

the values for $\gamma/v^{1/3}$ at 20° for carbon dioxide and nitrous oxide, we get 0.355 and 0.528, respectively. Now if we arrange these compounds in the Hildebrand series according to the decreasing order here indicated, we find that carbon dioxide is the first member, then nitrous oxide, and after a big gap we come to nickel carbonyl. According to the theory of solubility this can only mean that carbon dioxide and nitrous oxide in the liquid state are poor solvents for the common solutes and that of the two compounds we would expect nitrous oxide to be the better.

Summary

1. Surface tension measurements of liquid nitrous oxide have been made over a temperature range of 30 to -50°.

2. The equation of van der Waals for the change of surface tension with a change of temperature, when put in the form of $\gamma = 72.8 (1 - T/311.8)^{1.26}$ gave values for γ which were in fairly good agreement with those determined experimentally.

3. From the position of nitrous oxide in the internal pressure series of Hildebrand, it was predicted that it would be a poor solvent for the common solutes but that it was somewhat better than liquid carbon dioxide.

SALT LAKE CITY, UTAH

[CONTRIBUTION FROM THE LABORATORIES OF GENERAL CHEMISTRY, UNIVERSITY OF WISCONSIN]

THE COAGULATION OF FERRIC OXIDE SOLS BY GAS BUBBLES¹

BY HENRY M. STARK

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A ferric oxide sol of great purity has been prepared by C. H. Sorum² in this Laboratory. Due to its extremely low chloride content this sol has rather special properties. While making conductivity measurements on this sol Sorum observed that if streams of air bubbles were used as a stirring agent coagulation took place. Other gases were tried and the phenomenon seemed to be general. Since no mention had been made anywhere in the literature concerning the coagulation of colloid systems by gas bubbles, this phenomenon presented an interesting problem for investigation.

Coagulation of colloids such as ferric oxide is usually considered to be due either to destruction or neutralization of the charge on the particle by the

¹ An extract from a thesis presented in partial fulfillment of the requirements for the degree of Doctor of Philosophy, University of Wisconsin. The problem was suggested by Dr. C. H. Sorum and carried out under the supervision of Professor J. H. Walton. The author wishes to express his indebtedness to Mr. A. G. Jacques for many valuable suggestions.

² Sorum, *THIS JOURNAL*, 50, 1263 (1928).

oppositely charged ion of the coagulating electrolyte or to destruction by dehydration of the orientation of the molecules of the stabilizing layer of dispersion medium. Coagulation of a colloid by gas bubbles, because of the obvious difference in the nature of the process, cannot be attributed to these causes. Several possible factors might be considered as the direct cause of the coagulation, *viz.* (1) the neutralization of the charge on the ferric oxide particles by that on the gas bubbles, (2) the increased frequency and force of collision of the sol particles due to the agitation produced by the gas bubbles, or (3) adsorption of the colloid into the interface gas-liquid with consequent surface concentration. These factors will be discussed in detail after the experimental results have been described. The influence of such factors as the presence of impurities or of free electrons in the gas used for coagulation was reduced to as nearly a minimum as possible in the experimental part and will be given no further consideration.

Experimental

The ferric oxide sol used in this work was prepared and purified according to the method outlined by Sorum. A large volume of sol was prepared at one time and stored in 24-liter pyrex flasks. The sol used in most of this work contained 2.98 g. of iron per liter. Its flocculation value was between 5.5 and 6.0 millimoles of sodium chloride per liter, which is abnormally low for ferric oxide sols. The sol was so stable that neither its iron content nor its flocculation value changed appreciably on standing for one year. The average size of the particles of this sol as determined by the ultramicroscope-count method with a slit ultramicroscope was $59\mu\mu$.³

Cataphoresis Measurements.—A rather surprising property of this sol was that the charge on the particle, obtained from measurements of velocity of cataphoresis, was not abnormally low. Using the apparatus described by Burton⁴ a large number of measurements of velocity of cataphoresis were made. In order to obtain uniform values for the ascending and descending boundaries, it was necessary to produce what Mukherjee⁵ calls a "uniform ionic environment." This was done by adding to the liquid to be used above the ferric oxide layer, small quantities of an equimolecular mixture of ferric chloride and hydrochloric acid until the conductivity of the liquid and of the sol were equal. The results obtained from these cataphoresis measurements are compiled in Table I.

