cavendish Laboratory became the dominant center of scientific research in the world. Here was carried on more important research per square foot than in any other part of the earth. Here men's minds soared to heights never dreamed of before. The spirit of the boy Thomson was to pervade that sanctum of science for nearly half a century," p. 266.

"In 1912, at the age of twenty-six, Moseley published his results—he had discovered the Law of Atomic Numbers. He prepared a new Table of the Elements more fundamental than that of his Russian predecessor. He gave the world an infallible road map of all the elements of the universe—a chart based, not on atomic weights, but on atomic numbers. Mendeléeff's romantic blue-prints had served science for fifty years. Now a new and more enduring structure was reared, fashioned by the cunning brain of a youth," p. 298.

"Átoms, said Langmuir, differ from each other in chemical activity only because of their tendency to complete their outside shells and thus render the atom stable. Argon, the third inert gas in Moseley's Table of Elements, has an atomic number of 18. Its first shell is complete with two electrons, its second shell is also complete with eight additional electrons, while its third shell likewise contains eight electrons, showing once more a stable configuration. Hence argon is inert. Chemical affinity is thus a condition dependent upon the nature of the outermost shell electrons. When the outside shell of an atom contains very few electrons, its tendency is to lose them. Such an atom is a metal. If, on the other hand, the outermost shell of an atom contains an almost complete ring, it will strive to borrow some electrons from other atoms which are anxious to lose them. Such an atom is a non-metal. Metals are lenders of electrons and non-metals are borrowers. Hence metals and non-metals will combine energetically with each other and both, by an exchange of electrons, assume the stable condition. Chemical affinity or union, therefore, depends upon this transfer of electrons. In a polar union a positive atom loses its valence electrons to a negative atom and the two atoms are held by electrostatic attraction. In a non-polar union electrons are not actually transferred—the two atoms approach each other so that one or more valence electrons of one atom occupy the vacant positions in the valence shell of the second atom. Octets are thus formed by a process of sharing electrons," p. 329.

Cannizzaro's name is misspelled consistently and so are one or two others. It is only by a stretch of the imagination that one can call Moissan the inventor of the electric arc and Lippman the developer of color photography, p. 254.

Wilder D. Bancroft

The Wave Mechanics of Free Electrons. *By G. P. Thomson. 23 × 16 cm; pp. 173. New York and London: McGraw-Hill Book Company, 1930. Price: $2.50.* Professor Thomson was the George Fisher Baker non-resident lecturer at Cornell University during the Fall term of 1929. In his introductory lecture on "Waves and Particles," the author says: "Atoms can be made to emit light, and each atom emits its own characteristic wave-lengths. These are clearly a consequence of the structure of the particular atom, presumably of the arrangement of its electrons. Now *one* theory, and *one only*, was found capable of explaining these wave-lengths even in general terms. This was the theory due to Niels Bohr according to which the electrons were supposed to move in orbits round the nucleus rather like planets round the sun. But in order to make the theory fit the facts, Bohr had to assume a behavior of the electrons which is quite contrary to ordinary dynamics, and curiously enough the same quantity h came in, though in quite a different way. The real trouble was not so much that the electrons obeyed laws different from those of Maxwell and Newton, but that they were not consistent about it. Some of the things they did required the old laws to explain them; others required a new and inconsistent set. Sometimes both had to be used in different parts of the same calculation. The position of a physicist investigating an atom was rather like that of a man trying to make sense of an account of a game which started as golf and suddenly for no apparent reason turned into tennis and then back to golf again. Worse still, as time went on it became clear that the electrons did not play fair even at the game they had for the moment chosen. The results were nearly right but not quite. The only hint was that the quantity h came in whenever the atom chose to break the old rules, and this suggested a connection with the photo-electric paradox. The first really successful attempt to solve these difficulties is due to Prince L. de Broglie. He realized that the reason why the electron in the atom seemed to follow two different sets of rules at once was that it was behaving much more like a wave than a particle. Now if you think that you are reading of an account of a game played with a ball, when really the reporter was writing about a swimming match, it is not to be wondered at if the report does not make good sense. It is perhaps surprising that the physicists made as much of it as they did. De Broglie's theory was a mathematical one based on relativity. He reached the conclusion that any moving particle would be accompanied by a wave, and he postulated that this wave controlled the motion of the particle. Instead of Newton's laws of motion (motion in a straight line, acceleration proportional to the force, and so on) this view gives a motion governed by waves. Of course Newton's laws are true in every-day life. This is because a very short wave is indistinguishable in behavior from a particle, and the scale of de Broglie's waves is given by h, which is a very small quantity. But according to his theory the smaller the particle the longer the wave. For an electron in an atom the wave is quite comparable with the size of the atom, and the behavior of the electron is greatly different from what you would expect of a particle. It has been found, in fact, that this theory when fully applied mathematically, as it has been by Schrödinger and others, brings order out of chaos in the explanation of the properties of atoms," p. 6.

