COLLOIDAL CHEMISTRY.

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INTRODUCTION.

For an indefinitely long period in the history of chemistry, observations were constantly being made upon substances classed as amorphous and crystalline, and their properties were recorded in a more or less haphazard manner. It was not until the close of the 19th century, that an English physicist, Walter Graham, began his classic researches in this direction which resulted in the birth of a new phase of chemistry that has reared for itself today a monumental edifice which still promises a future of untold possibilities.

Walter Graham gave to the substances belonging in this new field of chemistry the somewhat phantastic name, "colloids," and its study is called "Colloidal Chemistry," or better still, "The Chemistry of Colloids," for he was chiefly concerned with the behavior of two different classes of substances. One class, comprising such compounds as NaCl , CuSO_4 , etc., he found would pass very readily through certain membranes such as parchment paper, while the other class, containing such substances as gelatine, agar-agar, albumen, etc., lacked this property or showed its presence to a very slight degree. The former class he called crystalloids, which means "like a crystal in structure" having the power to crystallize from a solution, and to the latter he gave the name colloids, from the Latin, which means like gelatine, lacking crystalline structure, or in other words, amorphous. Although new phrases and terms have been introduced since Graham's time, his original classification of substances into colloids and crystalloids is still retained.

Definition of a Colloid.

It would not be out of place at this stage to begin with the definition of a colloid, and then through experimentation to verify as far as possible the statements therein contained.

Colloidal solutions may be defined as being either solid or liquid mixtures of two or more substances which are not separated from each other by the action of gravity, by the ordinary mechanical methods of filtration or by decantation; but which are so separated when they are passed through certain animal or vegetable membranes. The substance, then remaining behind,

is designated the colloid. This distinguishes colloidal solutions at the outset from suspensions of fine visible particles which would ultimately settle out on the membrane and true solutions which would pass through and the colloid therefore lies somewhere between these two types in the size of the suspended particles. This process of separation is known as dialysis.

But there are two kinds of colloidal mixtures which are retained by the above mentioned membranes, a type of one being gelatine, agar-agar, etc., and of the other, colloidal arsenious sulphide, colloidal ferric hydroxide, etc. To the discussion of these we shall now turn our attention. For the sake of clearness and convenience I have designated the latter class as "Prepared Colloids" to distinguish them from the former class, the "Natural Colloids."

METHODS OF PREPARATION.

(1) *General Principle.*

When an insoluble substance is formed by the interaction of two or more compounds in the absence of an electrolyte or fairly well ionized substance, the insoluble precipitate thus produced will almost invariably be obtained as a colloid. Thus, if a saturated hydrogen sulphide solution, H_2S , from which all traces of any electrolyte have been removed (especially that of concentrated sulphuric acid or hydrochloric acid which may be carried over by the generated gas) is added to an aqueous solution of arsenious oxide, As_2O_3 , neutralized by the addition of sodium carbonate, Na_2CO_3 , an opalescent, orange-yellow solution will be formed which contains the exceedingly insoluble arsenious sulphide in solution. The solute in this solution will not settle out on prolonged standing or agitation, but appears as a perfectly homogeneous solution.

It will be profitable at this point to bring out the fact that we are not dealing with a supersaturated solution. It is well known, that if we dissolve considerable sodium thiosulphate (ordinary hypo) in boiling water we can obtain a solution which contains the solute dissolved far in excess of the amount required by a saturated solution, without any evidence of a solid phase appearing, but if we add the slightest crystal of the same substance, scratch the surface, or centrifuge it, immediate and spontaneous crystallization of the solute will take place. We are therefore dealing with a supersaturated solution. However, if we should add some ordinary solid arsenious sulphide to colloidal arsenious

sulphide, and agitate it, no crystallization will take place. We are therefore in this instance not dealing with a supersaturated solution, but with an insoluble substance in the colloidal condition. We shall postpone the proofs as to its colloidal nature at this part of the discussion.