These values were obtained by direct substitution into the equation of Helmholtz for the relation between particle charge and velocity of cataphoresis, $V = 4\pi n v / DX$, where V is the so-called zeta-potential, D is the dielectric constant of the liquid, n its viscosity, X the applied voltage and

³ Ayres, *J. Phys. Chem.*, **34**, 875 (1930).

⁴ Burton, *Phil. Mag.*, [6] **11**, 425 (1906); [6] **11**, 44 (1906).

⁵ Mukherjee, *J. Ind. Chem. Soc.*, **5**, 593 (1928).

TABLE I
VELOCITY OF CATAPHORESIS OF FERRIC OXIDE PARTICLES

Cat. vel. in cm./hr.	Temp., °C.	Volts	Cm./sec./volt/cm.	Charge in millivolts
2.65	23.0	108	46.4×10^{-5}	61.6
2.72	23.4	106	48.5×10^{-5}	65.0
2.88	22.3	107	51.0×10^{-5}	69.0
2.68	23.1	107	47.4×10^{-5}	62.3
2.35	17.6	107	41.6×10^{-5}	62.0
Average				63.98

v the velocity of movement of the particles. If, in the above formula, Debye's⁶ correction for spherical particles is made, in which 6π is substituted for 4π , the values for zeta-potential would be 50% higher. The value of 64 millivolts agrees fairly well with values determined by other investigators; Whitney and Blake⁷ give 42 millivolts while Burton⁸ gives 73 millivolts. Neither of these investigators made any special effort to make a sol of great purity.

On the basis of the results given in Table I, it appears that the low chloride content of this sol does not materially reduce the charge of its particles and that therefore the very low flocculation value must be accounted for in some other way.

Method of Coagulation.—Inert gases, after being carefully purified, were emitted as streams of small bubbles at the bottom of 8-inch pyrex tubes each containing 40 cc. of the sol. The volume of gas passing through was measured by means of a calibrated flowmeter and the number of bubbles forming per minute was counted. From these two values the size of the bubble was determined. Various kinds of tubes were used to conduct the gas to the bottom of the tube of sol and to serve as an emission tip, but in the greater portion of the work described below capillary tubing with one millimeter bore was used. When the gas was passed through the sol at rates varying from 0.63 to 6.80 liters per hour, noticeable coagulation took place within two to four hours, but complete coagulation required twenty-four to thirty-six hours.

Samples were removed at arbitrarily chosen intervals and the degree of coagulation was determined by centrifuging the sample of sol to separate the coagulated from the uncoagulated portion. Centrifuging for ten minutes at 2300 r. p. m. served to throw the larger particles to the bottom to such an extent that the supernatant liquid was again clear. Longer centrifuging caused no further reduction in the iron content of the supernatant liquid. Also, the same centrifuge treatment of the original sol caused no settling.

⁶ Debye and Hückel, *Physik Z.*, **25**, 49 (1924).

⁷ Whitney and Blake, *THIS JOURNAL*, **26**, 1339 (1904).

⁸ Burton, "The Physical Properties of Colloidal Solutions," Longmans, Green and Co., London, 2d ed., 1921, p. 143.

The iron content of the supernatant liquid was determined by titrating the reduced iron against potassium dichromate using diphenylamine as an inside indicator. In the calculation of the degree to which coagulation had taken place the iron content of the supernatant liquid after centrifuging was assumed to be proportional to the uncoagulated portion of the sol. This method of determining degree of coagulation is certainly open to criticism because of the "broom" effect of the larger particles sweeping down with them some of the smaller uncoagulated particles. It is doubtful, moreover, if the centrifuging would cause settling of aggregates only partially coagulated and containing two or three original particles. The values when obtained under constant conditions, however, do serve as an arbitrary measure of the extent of coagulation in the experiments described below.