"A question that inevitably arises is: What is the medium which transmits electron waves? I am sorry that I can give no entirely satisfactory answer. For the first time, physics is faced with waves in empty space which do not fit into the ordinary series of ether vibrations. All the ether vibrations differ only in wave-length; if the wave-length is given, the kind of 'light' is fixed. The electron waves have varying wave-lengths depending on the speed of the electron, but they usually fall in a region of wave-lengths which is already appropriated by X-rays. As we have seen, they are certainly not the same as X-rays. One must suppose some other medium, or at least that the ordinary ether is in some way profoundly modified by the presence of the electron. It is possible that they are waves in a 'subether.' But it is not a very attractive idea to have two ethers filling space, especially as the waves of protons—if they exist—would demand a third. Space is becoming overcrowded. Other suggestions are to regard the waves as a kind of mathematical abstraction, a sort of ghost waves. The whole question is getting very metaphysical," p. 11.

The chapters are entitled: general theory of waves; De Broglie's wave mechanics; theory of wave diffraction by crystals; the experimental evidence; effect of a continuous

medium on the waves; interaction between electrons and atoms; theoretical interpretation; physical theory; the magnetic properties of the electron; applications of electron diffraction.

"The results of the transmission experiments may be approximately explained by the following assumptions:

"(1) Each electron is associated with a wave of approximate wave-length h/mu, the length of the train being at least 50 waves and the breadth in the wave front at least 30×10^{-8} cm. in certain cases.

"(2) Each atom of the crystal is the center of a wavelet coherent with the original wave, and whose intensity varies with the angle to the original direction of motion of the electron, in a manner which can be calculated from the distribution of charge in the atom (p. 115).

"(3) The chance of the electron appearing at any place with its original energy is proportional to the intensity of the composite wave formed by the wavelets.

"It should be noticed that the electron is detected by any of a number of processes, such as the charging of a Faraday cylinder, the development of the grain of a photographic plate, or a scintillation on a screen, all of which can be interpreted only as the arrival of a particle with a certain charge and energy.

"(4) There is also a chance of the electron losing energy in passing through the crystal. In this case its deflection is governed by other laws of which little is known at present.

"The discrepancies between the above theory and the reflection experiments at low voltage apparently can be explained by considerations of the type presented at the end of Chapter V, which involve the investigation of the interaction of a wave train with the complicated periodic distribution of potential in the crystal. On this view assumption (2) is a convenient approximation to the result which should be obtained by a rigorous solution of Equation (5), p. 29, using for F the actual distribution of potential throughout the crystal. Mott's calculation of the scattering of single atoms also fall into line with this view.

"It seems, then, that we may regard the reflection experiments as accounted for by assumptions (1)-(4) above, if they are modified in the sense that the chance of an electron appearing is to be taken as proportional to the intensity of the scattered waves which satisfy Equation (5), page 29, using a value of F determined by the structures of the crystal and of its component atoms.

