LXII.—*The Coagulation of Colloidal Arsenious Sulphide by Electrolytes, and its Relation to the Potential Difference at the Surface of the Particles.*

By FRANK POWIS.

FROM a study of the relationship between the stability of an oil-water emulsion and the potential difference at the oil-water interface (P.D. will henceforth be used for the potential difference at the interface of the water and suspended particles), the author was led to conclude that the emulsion was comparatively stable whenever the P.D. exceeded a certain value (positive or negative), but coagulated whenever it was below this critical value (*Zeitsch. physikal. Chem.*, 1914, **89**, 186). It was also pointed out that the only suitable data regarding the relationship between the stability of colloidal solutions and the P.D., namely, those of Burton (*Phil. Mag.*, 1909, [vi], **17**, 583) indicated that the same held good for colloidal solutions, although Burton did not interpret them in this way. When starting the following experiments the author's intention was to test this idea in the case of several colloids, but since it is doubtful whether there will be opportunity to carry this work further, it seems advisable to publish the results already obtained.

A colloidal solution of arsenious sulphide was prepared by Freundlich's method (*Zeitsch. physikal. Chem.*, 1903, **44**, 129). Washed hydrogen was passed through it until it had almost no odour of hydrogen sulphide. It was then filtered, very little solid being retained by the filter. The resulting colloidal solution contained about 11 grams of arsenious sulphide per litre, and had a conductivity of 5×10^{-5} mho. at 17° . Before use, it was diluted with an equal volume of distilled water, the conductivity then being 4×10^{-5} mho., indicating that a large proportion of the electrolyte present was adsorbed on the particles. Only a small portion was diluted at one time, since the more concentrated solution kept better, perhaps simply because the bottle was not opened so frequently.

Coagulation Observations.

In determining the influence of electrolytes on the stability, 5 c.c. of the (diluted) colloidal solution were placed in a well-steamed test-tube and 5 c.c. of electrolyte solution of the requisite concentration added. The tube was immediately reversed twice so as to mix the contents, and the appearance then noted. It was

then allowed to remain, and the appearance again noted at suitable intervals. As there seems to be no description on record of the appearance presented when gradually increasing amounts of electrolyte are added to colloidal arsenious sulphide, or, so far as the author is aware, any colloid, and of the changes which occur on keeping or on shaking, the following observations with barium chloride may be given as typical. The concentration is in millimols. per litre in the final colloid-electrolyte mixture.

Concentration.	Appearance.
0.3 and all below	No turbidity either immediately or after twenty-four hours.
0.4	No immediate turbidity. After five hours no precipitate was present, but the whole of the liquid was turbid. After remaining undisturbed until the next day, the liquid was still turbid throughout, but on disturbing, some small flakes became visible, which slowly settled to the bottom. Most of the arsenious sulphide, however, still remained in such small particles or groups of particles that after again remaining undisturbed for twenty-four hours the liquid was turbid up to the top.
0.5	Very slight turbidity was noticeable after a few minutes. After one hour it was very turbid. After five hours there was a layer of clear liquid about 1 cm. deep at the top; no distinct precipitate was visible, perhaps because of the turbidity of the liquid. After remaining undisturbed for a day the precipitate still occupied a fairly large volume, but the liquid above was clear and colourless. On disturbing gently, the gel-like precipitate broke up into large flakes which settled rapidly and occupied a much smaller volume than before.
0.6	Became very turbid within a few minutes. It was disturbed again, when small flakes formed which settled slowly. After then remaining undisturbed for a day almost all the arsenious sulphide had separated in the precipitate, but the liquid above was slightly cloudy. (The cloudiness in this case, whereas the liquid in the preceding case is given as being clear, is due to the liquid being shaken, as will be described later.)
0.7	No distinct turbidity was produced immediately, but the liquid became very turbid within a few minutes. It was then disturbed again, when large flakes formed which settled fairly quickly. After remaining for twenty-four hours all the arsenious trisulphide was precipitated and the liquid above was quite clear.
0.8 and higher concentrations.	Became turbid when the electrolyte solution was poured in, and on reversing the tube so as to mix the contents, large flakes formed which settled rapidly. The liquid above was rather cloudy at first, but after twenty-four hours it had become quite clear.

