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ADSORPTION OF IONS AND THE
PHYSICAL CHARACTER OF PRECIPITATES

A Thesis

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by

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ADSORPTION OF IONS AND THE
PHYSICAL CHARACTER OF PRECIPITATES.

The first systematic investigation of the form in which substances precipitate from solution was made by von Weimarn*. He calls attention to a number of different factors on which precipitation depends: the solubility of the substance, the latent heat of precipitation, the concentration at which the precipitation takes place, the normal pressure at the surface of the solvent and the molecular weights of the solvent and solute. He points out the impossibility of taking all these factors into account and simplifies the problem by considering but two of the factors: the solubility of the precipitating substances and the concentration at which the precipitation begins. The process of condensation (precipitation) is considered as taking place in two stages: the first stage, in which the molecules condense to invisible or ultramicroscopic crystals; and the second, which is concerned with the growth of particles as the result of diffusion. The velocity of the condensation at the important first moment of the first stage of the process is formulated thus:

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*Kolloid.-Z., 2, 199, 230, 275, 301, 326; Supplement 2, LII (1907); 3, 89, 282 (1908); 4, 27 (1909); "Gründzüge der Dispersoidchemie" (1911); "Zur Lehre von den Zuständen der Materie" (1914).

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

in which W is the initial rate of precipitation, K a constant, Q the total concentration of the substance that is to precipitate, L the solubility of coarse crystals of the substance, $Q - L = P$ the amount of supersaturation. The ratio $\frac{P}{L} = U$ is the percentage supersaturation at the instant precipitation begins. To take care of other factors which may enter into the process, von Weimarn introduces a "variable multiplier", J , and the equation becomes:

$$W = KJ \frac{Q - L}{L} \quad (2)$$

The velocity of the second stage of the process is given by the Nernst-Noyes equation:

$$V = \frac{D}{S} \cdot O \cdot (C - l) \quad (3)$$

where D is the diffusion coefficient, S the thickness of the adherent film, O the surface, C the concentration of the surrounding solution and l the solubility of the disperse phase for a given degree of dispersity. $C - l$ may be termed the absolute supersaturation.

By the aid of these equations, several facts are interpreted. It will be seen that the velocity of precipitation depends not alone upon the supersaturation P , but upon the percentage supersaturation $\frac{P}{L}$. Thus, with a given value of P (say a few grams per 100 cubic centimeters), a very soluble substance, such as sodium chloride, will deposit nothing at first and finally a few crystals may form; but with the same

value of P an almost insoluble substance, such as alumina or silver chloride, will give an immediate gelatinous or curdy precipitate. The difference is, that the velocity of the precipitation is much smaller in the first case than in the second. On the other hand, if sodium chloride is formed by the interaction of sodium ethylate or sodium thiocyanate and hydrochloric acid in a mixture of ether and amyl alcohol, in which sodium chloride is practically insoluble, the precipitate is curdy like that of silver chloride.

While the value of P is not in itself of primary importance in determining the form of the precipitate, it is not without influence, since quite different results are obtained, depending on whether a given value of U is obtained by a large P or a small L . In the first case a large amount of disperse phase must be produced, and in the second very little. Hence, if U is large, the former will, in general, give a gelatinous precipitate or jelly, and the latter a larger number of highly dispersed particles — a sol.

Von Weimarn recognized that the velocity W of the first stage of precipitation cannot be measured in actual practice, and that, in many cases especially interesting in the synthesis of colloid systems, the velocity U of the growth of the particles cannot be determined. In due time, therefore, he introduced a specific coefficient called the "precipitate form coefficient" or "dispersity coefficient" N which is given by the expression:

$$N = \frac{P}{L} \cdot K_{ab} \cdot K_{cd} \cdot K_{bd} \cdot K_{ac} \cdot Z \quad (4)$$

in which $\frac{P}{L}$ is the percentage supersaturation as in the velocity equation, Z the viscosity, and K_{ab} , K_{cd} , etc. represent the "physical and chemical association" of the substances AB , CD , etc. which enter into the reaction AB (in solution) + CD (in solution) = AC (precipitate) + BD (in solution). The significance of "physical association" is known but it is not clear what von Weimarn means by "chemical association". This makes no difference, however, for the several factors are neglected and N is set down equal to $\frac{P}{L}$, that is,

$$N = \frac{P}{L} \quad (5)$$

or better,

$$N = J \frac{P}{L} \quad (6)$$

in which J has the same significance as in equation (2).

Now if N is taken as approximately equal to $\frac{P}{L}$, as von Weimarn first assumed, then for the different substances x , y and z ,

$$N_x = \frac{P_x}{L_x}; \quad N_y = \frac{P_y}{L_y}; \quad \text{and} \quad N_z = \frac{P_z}{L_z}.$$

If the character of the precipitate is to be the same in each case, irrespective of the chemical nature of the salt; in other words, if

$$N_x = N_y = N_z$$

then

$$\frac{P_x}{L_x} = \frac{P_y}{L_y} = \frac{P_z}{L_z}. \quad (7).$$

This is the simplest expression for von Weimarn's Law of Corresponding States for the Precipitation Process, which says that under corresponding conditions of precipitation the mean magnitude (expressed in gram molecules) of the crystals of substances capable of precipitation will be the same. In the form given in equation (7) the so-called law can hardly be regarded as a first approximation, even with substances that are related chemically. This is illustrated by the observations of Buchner and Kalf^{*} recorded in Table I. L is the solubility of the several salts and N is calculated from the concentrations of the solutions employed, using the expression $N = P/L$.

TABLE I. -- PHYSICAL STATE OF PRECIPITATES.

Salt	L	N	State of Precipitate
CaF_2	4×10^{-4}	3,400	Jelly
BaF_2	18×10^{-3}	75	Jelly
CaSO_4	3×10^{-2}	140	Jelly
BaSO_4	2×10^{-5}	100,000	Jelly
AgCl	1×10^{-5}	700,000	Colloidal, unstable
AgBr	$.7 \times 10^{-7}$	8,000,000	Colloidal, unstable
AgI	1.5×10^{-8}	30,000,000	Jelly, unstable
PbI_2	4.8×10^{-3}	360	Colloidal

^{*}Rec. trav. chim., 39, 135 (1920).