"It should be emphasized that, at least so far as present knowledge goes, the behavior of any particular electron must be expressed in terms of probability. For example, in a transmission experiment there is no way of knowing in advance whether any given electron will appear in the central spot or on a ring, and the same difficulty would arise even if the crystal were large and there were only one Laue spot to which diffraction could occur. In addition, there is always a probability of inelastic collision. It seems possible, however, at least in theory, to regard each electron as an individual particle fastened in such a way to a wave system obeying Equation (5), page 29, that it always moves along the wave normal. The expression for the necessary velocity has been given in practically equivalent forms by de Broglie and Schrödinger," p. 119.

"Towards the end of the history of the orbit theory of spectra it became apparent that a simple point electron was inadequate to explain the observed facts. To take only one difficulty, it was found that four quantum numbers had to be assigned to each electron. Now each quantum number may be regarded as fixing one degree of freedom, and a point has only three of these. This and other difficulties were overcome by Goudsmit and Uhlenbeck who suggested that the electron was to be regarded as a spinning body whose axis of spin could vary. Actually it was only necessary to suppose two possible directions for the axis, or rather one direction associated with a spin of either sense. One could think of the axis, for example, as always perpendicular to the oribt and the electron as spinning with or against its orbital motion. Such an electron would be expected to behave like a small magnet, and it was found in fact that agreement with experiment resulted if the moment was taken as $eh/4\pi mc$. This value fits in with the results of the Stern-Gerlach experiments.

"Nothing in the preceding theory at all corresponds with this conception of the electron as a magnet to whose axis a definite direction in space is to be assigned, and it is not surprising, therefore, that the theory in this form should fail to account for those facts which

made the hypothesis of the spinning electron necessary on the older theory. The necessary extension of the equations to cover this aspect of the electron has been made by Dirac, using the methods of non-commutative algebra; his results have been expressed in more ordinary form and considerably extended by Darwin whose methods we shall follow," p. 141.

Wilder D. Bancroft

Katalyse. *By W. Frankenburger and F. Dürr. 27 × 19 cm; pp. 58. Berlin: Urban and Schwarzenberg, 1930. Price: 3.50 marks.* This pamphlet is a reprint of the article on catalysis in the second edition of Ullmann's "Enzyklopaedie der technischen Chemie." The authors are in the research laboratory of the I.G. at Oppau. They are quite frank about admitting that there is no prospect at present of being able to predict theoretically what will be the best catalytic agent for any particular reaction, pp. 3, 30.

The authors group catalytic reactions under ten heads, p. 19:—

1. Hydrogen ion is often effective in causing addition of splitting off of water.
2. Hydroxyl ion is often effective in causing condensations, polymerizations, and racemizations.
3. Substances which can occur easily with two valences are often effective in causing oxidations.
4. Hydrogenations in presence of hydrogen gas are helped by presence of platinum, palladium, rhodium, nickel, cobalt, iron, and copper.
5. The splitting-off of water from the vapors of organic substances is facilitated by the oxides and phosphates of thorium, aluminum, and tungsten; also by kaolin which the authors for some unknown reason call bauxite.
6. Condensations in organic chemistry are often speeded up by metallic chlorides.
7. The introduction of carbon monoxide into an organic hydrocarbon can be done in presence of a mixture of hydrochloric acid with aluminum or cuprous chloride.
8. Halogenations are catalyzed by chlorides, iodine, sulphur, and charcoal.
9. Cuprous salts or copper powder favor the substitution of halides for the diazo group.
10. Cracking of hydrocarbons is catalyzed by aluminum chloride, metals, and active carbon.

The authors postulate the intermediate formation of something not necessarily a compound according to the laws of definite and multiple proportions, p. 27. This is of course perfectly safe, and absolutely useless. It is worse than useless because they think that they have said something and are therefore not especially interested in what actually happens in any particular case. They admit the existence of negative catalyzers which break up a chain reaction; but they do not believe in the existence of what people usually mean by negative catalyzers, p. 36.

