CRITICAL REVIEW.

THE PHYSICAL CHEMISTRY OF COLLOID SOLUTIONS.¹

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THE following short account of the physical chemistry of colloid solutions is, in the main, and in somewhat extended form, the introduction to a discussion on the subject at a joint meeting of physicists and biologists. It made no pretence of dealing in an exhaustive manner with the subject, nor even of touching upon all its aspects. Points of outstanding interest and importance were selected, with especial regard to those matters about which one may consider that there is some amount, at least, of scientific certainty.

Limited to colloid solutions, no mention is made of the large and equally important divisions of the subject of colloids which are concerned with the solid colloids, such as gelatinisation, the structure of gels, phenomena of imbibition, and of adsorption. And facts being, at the present moment, of more importance than hypotheses, no attempt has been made to discuss the merits or demerits of the many theories of the colloid state. It is sufficient to note that a colloid solution is best regarded as a two-phase system—solid and liquid—with an exceptionally large development of the surface bounding the two phases.

CRYSTALLOIDS AND COLLOIDS—DIFFUSION.

When Graham first divided substances into the two classes—the crystalloids which could diffuse through a parchment paper or other similar septum, and the colloids which were unable to do this—there was no reason to regard this classification as other than a rigorous one, and the crystalloid or colloid character to be an inherent property of the substance. The fact that the substances whose diffusion coefficients in water were high, diffused at about the same rate in a jelly of agar-agar or gelatin, and also could dialyse easily through a septum which separated the solution from pure water, whilst those substances which had very small diffusion co-efficients in water, did not diffuse at all in contact with gelatin or agar-agar jelly, and were also completely retained by the dialyser, led Graham (1876 ¹) to make his well-known dictum that “they appear like different worlds of matter, and give occasion to a corresponding division of chemical science. The distinction between these kinds of matter is that subsisting between the material of a mineral and the material of an organised mass.”

Unfortunately, the matter is not quite so simple as this; the crystalloid or colloid character is not a fundamental property of any given substance, but depends upon other circumstances, notably the nature of the solvent. Soaps, for instance, form colloid solutions when water is the solvent, but are normal in other liquids; still more striking is the fact that sodium chloride, sodium

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bromide, and sodium iodide, which are among the most typical crystalloids, according to Graham, have recently been found to form colloid solutions when certain organic reactions between halogen derivatives and sodium organic compounds are carried out in absolutely dry ether or benzene. Nor is the crystalline or amorphous condition of the solid substance a reliable guide in this matter, although the majority of crystalloids do crystallise more or less readily; for some of the hydrochlorides of primary amines of high molecular weight form beautiful crystals, and yet their solutions in water are typically colloid.

Later research has, in fact, modified Graham's results in several important directions. It has been found that in some instances a colloid will diffuse into water if it is mixed with an electrolyte (1887²), and that a mixture of colloid silicic acid with sodium chloride passes through a dialyser in considerable quantity, and that even gelatin solution can diffuse into a jelly of agar-agar (1901³). It must be concluded that there is no discontinuity between the slowest diffusing colloid and the crystalloids.

OSMOTIC PRESSURE—MOLECULAR WEIGHT.

The idea that colloids are substances which have necessarily a high molecular weight is still widely held. There is little doubt that the origin of this is to be found in Graham's observations, and especially in the conclusions which he drew from certain of the methods of preparation made use of by him. A colloid solution of ferric hydroxide was prepared by digesting precipitated ferric hydroxide with a hot solution of ferric chloride, and subsequent dialysis of the filtered solution. The colloid solution thus obtained always contained chloride, which could not be removed by dialysis, however prolonged; and the solution was considered to contain a chemical compound which was distinguished from ordinary ferric chloride, in that the ratio of iron to chlorine was very large. The combining weight of iron in this compound being so large, the compound must have a very high molecular weight. Similarly with silicic acid; a very small quantity of alkali was sufficient to cause a large quantity of gelatinous precipitated silicic acid to pass into solution, and, on the assumption that the process was exactly the same as the neutralisation of an acid and a base, it is obvious that this particular form of silicic acid must have a very large molecular weight. Graham distinguished them from the ordinary silicates and salts by the prefix "co."

