

THE THEORY OF PEPTIZATION

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Peptization consists in the disintegration of particles so that they form a colloidal solution. We get a permanent colloidal solution¹ whenever the particles are small enough to be kept in suspension by the Brownian movements and in some way are prevented from coalescing. Freundlich² has postulated that all adsorption is accompanied by a lowering of the surface tension of the adsorbing phase. The theoretical deduction is unsound because the Gibbs theorem applies explicitly to true solutions and not to suspensions. On the other hand, Freundlich's assumption seems to be true experimentally in all the cases which have been studied from this point of view. If we accept Freundlich's generalization as true empirically, a theory of peptization follows at once. Any substance which is adsorbed by a second will lower the surface tension of the second substance and will therefore tend to disintegrate it, in other words, to peptize it.³ If every adsorbed substance tends to peptize the adsorbing substance, we may expect to get peptization by a solvent; peptization by a dissolved non-electrolyte; peptization by an ion; peptization by a salt; peptization by a colloid. I shall take up these cases in detail.

Since glass adsorbs water, water should tend to peptize glass. At ordinary temperatures, the adsorbed surface film of water is not able to disintegrate the glass; but we get a very different state of things at higher temperatures where the cohesion of the glass is less.⁴ Barus⁵ found that when a

¹ Bancroft: *Jour. Phys. Chem.*, **18**, 552 (1914).

² *Kapillarchemie*, **52**, 154 (1909); Patrick: *Zeit. phys. Chem.*, **86**, 545 (1914).

³ I have used the word "peptonize" previously, but Graham coined the word "peptize," *Jour. Chem. Soc.*, **17**, 325 (1864), and it seems better to use that word since peptonize is used in a different sense by the biological chemists.

⁴ At higher temperatures the adsorption is less; but this is often more than counterbalanced by the decreased cohesion of the substance to be peptized.

⁵ *Am. Jour. Sci.*, (3) **41**, 110 (1891); (4) **6**, 270 (1898); **7**, 1 (1899); *Phil. Mag.*, (5) **47**, 104, 461 (1899).

thread of water in a capillary tube is heated to 185° , the thread of water becomes white and milky though translucent, and changes finally into semi-solid siliceous water. He was able to impregnate glass with water to such an extent that it was fusible below 200° . He concludes that glass as a colloid is miscible in all proportions with water. "On cooling, bubbles appear in the clear water-glass in great number, showing it to contract on solidifying from the center outward (centrifugally) like a Prince Rupert drop. The solid water-glass is in appearance as hard and brittle as ordinary glass, from which it differs in refraction and density * * * Made in quantities in a large digester, water-glass¹ is obtained as a nearly homogeneous compact body, adhering forcibly to the walls of the retort, from which it must be removed with wedge and hammer. A small lump held above a candle flame soon fuses with loss of water to a milk-white pumice. Left without interference in the cold for several weeks or months, it spontaneously cracks and crumbles, eventually becoming a loose mass breakable in the fingers, while the original lump could be broken only with a hammer. Water is set free, probably under great pressure, and hence the gradual crumbling of the mass. When compared with the disintegration of minerals, we have here an example of an enormously rapid chemical reaction in solids."

In another paper Barus² applied the same principle to the peptization of vulcanized rubber. "In my work on the solubility of glass in water, I showed that in proportion as the state of dissociation or the molecular instability of glass is increased with rise of temperature, the solvent action of water increases at an enormously rapid rate; that inasmuch as the solution takes place between a solid and a liquid, sufficient pressure must be applied to keep the fluid in the liquid state, whenever the vapor tension at the temperature in question exceeds the atmospheric pressure. Thus, at 100° , the action

¹ [Barus uses this term to mean glass impregnated with water and not to mean a solution of sodium silicate.]

² *Am. Jour. Sci.*, (3) **42**, 359 (1891).

of liquid water on glass is nearly negligible; but even at 185° solution occurs at so rapid a rate that capillary tubes may become filled with solid hydrated silicate in place of water, in an hour. Here, however, about 10 atm. must be applied to keep the solvent in the liquid state essential to speedy reaction.

"Having attempted to apply the same principle to the actual solution of vulcanized India rubber, I obtained confirmatory results at once. To my knowledge this material has not heretofore been advantageously dissolved in a volatile reagent, or in any reagent by which it is speedily and copiously taken into solution, and from which it may be conveniently obtained."

Barus worked with five samples of rubber of the following character:

a. Very elastic sheet rubber, usually not pigmented, translucent in thin films, brownish in color, used for rubber bands and sheeting, chemical rubber, tubing, etc.

b. Less elastic and harder rubber, pigmented gray, opaque, largely used for rubber tubing, etc.

c. Non-elastic, pigmented rubber, flexible, opaque gray, used for low class rubber tubing and low class merchandise in general.

d. Ebonite.

e. Same as *a*, rotted by age and exposure.

"From experiments made at 100° and 160° , it appears that elastic sheet rubber (*a*) is not fully soluble in CS_2 in a reasonable time, if at all. It is quite soluble at 185° , and soluble to a remarkable degree and at a remarkable rate at 210° . Hence the pressure under which solution is to take place, should here be greater than 15 atm., but need not exceed 30 or 40 atm. Inasmuch as CS_2 thus unites with rubber in any proportions, clear brown solutions of any viscosity may be obtained. Diluting such (thick) solutions with cold CS_2 , the solvent is first greedily absorbed; but the final solution of the unagitated syrupy rubber takes place very slowly. Finally, by exposing any of the solutions to

air, the CS_2 evaporates, and the dissolved vulcanized rubber is regained without sacrifice of its original non-viscid quality. Similarly, fissured brittle sheet rubber or tubing (*e*) which has become useless for practical purposes by age, is quite soluble in CS_2 at 200° , so far at least as its undecomposed portion is concerned. Elastic gray rubber (*b*) dissolves completely to a gray liquid, in which the pigment is suspended. The concentrated solution hardens at once on exposure to air, reproducing a rubber of nearly the qualities (*b*). The same is true of the non-elastic sample (*c*). Treatment at 310° resulted in a decomposition of the rubber.

"Commercial ebonite (*d*) is first partially devulcanized at 200° (excess of rubber) and eventually dissolved in excess of solvent. The partially devulcanized product is elastic on drying, but finally hardens to a tough solid having a leathery quality. The solution leaves a black stain, with free sulphur apparent after evaporation. Gases are frequently evolved during solution of highly vulcanized rubber in CS_2 . As a whole my experiments show that excess of sulphur is first removed by the solvent, after which the vulcanized rubber itself passed into solution.

"The elastic rubbers (*a* and *e*) dissolve easily in liquid mineral oils at 200° . The pressure necessarily will, of course, vary with the boiling point of the oil used, and may be as high as 50 atm. in the very volatile gasolenes. Commercial gasolene, though a good solvent of the rubbers *a* and *e*, is less powerful in case of *b* and *c*, unless excess of solvent be used. On exposure to air, the gasolene evaporated, leaving a residue which soon hardens. Mineral oils of a higher carbon order than gasolene, petroleum for instance, dissolves the rubbers *a* and *e* even more easily. The solution, however, dries only after much time and probably only in thin films. Solubility seems to increase as the oil lies higher in the carbon series. . . .