(2) The second method of obtaining colloidal preparations is through dialysis, which makes use of the fact to which reference has already been made, that certain animal or vegetable membranes will permit the passage of crystalloids, while they retain in the dialyzer any colloid. If a molar solution of ferric chloride, FeCl_3 (containing 161.5 grams of the salt to a liter) be carefully neutralized with a molar solution of ammonium carbonate $(\text{NH}_4)_2\text{CO}_3$ (96 grams to the liter) until the precipitate formed on each addition will barely dissolve, and then filtered and dialyzed against running water, distilled water, and finally conductivity water (it will then contain 2.40 grams Fe_2O_3 to the liter), ferric hydroxide, $\text{Fe}(\text{OH})_3$, a very insoluble substance, formed quantitatively according to the reaction, $\text{FeCl}_3 + 3\text{HOH} = \text{Fe}(\text{OH})_3 + 3\text{HCl}$, will be obtained in a perfectly soluble condition without forming any precipitate. It can be very easily verified as in the case of colloidal arsenious sulphide, that we are again not dealing with a case of supersaturation.

(3) There is still a third method known as that of "Bredig," the discoverer of this process. This consists in passing an electric current through fine wires of the noble metals, gold, silver or platinum, under pure distilled water, containing a 1/2000 N HCl solution, in such a manner that an electric arc is formed. Extremely fine particles of the metals are thus shorn off. If this liquid be now filtered it will be found that a clear and homogeneous appearing solution passes through the filter. If gold wires are used, a red-colored liquid is obtained and the intensity of the color will be indicative of the concentration of the gold particles in colloidal condition.

PROPERTIES OF COLLOIDS.

We have already seen that there are two distinct classes of colloids, one, the natural colloids as albumen, and the other, prepared colloids, as colloidal ferric hydroxide or colloidal arsenious sulphide.

For the sake of uniformity and logical treatment, I shall deal with the properties of both classes, first discussing those of the

natural colloids, and then contrasting them with similar properties of the other class, that is, prepared colloids, whenever feasible.

(1) *Density, Osmotic Pressure and Diffusion.*

(a) The first striking property that meets our attention in the treatment of colloids, is that their density is very great and that they therefore must have a very great molecular weight. They also exhibit a contraction in volume on increase of concentration, as shown by the following table:

1% gelatine gives a volume of 0.960 cc.

25% gelatine gives a volume of 0.937 cc.

50% gelatine gives a volume of 0.902 cc.

(b) If the osmotic pressure of both classes of colloids be taken, the important fact is brought to light that it is very small and in fact at times too minute for actual observation, whereas, true solutions such as cane sugar solution, etc., have very large pressures. The following table brings out these facts very strikingly.

Substance.	Concentration %	Osmotic Pressure cm. Hg.
Cane Sugar	1.0	53.0
Cane Sugar	5.0	265.0
Gum Arabic	1.0	6.9
As ₂ S ₃	4.0	1.7
Ferric Hydroxide	1.1	0.8
Ferric Hydroxide	2.0	2.8
Ferric Hydroxide	8.9	22.6

(c) As already noted in the introduction, colloids show practically no diffusive power through certain membranes, whereas, crystalloids pass through them very readily. It was this observation which led Graham to the conclusion that the size of the colloidal particles must be enormous, and therefore they could not pass through the small pores of such membranes, and led him to assign also a very great molecular weight to them as has already been stated. Upon this property of colloids, their slight diffusion, depends their separation in solution from ordinary crystalloids. If, then, such a mixture is placed in a collodion dialyzer¹ and the

¹ NOTE.—Among the many forms of dialyzers in use at the present time, the "parchment-paper" dialyzer is usually recommended as most suitable for dialysis. I have found it faulty in the following respects: First, the available dialyzing surface is small, and secondly, if large, the single

whole placed in running water, the crystalloid will soon pass out of solution, the water passing in either direction, while the colloid will be retained in the vessel, called the dialyzer. This process is known as dialysis, and it was extensively used by Graham in his many researches upon the properties of colloidal preparations.

-(2) *Opalescence.*

A general property of colloidal mixtures applying to both the natural and the prepared, is that they appear opalescent by reflected light. Colloidal arsenious sulphide and colloidal ferric hydroxide (when not too concentrated) will show this very conclusively. The true cause of opalescence is still a matter of dispute. Scientists differ widely in their statements.

covering under pressure breaks, after a short exposure to running water. It can be used to advantage only when the proper kind of paper is available, and then the conditions for such are difficult to obtain.