The problem was one which purely chemical methods were incapable of dealing with, and it was only when physical methods began to be applied that any new light could be thrown on it. We will pass over such isolated observations, though their importance can scarcely be exaggerated, as that of Hittorf—that a solution of stannic chloride in water behaves electrically as one of an equivalent solution of hydrochloric acid, from which he rightly concluded that water completely decomposes stannic chloride into hydrochloric acid and stannic acid, the latter of which, though in solution, takes no part in the electrical conduction—and will proceed at once to the consideration of van't Hoff's Law of Solutions, by means of which the molecular weight of a soluble substance may be determined.

Based, in the first instance, upon Pfeffer's measurements of osmotic pressure, van't Hoff's law is an extension of the gas laws—namely, Boyle's law, Charles's law, and Avogadro's law—to solutions of (non-volatile) substances, so that, just as the molecular weight of a gas or volatile substance may be determined by means of Avogadro's law, the molecular weight of a non-volatile substance may be obtained from a knowledge of its osmotic pressure. Chemists have thus a method of determining whether a substance has a high or a low molecular weight.

Some of Pfeffer's (1877⁴) results are of interest from the present point of view. According to his measurements, the osmotic pressure of a gum arabic

solution is about ten times smaller than the osmotic pressure of a sugar solution of the same percentage concentration, and the osmotic pressure of a gelatin solution is smaller still. From this one would conclude that gum arabic and gelatin have much larger molecular weights than cane sugar.

The direct measurement of the osmotic pressure of a solution is not generally made use of, owing to the experimental difficulties; instead of it, measurements are made of the diminution of vapour pressure, lowering of the freezing-point, or elevation of the boiling-point, which have been proved both experimentally and theoretically to be proportional to the osmotic pressure. Among others, Brown and Morris (1888, 1889⁵) determined the freezing-point of water to which known quantities of inulin, starch, maltodextrin, and arabic acid had been added. The observed lowerings of the freezing-points were very small, and the calculated molecular weights correspondingly large, but the relative experimental error was so considerable that no safe conclusions could be drawn from the results.

Sabanejew, Friedenthal, Meyer, and others made similar observations on colloid solutions of gallic acid, silicic acid, tungstic acid, glycogen, soluble starch, all with the same result. These determinations seem to have been very generally accepted as conclusive evidence that the molecular weight of the colloids was very large, and doubtless were so accepted because they fitted in with the prevalent ideas on the subject, in spite of the fact that Paterno (1889⁶) had already clearly shown that tannin and gallic acids do not appreciably lower the freezing-point of water, while in acetic acid the lowering of the freezing-point corresponds to the simplest chemical formula for the substances. Paterno stated his opinion that Raoult's law (van't Hoff's law as applied to the lowering of the freezing-point, and empirically discovered by Raoult) does not apply to colloid solutions, and that in them water is not truly a solvent. The molecular weights of albumins have been calculated from the depression of the freezing-point, *e.g.* Sabanejew and Alexandrow (1891⁷) found the molecular weight of albumin to be 14,700; Bugarsky and Liebermann (1898⁸), for egg albumin, after making a correction of the freezing-point of the soluble constituents of the ash, found it to be 6400.

In the light of more recent work there can be no doubt that these determinations are absolutely of no value, the observed freezing-point depressions, when not due to experimental error, being caused almost entirely by the impurities which are unavoidably present along with the colloid. Thus Ludeking, in 1888, observed that a 40 per cent. solution of gum arabic had the same boiling-point as water; Linder and Picton (1892⁹) obtained no depression of the freezing-point with a pure colloid solution of arsenious sulphide or of mercuric sulphide; and Lottermoser's experiments with stannic acid had the same result. The only conclusion that can be come to is that colloid solutions possess no appreciable osmotic pressure, and that therefore they are not solutions in the sense required by van't Hoff's law, and that the law cannot be applied to determine the molecular weight; in other words, Paterno's statement that in them the water does not act as a true solvent, is fully confirmed by later investigations.