"Elastic sheet rubber (*a*) dissolves at once in liquid CHCl_3 at 210° . Pressure should exceed 15 atm. and need not be larger than 25 or 30 atm. Solutions of any degree of viscosity seem to be obtainable. They dry at once on ex-

posure to air, leaving a hard residue relatively dark in color. Possibly this was due to the presence of sulphur in the chloroform. Gray rubber (*b*) is attacked with decomposition of the solvent and evolution of gas. The elastic sheet rubber (*a*) dissolves at once in liquid C_6H_6 at 200° . Pressure should exceed 7 atmospheres, but need never be higher than 30 atm. The solution exposed to air hardens rapidly. Solution of gray rubber (*b*) is less easy. Solution of elastic rubber (*a*) in liquid toluol at 200° also takes place with great ease. The liquid dries slowly. Pressures of less than 10 atm. suffice At 200° India rubber (*a*) is not dissolved in liquid methyl or in liquid ethyl alcohol, and only slightly so in liquid amyl alcohol In no case was there a trace of true solution at 210° [in water or mineral acids]. Water probably enters the physical pores of the elastic rubber (*a*), as this substance becomes superficially rough and warty on drying in steam at 200° , after being treated with liquid water at the same temperature. . . .

“Very interesting is the direct vulcanization of a rubber solution to liquid ebonite, by aid of a solution of sulphur. In case of elastic sheet rubber (*a*), this even begins at 160° ; but it is more complete at 185° and 210° . In case of pure (non-vulcanized) rubber dissolved in CS_2 with excess of sulphur, scarcely any change of the flesh color is observed at 160° , and the sulphur crystallizes out of the solvent in needles, on exposure. At 185° and 210° , however, the charge turns black, showing complete vulcanization. If equal masses of vulcanized rubber (*a*) and sulphur be treated, the product, after heating to 210° , is not dissolved nor soluble, until the excess of sulphur is removed. Gas is often evolved. In proportion as less sulphur is used relatively to the rubber, the product becomes more immediately soluble and less gas is evolved. Adding about 20 percent of dissolved sulphur to the elastic rubber (*a*), I obtained serviceable solutions of ebonite, on treating at 200° either in CS_2 alone, or in mixtures of this liquid with gasoline, benzol, etc. In most cases these harden very quickly to a jet-black enamel. With less sulphur the color is brown in thin films. . . .

"If vulcanized India rubber be impregnated or saturated by digesting it with the cold reagent (any solvent of pure rubber) for a suitable time (a few minutes to many hours), the swelled mass not only shows a relatively low melting point, but it remains liquid after cooling, provided the solvent is not allowed to escape. This is an observation of practical importance, since the retorts¹ can thus be charged with solid or dry rubber, a minimum of solvent be used in treating or lost by evaporation, and concentrated solutions be obtained often fit to be used at once. Finally the pressure necessary in this case is the smallest possible,² and may be below the data given for the divers solvents above.

"The quantity of solvent retained by solid rubber is very large: Thus elastic sheet rubber will hold 7 or 8 times its weight of CS_2 , or 1 to 2 times its weight of naphtha. Gray rubber (elastic) absorbs more than its weight of naphtha; etc. Experiments may be cited as follows: non-impregnated vulcanized rubbers (*a* to *e*) do not melt if exposed in a closed tube at 210° . Only in the case of very slightly vulcanized pure rubber gum is there a trace of fusion perceptible at the edges, and here it may even be due to a stain of dirt (oil) accidentally left there. Gray rubbers (*b*, *c*) with a superficial coating of exuded sulphur, turn black from the formation of a film of ebonite.

"All the India rubbers (*a* to *e*) fuse at 210° , when previously saturated, or nearly so, with cold carbon disulphide, and exposed in a close-fitting glass tube. If the pressure be reduced by a capillary aperture at one end of the otherwise closed glass tube, or if the tube be only partially filled and the empty end kept cool, the impregnating solvent is merely distilled off, and no fusion takes place. Whereas at 160° fusion scarcely occurs, melting seems to be complete in the well-impregnated elastic rubber (*a*) at 175° . There is there-

¹ The present experiments were made in *closed* glass tubes nearly filled with the impregnated rubber. After fusion the mass frequently appeared to have shrunk.

² [This is true only in case a real solution is formed. W. D. B.]

fore an approximate coincidence of the thermal data in the present and in the above paragraphs.

"Similar results were obtained with benzol, with gasolene and higher petroleum oils, etc. Fusion is absent or only incipient at 160° , and more than complete at 210° , provided the gasolene be not too volatile. In general the gray rubbers (*b*, *c*) fuse to a more viscous mass than the gum rubbers (*a*); the consistency of cold solutions in the latter case is about that of treacle.

"The occurrences of this paragraph therefore would resemble the fusion of a salt in its water of crystallization, but for the exceptional behavior that impregnated vulcanized rubber after fusion retains a consistency which is liquid relatively to the original non-impregnated charge. The analogy with the solution of starch, or of gluten, is thus more close and immediate. In all these cases the solid swells up when impregnated with the solvent, and fuses to a relatively less viscous consistency, or to a thin solution, when a certain temperature (below 100° in the case of starch and gluten and above 160° in case of vulcanized rubber) has been reached. Hence it is not unreasonable to suspect that even ordinary dry wood, or woody tissue, which swells to a marked degree when impregnated with water, may pass into actual solution if the temperature at which the water acts is sufficiently high, and the pressure above the vapor tension of water at that temperature.¹

"I mention finally that the reduction of melting point produced in vulcanized India rubber by the impregnating reagents may perhaps advantageously be discussed in accor-

¹ I have since tested this surmise at some length, but found in every case that cellulose is decomposed before solution in water takes place. In spite of the presence of water under pressure, the phenomenon seems to be a dry distillation. I may here refer to the remarkably close analogies in the thermal behavior of rubber and gelatine which have recently been discovered by Bjerken: *Wied. Ann.*, **43**, 817 (1891). The author has reason to believe that moist gelatines are heterogeneous mixtures of solid and liquid. The behavior of rubber, as discussed above, is characterized at low temperatures by a fixed maximum of absorbed solvent. The term mixture is scarcely applicable at once.

dance with Raoult's law; but owing to the difficulty of defining the melting point of the unimpregnated rubber, and the close proximity of the melting points after impregnation with different reagents (CS_2 , C_6H_6 , gasolene) my views on this subject have not taken shape. It is known that in general the melting point produced by a dissolved colloid is relatively very small, from which an exceedingly large molecular weight of the colloid has been inferred. The above results show that, in the converse experiment, where the melting point of the colloid is lowered by a solvent, the effects will probably be normal and pronounced.¹

"Nevertheless I doubt whether the thin rubber fluids obtained are true solutions, *i. e.*, represent a case in which the division of the solid has actually reached a definite molecule; for on long standing in sealed vessels a gradual thickening of the liquid with final coagulation seems to be the invariable result. Thus there must be a gradual growing together of the individual particles, until finally the whole solution forms one coherent gelatinous mass.

"To summarize: Suppose the coherence of rubber to be due to (cohesive) affinities, capable of being saturated like ordinary affinities. Then in case of impregnation with a solvent, a part of these combine with the similar affinities of the solvent. The result is the decided decrease of tenacity (observed). To liquefy the impregnated sample, the residual cohesive forces of the rubber must be withdrawn, and this can be done by heat. The liquid so obtained I do not conceive to be a true solution, but rather a suspension of particles, the exceeding fineness of which is determined by conditions discussed elsewhere.² Diffusion is thus an excessively slow process, and hence the liquid on cooling need not become solid again. In proportion as the individual particles unite however, coagulation gradually sets in, and its structure is probably that of a fine sponge holding solvent in its inter-

¹ [The error is in assuming that the rubber has fused; it has only been peptized. W. D. B.]

² Barus: *Am. Jour. Sci.*, (3) **37**, 126 (1889).

stances. If the coagulated solution be reheated (under pressure), a thin viscid solution is again obtained, which in its turn coagulates."

