ADSORPTION BY PRECIPITATES IV

BY HARRY B. WEISER

"Acclimatization"

It is an interesting fact that the amount of electrolyte necessary to coagulate a colloid completely is influenced by the rate at which the electrolyte is added. Since a quantity that will cause complete coagulation when the addition is rapid will not cause complete coagulation when the addition is slow, the colloid is said to become "acclimatized" to the presence of electrolyte and the phenomenon is called "acclimatization."¹

Historical

Several cases of "acclimatization" of colloids are referred to in the literature. Freundlich² observed this phenomenon first with colloidal arsenious sulphide: "In the course of the precipitation experiments described above, it was observed accidentally that, among other things, the rate with which the salt solution was added to the colloid had considerable influence on the precipitation value. This led to the conclusion that the precipitation process is not static but involves the element of time. In view of the investigations of Nernst who showed, for example, that marked differences in potential arise by the diffusion of ions, one might expect that diminution of the surface, that is precipitation, could result from the same cause. To test these points a series of experiments was carried out.

"The first experiment was as follows: The amount of barium chloride solution containing 9.55 millimoles of BaCl_2 per liter, necessary to precipitate completely in two hours an arsenious sulphide colloid containing 5.752 millimoles of As_2S_3 per liter, was first determined according to the method previously described. The same amount of electrolyte, 2 cc, was next added dropwise to the same amount of colloid, 20 cc, in 18

¹ Taylor: *The Chemistry of Colloids*, 98, 310 (1915).

² *Zeit. phys. Chem.*, **44**, 143 (1903).

hours, 27 days and 45 days, respectively. After the addition of each drop the solution was shaken once. Two hours after the addition of the last drop the solutions were filtered and it was found that the filtrate was still quite cloudy—the cloudy solution being the one to which the electrolyte was added slowest. In order to precipitate the remainder of the first solution completely, 1.5 cc of the same barium chloride solution was added; and after two hours it was clear. Likewise to the remainder of the second solution was added 1 cc and to the third 2 cc of electrolyte. Complete precipitation was observed in the second after two days and in the third after two hours. Nearly the same amount was required as if no slow addition had been made.

“These observations cannot be explained by assuming that they arise from the distribution equilibrium of the ion or on equilibrium conditions generally, since these depend solely on the concentration and the latter is as great after rapid addition as after slow, considering that the flocks resulting gradually by slow addition adsorb only a very small amount. On the other hand a process like diffusion which requires time undergoes a real change according as the addition is rapid or dropwise. In the first case a large difference in concentration is produced which causes a marked diffusion; in the second case the difference in concentration is kept so small that only inappreciable diffusion processes can go on. The latter case cannot be realized entirely, since at the point at which the drop enters the solution appreciable concentration differences are always present.

“A second deduction tested was whether small additions of salt which produce practically no diffusion will cause a distinct action on the colloid in the course of a long time. For this purpose 100 cc portions of colloidal arsenious sulphide were placed in each of three Jena glass flasks which were closed carefully after first adding 100 cc of pure water or like volume of potassium chloride solutions of different concentrations. After 340 days all these solutions possessed the same reddish yellow color as the freshly prepared colloids.

and there had separated only a fine scum and a few flocks of arsenious sulphide. All these were filtered and the content again determined. The results are given in the following table:

	I	II	III
KCl millimoles per liter	0	1.219	2.438
As ₂ S ₃ millimoles per liter (original solution)	11.272	11.272	11.272
As ₂ S ₃ millimoles per liter (after 340 days)	9.570	9.603	9.453

"It is evident that the addition of 1.219 millimoles of potassium chloride per liter has practically no influence, while the addition of 2.438 millimoles per liter has a very slight influence. These numbers lose some of their value on account of the fact that only the smallest part of the decrease in As₂S₃ content can be attributed to coagulation, the greater part being due to the decomposition into H₃AsO₃ and H₂S. Still, I believe that a certain amount of importance can be attached to the above values since a solution which contained 3.9 millimoles of potassium chloride per liter under the same conditions was as good as completely coagulated in the same time; the supernatant liquid had a faint yellow color and therefore contained but an unweighable amount of As₂S₃."

Similar experiments were carried out by Freundlich¹ on colloidal hydrous ferric oxide: "To 20 cc of a colloid containing 20.45 millimoles of Fe(OH)₃ per liter was added 2 cc of magnesium sulphate solution containing 4.82 millimoles per liter. The addition was made dropwise in the course of eight days; after each addition the flask was shaken once. Although a salt solution of this concentration precipitated the colloid completely after two hours, by this slow addition the solution was not entirely clear two hours after the last drop was added; and the filtrate still contained ferric hydroxide. The addition of three drops more (0.13 cc) of magnesium sulphate solution was sufficient to coagulate the remainder within an hour."