Considering the first four salts, it will be seen that the nature of the precipitate is the same although the value of N varies between 75 and 100,000. Von Weimarn obtained well defined crystals of barium sulphate at values of N varying between 50 and 20,000. The law of corresponding states in the simplest form would require that, under the conditions recorded in the table, CaSO_4 , CaF_2 and BaF_2 should give crystalline precipitates instead of transparent jellies. Considering next the silver halides: If von Weimarn's law in its simplest form held, these salts should give jellies more stable than BaSO_4 under the conditions used; but, instead, they form colloidal solutions which later come down in flocks of an entirely different physical character from the barium sulphate jelly. Finally, the small value of N for PbI_2 would lead one to expect the formation of a definitely crystalline precipitate under the conditions employed. Actually, a jelly results.

Von Weimarn's* explanation of these discrepancies is, of course, that the law of corresponding states for the precipitation process is not the simple expression

$$\frac{P_X}{L_X} = \frac{P_Y}{L_Y} = \frac{P_Z}{L_Z} \dots$$

but

$$J_X \cdot \frac{P_X}{L_X} = J_Y \cdot \frac{P_Y}{L_Y} = J_Z \cdot \frac{P_Z}{L_Z} \dots$$

*Kolloidchem. Beihefte, 18, 48 (1923).

in which J_x , J_y , and J_z are specific variable multipliers, the value for any substance being "the product of all other factors (in addition to P/L) which influence the crystallization process. These values must be expressed by abstract numbers such that the values of P/L are equivalent."* In other words, von Weimarn's equation for his so-called law becomes quantitative and generally applicable by putting in "variable multipliers", handy wastebaskets, as it were, into which are thrown all the variable factors known or unknown which have not been evaluated.

While facts may be expressed fairly accurately by means of such flexible formulas, it is doubtful whether anything is gained scientifically by regarding formulations of this kind as quantitative representations of natural laws. Von Weimarn evidently thinks so, but his opinion is not shared generally. Thus, Bancroft** prefers to discard the formulas altogether and state the whole thing from a different point of view. He points out that the mean size of the crystals is determined by the total amount of material crystallizing and the number of nuclei. The really important thing, therefore, is the number of nuclei which are formed under any given conditions. It is contended, very properly, that factors other than percentage of supersaturation influence the number of nuclei formed. Thus, the specific nature of the substance, stirring and temperature have a profound

 *VON WEIMARN: Kolloidchem. Beihefte, 18, 48 (1923).
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**Jour. Phys. Chem., 24, 100 (1920).
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effect on nucleus formation, and adsorption exerts a marked influence on the growth of particles*. Freundlich** likewise does not believe that the separation of a solid phase is generally and uniformly regulated by its solubility and the supersaturation prevailing: "What is known concerning the extraordinary sensitiveness to foreign substances of the velocities of formation of nuclei and crystallization makes it a priori improbable, and experience has not confirmed this theory."

The effect of adsorption on the physical character of precipitates is considered in the following way by von Weimarn***;

At constant $U = P/L$, foreign molecules have the same effect as greatly increasing U . The reason is that, during the growth of grains, the foreign matter keeps the reacting solutions away, so that not far away from a given grain a local supersaturation results in the formation of a new grain. This would not happen in the absence of foreign molecules.

As would be expected, von Weimarn**** includes the variable adsorption factor in his "variable multiplier": "According to my theory, the adsorption factor at constant P/L acts in the same way as simply increasing P/L ; that is, the precipitate is more highly dispersed. Now I have included the

*WEISER: Jour. Phys. Chem., 21, 514 (1917).

** "Kapillarchemie", 651 (1922).

*** "Grundsätze der Dispersoidchemie", 97 (1911).

**** Kolloidchem. Beihefte, 16, 68 (1923)

adsorption factor in the variable J of the precipitate form coefficient, $U = J \cdot (P/L)$. It follows, therefore, that J is increased by adsorption. If, however, P/L remains constant it follows that the value of N must likewise increase. A larger value of N corresponds to a higher degree of dispersion of the precipitate."

This dogmatic way of disposing of the effect of adsorption on the physical character of the precipitate is not helpful. Von Weimarn's view is that the foreign substance always forms a protective film around the particles and thereby prevents their growth. This is apparently what takes place when precipitation occurs in the presence of a strongly adsorbed protective colloid such as gelatine. However, the effect on the physical character of a precipitate, produced by the adsorption of the solvent and of ions of varying charge and degree of hydration, cannot be disposed of so simply as von Weimarn would lead one to expect. Any substance should form a gel provided a suitable amount of highly dispersed substance is precipitated, and provided the particles adsorb the dispersion medium very strongly. The amount of the dispersed phase that must be present in a given volume to form a jelly will depend on the size and orientation of the particles and the extent to which they adsorb the dispersing liquid, water in most cases. Now it is too well known to need comment that some substances adsorb water more strongly (that is, are much more hydrous) than others, so that at the same degree of dispersity some substances will form gels

while others will not. This specific capacity of the particles to adsorb the solvent is altogether independent of their size and the rate of precipitation. In many instances, this is of far more importance than the rate of precipitation in determining the form of the precipitate. A notable example is the case of manganese arsenate, which can be made to form a stiff jelly by mixing very dilute solutions of potassium arsenate and manganese sulphate. The value of L for the precipitate is so large that precipitation is slow and quantitative precipitation is impossible. $P/L = N$ is very small, and yet a typical transparent jelly results¹. Von Weimarn would take care of the variation in the adsorption of the solvent by the particles by putting it into the J of the expression $N = J \cdot (P/L)$, and so make the calculated values of N fit the facts. There is, of course, no objection to doing this, but it is difficult to see what is gained by such a procedure.