Results

Effects of Different Gases.—Five different gases were used and the coagulating power of each determined. The values given in Table II indicate that the nature of the gas was not a very important factor except in the case of carbon dioxide, in which case the hydrogen-ion concentration of

TABLE II
COAGULATING POWER OF VARIOUS GASES

Gas	Fe precipitated by 1 liter of gas, g.
Oxygen	453×10^{-7}
Nitrogen	273×10^{-7}
Air	317×10^{-7}
Hydrogen	428×10^{-7}
Carbon dioxide	Caused no coagulation

the sol was changed by the presence of the gas. The values are not the same for all gases but do not show the wide variations that are obtained for the coagulating action of electrolytes. That the reason for the failure of carbon dioxide to cause coagulation lay in its effect on the hydrogen-ion concentration was established by the following experiment. By means of a quinhydrone electrode apparatus for determination of hydrogen-ion concentrations, it was shown that the P_H of a sol saturated with carbon dioxide was about 4.3 at room temperature. Different members of a series of tubes of sol were brought to different P_H values by adding varying quantities of molar acetic acid and molar sodium acetate. The samples having a P_H value farther toward the alkaline side than 4.6 were very unstable toward air bubbling, while those with a P_H lower than 4.6 were not coagulated by air bubbles. The P_H of the sol alone was about 6.4. It appears, therefore, that carbon dioxide in dissolving in the water and lowering the P_H from about 6.4 to 4.3 causes the sol to pass from the region of instability toward gas bubbling to that of great stability.

As stated above, the gas was carefully purified before it passed into the tube of sol. However, in order to eliminate such factors as impurities in the gas or free electrons from consideration as possible causes of the coagulation, the following experiment was carried out. A given volume of gas was passed through a series of six tubes containing equal quantities of sol and arranged in such a manner that the gas emerging from the top of one tube was led to the bottom of the next. After the gas had passed at the rate of 0.29 liter per hour for thirteen hours, samples were withdrawn, centrifuged and the supernatant liquid analyzed. Table III shows that no loss in coagulating power of the gas took place as it passed through the

TABLE III
SHOWING CONSTANT COAGULATING POWER OF THE GAS

Tube	Fe precipitated, g.	Fe per liter after bubbling and centrifuging, g.
1	0.0060	1.82
2	.0056	1.87
3	.0056	1.87
4	.0063	1.81
5	.0052	1.86
6	.0061	1.83

series of six tubes. Since in passing through such a series of tubes impurities and free electrons would be largely absorbed in the first members of the series, we may infer from these data that these two factors are not responsible for the coagulating action of the gas.

Influence of Non-Electrolytes.—Janek and Jirgensons⁹ found that in low concentrations, alcohols decrease the stability of ferric oxide sols but when present in higher concentrations they increase the stability, as measured by the quantity of electrolyte required to cause complete precipitation in an arbitrarily chosen interval. Alcohols of high molecular weight had greater influence on stability than lower members of the alcohol series. In this investigation a study was made of the influence of various alcohols on the stability of ferric oxide sol toward gas bubbling. Ethyl and methyl alcohols had very little effect on the amount of colloid precipitated in a specified time, but higher members affected stability more markedly. The relationship between proportion of alcohol present and stability of the sol was similar to that found by Janek and Jirgensons. In Table IV are given the results obtained when small quantities of isopropyl, isobutyl and *n*-butyl alcohols were added to 40-cc. portions of sol just previous to coagulation by bubbling gas through them. Equal volumes of gas were passed through the different tubes. The data indicate that very small proportions of alcohol cause sensitization but that this sensitizing action decreases as more alcohol is added.

⁹ Janek and Jirgensons, *Kolloid-Z.*, 41, 40 (1927).