I have found the "collodion dialyzer" very convenient and besides its durability (being able to remain intact for considerable time in running water) it offers a much greater freedom for dialysis and therefore less time in which to complete the process. Directions for the preparation of such a dialyzer can be found in special articles, and they are therefore given for the sake of convenience and ready reference.

A few cubic centimeters of collodion are placed into a dry and clean four-ounce bottle having a wide neck. The bottle is then revolved horizontally spreading a uniform coating of collodion over the inside. The remaining collodion is poured back while rotating the neck of the small bottle. This process will insure a uniform coating. Working rapidly will prevent too thick a covering, which is to be avoided, thus preventing ultimate cracking of the collodion. When the proper coating is obtained, the bottle is then inverted and given a rotary motion between the palms of the hands. This causes evaporation of the ether which is hastened by blowing into the bottle. When all the ether has evaporated, water is poured into the bottle which will dissolve out the alcohol. (Collodion is a solution of guncotton in ether and alcohol.)

The film of collodion around the neck is then carefully detached, and a little water added between the neck of the bottle and the film. With a gentle, prying motion the water works its way around and loosens the collodion which can then be taken out of the bottle.

The solution is placed in the dialyzer thus prepared, a rubber stopper inserted in its neck, then attached to a clamp, placed in a jar of running water, and the whole apparatus is ready for dialysis.

Very useful dialyzers can be conveniently made by using small test-tubes of about 35 c.c. capacity as moulds, by following the above directions. I have found them to work extremely well. The liquid can be placed in these dialyzers and a space of about an inch left for the increase in volume of the liquid caused by the entrance of the outside water. The top is then closed tightly with a piece of cotton thread and placed in a large vessel of running water. These small "sausage collodion" dialyzers float around while the liquid dialyzes very quickly. In this manner, large amounts of liquid can be dialyzed at one operation and in one vessel.

(3) *Reversible and Irreversible Colloids.*

A striking difference between the two classes lies in their behavior towards heat and cold. If gelatine, albumen, agar-agar, gum arabic, etc., are heated, they form viscous liquids which on cooling return to their original solid condition and can again go through the same changes. Such colloids are said to be *reversible*, and this property is characteristic of all natural colloids.

Colloidal ferric hydroxide, colloidal arsenious sulphide, do not undergo such changes. If they are cooled no precipitation or coagulation takes place, and if coagulated, heating has no effect in bringing them back to their original condition.

Such colloids are called *irreversible*. This property is true of most of the prepared colloids.

(4) *Mutual Hindrance.*

Again, colloids mutually prevent each other's passage, while they allow the passage of crystalloids very readily. Thus, if a 4% solution of agar-agar be prepared, by dissolving 4 grams of the substance to every 100 cc. of boiling distilled water, and the resulting solution be poured into two large test-tubes tightly corked and then allowed to cool, a true natural colloid is obtained having the appearance of a jelly. If, then, one of the sticks thus prepared be immersed in an ammoniacal copper sulphate solution (prepared by adding strong ammonia water to the copper sulphate until the precipitate first formed just dissolves) and allowed to stand over night, it will then be found on cutting the sticks in two that the deep blue color has permeated the agar-agar uniformly to the center, imparting to the stick a deep blue color. On the other hand if the second stick be placed in any other colloid (preferably one that is highly colored) and allowed to stand the same amount of time and the stick is then cut open, no color will be found to have permeated it. Thus, agar-agar, a true natural colloid, has allowed the passage of a crystalloid while it prevented that of the colloid. The properties enumerated are only a few of the many that could be cited; but the most striking, characteristic in general of this great class of substances, have been given.

ELECTRICAL PHENOMENA.

Perhaps the most interesting of all the properties of colloids is that they appear to be charged electrically and exhibit under

certain conditions electrical phenomena. This can be shown in a number of ways.

