

ON THE COAGULATION OF PROTEID BY ELECTRICITY. BY W. B. HARDY, *Fellow of Gonville and Caius College, Cambridge.* With a note in the text by W. C. D. WHETHAM, *Fellow of Trinity College.*

THE material used in the experiments which form the subject-matter of this paper was the slightly opalescent fluid which is formed when white of egg is mixed with 8 or 9 times its volume of distilled water, filtered, and boiled. The proteid matter in solution is changed by the heat so that, according to Starke, the greater part presents all the characters of alkali albumen¹. In its physical characters the solution is indistinguishable from a solution of silicic acid. It belongs to the silicic acid and water type of colloidal mixtures². It contains, in addition to inorganic matter, organic matter which may be separated into two kinds by the passage of a constant current. One of these is the alkali-albumen-like body: it is present as a fine suspension of discrete particles the size of which may be increased by adding any electrolyte. These particles have a limited mobility in the solvent which is dependent solely upon the alkali present. Therefore, if the percentage of alkali is gradually lowered by dialysis against distilled water, or by slowly allowing free acid to diffuse into the fluid, demobilisation occurs with production of a coagulum. This may be called the specific relation of the substance to free acid or alkali as opposed to the generic relation which, in common with all colloidal solutions of the suspension type, it bears to electrolytes. Electrolytes when added to the solution cause an increase in the size of the colloidal particles. Different electrolytes vary in the power they possess: three stages in the process have been chosen for measuring this; the development of a clearly visible opalescence³; the formation of the

¹ J. Starke. Ref. in *Maly's Berichte*, xxvii. p. 19. 1897.

² This *Journal*, xxiv. p. 174. 1899.

³ Schulze. "Antimony and Arsenic Hydrosulphide," *Journ. f. prakt. Chem.* xxv. p. 431, 1882; *ibid.* xxvii. p. 320. 1883.

hydrogel¹; and the synæresis of the hydrogel². The results in the first two cases are absolutely concordant. They have been stated in various ways but I propose the following as the simplest method of indicating the relation.

If we define the coagulative power of a substance as the inverse of the concentration in gram molecules per litre necessary to convert a given hydrosol into a hydrogel then we can speak of the specific molecular coagulative power of a salt. If we denote this by k and the number of molecules per litre by m then for two salts,

$$\frac{k}{k'} = \frac{m'}{m}.$$

The value of k has been found to vary for different salts according to the valency of the metal when the hydrogel produced is not liquefiable by heat. The actual numbers may be obtained directly or by calculation from the papers quoted in the footnotes. Picton and Linder give the following figures:—if the value for salts of trivalent metals be taken as 1000, then the value for salts $R''Ac$, $R'Ac$ will be respectively 100 and ± 2 .

In the case of colloidal sulphides of arsenic, antimony or cadmium the salts of hydrogen—that is to say free acids—have the coagulative power proper to salts of univalent metals. In this respect the proteid solution is different as we have already noticed. Otherwise my experiments show that the action of neutral salts as coagulants agrees in this case with the law of the valency stated above.

The action of free acid or alkali varies according to the condition of the material. The original opalescent fluid is alkaline in reaction: on dialysing this against distilled water it at length coagulates, and the coagulum may be broken up and suspended in distilled water without solution. On the addition of acid a dispersion³ of the flakes of coagulum occurs with production of an opalescent fluid having an acid reaction. It therefore is necessary to distinguish three conditions which are according to the reaction with litmus (i) when the fluid is alkaline, (ii) when it is acid, (iii) when it is neutral. The electrical reactions show that the proteid substance is electro-positive or in an

¹ Prost. "Cadmium sulphide," *Bull. d. l'Acad. Roy. d. Sci. d. Belg.* Ser. 3, xiv. p. 312. 1887; Picton and Linder, "Antimony hydrosulphide," *Journ. Chem. Soc.* LXVII. p. 63. 1895.

² Spring and Lucion. "Copper hydrate," *Zeits. f. anorg. Chem.* II. p. 195. 1892.