The peptizing action of adsorbed ions may have a marked effect on the physical character of a precipitate. Thus, the analyst knows that barium sulphate, formed in ordinary analytical procedures, comes down very much finer when precipitated with barium chloride in excess than with sulphuric acid in excess. This happens notwithstanding the fact that barium ion and sulphate ion are adsorbed about equally, and yield positive and negative sols, respectively, when the precipitation is carried out under suitable conditions. Finer crystals are obtained from potassium sulphate solution than from sulphuric acid. The explanation of this behavior is as follows: In addition to

adsorbing its own ions strongly, barium sulphate adsorbs hydrogen ion more strongly than most cations. When sulphuric acid is treated with barium chloride in excess, the precipitate tends to come down in a finely divided state because of the peptizing action of the relatively strongly adsorbed barium and hydrogen ions. It would also come down in a finely divided state from a solution containing sulphuric acid in excess were it not that the strongly adsorbed hydrogen ion neutralizes the peptizing action of the sulphate ion. From potassium sulphate solution it comes down finely divided since potassium ion is not strongly adsorbed.*

That the effect of foreign material on the physical character of a precipitate may not be due chiefly to increasing the number of points of crystallization is well illustrated in the case of sulphur, which is thrown down from the sol in a variety of conditions in the presence of different electrolytes. Thus, Stingl and Morawski** showed that potassium and barium salts precipitate sulphur in a plastic form, while calcium, magnesium and sodium salts give flocculent sulphur. Oden*** states that sulphur is thrown down from the sol as a hard precipitate with potassium salts, fine grained with copper sulphate, plastic with barium salts, fluid with hydrochloric acid and slimy with other salts. Since the physical character of sulphur

*WEISER: Jour. Phys. Chem., 21, 314 (1917).

**J. prakt. Chem., (2) 20, 76 (1879).

***"Der kolloide Schwefel" 154, 157 (1912).

thrown down in the presence of different electrolytes shows so marked variations, it seemed to furnish a satisfactory substance for studying the general effect which the adsorption of ions may have on the physical character of precipitates.

EXPERIMENTAL.

Formation of Sulphur Sol. Colloidal solutions of sulphur are formed by the interaction of solutions of hydrogen sulphide¹, or alkali sulphides² and sulphurous acid; and by the decomposition of thiosulphate with hydrochloric acid³ or sulphuric acid⁴. A sol is formed also by pouring an alcoholic solution of sulphur into water⁵. In the latter case the dispersion is relatively unstable, the particles agglomerating and settling out in a short time.

The sols used in this investigation were prepared by an adaptation of the method used by Sobrero and Selmi¹, namely, by passing hydrogen sulphide and sulphur dioxide simultaneously

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(1) BERTHOLLET: Ann. chim., 25, 233 (1798); SOBRERO and SELMI: Ann. chim. phys., 28, 210 (1850).

(2) WACKENROEDER.

(3) ENGEL: Compt. rend., 112, 866 (1891); RAFFO: Kolloid-Z., 2, 358 (1908).

(4) ODEN: Z. physik. Chem., 80, 709 (1912); "Der Kolloide Schwefel" (1912); Novo Acta Upsala, 3, No. 4 (1913).

(5) VON WEIMARN and MALJISCHKEV: J. Russ. Phys. Chem. Soc., 42, 484 (1911); Kolloid-Z., 8, 216 (1911).

into a saturated solution of sulphur dioxide. By dissolving various amounts of sulphur dioxide in water and then saturating with hydrogen sulphide, Odén had found that a high initial concentration of sulphur dioxide favors the formation of a finely divided precipitate, whereas a low initial concentration of the same gas favors the formation of non-peptizable clumps. Accordingly, in order to obtain large quantities of colloidal sulphur, the water was first saturated with sulphur dioxide and the excess was then maintained throughout the reaction by passing the theoretical amount of sulphur dioxide for the reaction,

into the water simultaneously with the hydrogen sulphide.

By this method it was possible to carry on the reaction for several hours without changing the reaction medium. After the sol became highly concentrated, sulphur settled out as a yellow mass which was readily peptized by shaking with water. The constancy of the conditions of formation gave particles of a much more uniform degree of dispersion than could be obtained by strict adherence to Odén's method.

The characteristic hydrophilic properties of Odén's sulphur sol are attributed by Freundlich¹ to the presence of pentathionic acid in the micelles. This conclusion is based on the observation that the sols have different properties if obtained under conditions such that the pentathionic acid cannot form. There seems to be no good reason for believing that the only

 (1) Kolloidchem. Beihefte, 16, 234 (1922); also FREUNDLICH (HATFIELD): "Colloid and Capillary Chemistry", 618 (1927).

thionate present in the micelles is the pentathionate, since Debus¹ showed that the mixture formed by the interaction of sulphur dioxide and hydrogen sulphide contains, in addition to colloidal sulphur and pentathionic acid, di-, tri-, tetra- and probably hexathionic acids.

For the preliminary macro-observations on the physical character of the precipitated sulphur, the sol prepared as described above was purified by finally saturating the reaction liquid with hydrogen sulphide and then boiling out the excess gas. Any non-peptizable sulphur was removed by filtering through a fine filter paper. The sol obtained in this way contained nothing except the products of the reaction by which it was

(1) Chem. News, 57, 87 (1888).

formed, and required no dialyzing. Moreover, it was quite stable, a part of the colloidal particles remaining suspended for more than two years. On the other hand, due to the decrease in the concentration of sulphur dioxide at the end of the reaction, the particles showed considerable variation in size, and for the microscopic and submicroscopic investigations monodisperse sols were preferable.

The preparation of sols having particles of approximately uniform size was readily accomplished, since the sol thrown down by sodium chloride is reprecipitated by washing with water, and since the smaller particles are more stable and require a higher concentration of salt to cause coagulation¹. The following procedure was employed: The original sol was completely coagulated by the smallest possible concentration of sodium chloride, the coagulum collected by the aid of the centrifuge and reprecipitated with water. This process was repeated several times, until the supernatant liquid after coagulation gave no test for sulphite or sulphate with barium chloride. The sol then was split into fractions by adding sodium chloride stepwise to the sol and separating the sulphur not coagulated at each step. In order to insure complete fractionation, it was necessary to repeat the treatment with each concentration of sodium chloride several times. Each fraction was then concentrated by precipitating with sodium chloride and reprecipitating with a smaller volume of water. The same differential fractionation concentrations of

(1) ODEK: Z. physik. Chem., 78, 682 (19).

sodium chloride recommended by Odén and given in Table II were employed.