(1) *Migration.*

If an electric current is passed through colloidal ferric hydroxide and also through colloidal arsenious sulphide, contained in separate *U* tubes, one side of which contains the anode and the other the cathode, after a lapse of a few minutes migration will take place towards definite poles from which we argue that the colloidal particles are electrically charged. It will be found that in the former colloid, ferric hydroxide, migration takes place towards the cathode or negative electrode, and that therefore colloidal ferric hydroxide must have on it a positive charge; while colloidal arsenious sulphide will be found to move towards the anode or positive electrode, and is therefore negatively charged. It would be profitable to point out here that both the ferric hydroxide and arsenious sulphide (in colloidal form) move as an ion, the former as a positive ion, the latter as a negative one.

Before the current is turned on, the liquids appear perfectly homogeneous and as clear as solutions, having their characteristic opalescence. Just as soon as the current passes, the colloids not only begin to migrate, but they are precipitated around the electrodes as shown by characteristic colors which they assume, and they lose their opalescence.

The same is true of other colloids. Metallic hydroxides, silicic acid, basic dyes, as methyl violet, methylene blue, etc., are all charged positively and migrate to the cathode, while all metals, metallic sulphides, starch, acid, dyes, as aniline blue, indigo, fuchsin, etc., are all charged negatively and migrate to the anode. The natural colloids do not show this effect for they do not migrate when a current is passed through them, and they are therefore devoid of any charge whatsoever. It is for this reason that the addition of an electrolyte fails to produce any coagulation as will be pointed out later.

(2) *Change of Charge.*

Not only do colloids have definite electrical charges on them, but the character of the charge may vary with conditions. Thus colloidal platinum is negative in a medium such as water, but acquires a positive charge when prepared in a mixture of water and alcohol. Again, albumen, colloidal silicic acid, and colloidal stannic acid are negative in alkaline liquids and positive in those which are acid.

(3) *Coagulation.*

The use of the electric current is not the only source for demonstrating the electrical nature of colloids. Electrolytes, or highly ionized substances, will show the same behavior in discharging the colloids, and in ultimately precipitating them.

(1) *Electrolytes:* If to some colloidal ferric hydroxide or arsenious sulphide we add an electrolyte such as sodium chloride, NaCl, it will be found that the colloid is fairly rapidly precipitated when a sufficient amount of the salt is added. If, however, the same amount of sulphuric acid, H_2SO_4 , is added, almost immediate precipitation or coagulation takes place. The coagulation of the colloid will depend upon its charge and also that of the ions. Again, the increased speed of coagulation has been found to vary with the valency of the ion of opposite sign to the colloid and therefore sulphuric acid, valency of two, is a better reagent than sodium chloride, whose ions are only univalent. Trivalent ions will in turn be more effective in producing the desired result. Concentration also plays its role in this instance, for a definite concentration of the free ion is necessary to produce *complete* coagulation.

If separate 50 cc. portions of arsenious sulphide, in the colloidal condition, are poured into several large test-tubes, and 200 cc. of the following concentrations of the electrolytes in milli-equivalents per litre are used (non-electrolytes have no effect even if present in great concentration), as shown by the number preceding the electrolyte, immediate precipitation takes place with those having a dot prefixed, while the others will show less activity. It can be also readily shown that colloidal ferric hydroxide behaves in a similar manner.

Colloidal As_2S_3 .	Colloidal $\text{Fe}(\text{OH})_3$.
. (1) 0.6 AlCl_3	(1) 0.02 $\text{K}_3\text{Fe}(\text{CN})_6$
(2) 1.5 MgCl_2	. (2) 0.1 $\text{K}_3\text{Fe}(\text{CN})_6$
. (3) 20 MgCl_2	(3) 0.1 Na_2SO_4
(4) 60 NaCl	. (4) 1.6 Na_2SO_4
. (5) 400 NaCl	(5) 6 NaCl
(6) 60 Na_2SO_4	. (6) 50 NaCl
. (7) 400 Na_2SO_4	(7) 5 MgCl_2
	. (8) 50 MgCl_2

(2) *Mutual Colloidal Coagulation:* Still another method of coagulation depends upon the mutual neutralization of the charge on one colloid by that on the other. If colloidal ferric hydroxide be added to colloidal arsenious sulphide both will be immediately

precipitated. In short, colloids bearing opposite charges will mutually coagulate each other.

