

When moist oxygen is passed over the compound, the reaction shown in the preceding equation probably takes place to a slight extent, but the moisture acts much more vigorously on the substance than does the oxygen. The first stage is doubtless $\text{GeCl}_2 + 2\text{H}_2\text{O} = \text{Ge}(\text{OH})_2 + 2\text{HCl}$. The hydrogen chloride then instantly combines with unchanged germanium dichloride to form germanium chloroform, which is carried out of the tube by the current of oxygen.

Chlorine rapidly attacks germanium dichloride with the formation of pure germanium tetrachloride. Bromine forms a colorless liquid, which on fractionation was found to consist almost entirely of germanium tetrachloride and tetrabromide. Not more than a trace of a double halide was produced. Hydrogen sulfide acts at once upon germanium dichloride at room temperature. Quantitative examination of the products showed that the reaction is essentially $\text{GeCl}_2 + \text{H}_2\text{S} = \text{GeS} + 2\text{HCl}$.

Summary

This article describes the preparation and properties of germanium dichloride.

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A CONDUCTANCE-DIFFUSION METHOD FOR STUDYING THE COAGULATION OF COLLOIDAL FERRIC OXIDE^{1,2}

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Introduction

The knowledge that electrolytes will coagulate colloids dates back to the work of Thomas Graham.³ The study of this particular phenomenon from all of its various angles has proceeded almost without a halt from Graham's time up to the present, with the result that an enormous amount has been written on the subject of coagulation. To review this mass of literature would only be repeating items already summarized in a number of modern books on Colloid Chemistry. Sufficient if, passing in review the most important experimental facts gleaned from the work of a great

¹ The substance of this article was included in a paper presented at the Midwest Regional Meeting of the American Chemical Society, University of Chicago, May 27-28, 1927. A preliminary version was submitted for publication in *THIS JOURNAL*, October 10, 1927.

² An extract from a thesis presented in partial fulfillment of the requirements for the degree of Doctor of Philosophy, University of Wisconsin, June, 1927. All work was carried out under the direction of Professors F. C. Krauskopf and J. H. Walton, to whom the author is deeply and gratefully indebted.

³ Graham, *J. Chem. Soc.*, **15**, 216 (1862); **17**, 318 (1864).

many investigators, we mention four of the important current conclusions relating to coagulation. (1) Colloids may be coagulated by electrolytes, the ion of charge opposite to that of the colloid being the effective coagulant. (2) The coagulating power of an ion increases with the valency of that ion. (3) Each electrolyte appears to have a minimum concentration which must be reached before measurably rapid coagulation takes place.⁴ (4) Coagulation is, in general, accompanied or preceded by adsorption of the coagulating ion.⁵

Even a cursory examination of the literature impresses one with the fact that there is great lack of agreement in the results upon which these and other conclusions are based. Due to the inherent nature of colloids and their apparent failure to conform to the laws which regulate the composition and behavior of pure compounds, we probably should not expect quantitative exactness in coagulation data, but a higher degree of accuracy and uniformity certainly is to be desired. Possibly the technique involved in making coagulation studies may be largely at fault. If so it should be intensely important to Colloid Science to correct this fault by substituting methods qualified to give more exact results.

If we inquire into the experimental technique employed by the numerous investigators in the field of coagulation, we find practical agreement in the methods employed. In most cases they have followed the general plan of adding varying amounts of the electrolyte in question to equal samples of the sol and noting the minimum amount required to bring about complete coagulation. The choice of electrolyte concentration seems to have been arbitrary, the only requirement being that it must be high enough to be capable of causing coagulation. Each worker has his own standardized concentration of sol and electrolyte and his own method of procedure. Some have used dilute sols, others concentrated. Some have added a concentrated solution of the electrolyte, others a rather dilute solution. The electrolyte has been added with stirring, without stirring, with agitation, without agitation, has been added rapidly and slowly. The time element has varied all the way from several minutes to several days. The decision as to the exact point of complete coagulation has, as a rule, rested on the appearance of the supernatant liquid obtained by centrifuging the treated sol, the absence of all color in the case of sols such as ferric oxide being taken as a positive index.

A combination of what seemed to him to be the best features of all past methods was employed by Ward⁶ in connection with some unpublished

⁴ Hatschek, "Introduction to the Chemistry and Physics of Colloids," P. Blakiston's Sons, Philadelphia, 1926, p. 56.

⁵ Weiser, "Colloid Symposium Monograph," 4, 354 (1926); Bancroft, "Applied Colloid Chemistry," McGraw-Hill Book Co., Inc., New York, 1926.