With glass and water a temperature of at least 185° was necessary to cause peptization; with rubber and many organic liquids peptization becomes marked at 160° . Denaeyer¹ claims to have peptized coagulated albumin by heating it in water under pressure of one atmosphere. When silica is ground very fine, it is peptized by boiling water.² Water peptizes gelatine at about 30° and tannin instantaneously at ordinary temperatures. Pyroxylin is peptized by amyl acetate at ordinary temperatures. When a substance is peptized by water at moderate temperatures we call it a water-soluble colloid; but the phenomenon is general. Any substance which adsorbs a liquid will be peptized by that liquid at some temperature, provided decomposition does not take place before that temperature is reached. In the case of water and cellulose, it is not certain to what extent peptization takes place³ before decomposition takes place. The metallic fogs⁴ are apparently cases of peptization of liquid metals by melts at comparatively high temperatures.

Relatively little work has been done on direct peptization by means of a non-electrolyte; but a good deal of stress has been laid on the cases where a non-electrolyte prevents the formation of a visible precipitate. In all these cases the non-electrolyte would cause peptization under favorable conditions, so I am going to take up a few of the cases here.

Graham⁵ studied what he called the sucrate of copper. "The deep blue liquid obtained by adding potash to a mixed solution of chloride of copper and sugar appears to contain a colloidal substance. Placed on a dialyser for four days, the blue liquid became green, and no longer contained either

¹ Jour. Chem. Soc., 60, 1269 (1891).

² Desch: The Chemistry and Testing of Cement, 58 (1911).

³ Schwalbe: Die Chemie der Cellulose, 23 (1911).

⁴ Lorenz: Gedenkboek aan van Bemmelen, 395.

⁵ Jour. Chem. Soc., 15, 253 (1862).

potassium or chlorine; it, in fact, consisted of oxide of copper united with twice its weight of sugar. The external liquid remained colorless and gave no indication of copper when tested with sulphuretted hydrogen. The colloidal solution of sucrate of copper was sensitive in the extreme to pectizing agents. Salts and acids generally gave a bluish green precipitate; even acetic acid had that effect. The precipitate, or pectous sucrate after being well washed, consisted of copper oxide with about half its weight of sugar, and is therefore a subsucrate. When the green liquid is heated strongly, it gives a bluish green precipitate, and does not allow the copper to be readily reduced to the state of suboxide. The subsucrate of copper possesses considerable vivacity of color, and might be used as a pigment. A solution of sucrate of copper absorbs carbonic acid from the air with great avidity. The sucrate of copper dries up into transparent films of an emerald-green color. These films are not altered in appearance or dissolved in cold or boiling alcohol. In water they are resolved into sugar and the pectous subsucrate of copper.

"The perchloride of iron with an addition of sugar is not precipitated by potash, provided the temperature is not allowed to rise. The peroxide of iron combined with the sugar is colloidal, and remains on the dialyser without loss. At a certain stage, however, the sugar appears to leave the peroxide of iron, and a gelatinous subsucrate of iron pectizes. The subsucrate of iron thrown down from the soluble sucrate by the addition of sulphate of potash, consisted of about 22 parts of sugar to 78 parts of peroxide of iron.

"A similar solution may be obtained by adding potash to a mixture of the nitrate or chloride of uranium with sugar, avoiding heat. The solution is of a deep orange-yellow color, and on the dialyser soon loses the whole of its acid and alkali. This fluid sucrate has considerable stability, but, like the sucrate of copper, is readily pectized by salts. The subsucrate pectized has considerable solubility in pure water.

"The well-known solution of lime in sugar forms a solid coagulum when heated. It is probably, at a high tempera-

ture, entirely colloidal. The solution obtained on cooling passes through the septum, but requires a much longer time than a true crystalloid like the chloride of calcium."

Riffard¹ has based a method of analysis of sugar on the fact that sugar prevents the precipitation of hydrous ferric oxide from ferric chloride solution by ammonia. A weak point in the method is that invert sugar is about seven times as effective as cane sugar in holding up the hydrous ferric oxide. Grimaux² showed that glycerine prevents the precipitation of hydrous ferric oxide by caustic potash. Weisberg³ found that calcium silicate appears to dissolve in a sugar solution. What really happens is that it is peptized by a sugar solution. Lobry de Bruyn⁴ has prepared colloidal solutions of silver chromate and silver chloride in presence of sugar.

Peptization by a non-electrolyte is a familiar phenomenon in the pyroxylin industry, though even here the data are not in any way complete. Benzene, toluene, xylene, the petroleum naphthas, and the alcohols do not peptize cellulose nitrates. One may get peptization, however, by adding a liquid which does peptize pyroxylin. More interesting, however, is the case of alcohol and ether, neither of which peptizes collodion, while a mixture of the two does. Worden⁵ says that "the literature contains many statements of the solubility of cellulose nitrates in ether, but the author has never been able to dissolve a pyroxylin in ether free from alcohol. The lower nitrated celluloses gelatinize, but attempts to filter such a gelatinized mass does not give a filtrate with a nitrogen-containing residue. As is well known, ether containing as small amount as 2 % of alcohol dissolves pyroxylin appreciably, and as alcohol is the usual impurity in commercial ether, from which it is removed only with difficulty, all statements of the solvent action of ether on the cellulose nitrates, in the

¹ *Comptes rendus*, **77**, 1103 (1873).

² *Ibid.*, **98**, 1485, 1540 (1884).

³ *Bull. Soc. chim. Paris*, (3) **15**, 1097 (1896).

⁴ *Ber. deutsch. chem. Ges.*, **35**, 3079 (1902).

⁵ *Nitrocellulose Industry*, **1**, 167 (1911).

writer's judgment, should at least be accepted with some mental reservation. The phenomenon of two non-solvents, alcohol and ether, combining to a pyroxylin solvent is not an isolated instance, aqueous calcium chloride and alcohol, aniline and ether, phenol and ethyl alcohol, furnishing additional instances of two non-solvents uniting to a fluid of solvent action. The hygroscopicity and low boiling point (35°) would prevent the use of ether as a simple solvent, even if energetic."

Since ether is adsorbed by pyroxylin, it is probable that it would peptize the latter if the two were heated together in a sealed tube. If this is so, the problem then is to account for the fact that addition of alcohol lowers the temperature at which peptization takes place. There seems no reason to suppose that the alcohol exerts any appreciable effect on the cohesive power of the cotton; but, if not, we must then assume that it increases the disintegrating action of the ether. It seems to me quite probable that there is a greater difference of surface tension between ether adsorbed by pyroxylin and alcoholic ether than between ether adsorbed by pyroxylin and ether. If this be conceded, the increased peptization follows at once. While this is a plausible hypothesis, it should be tested quantitatively. Other cases are not unknown and many could probably be found if the matter were taken up systematically. Oudemanns¹ reports that cinchonine is more soluble in alcoholic chloroform than in alcohol or chloroform alone. It is at least a question whether he was not studying peptization² rather than one of solution. Galeotti and Giampalmo³ found that zein is soluble in a mixture of alcohol and water, but not in either liquid alone. This is undoubtedly a case of peptization.

If one ion of an electrolyte is adsorbed more than the other ion, it will tend to peptize the adsorbing material and to give rise to a colloidal solution containing positively or

¹ Zeit. anal. Chem., **11**, 287 (1872).

² Bancroft: Jour. Phys. Chem., **18**, 553 (1914).