When gold chloride is added to stannous chloride, a purple precipitate of colloidal gold particles which contains a negative charge, is formed, and this can be precipitated by colloidal stannic acid (carrying a positive charge) in the presence of HCl. If to this precipitate, an alkaline solution of ammonium hydroxide is added, the stannic acid now acquires a negative charge, is like the colloidal gold, the precipitate dissolves, and forms the beautiful tints of colloidal gold suspensions.

This negative solution is now extremely sensitive to the ions of a mixture of ammonium and magnesium nitrates.

(3) *Protective Colloids*: The point must be emphasized here that certain colloids, natural colloids, of the albumen type, may entirely prevent the coagulation of a colloid if present with the precipitating electrolyte; that is, when 200 cc. of a 0.05 Molar silver nitrate, AgNO_3 solution containing 2.5% HNO_3 (S. G. 1.42) is mixed with a 0.05 Molar sodium chloride NaCl solution, a white precipitate of silver chloride AgCl , immediately separates, but if repeated with 1% gelatine solution a white opalescence appears, and no precipitate separates even on prolonged standing. If hydrogen sulphide H_2S (containing no traces of electrolytes) is added, a black colloidal insoluble precipitate of Ag_2S , silver sulphide, is formed which will not settle on prolonged boiling or standing.

THEORIES ON COLLOIDS.

We have so far in our discussion concerned ourselves with certain properties peculiar and characteristic of colloids, without attempting to offer any explanation, and it remains to do so now.

As is true of a great many natural phenomena, so here no one explanation of their singular behavior can wholly suffice, though from time to time, many have been attempted with more or less success. Of all such attempts to explain their electrical charge, two deserve our special attention here, namely, that of Surface Contact and Ionization.

(1) *Surface Contact*.

We have first, a case of surface contact or surface electricity. It has been proven by experiment, that at the surface of two different substances there is always a potential difference and in the case of colloidal suspensions, there is a large surface contact, as compared with the surfaces exposed in ordinary cases of contact. A colloid like platinum or gold is negatively charged, and

the bathing medium receives the positive charge. This we have shown takes place when the medium is only water. Now, it was stated that colloidal platinum in water and alcohol is oppositely charged, positively, and according to this theory the bathing medium would then receive the negative charge. In the case of colloidal ferric hydroxide, positively charged, the bathing medium becomes negatively charged. Plausible as this explanation might seem, it still does not tell us which charge will be taken up by the colloid and which by the surrounding medium, and therefore the other theory which makes it a case of ionization seems to answer the question more conclusively.

(2) *Ionization.*

As a phenomenon of ionization, let us take colloidal ferric hydroxide as an example. This may dissociate and send a few hydroxyl ions into solution and leave a residual positively charged colloidal particle. With stannic acid or silicic acid, hydrogen ion would be sent into solution (positively charged) and leave behind a residual negatively charged colloidal particle.

Now, albumen is capable of forming salts, both with acids and with bases. As a salt, it would dissociate into ordinary positive ions and a colloidal negative one in alkaline solution and into an ordinary negative ion and positive colloidal one in acid solution, in harmony with the above theory.

But how are we to explain the action of the metallic colloids since metals cannot undergo ionization? To answer this question it is necessary here to make one further assumption. The surrounding medium ionizes, imparts the charge to the metal and causes it to assume the colloidal state. In a medium such as water its ionization charges the noble metals negatively.

The source of electrical charge must therefore be due to partial ionization and not to total ionization. That is, if the ferric hydroxide ionized totally, then it would send positive iron ions into solution and negative hydroxyl (OH) ions into solution and it would give rise to a simple case of ionization of an electrolyte. But the current does not throw out iron at the cathode nor (OH) at the anode, but red gelatinous ferric hydroxide is coagulated en masse at the cathode. It is therefore evident that by sending a few OH ions (negatively charged) into solution it leaves the opposite positive charge on the colloid as demanded by this theory of partial ionization.