³ The following pages show that it is inadvisable to use the word "solution" here.

alkaline phase when the fluid has an acid reaction, and it is electro-negative, or in the acid phase when the fluid has an alkaline reaction. This more exact nomenclature is however likely to be confusing if it is used before the actual experiments are described and discussed. I therefore propose to distinguish the three conditions according to the reaction of the fluid to litmus paper.

The similarity of this substance to a solution of silicic acid in water is complete. In the neutral condition it coagulates spontaneously unless the solution be very dilute. The coagulum is liquefied by an exceedingly minute trace of free alkali. One part by weight of caustic soda dissolved in 10000 of water will liquefy 200 parts by weight of silicic acid in 60 minutes at 100°¹. The proteid coagulum is perhaps even more sensitive to free alkali. If a pin point is just dipped in a strong solution of caustic soda, shaken, and then washed in 5 c.c. of distilled water an alkaline solution is produced which will rapidly liquefy the coagulum at the boiling point. Finally the coagulum, like the hydrogel of silicic acid, and unlike the hydrogel of gelatine, is not liquefied by a rise of temperature, but it shrinks with expression of "serum." The coagulum differs from a hydrogel of silicic acid in the fact that it is liquefiable by traces of acid as well as by traces of alkali. The coagulation of a solution of silicic acid is retarded or prevented by free acid although the process of coagulation is not reversed by acid, therefore the difference is probably one of degree rather than of kind. Still, in the ease with which it is liquefied by free alkali, the proteid coagulum reacts as an acid coagulum such as the hydrogel of silicic acid, and in the ease with which it is liquefied by free acid it resembles a basic coagulum such as the hydrogel of alumina or peroxide of iron.

The action of the acid or the alkali in liquefying these various hydrogels cannot be regarded as a simple chemical action such as the formation of a soluble salt, a silicate, or albuminate as the case may be, since the quantity of free acid or alkali necessary to produce the change is so excessively minute².

The minor part of the organic matter present in the boiled fluid is readily soluble and forms a fine film on drying. Supposing the separation which is effected by the electric current to be complete then

¹ Graham. *Trans. Chem. Soc.* II. p. 318. 1864.

² In the parallel case of silicic acid Thomsen's determination of the heat evolved, when different quantities of alkali are added, shows that there is no definite point of neutralisation.

the ratio by weight of this matter to the alkali-albumen-like matter would be about 1 to 12.

The action of a constant current.

The current was supplied by storage cells at 105 volts. Platinum electrodes were used and the electromotive force was varied from 8, 13, to 105 volts in various experiments. The resistance was always very great. It was not thought necessary to measure it but the current passing was always less than 0.000001 ampère. The cell employed had the shape of a U-tube with vertical limbs. The bend of the U was narrowed in order to make it easier to withdraw the contents from the limbs without mixing. The narrow and wide parts were joined by funnel-shaped regions each 14 mm. long. The transverse diameter of the limbs was 11 mm. The bending narrowed part was 80 mm. long and had a bore of 3 to 3.5 mm. It was found that this was wide enough to allow of an axial flow sufficient to neutralize the electrical endosmotic action so that, except when the tube became blocked, no alteration of level in the two limbs was produced by the potential gradient. Important endosmotic action was however noticed in the course of the experiments when a coagulum formed so as to block the tube. In one experiment the discharge from a Holz electrical machine was tried. In this case the voltage, as measured by the length of the spark in air, was about 25000. In this experiment a tube having throughout a transverse diameter of 13 mm. was used.

The fluid has an alkaline reaction. The effect of the passage of a constant current is the formation of an opaque white coagulum about the anode. The density of the coagulum is dependent upon the electromotive force: with 105 volts it is yellowish with transmitted light and of a tough almost rubber-like consistency as though the particles had been impacted with considerable force. When the coagulum forms as it sometimes does in the neck of the narrow part of the tube nearest to the + electrode it is of the dense yellow type, even though the electromotive force be only 13 volts; in the narrow part of the tube the lines of force which join the electrodes are closer together and therefore the intensity of the electric field is greater. The formation of the coagulum about the anode is accompanied by a diminution in the opalescence of the fluid in the cathode limb.