TABLE II
DIFFERENTIAL FRACTIONATING CONCENTRATIONS OF
SODIUM CHLORIDE FOR SULPHUR SOL.

Fraction Number.	Normal concentration of sodium chloride	
	Which coagulates	Which does not coagulate
1	0.25	∞
2	0.20	0.25
3	0.16	0.20
4	0.13	0.16
5	0.10	0.13
6	0.07	0.10
7	0.00	0.07

After the several fractions had been concentrated as described above they were dialyzed for two to three weeks, until the dialysate showed no residue on evaporation and gave no test for chloride. The first dialyses were done with parchment membranes, which gave trouble because of the tendency of the particles to diffuse through. A similar difficulty was reported by Nevinny¹. Later dialyses were done with "Cellophane" membranes, which were entirely satisfactory.

(1) Berl. klin. Wochenschr., 45, 1883 (1908).

Coagulation of Sulphur Sol by Electrolytes, and the Form of the Precipitate. The precipitation values of the sol for a series of electrolytes was determined using a mixing apparatus consisting of a small test tube sealed inside a larger one¹. Ten cubic centimeters of sol was placed in the inner compartment of the apparatus and a measured amount of standard electrolyte diluted to 10 cc. in the outer compartment. The stopper was inserted in the mixer and it was shaken vigorously, thus insuring rapid and uniform mixing. The mixture was then poured into a pyrex test tube and allowed to stand for 15 minutes, at the end of which time it was centrifuged for 3 minutes at 2000 r. p. m. By trial the concentration of electrolyte was determined which was just sufficient to leave a clear supernatant liquid. At the same time an amount of electrolyte slightly in excess of the precipitation concentration was added to the sol, and the nature and physical character of the precipitate was observed after allowing the mixture to stand 15 minutes and then shaking. The results are given in Table III.

Since the descriptions of the precipitates obtained with different precipitating ions are of necessity somewhat indefinite, some representative photographs of the clumps (actual sizes) which constitute the precipitates were made. The precipitations were carried out in the mixing apparatus, and the mixture was then poured into a flat-bottomed cell made by cementing a short length of hard rubber tube (2.5 inches

(1) WEISER and MIDDLETON: Jour. Phys. Chem., 24, 48(1920).

TABLE III
COAGULATION OF SULPHUR SOL BY ELECTROLYTES AND THE
PHYSICAL CHARACTER OF THE COAGULUM.

Electrolyte	Precipitation concentration milli-eq./cc.	Physical character of the precipitate
HCl	0.5	Slimy; reversible
LiCl	0.55	Gelatinous; reversible
NaCl	0.25	Gelatinous; reversible
KCl	0.12	Plastic flocks; irreversible
CsCl	0.12	Plastic flocks; irreversible
CuCl ₂	0.012	Gelatinous; reversible on repeated washing
MgCl ₂	0.015	Granular; reversible on repeated washing
ZnCl ₂	0.015	Granular; reversible on repeated washing
MnCl ₂	0.015	Granular; reversible on repeated washing
CaCl ₂	0.008	Granular; partly reversible
SrCl ₂	0.006	Curdy; irreversible
BaCl ₂	0.0076	Plastic; irreversible
FeCl ₃	0.00045	Curdy; almost entirely reversible
AlCl ₃	0.00035	Curdy; almost entirely reversible
H ₂ S	(Saturated)	Only a small amount of slimy precipitate formed in 4 hours; almost entirely reversible
NaOH	0.15	Curdy to plastic; slightly reversible

inside diameter) onto an optically plane glass plate. A camera was mounted above the cell and the precipitates were photographed on orthochromatic film by light filtered through a 1.5-inch thickness of saturated picric acid solution and reflected upward through the bottom of the cell.

(i) Precipitate formed with NaCl

(ii) Precipitate formed with KCl

(iii) Precipitate formed with BaCl_2

Figure 1. Macrographs of sulphur precipitates,
(a) immediately after neutralizing sol and (b) after agitating
to agglomerate coagulum.

In each case a photograph was made (a) immediately after pouring the mixture into the cell and (b) after agitating the cell to further agglomerate the coagulum. The results are shown in Figure 1.

The fact that the character of the precipitate is not determined by the rate of precipitation was shown in the following way: Ten cubic centimeters of sol was placed in a test tube, and 10 cc. of electrolyte solution containing enough NaCl or BaCl_2 for exact precipitation was poured into a "Cellophane" cup partly immersed in the sol. After about one hour precipitation was complete, and the nature of the precipitates formed was as indicated for the same salts in Table III.

As a further experiment, precipitates were formed by passing the sol forming gases into dilute solutions of LiCl, NaCl and KCl previously saturated with sulphur dioxide. After the concentration of the salt had been reduced below the precipitation value through adsorption by the precipitate, a sol was obtained in each case. However, the precipitate first formed was identical in character with that obtained by adding the electrolyte to the sol. It is therefore evident that in this case the nature of the precipitate is not determined by the degree of dispersity and percentage supersaturation at the beginning of the precipitation.

Microscopic Observations. Since the form of the precipitate is apparently due in the last analysis to the manner in which the individual colloidal particles come together after neutralization by the several electrolytes, attempts were made

to view the process microscopically. As might be expected this was unsuccessful, since the colloidal particles are invisible in the ordinary microscope. Moreover, little information is obtainable from the microscopic observation of the precipitates formed with the different electrolytes. From the observations recorded in the preceding section, it seemed probable that the precipitates thrown down by lithium and sodium ions consist of aggregates of colloidal particles which have not coalesced, while the precipitates obtained with barium ions consist of masses formed by the coalescence of the individual particles. However, this difference obviously cannot be demonstrated with the ordinary microscope. Further observations were therefore made with the ultramicroscope.