³ Zeit. Kolloidchemie, **3**, 118 (1908).

negatively charged particles according to the nature of the ion adsorbed preferentially. According to Schulze's law¹ the adsorption of an ion depends primarily on its valence and is greater the higher the valence. In a previous paper,² I have shown that Schulze's law is merely a first approximation. Univalent ions are not all adsorbed alike; nor are bivalent ions or trivalent ions. The order of adsorption is specific with each colloid. Certain univalent ions are adsorbed by certain colloids more than certain bivalent or trivalent ions. In many cases there is, however, a marked tendency to increased adsorption with increasing valence. It seems to be a general rule that insoluble electrolytes show marked adsorption for their own ions. Consequently a soluble salt having an ion in common with a sparingly soluble electrolyte should tend to peptize the latter.

Lottermoser³ titrated twentieth-molecular silver nitrate with twentieth-molecular potassium chloride, bromide, and iodide. With a slight excess of the alkali halide the silver halide remained in suspension. This was due to the adsorbed halogen ion as was shown by the fact that the colloidal silver halide moved to the anode under electrical stress. When a slight excess of silver nitrate was added to the alkali halide, the resulting silver halide remained suspended as in the previous case; but it then moved to the cathode under electrical stress, showing that it was the adsorbed silver ion which stabilized the colloidal solution. The potassium and nitrate ions are apparently adsorbed to a much less extent and Lottermoser considers that they may be neglected. This cannot be strictly true because a larger excess of silver nitrate or of alkali halide causes coagulation, which means the neutralization of the ion adsorbed preferentially.

A. Müller⁴ peptized thorium hydroxide in thorium nitrate

¹ Schulze: *Jour. prakt. Chem.*, (2) **25**, 431 (1882); **27**, 320 (1884).

² Bancroft: *Jour. Phys. Chem.*, **19**, 363 (1915).

³ *Jour. prakt. Chem.*, (2) **68**, 341 (1903); **72**, 39 (1905); **73**, 374 (1906); *Zeit. phys. Chem.*, **62**, 371 (1908).

⁴ *Ber. deutsch. chem. Ges.*, **39**, 2857 (1906); *Zeit. anorg. Chem.*, **52**, 316 (1907).

solution and zirconium hydroxide in zirconium nitrate solution; and Szilard¹ peptized a number of the rare earth hydroxides by means of the chlorides or nitrates of the same elements. A chromic chloride solution appears to dissolve a certain amount of hydrous chromic oxide; but Nagel² has shown that the oxide is peptized and not dissolved. It seems probable therefore that we are dealing with colloidal solutions in many cases of what have hitherto been considered solutions of basic salts. Hydrous chromic oxide gives an apparently clear green solution when treated with an excess of caustic potash; but the green oxide can be filtered out completely by means of a collodion filter, a colorless solution passing through.³ The oxide is therefore peptized and no chromite is formed. This is in accord with the earlier experiments of Fischer and Herz.⁴ Hantzsch⁵ considers that beryllium hydroxide is peptized by caustic potash. Hydrous copper oxide is apparently peptized to some extent by caustic alkali⁶ and so is cobalt oxide.⁷ In ammoniacal copper oxide solutions part of the copper oxide is apparently colloidal and part dissolved.⁸ The case of zinc oxide is more complex. Hantzsch⁹ claimed that alkaline solutions of zinc hydroxide were chiefly colloidal. Fischer and Herz¹⁰ decided that they were partly colloidal, while Klein¹¹ maintained that a definite sodium zincate was formed. Hantzsch¹² was so impressed by Klein's arguments that he changed his views. From experi-

¹ Jour. chim. phys., **5**, 488, 636 (1907).

² Jour. Phys. Chem., **19**, 569 (1915); cf. Graham: Jour. Chem. Soc., **15**, 254 (1862); Fischer: Zeit. anorg. Chem., **40**, 39 (1904).

³ Nagel: Jour. Phys. Chem., **19**, 331, 569 (1915).

⁴ Zeit. anorg. Chem., **31**, 352 (1902).

⁵ Ibid., **30**, 289 (1902).

⁶ Loew: Zeit. anal. Chem., **8**, 463 (1870); Fischer: Zeit. anorg. Chem., **40**, 39 (1904).

⁷ Tubandt: Zeit. anorg. Chem., **45**, 368 (1905).

⁸ Grimaux: Comptes rendus, **98**, 1434 (1889).

⁹ Zeit. anorg. Chem., **30**, 289 (1902).

¹⁰ Ibid., **31**, 352 (1902).

¹¹ Ibid., **74**, 157 (1912).

¹² Ibid., **75**, 371 (1912).

ments in the Cornell laboratory, which will be published later, it seems probable that everybody was right. Freshly precipitated zinc hydroxide is peptized by alkali; but the solution is very instable, the zinc hydroxide often coagulating inside of half an hour. The relatively small amount of zinc remaining in solution is present chiefly or entirely as sodium zincate. Depending on the moment selected for examination, the zinc oxide is chiefly colloidal, partly colloidal, or not colloidal at all. This was realized distinctly by Hantzsch¹ in his first paper; but he seems to have forgotten it later. The bulk of the evidence seems to be that alumina is not peptized appreciably by alkali and that it goes into solution as sodium aluminate,² though the other view has been supported.³

I have discussed the peptization of the hydrous oxides of chromium, beryllium, copper, cobalt, and zinc by alkali as a case of peptization by a common ion because we generally look upon these oxides as basic. This is not essential to the argument in any way. We can consider that these oxides are peptized by the preferentially adsorbed hydroxyl ion. We have to do this in the case of the peptization of silica or caseine by sodium hydroxide. Graham⁴ points out that gelatinous silicic acid may be liquefied by contact with a very moderate amount of alkali. The change "is gradual, one part of caustic soda, dissolved in 10,000 water, liquefying 200 parts of silicic acid (estimated dry) in 60 minutes at 100° C. Gelatinous stannic acid is also easily liquefied by a small proportion of alkali, even at the ordinary temperature. The alkali, too, after liquefying the gelatinous colloid, may be separated again from it by diffusion into water upon a dialyser." This

¹ Zeit. anorg. Chem., **30**, 300 (1902).

² Herz: Zeit. anorg. Chem., **25**, 155 (1900); Hantzsch: Ibid., **30**, 289 (1902); Rubenbauer: Ibid., **30**, 331 (1902); Fischer and Herz: Ibid., **31**, 355 (1902); Slade: Jour. Chem. Soc., **93**, 421 (1908); Zeit. anorg. Chem., **77**, 457 (1912); Trans. Far. Soc., **10**, 150 (1914); Blum: Jour. Am. Chem. Soc., **35**, 1499 (1913).

³ Mahin, Ingraham and Stewart: Jour. Am. Chem. Soc., **35**, 30 (1913).

⁴ Jour. Chem. Soc., **17**, 324 (1864).

last statement is inaccurate because the silicic acid forms a jelly before all the caustic soda is removed since the caustic soda is what stabilizes the hydrosol. What happened was that it was necessary to have more than enough soda if peptization is not to take place very slowly. The excess of caustic soda can then be removed by dialysis.

A. Müller¹ has prepared colloidal solutions of aluminum, iron, cobalt, thorium, and yttrium oxides by peptization with dilute hydrochloric acid (*M* 20). Bentley and Rose² obtained a colloidal solution of alumina by treating freshly precipitated alumina with 8 percent acetic acid. Since these colloids are positively charged, they have been peptized by a cation, presumably by hydrogen ion. It is possible of course that a slight formation of an aluminum salt has occurred in the last case and that the aluminum salt is the peptizing agent; but this does not seem very probable.