These changes in the aspect of the contents of the U-tube are due

to an actual movement of the proteid particles through the liquid from the cathode to the anode. This was determined by estimating the concentration of the solids in the two limbs after a current had been allowed to run for a certain time.

The following figures give the results in one experiment. I may note in passing that all the figures quoted in this paper are comparable, since the same cell, the same electrodes, the same electromotive force, and the same solution of egg-white were used to obtain them.

Exp. A. White of egg beaten thoroughly, to one volume 8 volumes of distilled water were added: filtered and filtrate boiled. Placed in dialysing trays in shallow layers a few millimetres deep and dialysed against distilled water in large volume, which was renewed every 24 hours for 6 days. At the close of the third day the fluid was removed and brought to the boiling point for a few seconds in order to check any bacterial action. The cups were thoroughly rinsed with distilled water. The fluid was again boiled at the close of the sixth day. The optical characters of the fluid were not modified by boiling. The total solids were now found to be 1.4 grams per 100 c.c. This fluid was used in experiments A, B, and C.

Some of the fluid was placed in a cell, E.M.F. = 105 volts, current < 0.000001 ampère, $T = 17^\circ$. After 24 hours a dense coagulum had formed about the anode; the fluid was at the same level in both limbs. The coagulum in the anode limb was thoroughly broken up and the solids in each limb determined.

Limb	Grams per 100 c.c.
+	2.5
-	0.2

The solid matter from the cathode limb formed a film of a much finer texture than the coarse-grained film produced by the dried solid of the anode limb.

If the coagulum which forms round the anode be broken up with a glass rod so as to convert it into a fine milky suspension it is found that the particles have changed their electrical characters, so that they now move in the reverse direction, namely towards the cathode. There is thus a primary movement of the proteid particles in the direction of the negative stream, and a secondary movement in the direction of the positive stream. The secondary movement is not manifested unless the coagulum be broken up because of the purely mechanical resistance. With a lower electrical pressure, say 8 to 13 volts, the coagulum is loose enough to allow of the secondary movement, so that after 48 hours

a membranous coagulum appears at the commencement of the narrow part of the tube on the side of the cathode—the flocculent coagulum as it were jams at this point on its reverse journey. In this way the proteid particles may be driven out of both limbs and impacted in a dense coagulum occupying a mean position.

The force which drives the proteid particles must be considerable. If one end of the narrow part of the tube be blocked by a plug of glass wool driven home as hard as possible the movement is not arrested though it is retarded. Now a pressure of about an atmosphere does not drive the particles through a similar plug of glass wool in the base of a funnel. The retardation is shown by the fact that with the same voltage—105—the amount of solids in the cathode limb was reduced only from 1.4 to 1.0 gram per 100 c.c. in 60 hours.

The experiments which I performed furnish the grounds for a qualitative statement only of the influence of the conductivity of the fluid upon the movement of the particles. A comparison of the results obtained with undialysed and dialysed solutions shows that in the former the rate of accumulation in the anode limb is less and the percentage of solids there does not rise to so high a level. This difference is in part due to the fact that the secondary or reverse movement is established sooner.

So far no mention has been made of any movement of the finely divided organic matter which is found in the cathode limb after the proteid particles have passed over to the anode limb. When a plug of glass wool is present in the narrow part of the U-tube the secondary movement forms a coagulum on the anode side which is dense, translucent, and yellow by transmitted light. On the cathode side however a much smaller amount of an entirely different coagulum appears. It forms a thin membrane only about 1 mm. thick, of an opaque Chinese white appearance. Sometimes (volts 105) the force of the secondary movement drives the yellow translucent coagulum through the glass wool so that it reaches the cathode side. In this case the opaque white coagulum abuts with a sharp line of junction on the yellow coagulum.

This white coagulum which is so scanty in amount is I take it formed by a movement, primary or secondary as the case may be, of the very finely divided organic matter which remains in the clear fluid of the cathode limb after the current has been flowing for say 24 hours.