There still remains, however, the question of the albumins, whether they are true solutions of substances with large molecular weight, or colloid solutions like the others. The chemical grounds for the belief that the molecules of albumins contain a very large number of atoms are certainly more cogent than those on which the large molecular weights of inorganic colloids was based, and accordingly there was a disposition to believe them to form true solutions to which van't Hoff's law could legitimately be applied. This question seems to have been finally settled by E. Waymouth Reid (1904¹⁰), who showed that carefully washed precipitated or recrystallised albumin gave solutions which had absolutely no osmotic effect, and that the small osmotic pressure usually obtained is caused by foreign impurities, or by decomposition products

of the albumin. From the osmotic pressure point of view, then, colloid solutions are not true solutions in the sense that sodium chloride or sugar form a solution in water; they are to be regarded as suspensions. It is not impossible that there may be a minimal osmotic effect not caused by impurities; this may be ascribed to surface phenomena such as condensation of liquid at the interface between the solid and the liquid phases, or it may be what Bredig (1901¹¹) has called a pseudo-osmotic pressure, due to mutual repulsion of the similarly electrically charged particles which results in a kind of diffusion.

HETEROGENEITY OF COLLOID SOLUTIONS.

Long ago Faraday (1857¹²) observed that a solution of gold, which he had prepared by reduction of auric chloride, appeared turbid when a concentrated beam of light was sent through it, and concluded that the gold was not dissolved but suspended in the water. Many other colloid solutions show the same phenomenon. Others present the appearance of fluorescence, but the light is not polarised in true fluorescence, whilst it is in the case of the colloids.

The particles are so small that they are not visible with even the best microscopes. Even with a magnification of 2250 Bredig and Swingle (1901¹³) were unable to detect solid particles in a colloid gold solution. With this magnification particles of a size of 0.14μ would have been visible. A very sensitive test of the heterogeneity of a medium is the Tyndall effect (1869¹⁴), namely, a ray of light sent through the medium is diffused and polarised owing to the numerous reflections from the surfaces of the particles. The Tyndall effect was first applied to colloid solutions by Linder and Picton (1892¹⁵), who observed it in the colloid solutions of metallic sulphides, ferric hydroxide, silicic acid, starch, cellulose, and the dye congo-red. Bredig observed it with the gold solution just mentioned.

But the Tyndall effect is so delicate a test of heterogeneity that it is difficult to obtain an "optically void" liquid. Neither filtration nor distillation is effective. According to Spring, the only certain method is to produce a precipitate in the liquid, and to allow the precipitate to settle down in absence of air. In this way he showed that aqueous solutions of salts of the sodium and calcium groups of metals are optically homogeneous, and that salts of iron, aluminium, copper, mercury, and lead are not so. In later investigations by Lobry de Bruyn it was found that solutions of phosphomolybdic acid, raffinose and cane sugar are not homogeneous.

The question as to the essentially heterogeneous character of colloid solutions could not be definitely settled by the Tyndall effect by reason of its sensitiveness. The invention of the ultra-microscope by Zsigmondy and Siedentopf enabled them to establish the essential heterogeneity of colloid solutions.

The method of Siedentopf and Zsigmondy (1903¹⁶) for rendering visible ultra-microscopic particles, is to illuminate the particles with an extremely powerful and very narrow beam of light in such a manner that no direct rays of the illuminating beam reach the eye of the observer. This is obtained by illuminating at right angles to the direction of vision. The feeble rays of diffracted light are then within the limits of microscopic visibility.¹

By means of this apparatus the existence of particles of the size $5 \mu\mu$ can be recognised. All solutions of colloids show an intense cone of light; in some individual bright particles (submicrons) are visible after suitable dilution,

¹ Full details of the apparatus, with figures, are given in a booklet issued by Zeiss, "Beschreibung der Einrichtungen zur Sichtbarmachung ultramikroskopischer Teilchen," Jena, 1904; also in Zsigmondy, "Zur Erkenntniss der Kolloide," Jena, 1905.

whilst in others, in which the particles are smaller, the cone of light gradually disappears on dilution (amicros).