TABLE IV

EFFECT OF ALCOHOLS ON STABILITY OF FERRIC OXIDE SOL TOWARD GAS BUBBLING

Isopropyl alcohol		Isobutyl alcohol		<i>n</i> -Butyl alcohol	
Volume per cent. of alcohol added	Iron precipitated, %	Volume per cent. of alcohol added	Iron precipitated, %	Volume per cent. of alcohol added	Iron precipitated, %
0.0	10.0	0.0	3.4	0.0	30.4
0.2	30.0	0.2	25.8	0.2	49.4
1.0	28.1	0.4	28.0	0.4	57.3
4.0	17.0	1.0	17.0	1.0	54.0
		2.0	9.0	2.0	47.2
		4.0	5.5	4.0	37.0

Influence of Electrolytes on Coagulation by Gas Bubbles.—Investigations carried out by Sorum and Judd¹⁰ in this Laboratory have shown that the specially purified sol used in this work may be coagulated by a lower concentration of electrolyte than ordinary ferric oxide sols. In this investigation it has been shown that coagulation of this ferric oxide sol takes place in still lower concentrations of electrolyte when streams of gas bubbles are passed through the sol. Determinations were made of the minimum concentrations in millimoles per liter of various electrolytes required to cause complete coagulation of the sol during twenty hours of gas bubbling. The gas was passed through the tubes of sol at the rate of 0.29 liter per minute. Complete coagulation was assumed to have taken place when after twenty hours' bubbling and ten minutes' centrifuging there remained less than 1% of the original iron of the sol in the supernatant liquid. In Table V this minimum concentration is called the "coagulation value."

TABLE V

COAGULATION VALUES FOR VARIOUS ELECTROLYTES

Electrolyte	Floculation value (Judd)		Electrolyte	Floculation value (Judd)	
	Coagulation value	Floculation value (Judd)		Coagulation value	Floculation value (Judd)
NaCl	2.0	3.8	Na ₂ SO ₄	0.10	0.46
KCl	4.0	13.0	K ₂ SO ₄	.30	.59
BaCl ₂	10.0	...	K ₂ Cr ₂ O ₇	.375	.399
MgCl ₂	5.0	...	MgSO ₄	.10	...
Th(NO ₃) ₄	Above 300	...	Na ₃ PO ₄	.025	...
ThCl ₄	..	395.0	K ₃ PO ₄	.050	...
AgNO ₃	10.0	47.0	K ₃ Fe(CN) ₆	.05	.084
NaNO ₃	2.5	56.0	K ₄ Fe(CN) ₆	.025	.033
Al(NO ₃) ₃	62.5	182.0			

The values given in the third column are the floculation values, *i. e.*, the concentrations of electrolyte required to cause complete coagulation in two hours without agitation, obtained by Judd in an investigation of this sol. It is obvious that the concentrations of electrolyte required to cause complete coagulation were uniformly lower when the sol was stirred with

¹⁰ Judd and Sorum, THIS JOURNAL, 52, 2598 (1930).

gas bubbles than when it was at rest. The amount of gas bubbling applied in this experiment was sufficient to coagulate approximately 25% of the particles of the sol in the absence of electrolyte. The values given in the second column represent the additive effects of gas bubbling and addition of electrolyte, which accounts for their being uniformly lower than the flocculation values given in the third column.

Coagulation Velocity.—Smoluchowski¹¹ developed the following equation to represent the decrease in the number of particles of a sol during the process of coagulation

$$n = \frac{n_0}{1 + 4\pi D r n_0 t}$$

where n is the total number of particles present at any time t , n_0 is the number originally present, D is the diffusion constant and r is the radius of the sphere of attraction of the particles. For the number of *single* particles present after a time t , the expression becomes

$$n_1 = \frac{n_0}{(1 + 4\pi D r n_0 t)^2}$$

or setting $4\pi D r = k$ the expression becomes

$$n_1 = \frac{n_0}{(1 + k n_0 t)^2} \text{ or } k = \frac{1}{t} \left(\sqrt{\frac{n_0}{n_1}} - 1 \right)$$

Smoluchowski is of the opinion that the laws of rapid coagulation should also apply to the phenomenon of slow coagulation except that there should be inserted a factor in the above expression, representing the proportion of the collisions between particles which are fruitful in producing coagulation. Freundlich and Basu¹² found that the decrease in the number of particles of copper oxide sol could be calculated from the Smoluchowski equation.