When an impacted coagulum is formed in the narrowed part of the

tube endosmotic phenomena are manifested in a change in the level of the water in the limbs. The fluid rises in the cathode limb so that the flow is from the anode to the cathode. To sum up therefore—in a fluid having an alkaline reaction the proteid particles move from the cathode to the anode, that is in the direction of the negative stream; the water moves from the anode to the cathode, that is to say in the direction of the positive stream. The proteid particles after completing their transit to the coagulum on the anode, or being in the anode region for some time, become altered so that they now tend to reverse their movement and to travel with the positive stream.

The discharge from a Holz machine in passing through the alkaline fluid also produces a coagulum about the anode. In this case the electricity was led into and from the fluid by two platinum wires. The voltage was ± 25000 . A tiny coagulum formed slowly on the point of the positive wire, and in about 30 minutes it grew to the size of a small pin's head.

The fluid has an acid reaction. The movements of the proteid particles and of the water are the reverse of those described. The particles now move with the positive stream from the anode to the cathode, the water moves with the negative stream. No attempt was made to demonstrate any secondary reverse movement of the particles.

Exp. B. To a part of the fluid in Exp. A which had been dialysed for 6 days, hydrochloric acid was added until it became opaque white. Acetic acid was then added until the fluid became again translucent. It was then dialysed in a very thin layer against a large volume of distilled water for 24 hours: the distilled water was twice changed. Current run for 24 hours: E.M.F. = 105 volts: current < 0.000001 ampère.

Limb	Solids in grams per 100 c.c.
+	0.625
-	2.20

In this case also endosmotic action is obvious when a coagulum blocks the tube. The water however now flows from the cathode to the anode. Therefore, in both acid and alkaline fluids the movements of the water and of the particles are in opposite directions.

Fluid is neutral. The coagulum which forms when dialysis is pushed far enough was broken up very thoroughly and suspended in distilled water. There is now so little movement of the particles under the influence of a current that it is difficult to detect, and what movement there is, is due to the fact that the material is not absolutely

neutral. Thus, if the coagulum be formed by dialysing an acid fluid the particles when suspended in distilled water will move to the cathode.

Exp. C. Remainder of acid fluid used in Exp. B dialysed until it formed a clear hydrogel. This was broken up in distilled water by shaking so that a milky fluid resulted. Some was exposed for 24 hours to the current, the electromotive force being again 105 volts. Fluid in both limbs still milky, though the particles have settled somewhat and to an equal extent in both limbs. This settling is due simply to gravity, seeing that it occurs at the same rate in a tube when no current is passing. The narrow part of the cell where the electrical density is greatest was however swept quite free from particles, and a small nodular mass of yellow coagulum had gathered round the cathode.

The movements of the particles and the water seem to be readily explained on the lines of Quincke's theory of Electric Endosmose. When a current passes through a fluid in a capillary tube there is movement of the fluid. The capillary tube in question may be a single capillary tube of for instance glass, or it may be the capillary spaces in a permeable membrane of china clay, or such organic membranes as frog's skin, cat's lung, &c., as in Engelmann's experiments. The movement of the fluid is almost always in the direction of the positive stream, it is however determined by the nature of the wall of the capillary tube and the nature of the liquid. Thus water in glass moves with the positive stream, turpentine in glass moves with the negative stream. Similarly solid particles, or minute gas-bubbles, are driven through a fluid by the passage of a current, the movement in this case is almost always in the direction of the negative stream.

An excellent account of the whole subject is given in Wiedemann, *Electricität*, 1. pp. 982—1023. Ed. 2, 1893. In addition to this a special discussion of the mathematical theory is to be found in a paper by Professor Lamb in the *Brit. Assoc. Report* for 1887, p. 495; and Picton and Linder have described the movement of colloidal particles under the influence of a current in the *Journal of the Chemical Society*, LXXI. p. 568, 1897.