⁶ Doctorate "Thesis," University of Wisconsin, 1926.

studies made at the University of Wisconsin. Although primarily intended as a coagulation study, Dr. Ward's work really developed into a critical examination of the accuracy of the method which he employed, and it is interesting to note that his conclusion was that the coagulation values obtained were "an estimate, in error by ten or twelve per cent." If technique of the caliber displayed by Dr. Ward and by others who have preceded him is capable of giving only an "estimate," in error by 10 or 12%, then apparently some improvement in the method of making coagulation studies is necessary, or at least desirable, if we are ever to learn the true mechanism of coagulation.

A possible course which an attempt at improvement might follow is suggested in the third and fourth of the previously listed conclusions relating to coagulation. The third states that "each electrolyte appears to have a minimum concentration which must be reached before measurably rapid coagulation takes place." Granting the truth of this statement, the incidence of rapid coagulation should be a function of electrolyte concentration. There should be a critical concentration at which noticeable coagulation should begin to take place instantly and throughout the entire sol. If we could gradually bring the electrolyte concentration up to this critical value the sol should then cloud and coagulate very suddenly. By accurately catching the value of this critical concentration we should, theoretically at least, have a method for determining what we might then call "critical coagulation concentration." Possibly the third conclusion is not entirely correct. Perhaps there is no such thing as a "stable" colloid. Stability may be only relative, the most "stable" colloid eventually undergoing complete coagulation without the assistance or intervention of any electrolyte. Still, since experimental evidence points to the fact that noticeable and measurably rapid coagulation is dependent upon the attainment of a minimum electrolyte concentration, any means of accurately catching the point at which this rapid rate becomes noticeable should be of value.

The fourth conclusion suggests a method by means of which we could catch this point. If "coagulation is, in general, preceded or accompanied by adsorption of the coagulating ion," the concentration of the electrolyte should experience an abrupt decrease at the coagulation point. The extent of this decrease would depend upon the degree to which the coagulating ion is adsorbed. If there is such a decrease we should have little difficulty in observing it because we have methods for following changes in electrolyte concentration. In the case of ferric oxide sols the conductance method would seem to be the only acceptable one. Using this method we could simply plot time against resistance as we brought the electrolyte concentration up to the "critical" value. The break in the time-resistance curve would represent the critical point.

To catch the "critical point" would then appear to be a simple matter. The main problem is to be able gradually and uniformly to bring the electrolyte concentration up to the critical value without getting preliminary coagulation. We cannot add the electrolyte directly, as past investigators have done, because that would give us local coagulation. This local coagulation would gradually deplete the supply of colloid and we would finally end up with a completely coagulated sol without having experienced the desired break in our curve. Obviously we must start with an electrolyte concentration too low to cause even the most minute trace of local coagulation and gradually increase it uniformly by evaporation; or else we must allow the electrolyte to diffuse in through a membrane, uniformly, slowly and in such minute quantities as to prevent any local effects. In this way we would get volume coagulation, that is, coagulation throughout the entire sol. Perhaps it may seem that we are frustrated at the very outset because there is no such thing as perfect volume concentration of a sol. Neither can there be diffusion without differences in concentration. But we should be able to come very close to the ideal state and get almost if not quite perfect volume coagulation. That, after all, is the best that we can hope for in any method.

Experimental

Concentration by evaporation was first resorted to, potassium nitrate being the added electrolyte. Twenty-five cc. of sol was diluted with 25 cc. of *N*/200 potassium nitrate, the mixture placed in a conductance cell consisting of a 2.5×20 cm. test-tube in the bottom of which was sealed two platinized platinum electrodes and the latter immersed in a bath of boiling water. A current of dry air was blown over the surface of the sol. The resistance of the solution was taken at frequent intervals up to and beyond the coagulation point. The time-resistance curves obtained from three runs showed slight but very noticeable "breaks." The sol clouded sharply at the same time as the break occurred; this was followed very shortly by the appearance of floccules of coagulum. Some localized coagulation took place at the surface in each run. In order to eliminate this, provision was made for stirring by bubbling clean air through the sol. The air bubbles caused coagulation, as did nitrogen, oxygen and hydrogen.⁷ A pyrex stirrer was then used.

The evaporation method served its purpose in that it indicated that the desired "breaks" could be obtained and that values could be checked. However, it was abandoned as unsatisfactory because it was too slow and tedious, about eight hours of constant attention being required for each determination.