The peptization of sulphides by hydrogen sulphide³ is a case where we are dealing with peptization by a common ion, the sulphide or hydrosulphide ion being the one adsorbed. Spring⁴ found that if copper sulphide, prepared by passing hydrogen sulphide through a dilute solution of copper sulphate in ammonia, is washed by decantation with water containing hydrogen sulphide, until the precipitate is perfectly free from ammoniacal salts, the copper sulphide dissolves, forming a dark brown solution. The solution may be boiled without decomposition, but the addition of small quantities of metallic salts causes the sulphide to precipitate. On evaporating the solution on a water bath, the copper sulphide remains as a dark resinous mass. If the copper sulphide is dried in a vacuum, it loses its property of dissolving in water. Pure dry copper sulphide has a dark green color. Under a pressure of 6500 atmospheres, it forms a dark blue compact mass, possessing metallic luster.

¹ Svedberg: *Die Methoden zur Herstellung kolloider Lösungen anorganischer Stoffe*, 400 (1909).

² *Jour. Am. Chem. Soc.*, **35**, 1490 (1913).

³ Linder and Picton: *Jour. Chem. Soc.*, **61**, 114; Picton, 137 (1892).

⁴ *Ber. deutsch. chem. Ges.*, **16**, 1142 (1883).

Prost¹ says that "colloidal cadmium can be prepared by completely precipitating an ammoniacal solution of cadmium sulphate with hydrogen sulphide, washing the sulphide with water by decantation, suspending the milky precipitate in water, and submitting it to a slow stream of hydrogen sulphide. The precipitate first becomes flocculent, then milky, and finally disappears entirely. The solution is then boiled until lead paper shows the absence of hydrogen sulphide. The solution is a beautiful golden yellow by transmitted light and fluorescent by reflected light. The composition of the dissolved substance is CdS. Dilute solutions remain unchanged for a long time. A solution containing four grams of sulphide to the liter remained clear many days; but another solution containing eleven grams to the liter coagulated in twenty-four hours."

Winssinger² states that colloidal zinc sulphide is easily obtained by washing freshly precipitated zinc sulphide with a dilute solution of hydrogen sulphide or by passing hydrogen sulphide through water containing pure zinc hydroxide in suspension. The solution is slightly opalescent, and can be boiled until the whole of the hydrogen sulphide is expelled without undergoing change; when boiled for a longer time the sulphide is precipitated, but, after cooling, it is readily dissolved when a stream of hydrogen sulphide is passed through the solution.

When authors state, as they so often do, that all the hydrogen sulphide can be removed without affecting the stability, they are speaking inaccurately. There must be an excess of hydrogen sulphide to cause peptization.³ What they mean is that the unadsorbed hydrogen sulphide can be removed. Linder and Picton⁴ showed that it was very difficult to remove all of the hydrogen sulphide even from the coagulated sulphides. "The first result of our experiments

¹ Jour. Chem. Soc., **54**, 653 (1888).

² Bull. Soc. chim. Paris, (3) **49**, 452 (1888).

³ Cf. Meunier: Comptes rendus, **124**, 1151 (1897).

⁴ Jour. Chem. Soc., **61**, 116 (1892).

was to prove that excess of sulphur was present in these precipitates; it was also found that the amount is not always constant. As in many cases the excess was small, the question naturally arose as to whether this could be free sulphur liberated during precipitation. To lessen the chances of such precipitation, boiled water was used in many cases. The only certain proof, however, was to make a searching examination in one of the cases where sulphur might most readily be expected to be formed; and for this purpose mercury sulphide was chosen; it gives a very small excess of sulphur and the liability to deposit sulphur unless due precautions are taken is well known. The precipitate, after washing with alcohol, was carefully extracted with carbon bisulphide, but still yielded the same excess as before; and in order to obviate the objection that this extraction might be imperfect, another method more easily applied was used. This consisted in heating the precipitated compound in a current of hydrogen; in this way the sulphuretted hydrogen was driven off and absorbed by soda, and there was no longer any possibility of the excess being due to free sulphur. But though washed to all appearance perfectly free from sulphuretted hydrogen, it might yet perhaps be thought that some small quantity of the gas was mechanically retained in the interstices of the precipitate. As a final test, therefore, the precipitate, after complete washing, was extracted carefully with carbon bisulphide, washed free from every trace of carbon bisulphide, and then completely dried in a vacuum. The substance so dried still retained sulphuretted hydrogen, however, which was slowly given off on heating and collected in soda. The same result was obtained in this case as in the others. The sulphur is, therefore, without any doubt *combined* with the freshly precipitated sulphide in the form of sulphuretted hydrogen."

The possibility of peptization by an adsorbed salt seems to have been pretty generally overlooked in the books on colloid chemistry, presumably because an increase in the concentration of a peptizing salt is apt to cause coagulation. Theoretically the matter is quite simple. We start with an

ion peptization because one ion is adsorbed more than the other. With increasing salt concentration we reach the point where the adsorption of the first ion varies but slightly with the concentration. The adsorption of the second ion continues to increase relatively to the first ion until we get what has been called neutralization of the adsorbed ion,¹ and consequently coagulation. At the same time the adsorbed salt is tending to peptize the substance; but if its peptizing action is relatively small, there may be quite a large range of concentrations over which the ion peptization has ceased to be effective and the salt peptization has not begun to be effective. With still greater salt concentration, we should expect to get salt peptization; but a number of disturbing factors may come in. The salt may not be sufficiently soluble at the temperature of the experiment or it may react with the substance to be peptized. If we increase the hydrochloric acid concentration with the oxides of aluminum, iron, cobalt, etc., we finally get the chlorides of these metals in true solution. If we increase the caustic soda concentration with silicic acid, we consider that we get sodium silicate in true solution. If we increase the potassium bromide concentration with silver bromide we say that we get a complex salt in true solution. It may be that we are wrong in this and that we are getting peptization in some of these cases. For years we thought that the so-called basic chlorides were definite compounds forming true solutions, whereas now we know that many of them are not.² With silver iodide and a concentrated silver nitrate solution³ we apparently get a definite compound, $2\text{AgNO}_3 \cdot \text{AgI}$; with silver bromide also a definite compound, $\text{AgNO}_3 \cdot \text{AgCl}$; but it is not probable that there is any such compound as $18\text{AgNO}_3 \cdot \text{AgCl}$, so it may be that here we have a case of peptization by an undissociated electrolyte.

It is possible that von Weimarn's peptization of cellulose⁴

¹ Bancroft: *Jour. Phys. Chem.*, **19**, 363 (1915).

² For optical turbidity see Picton and Linder: *Jour. Chem. Soc.*, **61**, 154 (1892).

³ Risse: *Liebig's Ann.*, **111**, 39 (1859).

⁴ Von Weimarn: *Zeit. Kolloidchemie*, **11**, 41 (1912).

by salt solutions may come under this head. Three grams of cellulose were heated with about 100 cc concentrated salt solution and were thereby peptized, the mixture usually cooling to a jelly. With NaI, CaI_2 , SrI_2 , CaBr_2 , $\text{Ca}(\text{SCN})_2$ and $\text{Ba}(\text{SCN})_2$ peptization took place at atmospheric pressure. With NaCl a temperature of 170° and a pressure of 8 atm. were necessary, and incipient decomposition seemed to take place. Deming¹ peptized cellulose with salts dissolved in acid solutions. In all these cases of possible peptization by undissociated salts, there may be an ion peptization and a water peptization superposed which, of course, complicates matters considerably. Oxides of mercury or less noble metals are adsorbed by mercury. I do not know any conditions under which they will peptize mercury unassisted, though it is very possible that this might take place at higher temperatures. If we disintegrate the mercury mechanically, it is possible to obtain a colloidal solution and here we unquestionably have an undissociated salt.