¹ Zeit. phys. Chem., **44**, 151 (1903).

Observations similar to the above were made by Freundlich¹ with colloidal platinum and by Höber and Gordon² with albumin. A similar behavior which is known as the Danysz effect, is observed in the toxin-antitoxin reaction.³ Thus when a diphtheria toxin is treated with its antitoxin, the reduction in toxicity depends on the manner in which it is added, that is, an amount of antitoxin which is exactly sufficient to neutralize a given amount of toxin when added all at once is not nearly sufficient to neutralize the same amount of toxin when added little by little, with moderate intervals between each addition. This similarity between the Danysz effect and true colloidal precipitation suggests that certain toxins and antitoxins are colloidal in nature.

Theoretical

As pointed out in the preceding section Freundlich suggests that the so-called "acclimatization" phenomenon may be due to difference in diffusion through the electrical film or layer which protects the particles. He argues that if the amount necessary to cause precipitation is added all at once, there is such a marked change in concentration that a marked diffusion through the colloid-liquid interface takes place, whereas, if the electrolyte is added very slowly there is no marked change in concentration at any instant and so the diffusion is inappreciable. It would seem that this explanation does not account for the fact that an amount of electrolyte added all at once, which will cause complete precipitation in two hours, say, will not cause complete precipitation in two hours after the same concentration is reached by slow addition. Later in discussing the cause of this phenomenon, Freundlich⁴ suggests that the difference in the effect of rapid and slow addition of an electrolyte to a colloid is traceable to the difference in the disturbance produced in the solution.

¹ Zeit. phys. Chem., **44**, 153 (1903).

² Beitr. chem. Physiol. Path., **5**, 436 (1904).

³ See Taylor: The Chemistry of Colloids, 310 (1915).

⁴ Kapillarchemie, 348 (1910).

"The discharge of the colloidal particles and the asymmetry, 'the disturbance,' resulting therefrom, vary with the nature, rapidity, etc., of the electrolyte additions. Hence, it has been found to be extremely difficult to obtain the same precipitation value under apparently identical conditions. The matter of the small disturbances which carry the colloid through all possible degrees of stability by slow addition of electrolyte naturally does not have the same effect as the rapid discharge and the rapid exceeding of the threshold value and growth of flocks resulting therefrom."

Freundlich's suggestions can scarcely be regarded as an explanation of the effect on the precipitation value of the rate of addition of electrolyte. Since a colloid stabilized by preferential adsorption of ions of a given charge is coagulated completely only after neutralization of the particles by adsorption of an equivalent amount of ions of opposite charge, it would seem that the rate of addition must have an effect on the adsorption which in turn determines the precipitation value. Approaching the matter from this point of view, we arrive at an explanation that is capable of experimental verification:

In previous communications¹ it has been pointed out that the adsorption of equivalent amounts of all the precipitating ions will effect neutralization of the charge on the particles of a given amount of colloid providing the stabilizing influence of the added ion having the same charge as the colloid is kept constant. Since the adsorption of a given ion depends on the concentration, it is usually, if not always, necessary to add to the colloid more of the precipitating ion than would be necessary to effect neutralization if all were adsorbed. The excess is then adsorbed wholly or in part by the electrically neutral particles. The actual amount of an ion carried down by a precipitated colloid is therefore determined (a) by the adsorption of the electrically charged particles during neutralization and (b) by the adsorption of the electrically neutral particles during the process of agglomera-

¹ Weiser and Middleton: *Jour. Phys. Chem.*, **24**, 30, 630 (1920).

tion and settling. The amounts of (a) are equivalent, but the amounts of (b) which have been pretty generally overlooked, vary with the nature and concentration of the ion concerned. Viewing the matter in this way, the precipitation value obtained by adding the electrolyte all at once is such a concentration of precipitating ion that sufficient adsorption to cause neutralization can result in a definite time. If this amount of electrolyte is added very slowly, there results a gradual increase in the size of the particles due to partial neutralization by adsorption. After the addition of enough electrolyte, partial agglomeration takes place. These coagulated particles have adsorbed not only enough ions to effect their complete neutralization; but the neutralized particles have carried down an additional amount during agglomeration. This adsorption by electrically neutral particles during the fractional precipitation accompanying slow addition of electrolyte, causes such a decrease in the ionic concentration that a greater amount must be added to effect complete neutralization by this fractional process. Rapid addition furnishes all at once the critical concentration of precipitating ion necessary for neutralization by adsorption. To obtain the same results by the very slow process, more electrolyte must be added to compensate for the loss of precipitating ion adsorbed by the electrically neutral particles that separate gradually during the process.