Coagulation velocity curves have been obtained for this ferric oxide sol in the presence of various electrolytes at different concentrations. The curves obtained by using potassium sulfate in varying concentrations are shown in Fig. 1. Curves for other electrolytes were similar to these except that ions of higher valence caused more rapid coagulation as is shown by the results recorded in Table V. Values of k were obtained by using the Smoluchowski equation. The iron content of the supernatant liquid at time t was assumed to be proportional to the number of single particles n_0 . These values of k for arbitrarily chosen intervals of time are given in Table VI.

It will be seen from this table that for low concentrations of electrolyte the coagulation velocity increases slowly with increasing electrolyte concentration, but for higher concentrations the velocity increases rapidly. This is shown graphically in Fig. 2, where the \log_e of $(k \times 100)$ is plotted against the concentration of electrolyte. It is evident from this figure that

¹¹ Smoluchowski, *Z. physik. Chem.*, **92**, 129 (1917).

¹² Freundlich and Basu, *ibid.*, **115**, 203 (1926).

TABLE VI
COAGULATION VELOCITY CONSTANTS FOR SOL CONTAINING K_2SO_4

Hours of agitation	Values of k at K_2SO_4 concentrations indicated concentrations given in millimols per liter					
	0.0	0.02	0.04	0.06	0.08	0.10
5	0.0126	0.014	0.014	0.018	0.045	0.29
10	.012	.014	.015	.018	.055	.39
15	.012	.014	.015	.019	.070	
20	.013	.014	.015	.020	.090	
25	.013	.015	.016	.022		
30	.013	.015	.017	.024		
40	.015	.017	.020	.031		

for lower concentrations of electrolyte a linear relation exists between the concentration of electrolyte and the logarithm of the coagulation velocity

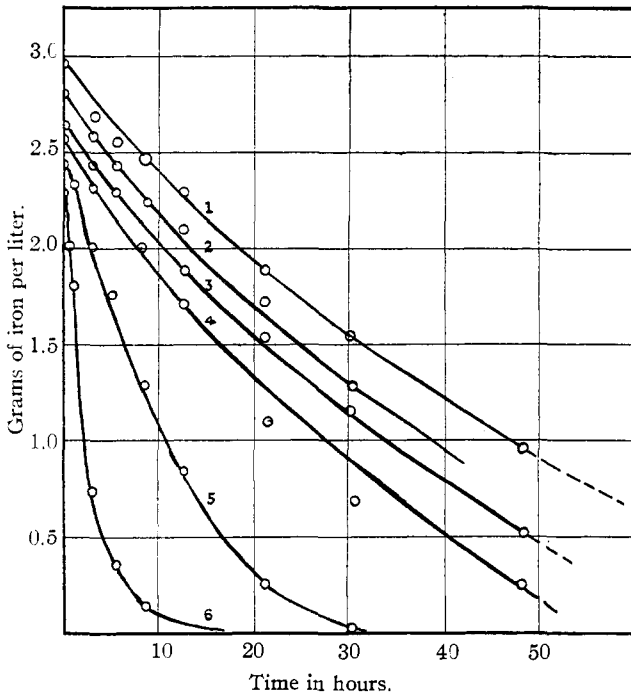


Fig. 1.—Influence of potassium sulfate on the velocity of coagulation of ferric oxide sols by gas bubbles. Coagulation velocity curves for: 1, sol alone; 2, sol containing 0.02 mmol. per liter; 3, 0.04; 4, 0.06; 5, 0.08; 6, 0.10.

constant. This relation was expressed by Schalek and Szegvari¹³ in the form of the equation

$$\log_e k = nc - 1$$

where n and 1 are new constants. Freundlich and Basu¹² found that this

¹³ Schalek and Szegvari, *Kolloid-Z.*, **33**, 326 (1923).

equation was valid for the coagulation of the copper oxide sol agitated by a mechanical stirrer.