The authors cite, p. 47, the work of Hoover and Rideal in which thorium causes the splitting-off of hydrogen from alcohol when the catalyst is poisoned by water and the splitting-off of water when the catalyst is poisoned by chloroform. This would seem to imply that the work of Adkins with catalysts made from aluminum ethylate for instance was affected by poisons, as suggested by H. S. Taylor. Experiments to decide this point are now being carried out in the Cornell laboratory. The belief is expressed, p. 50, that, with the nickel-molybdenum alloy for the synthesis of ammonia, the nickel activates the hydrogen and the molybdenum the nitrogen.

The last paragraph, p. 58, is especially interesting as coming from two industrialists. "A glance over the technical catalytical processes developed so far shows the extraordinarily manifold applications of the contact processes as time-savers in producing chemical products of the most varied nature. In spite of the number of catalytic industrial processes, they are far removed, economically and in changing the course of the reaction by gentle means, from what living nature shows us daily as a symphony of catalytic processes. In vegetable and animal organisms—without use of powerful reagents such as high gas pressures or high temperatures—there occur most remarkable catalytic reactions in harmonious interlocking. Homogeneous and microheterogeneous catalyses take place under the influence of inorganic and organic catalysts; also reactions at surfaces which under the influence of the sun's rays

convert chemically inert gases like carbon dioxide into compounds with high molecular weights; and processes by which the complicated substances of the vegetable and animal organisms are built up with ease from the simplest components. Most of these reactions have not even been studied yet in spite of all that has been done. It can be predicted that the industry of the future will have to model itself more than ever before on nature in order to exhaust the possibilities to come from the study and mastery of catalytic phenomena.

Wilder D. Bancroft

The Spirit of Chemistry. *By Alexander Findlay. 22 × 16 cm; pp. xvi + 480. London and New York: Longmans, Green and Co., 1930. Price: $3.50; 10 shillings, 6 pence.* "This book", the author states, "has been written as a text-book for those students, more especially, who, in the Universities of Great Britain and in the Colleges of the United States, in increasingly large numbers, pursue a course in chemistry as an element of general culture rather than as a part of their professional or technical training." This difficult task is one to which Professor Findlay has given much consideration and in which he made a beginning fifteen years ago by the publication of his well-known "Chemistry in the Service of Man". The scope of the present work is however much more comprehensive and in the twenty-nine chapters we have a display of the science in a great multitude of its implications with thought and life. The interest of the book is heightened by the blending of the history and philosophy of the science with a very carefully selected range of information on matters both abstract and concrete likely to interest a student of healthy intellectual appetite. The intercalation of biographical notices, the abundant and clear accounts of the industrial applications of chemistry, and the wealth of fine illustrations greatly enlighten the narrative.

To say more about the detail of the book is unnecessary; it can be confidently affirmed that it is an extremely interesting exposition of chemical science and its applications, reflecting the philosophic mind of a chemist thoroughly abreast of the times. It is a book that may surely be read with profit by chemistry students in general.

There remains the question how far Professor Findlay has accomplished the particular task to which he set himself as indicated by the title and sub-title of his book. There is no doubt an increasing demand from those concerned with what Professor Findlay calls "the liberal arts"—broadly speaking literary studies—that their curriculum shall include some measure of natural science. It is also a matter of great concern to science that the demand should be met. It is an exceedingly difficult question, and one on which we cannot expect to speak with confidence until much further experience has been gained. We are at the present day in a state of educational transition. Education is always changing, but there can be no doubt that the world-shaking discoveries and achievements of science of the last 20 years have shaken even the most somnolent or disdainful sections of thinking men into a lively conviction that science counts and is going to count immensely for good or evil. We may put the awakening no higher than a realisation that science has to be reckoned with and that to reckon with it you really will have to get to know a little more about it.