Extensive researches have been made, with the result that the presence of submicrons has been established in many cases, *e.g.* in colloid solutions of gold, silver, platinum, ferric hydroxide, aluminium hydroxide, silicic acid, etc.; of dye-stuffs—prussian-blue, carmine, naphthol-yellow, methyl-violet, anilin-blue; and in gold ruby-glass. The case of organic colloids—Much, Römer, and Siebert (1904¹⁷)—deserves closer attention. Albumins, albumoses, gelatin, and agar-agar solutions all contain submicrons. For purposes of comparison the solutions are diluted until only three or four particles are visible in the field; this ultra-value enables one to differentiate the various colloids. The behaviour of albumin solutions is somewhat complicated, for both submicrons and amicros are present. A specially pure glycogen was examined by Biltz and Grużewska (1904¹⁸) in “optically void” water, and the solution contained numerous white submicrons along with a distinct cone of light, which almost disappeared at a dilution of 1 in 300,000; addition of alcohol at this stage caused the appearance of submicrons from the amicros.

A 3 per cent. solution of soluble starch, prepared by boiling, contained amicros only, but on being kept at ordinary temperature for some time the solution contained many submicrons.

ELECTRICAL PHENOMENA OF COLLOID SOLUTIONS.

When an electric current is passed through a colloid solution the particles move to the cathode or to the anode, and are deposited there; if a diaphragm is inserted between the electrodes the colloid is deposited on that side of it which is opposed to the movement of the particles to the electrode. This was first observed by Linder and Picton (1892¹⁹) in the case of arsenious sulphide which moved to the anode, and of ferric hydroxide which moved in the opposite direction. The behaviour of many substances has since been investigated, and the following list, though far from complete, may be useful for reference:—

To the cathode.—Ferric hydroxide, aluminium hydroxide, chromic hydroxide, cadmium hydroxide, titanac acid, thorium hydroxide; methyl-violet, methylene-blue, magdala red.

To the anode.—The metals—gold, silver, platinum, and most of their compounds, *e.g.* AgI, AgCl, As₂S₃, PbS, CdS, etc.; anilin-blue, indigo; methyl-anilin-green, eosin, fuchsin, mastic; silicic acid, stannic acid.

This phenomenon must not be confused with electrolysis or electrical conductivity, with which it really has nothing in common.

The movement is due to the fact that there exists a difference of electric potential between the solid and the liquid. The origin of this potential difference is not definitely known. It has long been known that when any liquid and a solid insoluble in the liquid are brought in contact there is a difference of potential between them; as also have certain phenomena closely allied to the electrical movement of colloid particles. Thus if a moderate current of electricity is passed through a poor electrolyte which is divided into cathode and anode compartments by a porous earthenware or other similar diaphragm, there is a transference of liquid from one compartment to the other, until a definite difference of level is obtained; generally the level rises in the cathode chamber. Here the water becomes positively electrified with respect to the diaphragm, and, as the latter is immovable, the water is attracted to the cathode. The same effect has been observed with capillary tubes instead of a porous diaphragm.

If the diaphragm be reduced to very fine powder, and be suspended in the water, the water will still be positive and the solid negative, but now it is the

solid which can move more easily, and it will be attracted to the anode while the water level remains stationary throughout. This is precisely what happens with the great majority of colloids in water. In other liquids the movement may be in the opposite direction; platinum in water is negative, and moves to the anode, but addition of alcohol reduces the difference of potential to zero and finally reverses the sign of the charge, and with it the direction in which it moves. In general the addition of H ion displaces the charge on the solid to the + side, whilst OH ion displaces it to the - side. These two ions have a greater effect than any others, and the OH ion is much more effective than the H ion, a concentration of 1 grm. equivalent of alkali in 10^5 litres having a recognisable effect.