In an effort to gain some knowledge concerning the mechanism of this coagulation phenomenon a study was made of the influence of such factors

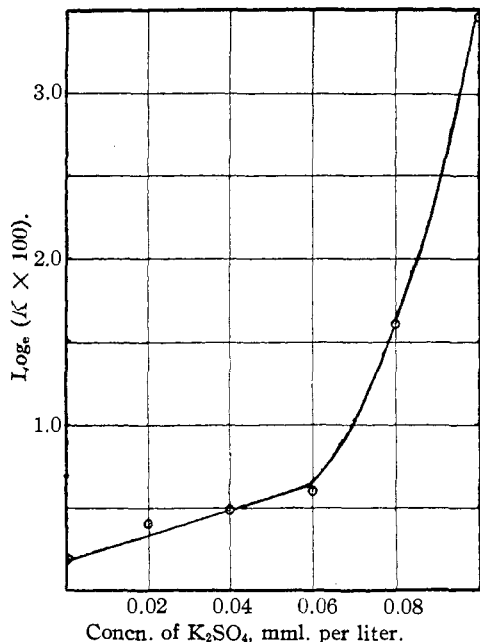


Fig. 2.—Relation between concentration of electrolyte and coagulation velocity constant.

as height of column, rate of bubbling gas through the sol, size of bubble and others. The influence of the height of the column through which the gas was bubbled is shown in Table VII.

A constant amount of gas was passed through each of the four tubes. It appears from these data that the height of the column influences the amount of coagulation taking place only to the extent that it affects the volume of liquid through which the gas passes. The total amount of sol coagulated in the above series was roughly proportional to the volume of sol present.

Rate of Flow of Gas.—The influence of the rate at which the bubbles of gas were passed through the tube of sol is shown in Table VIII.

These data indicate that up to a certain point increasing the rate of flow of the gas increases the rate at which the sol is coagulated, but that beyond

TABLE VII
INFLUENCE OF HEIGHT OF COLUMN ON AMOUNT OF COAGULATION

Sol, cc.	Height of column, cm.	Fe per liter after agitation by gas bubbles, g.
140	45	2.25
100	30	2.08
60	15	0.95
20	5	0.51

TABLE VIII
INFLUENCE OF THE RATE OF FLOW OF THE GAS ON ITS COAGULATING ACTION

Rate of flow in liters per hour	Fe precipitated by 1 liter of gas, g.	Rate of flow in liters per hour	Fe precipitated by 1 liter of gas, g.
0.63	0.052	10.63	0.018
1.06	.060	21.2	.010
2.51	.104	31.8	.009
6.80	.035		

this point a further increase in rate of flow causes a decrease in the coagulating power of the gas.

Size of Bubble.—Variations in the size of the bubble such as were produced by the use of tips ranging from 1 to 17 millimeters in diameter caused no appreciable difference in the rate of coagulation.

Mechanical Agitation.—The sol was coagulated by any form of mechanical agitation. Thus, shaking vigorously, either in the presence of air or in a tube from which the air above the sol had been removed, caused coagulation to take place at a rate approximately the same as with gas bubbles. Stirring with a glass stirrer in the absence of carbon dioxide caused coagulation. The same forms of coagulation velocity curves were obtained for stirring in this manner as when the bubbling method was used.

Discussion of Results.—The coagulation phenomenon described in the preceding pages might appear to be caused by one or more factors, such as those mentioned in the introductory paragraphs of this article. The suggested causes of the coagulation mentioned are discussed below in the light of the experimental evidence presented.