As above described, Freundlich has shown that the stability of colloidal arsenious sulphide is affected but slightly by a concentration of ion far below the precipitation value. This is due to the fact that complete precipitation cannot take place below the concentration of ion necessary for complete neutralization by adsorption.

Experimental

The theory set down in the preceding section emphasizes the importance of adsorption during agglomeration for explaining the so-called "acclimatization" phenomenon. Before taking up the work on adsorption an account will be given of

some experiments carried out in order to become acquainted with the effect of rate of addition of electrolyte on the precipitation value.

Precipitation Experiments

Experiments with Hydrous Ferric Oxide.—Colloidal hydrous ferric oxide was prepared by the method described in detail in a recent communication.¹ The approximate precipitation value for potassium oxalate was determined by titrating 10 cc of the colloid with $N/50$ $K_2C_2O_4$, using a 2 cc Ostwald pipette calibrated in tenths of a cubic centimeter. Knowing the approximate precipitation value, a series of experiments was carried out in which measured amounts of electrolyte were added all at once to 20 cc of colloid, employing a slightly modified form of the mixing apparatus which was found so useful in previous investigations.² The precipitation value on slow addition was determined as follows: Twenty cubic centimeters of colloid were measured into a pyrex flask supplied with a rubber stopper. This stopper contained a 2 cc Ostwald pipette to the upper end of which was sealed a stopcock for convenience in retaining the solution in the small pipette and in making the small additions of electrolyte. The latter was added in 0.1 cc portions every hour for 10 hours, after which the solution was allowed to stand over night and the additions completed the next day. After each addition the flask was shaken once to ensure mixing. Approximately 30 hours elapsed between the addition of the first portion of the electrolyte and the conclusion of the experiment. The results confirm those of Freundlich. Whereas 1.8 cc of $N/50$ $K_2C_2O_4$ was sufficient to cause complete precipitation in 1 hour when added all at once, the precipitation was not complete one hour after the addition of the same amount of electrolyte by the slow method. By adding 0.1 cc more and allowing the solution to stand for an hour, a filtrate free from colloidal oxide was obtained. Three parallel experiments gave the same results.

¹ Weiser: Jour. Phys. Chem., **24**, 277 (1920).

² Weiser and Middleton: Loc. cit.

In connection with these experiments it was of interest to note that no precipitation of the colloid took place until very near the precipitation value. In other words, the precipitation value was fairly sharp even when thirty hours was taken for the addition of electrolyte. Since but few ions were removed by adsorption by neutralized particles until very near the precipitation concentration, one should expect but little variation in precipitation with rate of addition of electrolyte. This view is confirmed by our own experiments and those of Freundlich.

Experiments with Colloidal Arsenious Sulphide.—Colloidal arsenious sulphide was prepared by the method of Linder and Picton,¹ which consists essentially of passing hydrogen sulphide into a dilute solution of arsenious sulphide until no further action takes place, removing the excess hydrogen sulphide with a current of hydrogen. The experiments described above were repeated with this colloid. In order to determine when coagulation was complete the solution after filtration, was examined in small Nessler tubes. Even a trace of colloidal sulphide was detectible in this way. Precipitation values were determined for strontium chloride and potassium chloride. On rapid addition, 2.05 cc of $N/50$ strontium chloride and 2.50 cc of $N/2$ potassium chloride were necessary to precipitate completely 20 cc of colloid. The slow addition of the electrolyte in 0.1 cc portions over a period of approximately 36 hours required 2.50 cc of strontium chloride and 2.70 cc of potassium chloride solutions.

Unlike colloidal hydrous ferric oxide, colloidal arsenious sulphide started to precipitate after the addition of a few tenths of a cubic centimeter of electrolyte and the fractional precipitation continued until coagulation was complete. These are the exact conditions which would tend to make a distinct difference between the precipitation values on rapid and slow addition. The results show this to be the case. The variations are not so marked as observed by Freundlich, but it is not known what procedure was followed by Freundlich to

¹ Jour. Chem. Soc., 61, 137 (1892).

determine just how much electrolyte must be added all at once after the initial titration in order to obtain complete coagulation. A source of error suggests itself: Freundlich may have used an old colloid, and it is well known that colloidal As_2S_3 decomposes on standing to give arsenious acid and hydrogen sulphide. Barium ions added very slowly to such a solution would be removed in part as insoluble barium arsenite before the concentration was sufficiently high for marked adsorption by the colloid.