Under the general heading of peptization by a colloid, we can distinguish several types. The most important is peptization by a water-soluble colloid, such as gelatine, agar-agar, dextrine, etc. Gelatine peptizes freshly precipitated silver bromide. The effect seems to be more striking in presence of a slight excess of potassium bromide or silver nitrate, in which case one gets the ion peptization in addition. Eder² says: "If we precipitate silver bromide from a cold aqueous solution containing no gelatine or other similar substance, we get a coarse, compact precipitate which can easily be washed on a filter. If we pour this precipitate into a warm solution of gelatine and shake, the silver bromide disintegrates and forms a fine emulsion. Under these circumstances the silver bromide behaves differently, depending on whether it has been precipitated in presence of an excess of bromide or of silver salt. This difference is noticeable no matter how carefully the silver bromide is washed."

¹ Jour. Am. Chem. Soc., 33, 1515 (1911).

² Eder's Handbuch der Photographie, 5th Ed., 31, 28 (1902).

Luppo-Cramer¹ points out that "the peptization of the silver iodide and silver bromide gels by the corresponding halogen ions takes place in quite a striking way in presence of gelatine. Starting from the coarsely flocculent silver bromide, obtained by precipitation in absence of a binder, we can obtain very fine-grained, homogeneous, though by no means colloidal, emulsions. Further experiments have shown that the same results can be obtained more rapidly with ammonia than with bromine ions. The reaction was carried on in precisely the same way as the preceding one, merely substituting 2 cc of ammonia (sp. gr. 0.91) for the bromide. The disintegration of the flocculent silver bromide in the gelatine took place immediately and the resulting completely homogeneous, creamy emulsion showed under the microscope (oil immersion) only very small particles which looked like fine splinters. Ammonia does not disintegrate the silver bromide in collodion, while an emulsion is very easily obtained under the influence of a bromide. . . .

"The state of the silver bromide was of fundamental importance for the emulsification in gelatine by means of bromine ions and the same thing is true for the emulsification by means of ammonia. The silver bromide gel loses completely its peptizable properties just by standing. Samples which had stood for one, three, six, ten, and twelve hours in the dark at ordinary temperature showed a gradual decrease in the tendency to form an emulsion. After twelve hours' standing, no emulsion could be formed at all.

"If the silver bromide is formed from ammoniacal silver oxide instead of from silver nitrate, it differs in shape and color from that precipitated from a neutral solution and it cannot be peptized in presence of gelatine.² Even when not precipitated in presence of ammonia, it only requires a few minutes' shaking of the silver bromide with a very dilute solution of ammonia to bring the silver into such a state that

¹ Phot. Correspondenz, 44, 578 (1907).

² [This should be repeated. It seems improbable that we have a full statement of the facts. W. D. B.]

ammonia does not cause an emulsification in presence of gelatine. Bromides cannot peptize a silver bromide precipitated from an ammoniacal silver oxide solution.

"Freshly precipitated silver iodide is quickly converted into an emulsion by the action of ammonia in presence of gelatine; but this does not take place after the silver iodide precipitate has stood for a day or two. An excess of silver nitrate at the time of precipitation has no appreciable effect on the peptizing action of ammonia on either silver bromide or silver iodide. The same thing is true in case the silver iodide is added after the precipitation and is then nearly all washed out of the precipitate."

Lefort and Thibault¹ found that mercuric sulphide precipitates rapidly when mercuric chloride is added to the sulphur springs at Bagnères de Luchon; but if solutions of gum arabic, sarsaparilla, wild cherry, beef tea, albumin, or apple jelly be added to the waters, no precipitation will take place on addition of mercuric chloride. It was thought at first that the non-precipitation of mercuric sulphide was due to the increased viscosity of the solution; but this was disproved by the fact that a precipitate is obtained if gum arabic is replaced by glycerine. Experiments with other sulphides showed that gum arabic prevents the precipitation of the sulphides of lead, silver, iron, manganese, mercury, copper, zinc, antimony, and arsenic, provided the solutions of the salts are dilute and that enough gum arabic is added. In presence of gum arabic, metallic hydroxides behave like sulphides.

"The formation of other precipitates is also prevented, as that of calcium phosphate in neutral solutions, uranium ferrocyanide, and ferric hydroxide when a dilute solution of ferric chloride is treated with ammonia. The alkaloids, quinine, cinchonine, morphine, strychnine, brucine, veratrine, are not precipitated by phospho-molybdic acid, potassium mercuric iodide, or tannin, in presence of gum arabic. . . . The intense colorations produced on adding the reagent to the

¹ Jour. Chem. Soc., 42, 1322 (1882).

metallic solutions containing gum, show that a reaction has taken place; it therefore remains to be proved whether the precipitation is soluble in gum arabic or held in suspension in an exceedingly fine state of subdivision. The authors are inclined to think that the latter is the more probable, since concentrated solutions of gum arabic fail to dissolve the precipitated substances even when recently formed." It is probable that the failure to obtain peptization was due to ignorance of the idiosyncrasies of the precipitates; but this matter certainly calls for more study. Wegelin¹ has overcome the cohesion of metals by grinding them with gelatine. So far as one can see this is a general method and can be applied in all cases where agglomeration has been too intense.

Lachaud² found that "dextrine is partially precipitated from its aqueous solutions by the addition of magnesia or any of the alkaline earth carbonates; but at the same time a part of the precipitating agent goes into solution. Similar results are obtained when solutions of such salts as aluminum sulphate, chrome alum, ferric sulphate, or lead nitrate are added to a solution of dextrine and then rendered alkaline with ammonia. Extended experiments with dextrine, ferric sulphate, and ammonia showed that the whole of the dextrine can be precipitated if the ferric hydroxide is in large excess; if, however, the dextrine is in large excess, no precipitate is formed, and all the iron remains in solution. Many other organic compounds behave in much the same way as dextrine." This seems to be exactly like the action of an alkaline chromic oxide solution on hydrous ferric oxide, which will be discussed a little later.

Saponin peptizes lead sulphate, barium carbonate, and other salts.³ Soap peptizes rouge, charcoal, etc.⁴ If a suspension of soot in water be filtered several times through filter paper, the water will finally run through clear and soot

¹ Zeit. Kolloidchemie, **14**, 65 (1914).

² Bull. Soc. chim. Paris, (3) **15**, 1105 (1896).

³ Schiaparelli: Jour. Chem. Soc., **46**, 333 (1884).

⁴ Spring: Zeit. Kolloidchemie, **4**, 161 (1909); **6**, 11, 109, 164 (1910).

will be held back by the filter paper. If a soap solution be poured on the filter, a black filtrate is obtained and the filter paper is no longer black. All the soot has passed through the filter paper. The same thing can be done with rouge except that a red filtrate is obtained instead of a black one. At first sight it seems as though the soap must have broken up the carbon or the rouge into finer particles, which then passed through the filter; but I think that this is erroneous. The filter paper is quite porous enough at first to let the particles of soot or rouge through, as is shown by the fact that some usually does pass through the filter at first. The cellulose adsorbs either carbon or rouge and this clogs the filter to such an extent that the pores are not large enough to let the remaining particles through. The soap removes the rouge or carbon from the paper because of its greater adsorbing power for these substances and everything goes through the paper. That this is the true explanation can be shown in two ways. In the first place the experiment does not succeed if the rouge or the carbon is too coarse. In the second place Spring showed that we are dealing with an adsorption of soot by filter paper. If the black filter paper be reversed and washed with water, only the carbon which is not in immediate contact with the paper is removed.