The case of albumin—Hardy (1904²⁰), Perrin (1903²⁰)—is particularly instructive. Coagulated egg albumin, brought into solution by means of a small quantity of alkali, wandered to the anode as a white coagulum; but if an acid solution was employed the albumin went to the cathode, and in neutral solution the albumin remained stationary; albumin must be iso-electric with pure water, and becomes negative in alkaline solution and positive in acids. Recently W. Pauli (1906²¹) extended and confirmed Hardy's experiments, using a pure dialysed albumin free from electrolytes. No cataphoresis took place; the albumin was therefore free from electric charges. In presence of acids or acid salts it was +, in presence of alkalies or basic salts it became -, neutral salts had no effect. The actual velocity of the colloid particles of gold and silver under a known electric force has been determined (Burton (1906²³)). The rate is of the same order as that of the slower moving ions in aqueous solution. An empirical rule as to the sign of the charge on the solid suspended in a liquid is that the substance with the higher dielectric constant is always positive; and since water has the highest known dielectric constant, with the exception of hydrocyanic acid and hydrogen peroxide, in water the colloid is negative, *e.g.* glass has a D.C. 4 to 7, and in contact with turpentine with D.C. 2.2 is positive, and if suspended in it, migrates to the cathode. But in water with a D.C. 80 the glass is negative, and migrates to the anode. This empirical rule does not always hold in the case of metallic compounds. As has been already mentioned, the migration of colloids in an electric field are not electric conductivity effects, nor directly connected with them. In fact, the electrical conductivity of colloid solutions has been the subject of careful investigation, and has been found to be exceedingly small. Whether the observed conductivity is not due to impurities is difficult to say. Billitzer found the conductivity of a colloid platinum solution to be two or three times greater than that of water (water = 0.81×10^{-6} ; platinum solution = 1.14×10^{-6} to 1.6×10^{-6}). Further evidence is afforded by the experiments of Malfitano (1904²³), in which filtration through collodion of a solution of ferric hydroxide, arsenious sulphide, or albumin did not change the conductivity of the solution, though the collodion retained considerable quantities of the colloid. According to Pauli (1906²⁴) very pure albumin solution is practically an insulator, the addition of 0.06 grm. NaCl to 1 litre of the solution increasing the conductivity eight times.

THE COAGULATION OF COLLOIDS.

Graham observed that many colloid solutions are precipitated by the addition of certain substances even in small quantity; a solution of aluminium hydroxide, made by digestion with aluminium chloride, gave a dense precipitate of aluminium hydroxide when a drop of dilute sulphuric acid was added. In certain cases the precipitate goes back into solution when the precipitant is removed, but in others it does not. A colloid can exist, then, in two forms which Graham called the "sol" and the "gel," a nomenclature

which is still in use; and further, there are two classes of colloids—the “reversible” and the “irreversible,” although this division is not quite correct, for some colloids are reversible or irreversible according to circumstances.

It will be convenient to deal with “*irreversible*” precipitation first. The inorganic colloids mainly belong to this class, and are coagulated by extremely small quantities of certain substances, while even large quantities of other substances have no effect. Electrolytes as a class have a coagulating action, non-electrolytes have none. The reversible colloids are not so sensitive to electrolytes unless some specific chemical action takes place, but, on the other hand, they are often coagulated by organic substances; albumin, for instance, is coagulated by alcohols, phenols by mercuric chloride, but not by small quantities of salts like sodium chloride.