(1) **Neutralization of the Charge on the Colloid by the Charge on the Bubble.**—The work of a large number of investigators supports the view that bubbles of inert gases suspended in water are negatively charged. Lenard¹⁴ found that at the bottom of waterfalls the water or mist is positively charged and the air through which it has fallen is negatively charged. Thomson, McLean and Galt¹⁵ and later Coehn and Mozer¹⁶ by means of the quadrant electrometer, measured the charge produced by bubbles of inert gases as they rose through water and solutions of electrolytes. McTaggart¹⁷ measured the charge on gas bubbles while they were immersed in a liquid by observing the rate of cataphoresis of small bubbles in water and solutions of electrolytes and non-electrolytes. He showed that all the inert gases which came under his investigation carried in water a negative charge, but that the magnitude and even the sign of this charge might be changed by the addition of small quantities of electrolytes. Also, the charge could be lowered by the addition of small quantities of alcohols and other non-electrolytes which lower the surface tension of water. Undoubtedly the electric charges encountered in these two instances are not of identical origin, and any charge gained by the bubbles in the experiments carried out in this investigation must be attributed to the same cause as in the case of McTaggart's work. The results obtained by adding small quantities of alcohols to the sol previous to coagulation, which are summarized in Table IV, indicate that the coagulation phenomenon here observed is not due

¹⁴ Lenard, *Ann. Physik*, [3] **46**, 584 (1892).

¹⁵ Thomson, McLean and Galt, *Proc. Roy. Soc. (London)*, **57**, 335 (1895).

¹⁶ Coehn and Mozer, *Ann. Physik*, [4] **43**, 1048 (1914).

¹⁷ McTaggart, *Phil. Mag.*, [6] **27**, 297 (1913); [6] **28**, 367 (1914); **44**, 386 (1922).

primarily to a neutralization of the charge on the colloid by that on the gas bubble; for as McTaggart has shown, the addition of small proportions of alcohols to a liquid continually lowers the negative charge on a bubble of inert gas suspended in the liquid, which would decrease its power to coagulate a positively charged colloid. In this investigation, however, the addition of small amounts of alcohols actually caused greater amount of coagulation. The influence of the charge on the bubble probably is overshadowed by some other stronger factor.

(2) **Coagulation by mechanical agitation produced by gas bubbles**, in spite of its apparent feasibility, is probably relatively unimportant. The bubbles used in this work were relatively large (average, 0.1 cc.) and moved through the sol rather sluggishly. Under these conditions definite flow portions would be set up in which both water and sol particles move in a direction governed by the resultant of forces acting on the various discrete portions produced by the haphazard agitation of the gas bubbles. In order for the agitation to produce the increased frequency and force of collisions necessary to cause coagulation, it would be necessary for the particles of one flow portion to meet those of another flow portion going in an opposite direction; but the only place where two oppositely directed flow portions can meet is at the edges where the particles are moving at a very slow rate in comparison with the rate nearer the center of the flow portion. Collisions between particles in the same flow portion are unlikely because all are moving in the same direction.

The results obtained in the investigation substantiate the statements made above to the effect that mechanical agitation is not the chief factor in the coagulation phenomenon by gas bubbles. Thus variation in two factors which influence the intensity of agitation, *viz.*, the height of the column and the rate of bubbling, failed to give proportionate variations in coagulation. In Table VII it is shown that the iron content of the supernatant liquid increased with the height of the column. It may appear from this that coagulation increased with decreasing height of column and, therefore, with increasing agitation, but when account is taken of the fact that the volume of sol also increased with increasing height of column, it is apparent that approximately the same total quantity of sol was coagulated in each case. Again in Table VII the amount of coagulation decreases with increase in the rate of bubbling over most of the range. If coagulation were due primarily to mechanical agitation, increase in rate of bubbling would give rise to increased coagulation.

(3) **Adsorption of the Colloid into the Interface Gas-Liquid with Consequent Concentration.**—It is well known from the work of McTaggart that bubbles of inert gases suspended in solutions of electrolytes adsorb on their surfaces the ions present in solution. In like manner colloids are adsorbed from dilute sols, such as those of thorium hydroxide. McTaggart

obtained experimental evidence of a relation between curvature of the surface of the bubble and its adsorptive power. Kenrick¹⁸ long ago worked out the potential difference relations for the interface gas solution and found that adsorption of anions was the cause of the potential difference between the two phases. He also showed that the potential difference was independent of the nature of the gas. Numerous other references might be cited in support of the view that ions and colloid particles are adsorbed on the surface of gas bubbles.