Aniline dyes which are insoluble in benzene can be peptized by a benzene-soluble colloid such as zinc or magnesium resinate so-called.¹

It is a little uncertain whether albumin is to be called a water-soluble colloid or one peptized by an ion; but the latter is probably the better way of considering it. In the case of caseine there is no question. It is not soluble in water and is peptized by acids or alkalies. Both have been used as protecting colloids and would undoubtedly act as peptizing agents under favorable conditions. A more interesting case than either of these is that of hydrous chromic oxide, an alkali-soluble colloid.² Hydrous chromic oxide adsorbs the

¹ Soxhlet: *Art of Dyeing and Staining Marble, etc.*, 76 (1902).

² Northcote and Church: *Jour. Chem. Soc.*, 6, 54 (1854); Nagel: *Jour. Phys. Chem.*, 19, 331 (1915).

hydrous oxides of iron, nickel, cobalt, manganese, and copper; and consequently peptizes them to a certain extent, making them apparently soluble in caustic potash solution. The converse is also true, of course, that these hydrous oxides adsorb hydrous chromic oxide and consequently tend to make the latter apparently insoluble in caustic potash. When chromium salt is present in large excess relatively to the iron salt, no iron oxide is precipitated; when the iron salt is present in excess, no chromium oxide remains in the water phase, the latter becoming colorless. Colloidal copper oxide peptized by ammonia causes the peptization of hydrous chromic oxide by ammonia.¹ These cases are precisely analogous to that of dextrine and ferric hydroxide previously referred to.

Miss Hitchcock² points out that molybdic acid is not precipitated from its salts by uranyl salts while tungstic acid is. In presence of tungstic acid, however, practically all the molybdic acid is precipitated. This is obviously a case of adsorption and the converse is undoubtedly true that no tungstic acid would be precipitated in presence of a sufficient excess of a molybdate.³

Hydrous chromic oxide peptized by alkali forms a relatively stable colloidal solution. The ordinary ion-peptized solutions of arsenic sulphide and ferric oxide, for instance, are relatively instable. If a positively charged hydrosol of this type be mixed with a negatively charged one in suitable proportions, the two will be precipitated practically completely but this precipitate is peptized by an excess of either hydrosol.⁴

While I have made no effort to consider all possible cases, I think that I have taken up enough to show that we have a good working theory of peptization which is generally applicable. It is based explicitly on Freundlich's assumption

¹ Prud'homme: Jour. Chem. Soc., **25**, 672 (1872).

² Jour. Am. Chem. Soc., **17**, 483, 520 (1895).

³ Cf. Wöhler: Zeit. Elektrochemie, **16**, 693 (1910).

⁴ Freundlich: Kapillarchemie, 446 (1909).

that adsorption is accompanied by a lowering of the surface tension of the adsorbing phase. This is purely an empirical generalization and may not be true. If it should prove later not to be true, it will be a simple matter to restate this theory of peptization in terms of our wider knowledge; but there is nothing to be gained now by discussing that.

It will be well, however, to consider some points which have been brought out by others. Lottermoser¹ studied peptization by adsorbed ions and formulated the following general rule: "If one adds to an amorphous substance an ion—or a closely allied ion—at a higher concentration than the substance itself can generate in the solution, the substance will be converted back into a hydrosol. The essential condition for the success of this reaction is that the substance shall be in such a state that it is capable of swelling or of a decrease in the molecular complex by peptization or addition of the ion; in other words it must be in a definite physical state." The underlying idea is sound but the wording of it could hardly be worse. If the solid phase sends out ions into the solution up to equilibrium, any addition of a salt with a common ion will mean a higher concentration than the substance can generate and why not say so. If he means something else, why not say that? Of course the substance cannot generate a closely allied ion at all. It is also unfortunate, because inaccurate, to insist that the substance shall be amorphous. What Lottermoser really meant was that addition of a readily adsorbed ion will tend to cause peptization, though this is an empirical statement so far as he is concerned. If we bring in the lowering of the surface tension, we at least make the disintegration seem plausible. What Lottermoser says in regard to the physical state is the same thing as my statement that the agglomeration must not have proceeded too far. Both are non-committal phrases because we have no means as yet of measuring the property in question.

In his work on the stannic acids, Mecklenburg² has

¹ Cf. *Jour. Phys. Chem.*, **14**, 17 (1910).

² *Zeit. anorg. Chem.*, **74**, 260 (1912).

brought out some very important facts in regard to agglomeration. "Adsorption is a surface phenomenon and becomes noticeable only when the adsorbing phase is very finely divided and consequently has a very large surface. The starting-point for a colloid chemical theory of the stannic acids is that under otherwise equal conditions the adsorbing power of a substance increases within certain limits¹ with increasing surface, in other words with increasing degree of dispersion. Since the five stannic acids [prepared at five temperatures] behave qualitatively alike but quantitatively different in regard to the adsorption of phosphoric acid, the five must differ in surface, and the size of grain must increase the higher the temperature of preparation. The 0° acid should have the finest grain and the 100° acid the coarsest; the 25° acid should approximate to the 0° acid and the 75° acid to the 100° acid, while the 50° acid should assume an intermediate position. This view is supported by the way in which the samples react with hydrochloric acid and by the fact that, when dried in air, the five stannic acids hold water more firmly and therefore contain more water, the lower the temperature of preparation.

"The conception of size of grain as here used calls for more discussion. In his classical contributions to our knowledge of colloids,² Zsigmondy has pointed out that the precipitation of colloids from solutions may occur either because the single particles agglomerate to complexes in which each particle keeps its identity or because the single particles themselves become larger just as crystals grow in a supersaturated solution.

"The colloid chemist is not unfamiliar with cases of the first sort, instances of which probably occur with stannic acids, as was pointed out in the first paper on the isomerism of the stannic acids. Zsigmondy³ himself has recently studied

¹ If this assumption were true without limit, the adsorbing power would be greatest when the substance was disintegrated to the molecules or ions. This seems not to be the case.

² Zsigmondy: *Zur Erkenntniss der Kolloide*, 13, 175 (1905).

³ *Zeit. anorg. Chem.*, 71, 356 (1911).

the silicic acid gel with the ultra-microscope and has come to the conclusion that the particles forming the clear transparent gel are amicrons, in other words, so small that they cannot even be detected by means of the ultra-microscope. This result is not to be reconciled with the conclusion that gelatinization results from the increase in size of the single particles. An additional argument is that red colloidal gold solutions become blue before coagulating, for according to Maxwell Garnett a gold sol which contains very small and widely scattered gold spheres should be red, while it should turn blue if the particles agglomerate to larger complexes. As a matter of fact Steubing¹ has made the observation that, while the particles of a red-gold sol appear round when examined in the ultra-microscope, the particles of the blue-gold sols show peculiar distortions—an observation which fits in well with the theory under discussion.

“If the individuality of the single or ‘primary’ particles of the stannic acid do not remain when the primary particles agglomerate to secondary particles, it is not easy to see why the relative surfaces of the five stannic acids should depend even after coagulation on the temperatures at which the stannic sulphate hydrolyzed. One would rather assume that the adsorption would depend on the greater or less care with which the solid masses afterwards were pulverized. As a matter of fact direct proof can be given that the microscopic size of the grains of the secondary particles has nothing to do with the surface of the primary particles as measured by adsorption. This proof is given by determining the volume occupied by one gram. Into weighed measuring glasses of 10 cc capacity and graduated to 0.1 cc, there were placed 2 cc portions of the stannic acids in the form in which they were used for the other experiments. By tapping carefully on the tops of the glasses the stannic acids were made to settle to the minimum volume. Then another 2 cc of the powder was added and made to settle; this was repeated until the measur-

¹ Drude's Ann., 26, 339 (1908).

ing glasses were practically full, after which the volumes were read off and the weights determined. Especial stress was laid on making the experiments as uniform as possible. The [mean of the] data are given in Table I.