The first point of importance is that there is a minimal concentration below which coagulation is not produced. For purposes of comparison, the reciprocal of the equivalent concentration which just causes complete coagulation under fixed conditions is made use of. This value is strikingly different for different salts, as the following table for arsenious sulphide shows:—

KI	= 1	MgCl ₂	= 182
KCl	= 2·5	ZnSO ₄	= 60
Na ₂ SO ₄	= 2·5	Al ₂ Cl ₆	= 1518
CaCl ₂	= 80	Al ₂ (SO ₄) ₃	= 957

It is obvious that the coagulating power depends more on the cation than on the anion. Then again of the cations, the univalent K' and Na' have about the same effect, the bivalent Ca'', Mg'', and Zn'' are together with a much greater effect, whilst the trivalent Al''' has an enormously greater effect. The ratios of the three sets of ions are

$$K' : K'' : K''' = 350 : 20 : 1.$$

Subsequent investigation has shown that this is not an exceptional example, colloid cadmium sulphide, silver, antimonious sulphide, and cupric hydroxide all exhibit the same behaviour. Hardy (1899²⁵) examined solutions of gold and of ferric hydroxide. With the latter, which is positively charged, the equivalent coagulating power no longer depends on the cation, but on the anion, and in the same ratio as before. Hardy's conclusion is that the coagulating power of a salt depends on the valency of one of its ions, and that the coagulating ion has always the opposite sign to that of the colloid.

This is of fundamental importance in the theory of coagulation, and has led to important results. Whetham, by the aid of the theory of probabilities, and on the assumption that the electric charge on a trivalent ion is just sufficient to cause aggregation of a given number of colloid particles, has shown that the coagulating power of univalent, bivalent, and trivalent ions should be in the ratio previously mentioned. Burton (1906²⁶) investigated the effect of the addition of increasing quantities of aluminium sulphate to colloid gold and silver; at first the velocity diminished, and finally the direction of migration was reversed. At the reversal point the solution was at its maximum instability. Assuming that at this point all the metal ions go to neutralise the charges on the particles, he calculates the charge on a gm. equivalent of silver to be 0·04 of the charge on a univalent ion, and of gold to be 0·12 of that on a univalent ion.

The second point of importance is that on coagulation the colloid carries down some of the electrolyte, or rather of the ion, which causes the coagulation. This was first observed by Linder and Picton (1895²⁷) with barium chloride and arsenious sulphide, barium being taken down and the remaining solution being acid in reaction. The barium could not be removed by washing, but could be replaced by other cations when the precipitate was washed with solutions of other salts.

The different ions are carried down in chemically equivalent amounts. It may be that the hydrolysis of the salts exerts an influence in this respect, for in the case of univalent ions it is negligible, is noticeable in the case of the bivalent ions, and very marked with salts of trivalent metals.

A third point of outstanding interest is that small amounts of reversible (organic) colloids can "protect" an irreversible colloid from the coagulating effect of salts. It was noticed by E. von Meyer and Lottermoser (1902²⁸) with albumin and colloid silver. Later researches have shown it to be a general property, and in an elaborate research Zsigmondy (1897²⁹) found that the protecting power differed enormously for different organic colloids, and that the differences could be used to characterise the substances. The number of milligrammes of colloid which just failed to prevent coagulation of a given gold solution to which a definite quantity of sodium chloride was added he called the "gold number." A few of his results are given:—

Gelatin	0.005 to 0.01
Isinglass	0.01 „ 0.02
Casein	0.01 (+ NH ₃)
Egg albumin	{ 0.15 to 0.25
Gum arabic	{ 0.1 „ 0.2 (two different kinds)
Dextrin	0.15 „ 0.25
Wheat starch	6 „ 12
Potato starch	4 „ 6
Cane sugar	25 „ 8

The "gold number" can be used as a test for adulteration, etc., *e.g.* a dextrin solution with 1 per cent. of gelatin has a "gold number" of 0.5 to 1 instead of 10. It has also been used (Schulz u. Zsigmondy (1902³⁰)) in the fractional precipitation of white of egg, and to albumoses (Zunz (1904³¹)) derived from egg albumin by means of pepsin, and the "gold numbers" of various sera and antitoxins (Biltz (1902³²)) have been determined.

It should be mentioned that "protection" is not afforded by organic colloids only—zirconium hydroxide solution protects gold solution, and colloid ferric hydroxide solution derived by dialysis of ferric chloride contains chloride which is not precipitated by silver nitrate, the colloid silver chloride being protected by the ferric hydroxide. No very satisfactory explanation of "protection" has been put forward. It is not due to differences of potential, nor is it simply an enclosure of the one particle by the other, for the ultra-microscope shows the sizes not to be much different.