Experiments on Adsorption

As I have pointed out, it is usually considered that equivalent amounts of various ions are adsorbed by a precipitated colloid at the precipitation concentration. This conclusion is deduced from the fact that the adsorption of equivalent amounts of various ions will produce neutralization; but fails to take into account the adsorption of the neutralized particles during agglomeration. In order to get some idea of the magnitude of the adsorption of neutralized particles a series of experiments was carried out in which the adsorption of various ions by precipitated hydrous ferric oxide was determined at and above the precipitation concentration. The colloid employed contained 1.824 grams of Fe_2O_3 per liter. The method of procedure was as follows: The precipitation value of the ion under consideration was first determined in the usual way, after which a quantity of electrolyte of known concentration was added all at once to 125 cc of colloid contained in a 200 cc wide-mouth bottle. The solution was allowed to stand for an hour after which it was centrifuged for 20 minutes at 3000 r. p. m. By this process the precipitated oxide was matted firmly in the bottom of the container so that the supernatant liquid could be removed quantitatively and the vessel thoroughly rinsed. It was intended to wash the precipitate by shaking with distilled water and repeating the centrifuging as was done in previous experiments.¹ This was found to be impossible even with divalent ions since at

¹ Weiser and Middleton: Loc. cit.

concentrations so near the precipitation value, immediate washing resulted in slight peptization. However, since the solutions were quite dilute, the amounts remaining in the small space occupied by the precipitated oxide were very slight. Moreover, absolute adsorption values were not necessary, so that the washing could be dispensed with. The supernatant liquid was analyzed and the amount adsorbed was determined by difference. Experiments of this character were carried out with the potassium salts of oxalic, chromic and dichromic acids.

Adsorption of Oxalate Ion

Method of Analysis.—A solution of $N/50$ potassium oxalate was prepared in the usual way by direct weighing. This was used for standardizing a solution of potassium permanganate of similar concentration, which was subsequently employed to analyze for oxalate in the supernatant solution after precipitation. This standardization was effected in a volume of 150 cc in the presence of a constant amount of sulphuric acid and at a temperature of 70° . The analysis showed that 0.935 cc of permanganate was equivalent to 1 cc of oxalate.

Determination of Adsorption.—It was found that 8.25 cc of $N/50$ $K_2C_2O_4$ was necessary to precipitate completely 125 cc of colloid. The adsorption was determined at this concentration and at higher concentrations as shown in Table I. The final titrations were made with a 2 cc burette prepared from an Ostwald pipette. In the curve shown in Fig. 1 the amount adsorbed (in milliequivalents per gram of Fe_2O_3) is plotted against the concentration of electrolyte (in milliequivalents per liter) from which the precipitate separates.

The determination of adsorption with 15 cc of oxalate was repeated in the usual way except that the precipitate was washed once by shaking with 50 cc of distilled water followed by centrifuging for 10 minutes. The amount adsorbed was 12.24 cc as compared with 12.3 cc without the washing. This shows not only that the oxalate ion is strongly adsorbed but that little solution remains in the space occupied by the oxide after prolonged centrifuging.

TABLE I
Adsorption of Oxalate Ion

KMnO ₄ to oxidize unadsorbed K ₂ C ₂ O ₄ cc			N/50 potassium oxalate cc			Concentra- of electro- lyte (milli- equivalents per liter)	Amount ad- sorbed (milli- equivalents per gram Fe ₂ O ₃)
I	II	Av.	Taken	Re- maining	Ad- sorbed		
0.27	0.25	0.260	8.25	0.28	7.97	1.238*	0.7000
0.26	0.26	0.260	8.75	0.28	8.47	1.308	0.7430
0.30	0.27	0.285	9.25	0.30	8.95	1.378	0.7807
0.35	0.30	0.325	9.75	0.34	9.41	1.447	0.8254
0.45	0.47	0.465	10.75	0.50	10.25	1.584	0.9000
0.84	0.87	0.855	12.00	0.84	11.08	1.752	0.9720
1.70	1.68	1.690	13.50	1.80	11.70	1.949	1.0263
2.50	2.54	2.520	15.00	2.70	12.30	2.144	1.0790

* Precipitation concentration.