After the first day the only mixtures showing any appreciable change compared with the mixture of 5 c.c. (diluted) colloid + 5 c.c.

water were those with concentrations between 0.4 and 0.6 millimol. per litre, and in these the change was very slow. After four days the liquid in the 0.6 tube had become quite clear, and that in the 0.5 tube was only slightly cloudy, but the 0.4 mixture was still yellow and turbid, and only a small amount of precipitate had settled at the bottom. This 0.4 millimolar mixture slowly underwent further change, so that after eight days nearly all the arsenious sulphide had settled to the bottom, but the liquid was still turbid, with a yellowish-white appearance; after thirty-two days the liquid was only slightly cloudy, and had a bluish-white tinge. The difference in the light reflected from the mixture as it changed from turbid through cloudy to almost clear, is no doubt due to the settling of the larger particles, so that the average size of those remaining suspended gradually decreased.

After two months the mixture containing 0.3 millimol. per litre was still like the pure colloid; both contained a very small amount of precipitate, and appeared almost clear in transmitted light, but turbid in reflected sunlight; the yellow colour of both was much less intense than at first, probably due to slow chemical action, for example, hydrolysis of the arsenious sulphide.

Examination of the above observations shows that there is no definite concentration above which coagulation occurs almost immediately, but below which no coagulation occurs. Yet the limits of concentration for these are fairly narrow, being below 0.8 but above 0.3 millimol. per litre. Odén (*Zeitsch. physikal. Chem.*, 1912, **78**, 682) obtained results with colloidal sulphur which are important in this respect. He found that when all the particles in the colloidal solution were of approximately the same size, the concentration at which coagulation occurred was much more sharply defined than when particles of widely different size were present. Moreover, the smaller the size of the particles in these solutions the larger was the concentration of electrolyte necessary for coagulation, indicating that the larger particles of any colloidal solution coagulate more easily than the small ones. Galecki (*Zeitsch. anorg. Chem.*, 1912, **74**, 174) has shown that in the coagulation of gold sols. the larger particles act as nuclei for the smaller ones. The presence of particles of very different size is therefore probably the reason why the coagulation concentration with arsenious sulphide is not very sharply defined.

In determining the influence of electrolytes on the stability of colloids the usual method has been to add the requisite number of drops of a concentrated solution of the electrolyte. This would appear to be very unsatisfactory, since even if this is done in a flask which is shaken, some of the colloidal particles must for a

small interval of time be in contact with an electrolyte solution of much higher concentration than that finally present. This may cause part of the colloid to coagulate, and according to Galecki's results the groups of particles so formed would tend to act as nuclei for the deposition of the remaining particles; so coagulation might occur at a concentration less than the real coagulation concentration. Such a possibility can, however, be almost eliminated by the use of an electrolyte solution not much more concentrated than that required in the final mixture, and running it in slowly while shaking the flask containing the colloidal solution. (In investigating the effect of an electrolyte like thorium chloride in sufficient concentration to reverse the sign on the colloid, it is better to add the colloid to the electrolyte.)

Influence of Shaking.—If equal quantities of colloid and electrolyte solutions are mixed in a tube as described above, the progress of coagulation and settling is little influenced by subsequent shaking of the tube unless the electrolyte concentration is near that which causes immediate turbidity but not immediate coagulation and settling, for example, 0.5 millimolar in the case quoted above. At concentrations near this, shaking greatly facilitates, or one might even say is necessary for, the formation of large, separated flakes; these then settle quickly, but leave the liquid above turbid or cloudy owing to the slow settlement of the remaining smaller particles or groups of particles. If, however, a turbid mixture is left undisturbed, no separate coagula are formed, but the surface of the turbidity slowly sinks in the liquid and leaves it clear and free from particles. As an example, a few of the observations made with barium chloride may be quoted. The test-tube was gently shaken for a few seconds at intervals of half an hour for two hours, then of one hour for three hours, then occasionally as indicated on page 738.

The shaken tube had not been disturbed for nineteen hours before making the last observation, and therefore the difference in appearance of the two tubes was not due to re-suspension of the particles by shaking. After a week, the tube not having been disturbed for four days, the liquid in the "shaken" tube was still slightly cloudy, a few very fine particles still remaining suspended.

With a concentration of 0.8 millimol. per litre or higher than this, large flakes tend to be formed during the initial shaking adopted to mix the two solutions, so that without subsequent shaking the behaviour approximates to that in the tube containing 0.6 millimol. per litre which was shaken at intervals. There was evidence, however, that this would not have been so if the initial shaking had been less vigorous.

Concentration of Barium Chloride, 0.6 millimol. per litre.