The method of increasing the concentration by allowing the electrolyte to diffuse in through a membrane was then resorted to. The conductance-diffusion cell (Fig. 1) consisted of two platinum electrodes, D, sealed into glass tubes which were firmly embedded in sealing wax contained in the space between the inner, K, and outer, J, collars. The outer collar was flanged out at the lower edge to facilitate attachment of the collodion bag. The inner collar, being open at both ends, permitted introduction of the pyrex stirrer, C. The electrodes were protected by four solid glass guard posts,

⁷ A detailed study of the coagulation of sols by gas bubbles is now under way in this Laboratory.

G, which were embedded in the sealing wax. These posts extended a short distance below the lower edge of the electrodes and prevented their coming in contact with the collodion bag.

The collodion bag, B, was molded in an ordinary 3-cm. pyrex test-tube of convenient length. It was slipped over the flanged edge of the outer collar to the position shown and was held in place by a rubber band. Fifty cubic centimeters of sol, or sol-electrolyte mixture, was then introduced by means of a pipet, after which the cell was clamped in the position indicated in the figure and lowered into a beaker, A, containing electrolyte of the same concentration as that used in the preparation of the sol-electrolyte mixtures. By means of a simple constant-level device the level of the electrolyte in A was adjusted and maintained about equal to that of the sol in the bag, B. Beaker A was kept in a water thermostat bath at 25°, all determinations being made at this temperature. The motor-driven stirrers, C and C', which were started as soon as the cell had been lowered to its proper position, were operated at 220 and 400 r.p.m., respectively.

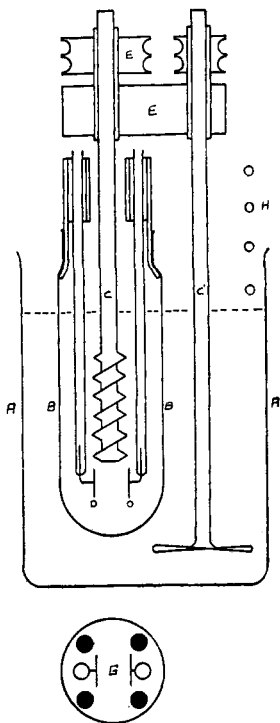


Fig. 1.

When the cell and its contents had come to the temperature of the thermostat, the desired electrolyte was introduced, drop by drop, at H from a water-jacketed buret whose temperature was kept constant at 25°. Time-resistance readings were then taken at frequent intervals until coagulation of the sol took place, the uniform drop-by-drop addition of electrolyte being continuously kept up. The location of the coagulation point was based on two criteria, the change in the appearance of the sol and the break in the time-resistance curve.

The break in the time-resistance curve having been properly located, the specific conductance corresponding to this break was calculated, and the electrolyte concentration corresponding to this specific conductance was read from an experimentally determined conductance-concentration curve. The final concentration was expressed in terms of normality and represented the critical coagulation concentration, that is, the concentration to

which the electrolyte had to be raised before coagulation of the sol would take place.

The concentration of electrolyte run in at H was generally about ten times as great as that used in preparing the sol-electrolyte mixtures. The choice of this latter concentration was determined by elimination, a series of ranging concentrations being tried out and that one selected which just failed to show any signs of coagulation on twenty-four hours' standing.

The rate of addition of electrolyte at H was found to be important. If added too rapidly the high concentration gradient developed between the inside and outside of the membrane promoted such rapid diffusion into the sol that localized coagulation took place near the inner surface. Slower rate of addition was better since localized coagulation was then almost entirely avoided. However, regardless of how much care was exercised and how slowly diffusion took place, there was always some localized coagulation near the walls of the bag. Furthermore, the critical

coagulation concentration was found to change with rate of addition of electrolyte, being greater with slow addition and less with rapid addition. When the rate of addition was kept constant, whether high, low or intermediate, results could be duplicated very closely.

The conductance-concentration curves from which the concentration of electrolyte at the "break" was read were drawn from values obtained