TABLE I

Sample	Weight in grams	Volume in cc	Specific volume in cc
0° acid	12.27	9.12	0.74
25° acid	22.58	9.27	0.41
50° acid	16.55	9.52	0.58
75° acid	15.08	9.86	0.65
100° acid	8.56	9.26	1.08

"The figures show that the 100° acid is by far the most bulky, which is the more surprising because it has the largest content of the denser SnO₂ [less water]. The 25° acid, which contains relatively little SnO₂, is the densest. The 50° acid is more bulky and then come the 75° acid and the 0° acid. The bulkiness of the powder as thus measured is a haphazard value depending primarily on the resistance to grinding. Though it may be used as an approximate measure of the microscopic fineness of the powder, it of course has nothing to do with the temperature at which the sample was prepared and has no connection with the size of grain as determined by the behavior towards hydrochloric acid or by the adsorption of phosphoric acid.

"This lack of connection between the microscopic size of grain of fine powders and their activity is confirmed by very interesting experiments in an entirely different field. In Lothar Wöhler's laboratory Pluddeman¹ showed that the catalytic action of the oxides Cr₂O₃, Fe₂O₃, etc., on the reaction $2\text{SO}_2 + \text{O}_2 \longrightarrow 2\text{SO}_3$ does not stand in any relation to the size of the particles even with the same catalytic agent. The surface on which this surface action depends must there-

¹ Dissertation Techn. Hochschule Karlsruhe (1907).

fore lie deeper, a point which is of great importance for the surface action theory of catalytic agents.¹

"According to the theory of primary and secondary particles the peptization of the stannic acids consists in the splitting up of the secondary particles into the primary particles. It does not seem necessary, however, that the breakdown of the secondary particles shall be complete; a colloidal solution will be formed whenever the disintegration has gone so far that the products, whether they be primary particles or aggregates thereof, can be kept floating in the liquid under the existing conditions. This conception of the process of peptization makes intelligible a number of phenomena which were difficult to account for on the usual theory which makes no distinction between primary and secondary particles. According to the old conception a stannic acid must be peptized more readily the greater its power of adsorption, a conclusion which is not confirmed by experiment, for the 100° acid is not perceptibly more difficult to peptize than the 0° acid, and the 50° acid is not characterized by a lesser power of adsorption even though it is much less readily peptized than any of the other four standard samples. According to the theory of primary and secondary particles, the readiness with which a substance is peptized varies inversely with the force with which the primary particles are held together in the secondary complex. It has nothing to

¹ In connection with this the fact may be recalled that the natural inorganic products such as cassiterite, chromite, corundum, etc., even when very finely powdered are much less readily attacked by chemical reagents than the corresponding synthetic compounds. Here also the size of the grain, on which the behavior of these substances depends primarily, seems to be beyond the limit to be reached by mechanical disintegration. The crystal fragments produced by the very best grinding, are still very much larger than the primary particles of the synthetic products. The fact that the laboratory products are not crystalline does not prevent a comparison between the natural and the synthetic products because it has been proved for silver iodide by Tammann [Zeit. phys. Chem., **75**, 740 (1911)] and has been made probable for silicon by Wilke [Wallach-Festschrift, 682 (1909)] that these substances which are usually considered amorphous are really "cryptocrystalline."

do with the absolute size of the secondary particles,¹ a value which is not defined in any way."

This statement of Mecklenburg brings out pretty clearly how much we have yet to learn in regard to agglomeration and to cohesion in agglomerated particles. The surface for adsorption depends on the porosity. With a metal, which is not porous, the surface is increased enormously by grinding. With a porous material like charcoal, grinding has an almost negligible effect on the degree of adsorption. A colloidal mass, which has only just agglomerated, can often be peptized without difficulty. If the coalescing surfaces are allowed to set or if the substance is heated so that sintering takes place, peptization becomes extremely difficult.

A theory of peptization has been put forward by von Weimarn.² He considers that the solid always dissolves in the peptizing agent, forming instable compounds which then break down, the precipitate forming a hydrosol. According to this view all methods of making sols are really condensation methods, the so-called dispersion methods really involving solution and then condensation. According to von Weimarn the necessary and sufficient conditions for peptization are:

1. The solid crystalline substance must consist of such small crystals that the physical and chemical properties vary with the size of the crystals.

2. The peptizing substance must have the power at sufficiently high concentrations to form a stable, soluble, chemical compound with the substance which is peptized. When the concentration of the peptizing agent is sufficiently low, no such compound must be formed.

¹ It is self-evident that when secondary particles are hard to peptize they disintegrate slowly and a longer action of the solvent is necessary to produce a colloidal solution. This is not a factor in the present discussion, however. The resistance to peptization of the 30° acid stands in no relation to the specific volume as measured. The 25° acid which is easily peptized is considerably denser (1/0.41 than the 50° acid (1/0.58)). When the 50° acid was ground further in an agate mortar, the specific volume was brought to the relatively high value of 0.87; but the resistance to peptization was not changed perceptibly.

² Zur Lehre von den Zuständen der Materie, 1, 60 (1914).

3. The medium in which peptization takes place must have practically no solvent action on the substance to be peptized when no peptizing agent is present.

It is true that soluble compounds may be formed in many cases when the peptizing agent is present in high concentration. Instances of this are alumina and hydrochloric acid, silica and caustic soda, silver bromide and potassium bromide; but there seems to be no reason to assume that soap forms a definite chemical compound with carbon, gold with gelatine, or chromic oxide with the oxides of iron, cobalt, copper, etc. In the cases of mechanical disintegration there is not necessarily any solution and subsequent precipitation. So far as I can see the hypothesis of an intermediate soluble compound does not account for the fact that in alkaline solutions hydrous chromic oxide will peptize a relatively small amount of hydrous ferric oxide; but will be carried down completely by a relatively large amount of ferric oxide. In fact von Weimarn has overlooked the conditions for the stability of a colloidal solution completely and he seems also not to have taken into account the peptizing action of the solvent. For these and other reasons I consider that von Weimarn's theory of peptization is inadequate.

The general results of this paper are as follows:

1. If we adopt Freundlich's generalization that adsorption involves a lowering of the surface tension of the adsorbing phase, a theory of peptization follows at once.

2. If Freundlich's generalization proves not to be universally true, it will be easy to modify the theory of peptization so as to account for the new facts.

3. Any substance which is adsorbed by a second will tend to disintegrate or peptize the latter.

4. We may have peptization by a solvent; by a dissolved non-electrolyte; by an ion; by an undissociated salt; by a colloid.

5. Adsorption decreases in general with rising temperature; but so does the cohesion of the adsorbing substance. We may therefore have peptization by a solvent at high tem-

peratures when we do not get it at lower ones. Instances of this are glass and water, vulcanized rubber and many organic solvents, gelatine and water.

6. Instances of peptization by a dissolved non-electrolyte are sugar or glycerine and hydroxides in water, ether and pyroxylin in alcohol.

7. Typical cases under ion peptization in water are silver bromide and potassium bromide, silica or chromic oxide and caustic potash, alumina and acids, chromic oxide and chromic chloride.

8. No cases of peptization by a soluble undissociated salt have been studied as such. If impure mercury is shaken with water we get peptization by an oxide film.

9. Typical instances of peptization by a colloid in water are silver bromide and gelatine, alkaline chromic oxide and hydrous ferric oxide, gold and stannic oxide.

10. Since the adsorption depends on the surface and since peptization involves breaking down the cohesion of particles, there is no necessary connection between amount of adsorption and ease of peptization.

11. A coarse-grained porous precipitate may be peptized more readily than the same mass in a more dense form.

12. Von Weimarn's theory of peptization is inadequate.

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