The phenomenon described above of the coagulation of a positively charged sol by gas bubbles might be attributed to adsorption at a gas-liquid interface as described above. We might picture the coagulation process as taking place in the following manner. The bubble in rising sluggishly through the sol adsorbs particles of colloid, carrying them to the surface of the liquid where the bubble collapses. The concentration of colloid particles in the interface gas-liquid at the surface of the bubbles is greater than in the remainder of the liquid and when these bubbles burst there is formed a very thin layer of liquid containing a much higher concentration of colloid particles. In these local areas at the upper surface of the sol, the concentration exceeds that at which the sol is stable and coagulation takes place by ordinary kinetic methods.

The data obtained in this investigation are in substantial agreement with the explanation of coagulation outlined above. Thus according to this view we would expect all inert gases to have approximately the same coagulating power, for the work of McTaggart and of Kenrick cited above and of Frumkin¹⁹ indicates that adsorption at the surface of gas bubbles and hence the charge on the bubble are independent of the nature of the gas. The values given in Table II for the relative effects of different gases in coagulating the sol indicate that no wide differences exist for the inert gases. Gases exerting a chemical action come under a different category and undoubtedly show wide differences in their action toward this sol such as are shown in Table V to exist for electrolytes. The fact that the gas loses none of its coagulating power in passing through a series of tubes shown by the data in Table III would be expected as a result of the proposed mechanism of coagulation.

The effect of alcohols on the coagulation of ferric oxide by gas bubbles is similar to their effect on coagulation by electrolytes, *i. e.*, small quantities cause increased coagulation while larger amounts cause stabilization. Explanations offered for this anomalous effect of alcohols are not wholly concordant. In case of coagulation by gas bubbles the first small addition increases coagulation probably by increasing the size of the bubble and hence the adsorbing surface due to the decrease in surface tension of the liquid

¹⁸ Kenrick, *Z. physik. Chem.*, **19**, 625 (1896).

¹⁹ Frumkin, *ibid.*, **109**, 34 (1924).

caused by the addition of the non-electrolyte. Further addition of alcohol while lowering the surface tension still more decreases the specific adsorption of the liquid-gas interface and in this manner decreases the amount of colloid carried to the surface to become coagulated.

In case of coagulation by gas bubbles in presence of small quantities of electrolytes, the colloid is sensitized by the electrolyte and coagulation takes place in the same way as outlined above. We also should expect coagulation to take place at a lower electrolyte concentration when gas bubbles are passed through than when they are not. The coagulation values given in Table V indicate the additive effect of electrolyte and coagulation by adsorption on the gas bubbles.

The data obtained in studies on velocity of coagulation support the view that the relation of Smoluchowski, which was originally developed for a sol at the isoelectric point, holds also for this sol which still has considerable charge on its particles. Freundlich and Basu¹² have shown that copper oxide sol when agitated by a glass stirrer coagulates in such a way as to follow the Smoluchowski equation. The velocity constants given in Table VI for coagulation of ferric oxide in presence of small quantities of potassium sulfate are undoubtedly larger than would have been obtained with no gas bubbling and with the same electrolyte concentration since the coagulation process is the combined effect, first, of lowering of zeta-potential by the electrolyte and thus increasing the frequency of collision of the particles and, second, of adsorption of the particles in the gas-liquid interface and subsequent concentration of the sol particles at the surface of the liquid.

Mechanical agitation such as shaking and stirring causes the formation of large areas of gas-liquid interface on which temporary adsorption and concentration of particles beyond the limits of stability take place and in this way bring about coagulation.

Summary

1. Experiments have been carried out on the coagulation of ferric oxide sol by the following gases: oxygen, nitrogen, hydrogen, air and carbon dioxide.

2. The influence of various electrolytes and non-electrolytes on the coagulation by air bubbles has been determined.

3. Coagulation velocity studies have been made and the Smoluchowski equation for rapid coagulation found to hold. Also, the relation of Schalek and Szegvari was found to hold over a limited range of concentration of electrolyte.

4. An explanation concerning the mechanism of the coagulation process has been offered and discussed in the light of the data obtained.