Ultramicroscopic Observations. Attempts were made to view the coagulation process in the presence of electrolytes by means of the Jentzsch (Leitz) and the Siedentopf Cardioid¹ (Zeiss) ultramicroscopes. The results were not satisfactory with either apparatus. On account of the depth of the Jentzsch cell, the precipitated clumps settled out of the range of the objective as they formed and therefore could not be kept in focus. On the other hand, the Cardioid cell is too shallow (depth of liquid under observation, 0.002 mm.) to allow the clumps to form, the individual neutralized particles merely settling out after the Brownian movement had ceased.

(1) For a theoretical discussion of the Cardioid Condenser, see SIEDENTOPF: Kolloidchem. Beihefte, 25, 218 (1926)/

Since the process of clump formation was not readily followed, observations were made, by means of the Cardioid ultramicroscope, of the nature and behavior of previously formed clumps. These observations were accomplished in the following way: About 1 cc. of sulphur sol was mixed with slightly more of the electrolyte than the amount necessary for complete precipitation and the mixture was allowed to stand for several minutes, after which a drop of the liquid containing a considerable amount of precipitate was placed in the ultramicroscope cell and examined. Differences in the ultimate structures of the precipitates are brought out in a striking way in the plates, Figure 2. The first row of ultramicroscopic pictures, Figure 2 (i), shows the precipitate obtained with lithium chloride, focussed at different levels in the clump. The individual particles are clearly discernible, separated by a film of water. In the second row of pictures, Figure 2 (ii), is shown a portion of a large clump formed with potassium chloride, and Figure 2 (iii) shows a portion of a clump formed with barium chloride. In the last two cases it is clear that the individual particles have coalesced into a more or less uniform anhydrous clump of plastic sulphur. The smoothness of the edges of these two clumps shows particularly well the effect of the coalescence of the particles and the surface tension of the plastic mass.

Still more illuminating is the behavior of a hydrous clump formed in the presence of lithium or sodium ion, when

(i) Clump formed with LiCl

(ii) Clump formed with KCl

(iii) Clump formed with BaCl_2

Figure 2. Ultramicroscopic views of clumps of precipitated sulphur, focussed at different levels.

treated with a solution containing the more readily adsorbed and less hydrated potassium, caesium or barium ion. The observations were made, as before, with the Cardioid ultra-microscope. In this apparatus the container for the sol is a quartz disc with a central depression 0.002 mm. deep and about 12 mm. in diameter, surrounded by a circular moat about 2 mm. deep and 5 mm. wide, into which any excess liquid is expelled when the quartz cover glass is put on. Two holes were bored on opposite sides of this cover glass in the same position as the moat, so that the latter could be cleaned out and refilled with any solution desired. The removal of liquid from the moat was accomplished by means of a narrow strip of filter paper rolled into a pointed rod, which was inserted into a hole in the cover glass and served as a wick. The moat was refilled by means of a medicine dropper drawn out to a capillary.

To make the observations, the Cardioid cell was filled with a suspension of sulphur neutralized with lithium or sodium chloride. The moat was cleaned out and a satisfactory clump was brought into the field of view. The moat then was filled with a second solution containing the more strongly adsorbed ion, such as potassium, caesium or barium chloride, which diffused into the liquid bathing the precipitate and gradually, with repeated changing of the liquid in the moat, displaced the more weakly adsorbed sodium or lithium ion. This was accompanied by a marked change in the physical character of the

clump, which change was followed photographically by means of an Ernemann motion picture camera especially constructed for microscopic work. The microscope used a glycerine-immersion objective of 3 mm. focal length (N. A. 0.85), and the ocular employed had a magnifying power of 20 diameters. The magnification is roughly estimated at 1,500 diameters. The light for the microscope was supplied by a 17.5-ampere carbon arc, a single quartz lens placed near the arc serving as a collimator. The beam of light was passed through a 2-inch thickness of 5 per cent copper sulphate solution and a 12-inch thickness of water in order to cool it. For the purpose of minimizing vibration it was found necessary to mount the camera and microscope on separate bases.

The motion pictures of the changes taking place in the precipitates were made by taking one exposure every two seconds. Projection at normal speed increases the apparent velocity of the change approximately thirty times. The photographs accompanying this paper were made from sections of the motion picture negative taken at suitable intervals to show the nature of the change. The phenomena observed under different conditions will be considered in order:

Dehydration and Coalescence of Particles. Experiment 1.

The first observations were made on a clump thrown down by sodium chloride, in which the individual colloidal particles were rather widely scattered but were imbedded in a sheath of adsorbed water. When the adsorbed sodium ion was replaced by

barium ion in the manner described above, the excess water flowed out of the clump, leaving the colloidal particles stranded in approximately their original positions. At the same time there was an apparent contraction in the volume of the ultramicros. The photograph of the original clump, Figure 3 (1)(a), discloses the individual particles, but the voluminous hydrous character of the clump gives it a somewhat hazy appearance since all portions could not be brought into focus at the same time. Figure 3 (1)(b) shows the same clump after the excess water had flowed out of it, leaving the contracted particles.

Experiment 2. Since in the first experiment the particles were too widely scattered to come into contact after the excess adsorbed water was removed, attention was then directed to a more compact clump obtained with sodium chloride, in which the ultramicros were somewhat unevenly distributed. In this case, replacing the sodium ion with barium ion produced the same phenomena described in Experiment 1, but in addition the particles in intimate contact flowed together or coalesced into three or four minute, slightly hydrous particles. This transformation is pictured in Figure 3(1)(c, d, e).

Experiment 3. Experiment 2 was repeated with a somewhat more uniform clump. In this case, the substitution of the barium ion for sodium ion caused the entire gelatinous mass to coalesce into a single particle. See Figure 3(ii).

Experiment 4. On account of the more gelatinous character of the precipitate obtained with lithium chloride, ultramicroscopic observations were made on a relatively large gelatinous

clump as barium ion displaced the lithium ion. In this case there was a very marked shrinkage in volume, all the particles coalescing into a small uniform ball. This change is illustrated in Figure 3 (iii).