The explanation of electrical endosmose and of the movement of particles suspended in a fluid through which a current is passing which was furnished by Quincke, is based upon the assumption that there is a discontinuity of potential at the surface between the liquid and the solid particles or the wall of the capillary tube; there is thus developed

a double layer of positive and negative electricity. The direction of the flow of the fluid or of the movement of the particles therefore is an indication of the nature of the charge which is carried by the one or the other. Thus since water in a glass tube flows with the positive stream the charge it carries at the surface will be positive, that of the glass negative.

The application of Quincke's theory to the experimental facts set forth in the first part of this paper yields very interesting results. When the fluid is alkaline the proteid particles move with the negative stream and therefore they carry a negative charge, while the water moves with the positive stream and therefore carries a positive charge. When the fluid is acid, however, the proteid particles carry a positive charge and they therefore are positive to the water. When the fluid is neutral there is little or no difference of potential between the water and the particles—that is to say, the water and the particles form an electrically homogeneous mass.

The proteid particles therefore have this interesting property that their electrical characters are conferred upon them by the nature of the reaction, acid or alkaline, of the fluid. If the latter is alkaline the particles become electro-negative; and vice versâ.

The secondary or reverse movement of the proteid particles must on Quincke's theory be a result of a change in their electrical characters as referred to the water, so that whereas they may have been for instance negative to the water, they become positive to the water after a long or short sojourn in the neighbourhood of the anode. This change may I think be referred to the electrolytic action of the current upon the electrolytes present. Owing to this an electro-negative particle which moved to the anode would there reach an acid region in which its character would change from the electro-negative to the electro-positive character. This view is supported by the observation that the reverse movement is more pronounced the higher the concentration of electrolytes and therefore the greater the concentration of acid or alkali about the electrodes. In an undialysed solution the particles do not as a rule reach the electrodes to which they are travelling; they are arrested and form a coagulum at some intermediate point the position of which with regard to the electrodes is determined by the fall in potential in the cell.

The movement of the fluid may be explained as follows. When the tube remains patent throughout the experiment the level remains the same in both limbs. When a coagulum forms so as to block the

tube the fluid flows with the positive stream if it is positive to the proteid particles; with the negative stream if it is negative to the latter. Quincke and von Helmholtz refer the movement of particles in a fluid which is conveying a current to the contact difference of potential between them, whereby the particle and the fluid are urged in opposite directions. If the particles are free the result will be that they will move through the mass of the fluid; if however they become fixed, as happens when they aggregate to a clot which becomes jammed in the tube, the fluid is urged past the particles though of course in a direction opposite to that of the free particle¹. Therefore when the particles are electro-positive, as is the case when the fluid is acid, the water moves with the negative stream, a direction which is most unusual in the electrical endosmose of this fluid.

If the proteid in the boiled solution of egg-white be, as Starke affirms, a representative of the derived albumens, then the experiments perhaps throw a little light on the relation of the proteid to the acid or base in this class.

The proteid molecules in distilled water form large aggregates so that a coarse suspension or a coagulum is the result. A minute quantity of acid or base will disperse these aggregates so that a much finer suspension is produced; and the particles at the same time assume the electrical characters of basic, or acid particles respectively. The proteid molecules seem therefore to act as basic or acid particles according to the circumstances in which they find themselves. This conclusion is justified by the relation which Picton and Linder have established, namely, that the direction of the movement of colloidal particles under the influence of an electric current is determined by their chemical nature. Thus basic ferric hydrate moves with the positive stream, acid arsenious sulphide moves with the negative stream.

The oxides of silicon and iron which form colloidal hydrates also act as acid, and as base. Thus from silicon we can get a silicate of potassium, or a sulphide, or tetrachloride of silicon. Similarly there are ferrous or ferric salts, and ferrites and ferrates in which the iron oxide forms the acid ion.

¹ The statement in the text is purely a qualitative one. I have therefore omitted any mention of the movement of the water in the narrow part of the cell which will result from the difference of potential between it and the glass wall.