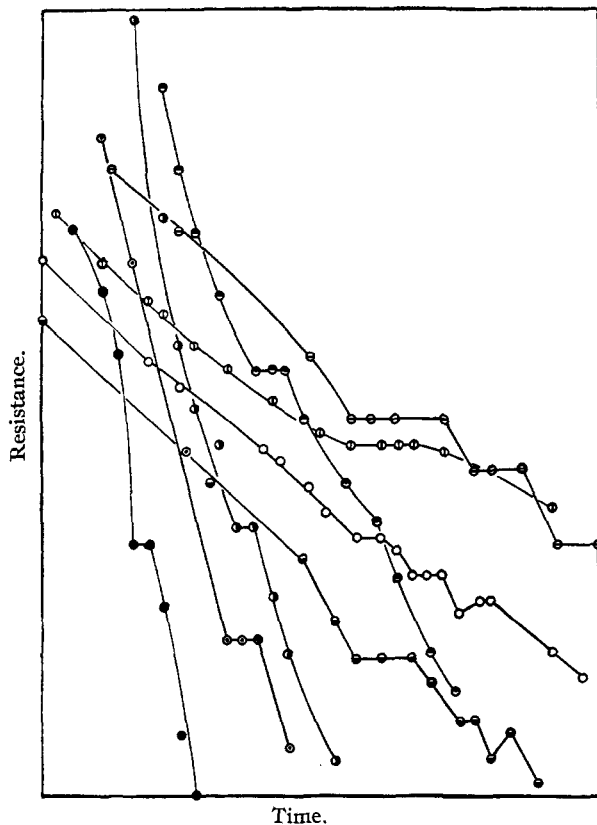


Fig. 2.

from determinations made in aqueous solutions of the pure salts. Possibly it may seem that these curves should have been drawn from values obtained using ferric oxide sol as the diluent rather than conductivity water, but since we are interested in the effective electrolyte concentration at the coagulation point and not after coagulation has taken place, it is evident that the ordinary conductance-concentration curve is the one that should be used.

Coagulation studies were made with various electrolytes using various dilutions of sol. The particular sol employed was free from detectable

amounts of chloride and was prepared in accordance with the method already described.⁸ The iron content of the undiluted sol was 2.90 g. per liter.

Parts 1, 2, 3, 4, 5 and 6 of Table I show representative data obtained with six different electrolytes. Fig. 2 represents typical time-resistance curves, the resistance of the sol in ohms being plotted against time in

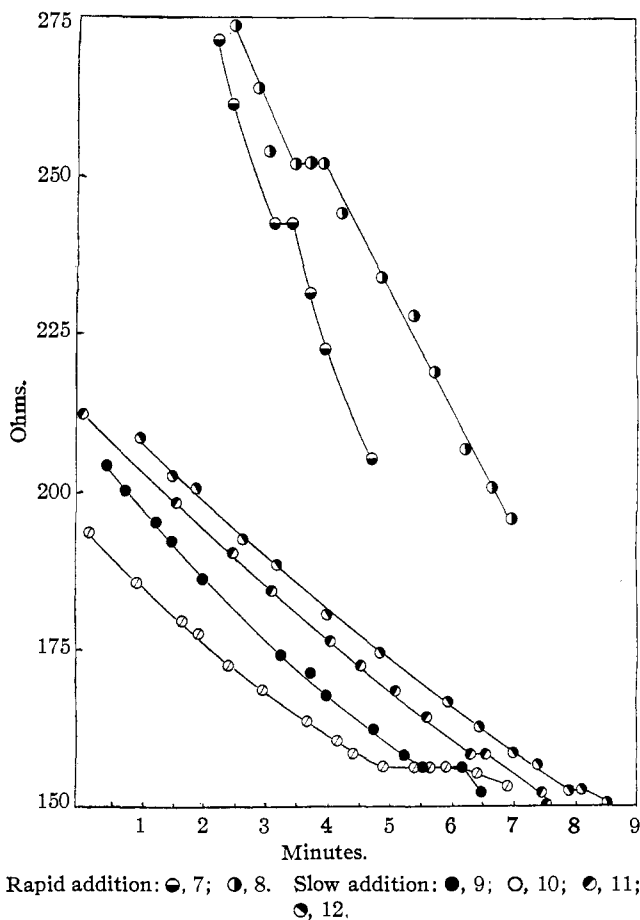


Fig. 3.—Coagulation of ferric oxide by potassium nitrate.

minutes.⁹ Parts 7 and 8, 9 and 10 and 11 and 12 of the table, with the corresponding curves (Fig. 3), show duplicate runs for potassium nitrate

⁸ Sorum, *THIS JOURNAL*, 50, 1263 (1928).

⁹ The conductance of the purified sol at 20° was found to be less than that of the conductivity water used in its preparation. This is in agreement with results described in a private communication from Dr. H. R. Kruyt, University of Utrecht, in whose laboratory purified sols with conductance lower than that of the water used in dialysis have been prepared.