Observation of a projection of the motion picture film of which this plate is a sectional copy shows clearly the optical effects produced by the outflow of the adsorbed water. By visual observations in diffused light too dim to photograph, it is possible to actually see the convection currents in the water surrounding the clump. The striking character of this phenomenon can scarcely be imagined from the still pictures alone.

Experiment 5. Since potassium ion gives plastic sulphur, a clump formed with lithium ion was treated with potassium chloride. The loss of water and coalescence is illustrated in Figure 3(iv).

Experiment 6. Since the precipitate formed with caesium ion is even more plastic than that formed with potassium, Experiment 5 was repeated, substituting caesium chloride for potassium chloride with the results shown in Figure 3(v).

Reversibility of Precipitation. Attention has been called to the fact that the coagulum obtained with lithium or sodium ions is (1) gelatinous, (2) composed of the individual particles which have not coalesced and (3) readily reversible on washing out the precipitating ion. On the other hand, the precipitates obtained with potassium, caesium and barium ions are (1) plastic,

(i) Na displaced by Ba

(ii) Na displaced by Ba

(iii) Li displaced by Ba

(iv) Li displaced by K

(v) Li displaced by Cs

Figure 3. Ultramicroscopic views of the behavior of hydrous sulphur clumps on displacing a highly hydrated neutralizing ion with a less hydrated ion.

(2) formed by the coalescence of the ultramicros and (3) practically completely irreversible. It has been shown also that if the neutralization of the ultramicros is carried out in the shallow Cardioid cell clumps do not form, but, instead, the individual particles settle out and remain at rest. This latter observation suggested experiments to show the factors which determine the reversibility of a precipitate. The method of procedure was as follows:

A monodisperse sol was placed in the Cardioid cell, the excess sol was removed from the moat, which was filled with the solution containing the desired coagulating ion. After a sufficient amount of electrolyte had diffused into the cell to cause complete neutralization of the particles, the electrolyte was removed from the cell and pure water substituted. The electrolyte gradually diffused into the pure water, which was changed repeatedly.

Experiment 1. The sol was first neutralized by sodium chloride. After removing the excess electrolyte, the Brownian movement was resumed by all the particles, showing that the neutralization was completely reversible.

Experiment 2. Experiment 1 was repeated, substituting sodium hydroxide for sodium chloride. Identical results were obtained, the neutralization being reversible.

Experiment 3. A dilute solution of barium chloride was used as the precipitating electrolyte. In spite of repeated changing of the water through a period of 48 hours, the particles showed no signs of again taking on the Brownian movement. This

experiment demonstrates quite clearly that the neutralization process is irreversible even in the absence of coalescence if the adsorption of the precipitating ion is too strong.

Experiment 4. Since potassium and barium ions give a similar type of precipitate when the particles are allowed to coalesce, and since the adsorption of the univalent potassium ion is much weaker than that of the bivalent barium ion, it seemed possible that the precipitation with potassium ion in the Cardioid cell, where there is no coalescence, would be reversible. This proved to be the case, the neutralized particles taking on the Brownian movement in 30 to 40 minutes after the beginning of the washing to remove the potassium ion.

As we have seen, Freundlich¹ attributes the characteristic properties of Odén's sol to the presence of pentathionic acid in the micelles. He is therefore led to the conclusion that the reversibility of a sulphur precipitate depends on the formation of a stable pentathionate with the precipitating ion, that is, a pentathionate which does not decompose and thereby destroy the pentathionate ion. On a basis of the same theory he concludes that a strong base, such as sodium hydroxide, gives an irreversible precipitate because it destroys the pentathionic acid. It is rather difficult to see why sodium pentathionate formed from sodium hydroxide should have properties which are different from sodium pentathionate formed from sodium chloride. These views are not tenable, for in the case of potassium we have a precipitate which is reversible or irreversible depending on whether or not the particles are allowed to coalesce, and in

(1) Kolloidchem. Beihefte, 16, 234 (1922).

the case of sodium hydroxide we have a similar phenomenon. The slight reversibility of the precipitate formed by neutralization of the sol en masse with sodium hydroxide is obviously due to some other cause than the destruction of pentathionic acid. It is probably related in some way to the influence of the excess of (OH) ion on the degree of hydration of the neutralized particles. Moreover, there appears to be no reason for believing that the lithium and sodium pentathionates should be any more stable than the corresponding potassium or barium salts. Certainly this is not true of the well known, closely related dithionates.

THEORETICAL.

From a survey of the observations recorded in the preceding section, it appears that the physical character of precipitated sulphur thrown down in the presence of alkali cations varies from gelatinous to plastic as we go down in the series from lithium to caesium. Likewise, the precipitate thrown down by alkaline earth cations changes in the same way as we go down in the series from magnesium to barium. In other words, precipitates formed in the presence of those ions which are generally recognized as the most highly hydrated are the most gelatinous, and the precipitation is reversed by washing, while the precipitates thrown down in the presence of the less hydrated ions are dense and plastic, and the precipitation is not reversed by washing.

The order of hydration of the alkali cations is believed to be: $\text{Li} > \text{Na} > \text{K} > \text{Rb} > \text{Cs}$; and of the alkaline earth cations: $\text{Mg} > \text{Ca} > \text{Sr} > \text{Ba}$. Unfortunately, no one has yet succeeded in measuring quantitatively the ion hydration, much less its dependence on concentration, temperature and the presence of foreign substances in the solution. Nevertheless, ion hydration numbers are frequently given. Thus, Remy¹ assumed that an ion moves like a sphere in a viscous liquid according to the well known Stokes formula $u = \frac{2 r^2 (d_1 - d_2) g}{9 \eta}$, where u is the velocity, r the radius and d_1 the density of the sphere, and d_2 and η the density and viscosity of the medium, respectively. The mobility of the ions calculated in this way is too

(1) Z. physik. Chem., 89, 467 (1915).