IMMUNITY.

Bredig noticed that a freshly prepared gold solution was very sensitive to the action of ammonia, and that the sensitiveness diminished when the solution was old. When he mixed a quantity of "old" solution which was added to a freshly prepared solution, the latter became "immune" to ammonia; in other words, the old solution "protected" the new solution against the coagulating action of ammonia.

In this connection another interesting and suggestive observation must be mentioned. When a coagulating solution is added a little at a time to the colloid solution, a larger quantity is necessary to cause coagulation than if it were added at once. The solution becomes accustomed, as it were, to that particular precipitant, and can bear a larger concentration of it than it could at first.

THE MUTUAL PRECIPITATION OF COLLOIDS.

Since the coagulation of an irreversible colloid solution, by means of an electrolyte, is certainly a result of the neutralisation of the electric charge on

the particles by the opposite electric charge on the coagulating ion, it is not surprising that negatively charged colloids are coagulated by positively charged colloids, and as a result both colloids are precipitated together. That a certain proportionality between the two colloids should be necessary for precipitation follows from this conception of the nature of the changes on coagulation. This conclusion is fully borne out by the facts; an insufficiency of the one, which of course is an excess of the other, does not cause coagulation of either. This behaviour, which is similar to some processes of dyeing, and to the agglutination of bacteria, has been thoroughly studied by Biltz⁽⁸⁸⁾ and, in numerous instances, the existence was established of an "optimum precipitation" when a definite proportion of the one colloid was added to the other. Billitzer (1904³⁴) further demonstrated that this "optimum precipitation" took place when the proportion of the two colloids was in the inverse ratio of the electric charge on unit mass of the particles. This latter ratio he determined in a simple manner by estimating volumetrically the amount of barium carried down by the different colloids when coagulated by barium chloride solution.

This constancy of proportion in the mutually precipitated colloids has undoubtedly misled many people into the notion that these precipitates are true chemical compounds.

When two colloid solutions of like electric charge are mixed no precipitation takes place; on the other hand, the more stable of the two "protects" the other against the action of electrolytes, and the mixed solution has the same stability as the more stable component. The phenomena are again more complicated in the case of organic colloids. Dialysed albumin, which in water is electrically neutral, is not coagulated by either positive or negative colloids. In acid solutions it becomes positive, and can then be coagulated by negative colloids such as phospho-tungstic acid, phospho-molybdic acid, and acid-colouring matters. As ordinary albumin is precipitated by solutions of heavy metals, which on account of hydrolysis contain positive colloids, it must be negative. This negative charge is attributed by Pauli to the alkaline salts normally contained in it, such as sodium bicarbonate and disodium hydrogen phosphate.

EFFECT OF RADIUM RAYS ON COLLOID SOLUTIONS.

The effect of radium rays on colloid solutions is in agreement with the view that the coagulation of colloids is brought about by the removal of the electric charges on the solid particles. Henri and Mayer⁽⁴¹⁾ found that the negative rays from radium had no action on ferric hydroxide or silver solutions, even after four days. After the addition of a trace of sodium nitrate, in insufficient quantity to coagulate the solutions, the positive ferric hydroxide was coagulated by the radium rays, the silver not coagulated. Later experiments with the positive colloids magdala red and methyl-violet, and the negative colloids anilin blue and cupric ferrocyanide, confirmed this result.

REVERSIBLE COAGULATION.

The subject of the coagulation of "reversible" colloids is very large, and much less is known with certainty as to the nature of the changes and the causes leading to them. The behaviour on desiccation is strikingly different from that of irreversible colloids. Most if not all inorganic colloids become insoluble when evaporated to dryness, or when the liquid is frozen; most of the organic colloids dry up to an amorphous, semi-solid mass which redissolves completely when allowed to stand in contact with the liquid. They may be considered to form "solid sols."