Adsorption of Chromate Ion

Method of Analysis.—A solution of sodium chromate N/50 with respect to chromate ion was prepared using the volumetric method of Seubert and Hinke¹ to make the analyses. The method of procedure was identical with that described in detail in earlier investigations.² It consists essentially in liberating iodine from potassium iodide by the action of chromate in acid solution—the liberated iodine being titrated with standard thiosulphate. A fiftieth molar solution of thiosulphate solution was employed. The standard solutions bore the following relationship to each other: 2 cc K₂CrO₄ = 3 cc Na₂S₂O₃.

Adsorption of Chromate Ion.—It was found that 9.50 cc of the chromate solution would just precipitate 125 cc of the colloidal oxide. Adsorption experiments were carried out at this and greater concentrations. A 10 cc burette was used in making the final titrations. The results are given in Table II and plotted in Fig. 1.

¹ Zeit. anorg. Chem., **14**, 1147 (1902).

² Weiser and Middleton: Jour Phys. Chem., **24**, 57, 645 (1920).

Fig. 1

The adsorption in the presence of 15 cc of chromate determined, washing the precipitate before making

TABLE II
Adsorption of Chromate Ion

N/50 Na ₂ S ₂ O ₃ required cc	N/50 potassium chromate cc			Concentration of electrolyte (milliequiva- lents per liter)	An sorl equi gra
	Taken	Remain- ing	Absorbed		
1.43	9.50	0.95	8.55	1.413*	(
1.53	10.00	1.03	8.97	1.474	(
2.28	11.00	1.52	9.48	1.618	(
3.20	12.00	2.13	9.87	1.752	(
4.16	13.00	2.77	10.23	1.885	(
5.12	14.00	3.41	10.59	2.015	(
6.15	15.00	4.10	10.90	2.144	(

* Precipitation value.

analysis. The adsorption was slightly less, 10.70 cc compared with 10.90 cc, the value obtained without wash

Adsorption of Dichromate Ion

Method of Analysis.—A solution of sodium dichromate N/50 with respect to dichromate ion was prepared by the same method of analysis as with chromate. In this $K_2Cr_2O_7$ is equivalent to 3 cc of $Na_2S_2O_3$.

Determination of Adsorption.—6.50 cc of N/50 dichromate was required to precipitate 125 cc of colloid. The ac

at this and higher concentrations was determined in the usual way. The results are given in Table III and plotted in Fig. 1.

TABLE III
Adsorption of Dichromate Ion

<i>N</i> /50 $\text{Na}_2\text{S}_2\text{O}_8$ required cc	<i>N</i> /50 potassium dichromate cc			Concentration of electrolyte (milliequiva- lents per liter)	Amount ad- sorbed (milli- equivalents per gram Fe_2O_3)
	Taken	Remain- ing	Adsorbed		
3.18	6.50	1.06	5.44	0.990*	0.3778
4.00	7.00	1.33	5.67	1.061	0.3938
6.10	8.00	2.03	5.97	1.203	0.4146
8.38	9.00	2.79	6.21	1.343	0.4313
10.80	10.00	3.60	6.40	1.474	0.4444
23.70	15.00	7.90	7.10	2.144	0.4930

* Precipitation value.

The adsorption was determined in the presence of 15 cc of electrolyte, washing the precipitate before the final analysis. 6.10 cc was adsorbed as compared with 7.10 when the precipitate was not washed. The ion was adsorbed less strongly than oxalate and chromate and more was removed from the precipitate by washing.

Discussion of Results

The results of the experiments above described emphasize the importance of adsorption by the neutralized particles in determining the amount of electrolyte carried down by a precipitated colloid. Take the case of oxalate ion: The addition of 8.25 cc of *N*/50 potassium oxalate was just sufficient to cause coagulation of 125 cc of colloidal ferric oxide within an hour. Of this amount of electrolyte, but 0.3 cc was not adsorbed. When 8.75, 9.25 and 9.75 cc, respectively, were added to the colloid, the same amount, 0.3 cc, remained unadsorbed. On gradually increasing the concentration of electrolyte, the amount unadsorbed increased; but this was less than 1 cc even when 12 cc of electrolyte were added. In the presence of 15 cc, 1.5 times as much electrolyte was carried down as at the precipitation concentration and the adsorp-