large when the atomic radius is assumed to be the radius of the ion. From the greater radius which must be assumed to obtain agreement with the Stokes formula — an increase which is attributed to a sheath of water — it is calculated that the lithium ion is associated with more than 120 molecules of water; the sodium ion with more than 66; potassium ion, 16; rubidium ion, 14; and caesium ion, 13. (Hydrogen is assumed to be anhydrous.) The order of magnitude of the hydration numbers determined from transference experiments by Washburn and Millard¹ is quite different from the results of Remy. Thus, if chloride ion is assumed to be anhydrous the number of molecules of water on the several cations is calculated to be: lithium, 4.7; sodium, 2; potassium, 1.3; caesium, 0.7; and hydrogen, 0.3. If the chloride ion is assumed to have 4 molecules of water, the values for the cations become: lithium, 14; sodium, 8.4; potassium, 5.4; caesium, 4.7; and hydrogen, 1. Recent theories of strong electrolytes would indicate that hydrogen is relatively highly hydrated. Bjerrum² calculates the hydration number of hydrogen to be 8 and that of potassium 0. Jablscynski and Wiesnewski³ conclude from freezing point measurements that lithium is combined with 11 molecules of water, sodium with 3 and potassium with 0. Schremer gives for hydrogen 10-11 and for lithium 6.5-7.5 molecules of water, respectively. On the assumption that

(1)Jour. Am. Chem. Soc., 37, 694 (1915).

(2)Z. anorg. Chem., 109, 275 (1920).

(3)Roczniki Chem., 1, 116 (1921).

hydrogen is monohydrated, Baborovsky¹ concludes that lithium holds 35 molecules of water, sodium 22 to 25 and potassium 6. Other investigators give still different values, but those recorded suffice to show that the absolute value of the degree of hydration of the ions under any specified conditions is not known. All observers agree, however, that the hydration falls off in the alkali series from lithium to caesium and in the alkaline earth series from magnesium to barium. Born² has shown further that the radius of the ions increases in the series from lithium to caesium, and Fajans³ and Born⁴ have calculated the heats of hydration of the ions from the lattice energies of binary salts and have found them to decrease from lithium to caesium and from magnesium to barium. This merely confirms the order of hydration of ions in the two series, but gives no indication of the degree of hydration. Indeed, Fajans is of the opinion that the so called hydration of ions does not connote the formation of ion hydrates of definite stoichiometric composition⁵, but rather that, due to the electrostatic charge of the ions, the oppositely charged part of the polar water molecule is turned toward the ion and this in its turn exerts an attractive force

(1) Chem. Listy, 19, 297 (1925).

(2) Z. Elektrochem., 26, 401 (1920).

(3) Ber. deutsch Phys. Ges., 21, 709 (1919).

(4) Z. Physik, 1, 45 (1920).

(5) Cf. also BABOROVSKY and VELISEK; Chem. Listy, 21, 227 (1927).

on the next molecule. This type of dielectric polarization would proceed continuously in the water surrounding the ion. From this point of view it would follow that the so called hydration values will be relative numbers only. For a series of ions having the same valence, the dielectric polarization will vary with the specific nature of the ion and with its size. In general, the concentration of the charge on a very small ion will exert a greater attractive force on the polar water molecules than the same charge on a larger ion.

Observations on the precipitation of sols with cations having the same valence disclose that the adsorption of an ion, which determines its precipitating power, may be closely related to its degree of hydration¹. If one accepts Fajans' view that the hydration consists in the formation of a polarized water envelope, the process being accompanied by a positive heat effect, one should expect the adsorption of an ion to be accompanied by a partial dehydration, the extent of which will be determined by the heat of hydration of the ions. Since we have seen that both the heat of hydration and the amount of hydration decrease in the alkali series from lithium to caesium and in the alkaline earth series from magnesium to barium, it follows that the adsorptive capacity and coagulative action should likewise decrease in the same direction, as the results show².

(1) Cf. LACHS and LACHMAN: Z. physik. Chem., 123, 303(1926).

(2) Cf. WEISER: Jour. Phys. Chem., 29, 955 (1923).

It is of interest to inquire into the probable thickness of the film of water surrounding the sulphur particles.

Pettijohn¹ found the maximum thickness of a water film on some glass pearls made in Germany to be about 128μ . With another lot of glass of different origin the maximum was about 68μ . With river sand the estimated thickness varied from 285μ with 10-mesh sand to 114μ with 60-mesh sand. From observations by Barus² on the formation of fog it is calculated that the thickness of the water film under the conditions of the experiments is 0.1 to 0.8μ when the nucleus has a diameter of 2.6μ and 0.05 to 0.5μ when the nucleus has a diameter of 3.6μ . With sugar charcoal, Bijl³ was able to show that the Gibbs layer of water was more dense than the main bulk of the liquid. He calculated the thickness of this layer to be 0.68μ , which is below the limit of visibility with the ultramicroscope.⁴ The high visibility of the film between the discharged sulphur particles would seem to indicate that the density of the adsorbed water is relatively high, the refractivity being of a similar order to that of sulphur. The visual observation of ultramicroscopic convection currents accompanying the dehydration supports this view. In a relatively dense gelatinous mass of sulphur precipitate, the thickness of the film of water between the ultramicros appears to be, by comparison with the size of the ultramicros, about 50μ .

(1) Jour. Am. Chem. Soc., 41, 477 (1919).

(2) Phil. Mag., (6) 4, 24, 262 (1902)

(3) Rec. trav. chim., 46, 763 (1927).

(4) Cf. page 32 (a).

Harkins and Erving¹ found that when 10 grams of ignited charcoal was treated with 1 gram of water, the water was attracted onto the surface of the charcoal by an attractive force equivalent to 37,000 atmospheres, and that under this pressure the water was compressed to 75 per cent of its original bulk.

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(1) Jour. Am. Chem. Soc., 43, 1787 (1921).