Time after mixing	Appearance.	
	Tube shaken	Tube not shaken except the reversal immediately after adding the electrolyte.
Immediately	Turbid	Turbid.
Two hours	Much precipitate at bottom; rest turbid	Layer of clear liquid at top, about 1 mm. deep; rest very turbid. No distinct precipitate at bottom.
Five hours	Large precipitate; liquid above slightly turbid	Some precipitate at bottom. Liquid at top clear for about 7 mm. Rest very turbid, but no separate particles visible.
One day	Dense precipitate containing almost all the arsenious trisulphide. Liquid above slightly turbid except 1 mm. at top.	All the arsenious sulphide contained in precipitate of small bulk. Liquid above quite clear.

With 0.5 millimol. per litre the results were similar in character to those with 0.6. With a 0.4 millimolar solution the two tubes had almost the same appearance when examined after various intervals of time up to a week. After five hours both had become turbid, but gentle shaking did not cause large coagula to form as it did with the turbid 0.6 millimolar solution.

During the first few days the arsenious sulphide in the 0.5 and 0.6 millimolar solutions which were not disturbed after they had once been thoroughly mixed, resembled gelatinous precipitates like ferric hydroxide, and the existence of a honeycomb or network structure would explain the carrying down of the very fine particles which occurred under these conditions, but not when the tube was frequently shaken.

The Relation between the Stability and the Potential Difference at the Surface of the Particles.

In determining the value of the P.D. the method employed by Burton (*Phil. Mag.*, 1906, [vi], **11**, 425) was used. For this a clear solution is required for the upper half of the U-tube, which has a conductivity equal to that of the colloid-electrolyte mixture in the lower half. Moreover, the kind and concentration of the electrolyte or electrolytes present must be the same, although this has not always been attended to.

The simple method adopted for attaining this is illustrated by the following for the determination in presence of 0.05 millimolar aluminium chloride. For the lower half of the tube 50 c.c. of 0.1 millimolar aluminium chloride solution were added to 50 c.c. of (diluted) colloid. For the upper liquid 25 c.c. of 0.2 millimolar aluminium chloride were added to 25 c.c. of undiluted colloid (having, therefore, twice the concentration of the 50 c.c. used above and of that used for the stability determinations). After remaining undisturbed for a few minutes the mixture was shaken and then filtered. In this mixture the concentration of aluminium chloride is sufficient to cause coagulation, and by waiting for some time before shaking, the very small particles stick to or are entangled amongst others, and so a colourless, clear filtrate is obtained. Neglecting the first portion, the rest was diluted with an equal volume of water. It will readily be seen that the concentration of both the aluminium chloride and any electrolyte contained in the colloidal solution will be the same as in the colloid-electrolyte solution used in the bottom half of the tube, or, at any rate, very nearly so, whereas a pure 0.05 millimolar aluminium chloride solution would have a much smaller conductivity.

Table I contains the results of determinations made in the presence of four different electrolytes, the cations of which varied in valency from one to four. For each electrolyte a series of stability determinations was made similar to that given earlier for barium chloride, and the concentration used for the P.D. determination was that at which the colloid had the same stability (or instability) as in presence of 0.5 millimolar barium chloride, that is, the lowest concentration at which rapid coagulation occurred.

TABLE I.

Electrolyte.	Concentration millimols. per litre.	P.D. in volt.*
Potassium chloride.....	40.0	0.044
Barium chloride	0.5	0.026
Aluminium chloride	0.05	0.025
Thorium nitrate	{ 0.05	0.027
	{ 0.07	0.026
	{ 0.1	0.024

* Arsenious sulphide is a so-called negative colloid, since, as usually prepared, the particles travel towards the anode in an electric field. According to the usual nomenclature, all the P.D. values given in this paper should therefore be preceded by the negative sign, except the value +0.03 volt for ferric hydroxide on p. 741, and +0.03 volt for arsenious sulphide on p. 742, where the + is inserted for distinction.