tion was so strong that but a trace of the 12.5 cc was removed by washing. Moreover, the adsorption had not reached saturation value as is evident from the adsorption isotherm in Fig 1. The experiments with chromate and dichromate ions gave similar results. The increasing amount of electrolyte adsorbed above the precipitation concentration was all due to adsorption by the electrically neutral particles; and it is altogether likely that a large part of the electrolyte carried down at the precipitation value was adsorbed during agglomeration. It is obviously incorrect to assume as Freundlich does that equivalent amounts are adsorbed at the precipitation concentration, since this would mean either that the neutralized particles do not act as an adsorbent or adsorb all ions to the same extent. On account of adsorption during agglomeration it has been deduced¹ that equivalent amounts of various ions should not be carried down at the precipitation concentration on account of the variability of the latter and consequent variability in the degree of saturation of the adsorbent by the adsorbed phase. The experimental results already described confirm this conclusion. Instead of having equivalent amounts adsorbed at the precipitation value of oxalate, dichromate and chromate ions, the adsorption is in the ratio 7.97:5.44:8.55.

Further consideration of the results disclose that the ion which has the highest precipitation value is adsorbed most at this concentration whereas one should expect the ion which precipitates in highest concentration to be adsorbed least. This behavior is readily understood when we consider that the adsorption of neutral particles during agglomeration was so great that but little of the electrolytes remained unadsorbed at their precipitation value. Obviously, under these conditions the electrolyte with the greatest precipitation value will be adsorbed the most at this concentration—again emphasizing the impossibility of obtaining comparable adsorption values in the immediate region of the precipitation value.

¹ Weiser and Middleton: *Loc. cit.*

² Weiser and Middleton: *Jour. Phys. Chem.*, **24**, 43 (1920).

Since the adsorption by neutralized colloidal particles during agglomeration is not negligible in any case and may rise to large proportions, we have the experimental evidence for the theory outlined to account for the so-called "acclimatization" phenomenon. From this point of view the term is a misnomer since the colloid does not become acclimatized to the presence of electrolyte in the ordinary sense. The necessity for using more electrolyte to effect complete precipitation on slow addition arises not from the adaptability of the colloid to the presence of electrolyte but from the fact that the fractional precipitation during slow addition continually removes ions owing to adsorption by neutralized particles; and this loss must be compensated for. The factors which determine the excess required for a given slow rate of addition are (1) the extent to which the colloid undergoes fractional precipitation, (2) the adsorbing power of the precipitated colloid and, (3) the adsorbability of the precipitating ion.

Summary

The results of this investigation may be summarized briefly as follows:

(1) The amount of electrolyte required to coagulate a colloid is influenced by the rate of addition. Since a quantity of electrolyte that will cause complete coagulation when the addition is rapid will not cause complete coagulation when the addition is slow, the colloid is said to become acclimatized and the phenomenon is called "acclimatization." The term is a misnomer since the colloid does not become "acclimatized" to the presence of electrolyte in the ordinary sense.

(2) The amount of precipitating ion carried down by a colloid is determined by (a) the adsorption of the electrically charged particles during neutralization and (b) the adsorption of the electrically neutral particles during agglomeration.

(3) The adsorption of oxalate, chromate and dichromate ions by colloidal hydrous ferric oxide has been determined at the precipitation value and at several concentrations above the precipitation value of the respective ions. The results em-

phasize the importance of adsorption by neutralized particles in determining the amount of electrolyte carried down by the precipitated colloid.

(4) The dropwise addition of an electrolyte to a colloid throughout a prolonged period is accompanied by fractional precipitation of the colloid. For a given rate of addition the extent of this fractional precipitation depends on the nature of the colloid and the precipitating ion.

(5) The precipitation value is such a concentration of precipitating ion added all at once that sufficient adsorption to cause neutralization of the colloidal particles can take place promptly. The necessity for using more electrolyte to effect complete precipitation on slow addition arises not from the adaptability of the colloid to the presence of electrolyte but from the fact that the fractional precipitation during slow addition continually removes ions owing to adsorption on the neutralized particles during agglomeration; and this loss must be compensated for.

(6) The factors which determine the excess electrolyte required for a given slow rate of addition are, (a) the extent to which the colloid undergoes fractional precipitation, (b) the adsorbing power of the precipitated colloid and, (c) the adsorbability of the precipitating ion.

(7) The amounts adsorbed at the precipitation concentration of the various ions are not equivalent as Freundlich assumes. Adsorption of equivalent amounts effect neutralization of the charged particles; but adsorption during agglomeration varies with the concentration and adsorbability of the ion. Comparable adsorption values cannot be obtained for the precipitation concentration on account of the variability of the latter.

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