Concluding our brief remarks we must say that no definite knowledge has as yet been obtained as to whether contact or a case

of partial ionization, is the correct view. At present, experimental evidence is hard to obtain, and time bringing better methods for research may decide definitely in our favor.

SOLUTION AND SUSPENSION.

Having noted the fact that colloidal solutions give very low osmotic pressures, little lowering of the freezing point and but small increase of the boiling point, and also only slight variations in vapor pressure, while true solutions such as cane sugar solution or one of copper sulphate give very high osmotic pressures and so forth, it becomes necessary to investigate whether these colloids are true solutions or simply cases of finely suspended particles of matter.

Before attempting in the face of contradictory and much disputed opinions, an explanation of such vast importance to chemistry, it will be advisable to review the more salient points gathered by experiment and observation, which may throw light upon this phase of the subject.

First, a very powerful microscope, known as an ultra-microscope (that is beyond the power of an ordinary one) through which has been passed a very powerful and strongly illuminated beam of white light, which has previously passed a colloid, will reveal the presence of finely divided particles seemingly in a suspension. Not only does this microscope reveal these suspended particles, but a peculiar vibratory motion of the particles, which dart across the field of vision with more or less speed depending upon their size, can also be seen. The larger particles are seen to move very slowly in comparison with the smaller ones. This peculiar movement is known as the "Brownian Movement" after Professor Brown, its discoverer. It is probably caused by internal heat. Another view held by many scientists is that the tendency to move downwards by the action of gravity, and the viscosity of the surrounding medium to retain the particles in suspension, produce a sort of "see-saw" effect, an up and down motion. Should one of the factors, viscosity or gravity, gain the upper hand, then the particles will remain suspended or settle out. This takes place in a case of precipitation, where the particles become great enough to be influenced by the action of gravity and settle out. Should viscosity gain the upper hand, then the particles rise to the surface sometimes in the form of a fine scum. True solutions do not show this peculiar behavior, and we are therefore, in the case of colloids, not dealing with true solutions.

Again, when a beam of light is passed through any medium containing suspended particles, the beam becomes visible as does a sunbeam in dusty air, causing diffuse reflection of the light. Not only this, but the light becomes polarized and can be made to give a dark field when viewed through a polarizer or Nicol prism. This can be shown to be the case with colloidal arsenious sulphide, colloidal ferric hydroxide, but true solutions show no such behavior and again proves the colloid to be different from them.

HOMOGENEITY.

It appears from investigations of colloids as to the degree of divisibility of their suspended particles, that all solutions must be considered as suspensions of their dissolved particles, and that homogeneity, a characteristic of all true solutions, is also simply a case of suspension in which the particles are so finely divided that they can not be detected by our present optical methods. The size of such a particle would fall within the limits of $0.1\ \mu$ in diameter ($1\ \mu$ equals $0.001\ \text{mm.}$), the calculated limit of molecular divisibility. Granting this as the extreme limit of divisibility for particles in true solution, colloidal solutions must be those that lie somewhere between this extreme limit ($0.1\ \mu$) and some greater limit, that is $20\ \mu$. Such a colloidal particle then becomes visible under the ultramicroscope, but is still invisible to the naked eye, or under the ordinary microscope. Should, however, the divisibility approach the value $1\ \mu$, then the suspended particles become visible under the microscope and we have a case of ordinary coarse suspension. From this rough classification it would follow that colloids are simply suspensions whose particles lie somewhere between the above limits, $0.1\ \mu$ for true solutions and $1\ \mu$ for ordinary suspensions.

From the above remarks, homogeneity, a characteristic of true solutions, and heterogeneity, that of colloidal solutions, must be due especially to the extreme divisibility of their suspended particles and the discussion would therefore resolve itself around the heterogeneity of solutions in general.

In conclusion, let it be stated that the field of the investigation of the properties of colloids offers enormous opportunities. Whether colloids are true solutions or not, whether they are homogeneous or heterogeneous only time will tell, thus terminating the present necessity for involved and hairsplitting distinctions. Here, however, is a field, teeming with a harvest of truth, which must ultimately yield to the implements of industrious application and research.