With regard to stability, the behaviour of the colloid towards thorium nitrate was a little different from its behaviour towards

the other electrolytes tried. With 0.05 millimol. per litre there was no turbidity even after twenty-four hours, but with 0.06 there was immediate turbidity and formation of small flakes. These small flakes settled slowly, but instead of leaving the liquid quite clear and colourless, as might have been expected from the behaviour with barium chloride, the liquid remained yellow and like the pure colloid in appearance. In the presence of 0.1 millimol. per litre the behaviour was very similar, although 0.2 millimol. did cause the formation of large flakes, and after a few hours the liquid above was quite clear and colourless. On comparison with barium chloride, it will be seen that there is a much smaller change in concentration with thorium nitrate in passing from that which does not cause turbidity in twenty-four hours to that which causes immediate turbidity, but a greater change in passing from this to the concentration which causes the liquid to become quite clear and colourless in a few hours. The reason for this difference in behaviour was not ascertained; one would certainly not expect the use of the nitrate instead of the chloride to have this effect. On account of this difference in behaviour, potential measurements were made with 0.05, 0.07, and 0.10 millimol. per litre, the concentration having a coagulative effect equal to that of 0.5 millimolar barium chloride being certainly within this range.

The concentrations of the four electrolytes having equal coagulative effect, as given in table I, by no means form the geometric series which is often said to hold for the coagulation of negative colloids by electrolytes having cations of different valency—a point which was discussed in a previous paper (*loc. cit.*, p. 734).

The P.D. with the "pure" colloid was not determined owing to the difficulty of obtaining for the upper part of the U-tube a solution fulfilling the conditions previously mentioned; one attempt to obtain this by dialysis against distilled water resulted in coagulation before the conductivities of the colloid and outside water became equal. Many such determinations by different observers with other colloids have all given values less than 0.8 volt (for table, see Burton, "The Physical Properties of Colloidal Solutions," p. 135); with a pure oil emulsion the present author found $(-)$ 0.046 volt, the highest value in the presence of any concentration of potassium ferrocyanide, which is very powerful in increasing the charge on a negative colloid, being $(-)$ 0.07 volt. We may therefore safely conclude that the value for the "pure" arsenious sulphide would be less than 0.1 volt, and probably less than 0.06 volt.

The values given above for the P.D. at the concentration of each electrolyte which is just sufficient to cause rapid coagulation, all

exceed 0.02 volt. They therefore confirm the conclusion drawn by the author (*loc. cit.*, p. 734) from the behaviour of an oil emulsion that the "coagulation concentration" is not that at which the P.D. becomes zero, that is, the isoelectric point, but is much lower, and that here the P.D. has still a relatively high value. As further evidence in support of this, I may mention that a sample of positive colloidal ferric hydroxide coagulated rapidly in the presence of 0.4 millimolar sodium sulphate, although the value of the P.D. at this concentration was +0.03 volt.

With regard to the further question of whether the colloidal solution is stable when the P.D. has a value exceeding a certain critical value, but coagulates if it is below this, the determinations yet made do not allow quite definite conclusions to be drawn. Certainly the figures in the above table for the mean results with barium chloride, aluminium chloride, and thorium nitrate agree quite well with each other, better, in fact, than the separate values for the same electrolyte, as seen from the appendix. The value for potassium chloride, however, is distinctly higher. With hydrochloric acid the coagulation concentration was 30 millimols. per litre, and a single P.D. determination at this concentration gave a value 0.050 volt, and therefore, considering only one determination was made, within the limits of error for the value for potassium chloride.

In dealing with an oil emulsion it was only after taking into account the slow change which occurs in the value of the P.D. when an emulsion containing electrolyte is allowed to remain, that a relationship was found between the P.D. and the stability. The coagulation of the colloid in the presence of 40 millimolar potassium chloride could not, however, be explained in this way, since in some cases the colloid had coagulated to a large extent before the determination was finished. In order to be certain, however, a determination was made with a mixture which had been kept six hours. By this time most of the arsenious sulphide had settled out, but sufficient of the finer particles remained suspended to make the division in the U-tube easily visible. The value obtained was 0.044 volt (first value 0.043, second 0.045), which agrees with the mean of the four determinations made soon after adding the potassium chloride. Consequently, if any change does occur on keeping, it is very slow, and would not explain the high value given for potassium chloride in table I.

The results, therefore, agree with the idea of a critical P.D. as determining the stability or instability of a colloidal solution in so far as barium chloride, aluminium chloride, and thorium nitrate are concerned, but the behaviour with potassium chloride suggests

that electrolytes also exert a kind of salting out effect, so that when an electrolyte is used which has only a weak influence on the P.D., and therefore a relatively high concentration is required for coagulation, this coagulation occurs when the P.D. has a value so high that without this superimposed salting out effect the mixture would be quite stable. Since such an effect was not observed in the author's experiments with an oil emulsion where the number of suspended particles per unit volume was very small compared with the number in the colloidal arsenious sulphide, and also does not appear to have occurred to any appreciable extent in Burton's determinations (*loc. cit.*, p. 734), it is perhaps only important when the concentration of the suspended particles is very large. Further experimental investigation is necessary, however, before definite conclusions can be drawn regarding the cause of the value found for potassium chloride being much higher than the values for the other three electrolytes, which agree closely with each other.