There is however this great difficulty that custom has so long sanctioned the neglect of science as a normal part of a liberal education that in those who come to universities for literary studies we cannot for the time being assume that they have learned even the ABC of natural science. We are really called upon to do with mature minds in a university what should have been done upon the child mind in school.

The bearing of these observations upon Professor Findlay's book is that they raise the question, first, whether he has not provided too rich a table of chemical erudition, and, secondly, what place does he give to the craftsmanship of chemistry in his scheme, that is, to laboratory work and the actual practice of the experimental method. To the second question Professor Findlay has kindly replied in private correspondence. As was to be expected he is strongly in favour of practical work being pursued; he believes that "it is absolutely essential for the full development of the scientific spirit" and as a matter of

fact he requires it of all his students. But he alludes to the time difficulty, which all will acknowledge, and on the principle of half a loaf being better than no bread, he feels that "a suitable lecture course would prove of great value to an Arts student even if he does no laboratory work at all."

The writer of this notice has been sufficiently concerned with the problem to know its difficulty and to refrain from laying down the law. He has consorted with those who believe that inasmuch as the primary and distinctive power of science lies in the experimental method, it is a comprehension of this above all else that we should try to impart to those who come late even with small pitchers to our wells. He is convinced that to attain this end the actual practice of the science is indispensable. And so whilst believing that a course of experimental lectures given by teachers like Professor Findlay—a scarce kind it is to be feared—would be invaluable, he would himself be content to make a greater sacrifice of substance to method than the author has made in this interesting book.

Arthur Smithells.

Errata

Owing to the proof not having been read by the author and to errors in the manuscript, some corrections must be made in the paper by Maurice Lecat: **34**, 2508 (1930).

p. 2508 line 28, read azeotrope A for azotropea.
p. 2511 line 18, read Chavanne instead of Chaname.
p. 2511, footnote 19, read unicity for constancy, phenyldiimine for phenyldiamine, and cyclohexane for cyclohexene.
p. 2512 line 21, read eutectism for eutexi.
p. 2513 line 6 from bottom, read Z$\sim$ either to zero or instead of or.
p. 2514 line 3, read nature instead of mixture.
p. 2514 line 11 from bottom, read $\sim$ instead of M.
p. 2515 line 2, read $|\delta|$ instead of $1\delta|$.
p. 2516 line 4, read *L* instead of to.
p. 2516 line 9 from bottom, read apparatus instead of approach.
p. 2517 line 12, read two instead of four.
p. 2517 line 18 from bottom, read missing instead of mixing.
p. 2517 line 1 from bottom, read small instead of final.
p. 2518 line 14, read step instead of X-step.

Errata

Owing to the proof not having been read by the authors and to errors in the manuscripts, some corrections must be made in the papers by Messrs. Miles and Milbourn and Miles and Craik: **34**, 2598, 2607 (1930).

p. 2602 Fig. 4, read 7.10% for 71.0%.
p. 2603 line 12, read solution for swelling.
p. 2604 line 2, read No. 20 for No. 42.
p. 2604 line 6, read nitrating acid for nitrating.
p. 2604 line 16, read Fig. 1 instead of Fig. 7.
p. 2606 line 22, read Mr. T. Donaldson instead of Mr. J. Donaldson.
p. 2606 line 23, read Dr. J. Weir instead of A. J. Weir.
p. 2607 line 30, read portions for positions.
p. 2608 line 32, read advisable at 0° for advisable at 20°.
p. 2609 line 8, read or mercerised for of mercerised.
p. 2610 line 2, read of them for of the.
p. 2613 line 1, read solution for swelling.
p. 2613 line 3, read condition for conditions.
p. 2616 line 3, read small definite for shall definite.
p. 2620 line 8, read solution for swelling.
p. 2620 line 21, read Mr. T. Donaldson instead of Mr. J. Donaldson.
p. 2620 line 22, read Dr. J. Weir instead of Mr. J. Weir.