The protective action of reversible colloids on irreversible ones with regard

to coagulation by electrolytes also extends to these processes. A gold sol to which gelatin has been added may be evaporated to dryness or be frozen, and on addition of water or on the solution being melted the gelatin goes into solution, and takes the gold into solution with it.

The processes of solidification and liquefaction of gelatin and agar-agar solutions have been extensively investigated by Hardy (1900³⁵), Pauli and Rona (1902³⁶), Schroeder (1903³⁷), and others. Pauli and Rona found that sulphate, citrate, tartrate, urea, and glucose raise the solidification temperature, and that chloride, chlorate, nitrate, bromide, and iodide lower it. That precipitation of gelatin and gelatinisation are two distinct processes follows from this observation, and the fact that aqueous gelatin solutions are precipitated only by electrolytes, and that non-electrolytes, especially urea and glucose, influence or prevent the precipitation by salts.

The process of "salting out" of albumins, by neutral solutions of salts of the alkalis, ammonium, and magnesium, a process which is of so great technical importance, is at first a reversible coagulation, but slowly passes into an irreversible one. The nature of the changes is not certainly known. One characteristic feature of salting out is that it only takes place with relatively strong solutions of salts, and for each albumin there appear to be definite limits of concentration between which the coagulation is commenced and completed. According to Spiro (1903³⁸), two phases are always formed in typical "salting out," each phase containing all three components, but in different proportions. It is thus a partition process, comparable, for instance, to the partition of an organic substance between ether and water.

The heat coagulation of albumins is also irreversible, but pure dialysed albumin is not coagulated by heat; subsequent addition of salt causes coagulation. The acid or alkaline reaction of the solution is also of importance. In this connection it is worthy of note that salt-free albumin is not readily precipitated by alcohol. Passing reference must here be made to Ramsden's (1894, 1903³⁹) ingenious and highly suggestive researches on the formation of solid albumin by mechanical agitation, gas bubbles, surface action, etc. In some instances the solid formed is insoluble in the liquid, in others it is soluble. The bearings of his investigations on many of the phenomena shown by reversible colloids are obvious.

THE FILTRATION OF COLLOIDS.

The pores of filter paper are so large in comparison with the sizes of colloid particles that colloid solutions pass through it without change, apart from adsorption. Porous earthenware, Pukall's cells, Maassen or Chamberland filters allow arsenious sulphide or gold solution to pass unchanged; the pores may become clogged up with particles, and then the filtrate may become colourless.

Bechhold's (1906, 1907⁴⁰) experiments are particularly important. By suitable regulation of the size of pore of the filter he was able to separate colloid particles from the liquid or from crystalloids dissolved in the liquid. His filters consisted of filter paper, woven fabrics, or wire gauze impregnated with jellies of different concentrations. By means of them he removed arsenious sulphide, and ferric hydroxide from water, and concentrated solutions of albumin and of hæmoglobin, the filtrate being quite free from albumin. The relative sizes of particles can be readily determined in this way by using filters of graduated density, and the results agree well with the ultra-microscopic determinations. The most important application of this filtration process is that it enables one to carry out fractional filtrations on mixtures of colloids. Thus the albumoses of a mixture have been separated in this way.

But useful in practice as the process undoubtedly is, it is by no means such a simple matter as it was first thought to be, namely, a difference in size

of pores through which the particles were, or were not, too large to pass. Besides plugging up of the original pores, adsorption, and, in particular, the mutual action of one colloid on another by which insoluble mixtures are formed, must play an important part in gelatin filtration. The facts are in agreement with this view; filtration is at first fairly rapid, gradually slackens off, and at last ceases entirely. Moreover, a solution of arachnolysin cannot pass through a gelatin filter, not because its particles are large, but because it combines with the gelatin. Collodion filtrations are probably intermediate between filtration through a finely porous diaphragm and a colloid filter such as Bechhold's gelatin filter.

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See also Zsigmondy, "Z. Erkenntnis der Kolloide," Jena, 1905, S. 119.