The fact that negative colloids coagulated by salts with a univalent cation pass into the colloidal form again on washing away the electrolyte much more readily than when salts with cations of higher valency are used, may be connected with the difference in the P.D. values found above for the two classes of electrolyte.

So far as the stability of a colloidal solution is determined by the P.D. having a value greater than a certain critical value, the lack of sharpness in the coagulation concentration will be due to the critical value being slightly different for particles of different size, Odén's results indicating that the smaller the particle of any one colloid the smaller the value of the critical P.D. In the oil emulsion the limits of size of the particles were only about 1 to 6.

According to the views advanced by the author (*Zeitsch. physikal. Chem.*, 1914, **89**, 91; T., 1915, **107**, 818), addition of sufficient thorium nitrate should cause the P.D. at the surface of the arsenious sulphide particles to become positive, and this was found to be so. For instance, in presence of a 0.5 millimolar solution the value was +0.03 volt. Although this exceeds (numerically) the value given above for the coagulation of the negative arsenious sulphide, namely, 0.026 volt, no range of concentration was found in which the arsenious sulphide was present as a stable positive colloid, even although the arsenious sulphide was added to the thorium nitrate solution. This was no doubt due to the particles adhering before the two solutions had time to mix sufficiently to give 0.5 millimolar thorium nitrate in contact with all the arsenious sulphide particles; in support of this it was observed that although most of the sulphide coagulated and settled almost immediately,

yet a small amount remained suspended, and the upper liquid did not clear anything like so rapidly as with a concentration of 0.1 millimol. per litre; moreover, this was more marked when the colloid was added to the electrolyte than when they were mixed in the opposite order. It is therefore probable that if the colloidal arsenious sulphide had been considerably diluted and slowly run into a flask containing the thorium nitrate, with constant shaking, instead of mixing in a test-tube, it would have been possible to convert it to a positive colloid without coagulation.

Appendix.

In calculating the P.D., the usual formula, $e = \frac{4\pi\eta\mu}{H.D.}$ was used (Freundlich, "Kapillarchemie," p. 229), D being taken as 81, and η as the viscosity of pure water at the temperature during the determination.

Each value given in the following table is calculated from the mean velocity of the dividing surface up one limb and down the other, the latter being generally slightly greater than the former. The current was then reversed, and a second value thus obtained.

TABLE II.

Electrolyte.	Concentration in millimols. per litre.	P.D.			Remarks.
		First value, volt.	Second value, volt.	Mean value, volt.	
Potassium chloride	40.0	0.054 0.054 0.046 0.045	0.037 0.036 0.041 0.041	0.044	With copper sulphate.
Barium chloride	0.5	0.0275 0.022	0.027 0.029	0.026	
Aluminium chloride	0.05	0.022 0.021	0.027 0.030	0.025	With thorium nitrate, after reversing the current the division going down the tube moved abnormally quickly; hence the high value for the second determination, which has been neglected in taking the mean.
Thorium nitrate	0.05	0.025 0.029	0.041 0.034	0.027	
	0.07	0.022 0.030		0.026	
	0.1	0.025 0.023	0.042	0.024	

Often the colloid had coagulated to a fair extent before the end of the measurements, but sufficient remained suspended to mark the division. The line of division did not always remain quite horizontal, and since the total distance traversed was usually only 0.4 cm., this may introduce an appreciable error. The results obtained are given in table II.

For the determinations with potassium chloride the U-tube was immersed in water. The rise in temperature during the determination was thus reduced to less than 2°. With the lower concentrations required for the other electrolytes the heating effect of the current was only small. In order to be certain that the higher values obtained with potassium chloride were not due to contamination of the liquid near the particles by the products of electrolysis, although the electrodes were 4 cm. away, a determination was made in which above the potassium chloride layer was one of copper sulphate-sulphuric acid solution of the same conductivity, copper electrodes being immersed in it (platinum ones being used for the other determinations), but as seen in the table the same value was obtained.

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