In the light of these considerations it seems reasonable to conclude that when the sulphur particles are neutralized by the adsorption of highly hydrated ions the particles retain an envelope of water, so that the coagulated mass is an agglomerate of ultramicroscopic particles which have not coalesced. The film of adsorbed water together with the water entrained during the agglomeration process gives a flexible hydrous mass, which is known as a gelatinous precipitate. The ultramicroscopic observations on gelatinous sulphur formed by coagulation of the sol with highly hydrated lithium, sodium or magnesium ion gives definite visual confirmation of the nature of a gelatinous precipitate deduced by Weiser¹ several years ago.

Since the highly hydrated ions that yield gelatinous precipitates are not adsorbed strongly, and since the ultramicros retain their individuality in such precipitates, it follows that washing out the excess of precipitating ion should cause reprecipitation. This is very readily accomplished with the precipitates formed with the univalent lithium and sodium ions. Practically complete reprecipitation of precipitates formed in the presence of magnesium and zinc ions can also be effected, but the washing must be more thorough because of the stronger adsorption of the divalent ions.

Conditions are quite different if the neutralisation of the particles is accomplished by the adsorption of ions that are not sufficiently hydrated to maintain a film of water of

(Cf. BOGUE: "Colloidal Behavior", 387 (1924).)

sufficient thickness or rigidity to prevent coalescence of the individual ultramicros. This condition is realized with potassium, caesium and barium ions. After neutralization the ultramicros collide and coalesce, giving a more or less uniform mass of plastic sulphur which cannot be reprecipitated to give a sol no matter how thoroughly the precipitate is washed. If the individual particles are prevented from coming together by precipitating in the shallow Cardioid cell, reversal can be accomplished by washing if the relatively weakly adsorbed potassium ion has been used to effect neutralization, whereas if the more strongly adsorbed, bivalent barium ion is employed it cannot be displaced by washing and reversal is impossible.

The formation of sulphur precipitates in quantity either by neutralizing the sol by the addition of electrolytes or by carrying on the reaction between sulphur dioxide and hydrogen sulphide in the presence of electrolytes can be visualized as follows: The first step following the formation of colloidal particles is their neutralization below the critical value necessary for agglomeration. When two or more such particles collide they either adhere or coalesce, the combination forming the nucleus for a larger clump. In the formation of a large coagulum it is immaterial whether the particles actually coalesce or are held apart by a cushion of water. From the first collisions of discharged particles to form submicroscopic or microscopic nuclei the general mechanism is the same.

A larger clump inmeshes a smaller one, and is in turn inmeshed by a clump larger than itself. The entire process resembles the accumulation of driftwood in a swollen stream. The growth of a clump therefore may be regarded as autocatalytic in nature. The shapes and sizes of the ultimate clumps depend upon the number and manner of chance collisions, except that the weakness of the binding forces in the gelatinous precipitates makes impossible the formation of very large clumps in the absence of packing (cf. Figure 1 (1)). When the particles coalesce the size of the clumps is limited only by the quantity of material available. The fundamental nature of the clumps, that is whether they are flexible, gelatinous and readily reprecipitated or are hard or plastic and non-precipitable, depends on whether or not the conditions are favorable for the coalescence of the ultramicros. This in turn depends on the nature and hydration of the adsorbed precipitating ion in the manner above described.

SUMMARY.

(1) A critical discussion of the von Weimarn Law of Corresponding States for the Precipitation Process has been given. It has been shown that the law in its simplest form is frequently inapplicable, and that, in certain cases, it may be of little value for predicting the form of a precipitate in advance of the precipitation experiments.

(2) Among the factors other than the percentage supersaturation which influence the physical character of precipitates are: (1) the specific tendency of the particles to adsorb the solvent; (2) the shape of the particles and (3) the effect of the adsorption of ions.

(3) The element sulphur furnishes a satisfactory substance for studying the specific influence of the adsorption of ions on the form of a precipitate, since the physical character of precipitated sulphur varies more or less continuously from gelatinous and reversible to plastic and completely non-reversible when thrown down in the presence of the lyotropic series of ions from lithium to caesium and from magnesium to barium.

(4) Neutralization of Odén's sulphur sol with a highly hydrated, weakly adsorbed ion, such as lithium or sodium, gives a gelatinous precipitate composed of the individual micelles separated by a film of adsorbed water. Such a precipitate is readily reprecipitated by washing out the neutralizing ion. Photographs are given showing the macroscopic and ultramicroscopic appearance of typical clumps.

(5) When the sulphur sol is neutralized with a slightly hydrated, strongly adsorbed ion, a plastic precipitate is obtained in which the individual particles have lost their identity due to coalescence. A precipitate of this type is not reversed by very thorough washing. Photographs are given showing the macroscopic and ultramicroscopic appearance of the clumps.

(6) Ultramicroscopic observation of the change taking place when a highly hydrated cation is removed from a gelatinous sulphur clump, by displacing with a less hydrated, more strongly adsorbed cation, shows a very marked shrinkage as the result of the loss of adsorbed water and the coalescence of the particles. Ultramicroscopic convection currents in the surrounding liquid, due to the outflow of the adsorbed water, are visible during the change. Motion pictures have been made of this change in the physical character of the clumps under the influence of various ions, and selected views from the motion pictures are included in this paper.

(7) When the sulphur sol is neutralized in the cell of the Gardioid ultramicroscope, so that the neutralized particles do not collide with one another, the precipitation is reversible or irreversible depending on whether or not the adsorbed neutralizing ion may be removed by washing, and independently of whether the particles would coalesce if allowed to collide.

(8) It is concluded that: A reversible precipitate of any substance will be obtained when a sol is neutralized under such conditions as to prevent coalescence, either (1) by the intervention of a film of adsorbed solvent or (2) by preventing collisions of the neutralized particles. In either case it is essential that the adsorption of the neutralizing ion be sufficiently weak to permit its removal by washing.

(9) The shapes and sizes of the individual precipitated clumps of sulphur depend upon the number and manner of chance collisions during the precipitation process.

(10) The fundamental nature of the precipitated sulphur clumps depends upon whether or not the conditions under which the precipitation is carried out favor the coalescence of the ultramicros, which is in turn dependent upon the nature and degree of hydration of the adsorbed neutralizing ions.