TABLE I

REPRESENTATIVE DATA ON COAGULATION OF FERRIC OXIDE

Time	Resistance	Time	Resistance	Time	Resistance	Time	Resistance
1. By KNO ₃		4. By KBr		8. By KNO ₃		13:45	156
19:30	247	21:30	126	(Duplicate)		14:00	156
20:15	241	23:04	119	16:40	313	14:30	155
21:00	232	25:06	106	17:00	308	15:00	153
21:35	225	26:12	98	17:15	290	16:15	146
22:15	217	26:42	95	17:32	280	KNO ₃ 0.0154 N at coagulation point	
22:45	212	27:30	95	17:50	270	11. By KNO ₃	
23:26	205	28:07	95	18:07	260	12:00	161
23:45	200	28:45	95	18:30	258	12:21	160
24:15	196	29:10	94	18:45	258	12:36	159
24:45	190	29:30	95	18:55	258	13:06	157
25:15	182	29:42	95	19:15	250	13:24	156
25:50	177	30:00	97	19:50	240	13:45	154
26:15	171	5. By K ₂ CrO ₄		20:25	234	14:00	154
26:45	162	23:15	18400	20:45	225	14:21	152
27:15	156	29:30	16300	21:15	213	14:50	151
27:40	158	34:15	14800	21:40	207	15:00	150
28:00	157	45:15	11940	22:00	202	15:35	148
28:15	154	47:30	11440	KNO ₃ 0.01135 N at coagulation point		16:00	147
28:45	148	49:30	11000	9. By KNO ₃		KNO ₃ 0.01906 N at coagulation point	
29:05	145	51:00	10500	14:15	174	12. By KNO ₃	
2. By KCl		52:00	10300	15:00	167	(Duplicate)	
11:36	104	6. By K ₄ Fe(CN) ₆		15:15	165	13:48	162
12:45	91	77:30	18000	15:45	162	15:38	160
13:30	83	84:45	16800	16:12	158	16:00	158
14:00	78	90:15	15700	16:35	156	16:32	156
14:30	75	94:15	13500	17:10	156	17:06	154
14:45	74	95:45	12400	17:30	152	17:26	153
15:00	74	96:45	11500	18:15	147	17:55	151
15:30	74	98:15	10000	19:50	140	18:20	151
15:45	74	99:15	9000	KNO ₃ 0.0154 N at coagulation point		18:40	150
16:08	73	7. By KNO ₃		10. By KNO ₃		19:00	149
16:18	72	13:16	324	(Duplicate)		19:15	148
16:45	71	13:30	320	10:30	172	19:36	147
3. By K ₃ Fe(CN) ₆		14:00	292	10:50	170	KNO ₃ 0.01973 N at coagulation point	
149:00	13500	14:18	272	11:05	168		
149:24	13100	14:32	262	11:25	166		
150:15	12100	14:52	256	11:40	164		
151:00	11400	15:08	243	11:45	163		
151:30	11000	15:25	243	12:00	161		
152:00	10800	15:45	232	12:15	160		
152:36	10600	16:05	223	12:30	158		
153:06	10100	16:22	218	13:00	156		
153:45	9600	16:45	206	13:30	156		
154:12	9400	KNO ₃ 0.01186 N at coagulation point					

with a sample of sol whose iron content was 1.45 g. per liter. These latter curves emphasize the fact that the critical coagulation concentration changes with rate of addition of electrolyte, being greater with slow addition and less with rapid addition. They show, further, that results can be duplicated quite closely when the rate of addition is kept reasonably constant.

Discussion

Since there is no standard by which the accuracy or inaccuracy of any method of making coagulation studies can be correctly judged, one cannot say that the conductance-diffusion method as outlined is capable of either greater or less accuracy than the classical method used by past investigators. Certainly the conductance-diffusion method does not give quantitative values, but when a standardized method of procedure is used results can be duplicated very accurately. The personal factor is largely eliminated since the location of the critical coagulation point is determined by the change in the course of a time-resistance curve.

The "break" in the time-resistance curve is an experimental fact, as the graphs will show. It was assumed at the outset that this "break" was due to the adsorption of electrolyte during coagulation. Such may or may not be the case. Perhaps the voluminous coagulation at the critical point impairs free diffusion, thereby creating a break in the curve. The fact that the majority of "breaks" are "plateaus" lends support to this view. The irregularities in the course of the curve following the first "break" lend further support, uniform diffusion of the electrolyte being impossible in the presence of a large volume of coagulum. This interference with free diffusion may also be the cause of the successive "breaks" that are to be observed in some of the curves.

Further study of the conductance-diffusion method is now under way in this Laboratory.

Summary

1. A conductance-diffusion method for studying the coagulation of colloidal ferric oxide by electrolytes has been described.
2. Data are presented to show the application of the method.

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