The experiments suggest certain ideas concerning the nature of the directive force which determines the aggregation and arrangement of the colloid particles in the formation of a hydrogel. Graham attributes it to a quality of "idio-attraction" possessed by colloid molecules. Many colloidal solutions are however stable unless an electrolyte be added, and in this fact a clue to the nature of the force may perhaps be found.

In speaking of the precipitating action of crystalloids upon colloids, Hofmeister referred the property to the "water-attracting power" of the former, and the phrase has become current in physiological literature. It may I think be put aside once and for all. It is vague and meaningless in that it cannot be expressed in terms of any definite stoichiometrical quantity. Also any possible meaning it can bear must be shared by non-electrolytes, and these apparently possess no aggregating action upon colloid particles. The boiled egg-white solution, for instance, is freely miscible with alcohol.

I endeavoured to arrive at the nature of the action of electrolytes by assuming that if the electrolyte acts by modifying the characters of the solvent it must be possible to find some value for one of their properties such as osmotic pressure, surface tension, viscosity, &c., which is approximately constant for all those solutions which are of the strength which is just necessary to produce coagulation. I calculated the concentration of Schulze's equicoagulative solutions¹ in gram equivalents and used these figures as the basis for further calculations. No agreement in any values was found for equicoagulative solutions.

The following table shows the values for the product of the number of gram molecules and the coefficient of osmotic pressure (mi) for chlorides.

Equicoagulative solutions of chlorides of	Gram equivs. per litre	Calculated value of mi
Am	0.090	0.16
K	0.098	0.18
Na	0.07	0.13
Mg	0.002	0.003
Ba	0.003	0.004
Ca	0.004	0.006
Al	0.0002	0.0003

¹ *Journ. f. prakt. Chem.* xxv. p. 431. 1882.

As little agreement was found in the viscosity of equicoagulative solutions. Thus for the solutions of potassium and barium chloride Wagner's constant gave the respective values 0.0947 and 0.00367. Lastly, a comparison of the way in which surface tension of the free surface of solutions of various salts varies with the valency of the metal shows a complete lack of agreement with coagulative action. Thus for chlorides we have :

	R'	R''	R'''
Surface tension ¹	1	1.7	4
Coagulative power	1	30	1650

Also the amount of the salts of bi or trivalent metals necessary to produce coagulation is so small as to produce negligible changes in the surface tension of the free surface, though it is of course possible that by electrical action the ions may largely alter the surface tension between the colloid particles and the water. The amount of zinc sulphate necessary to produce coagulation of the solution of arsenious sulphide used by Schulze was 0.0037 gram equivalents per litre. Dorsay by actual measurement with the ripple method found the tension of the free surface of a solution holding 0.0199 gram equivalents to be 73.17. This value is below that which he obtained for distilled water, namely, 73.27. The conclusion I would draw from these results is that an electrolyte does not act as a coagulant by modifying in any simple manner the stoichiometrical characters of the solvent. The same conclusion indeed might be drawn at once from the effect of valency upon coagulative power. Stoichiometrical values vary generally with valency according to the ratio $x : 2x : 3x$ and not according to the square and the cube as coagulative power approximately does.

The dependence of coagulative power upon electrical conductivity is however very clear. Non-electrolytes are almost if not quite without any coagulative power, that is unless they act chemically. Feeble electrolytes possess an equally feeble power. Cane sugar, absolute alcohol, glycerine, chloral hydrate, boracic acid, benzoic acid, salicylic acid, and tartaric acid are miscible in all degrees with a solution of arsenious sulphide. The conductivity of an electrolyte increases with a rise of temperature, therefore at high temperatures tartaric, boracic, and glacial acetic acids coagulate antimony trisulphide². If Linder

¹ The value for the constant K and the formula given by Dorsay, *Phil. Mag.* ser. 5, XLIV. p. 369, 1897, were used.

² Schulze. *Journ. f. prakt. Chem.* xxvii. p. 320. 1883.

and Picton's measurements of the coagulative powers of various acids are set beside the values for the specific molecular conductivity of solutions of the acids holding 1 gram per litre the same relation is clearly shown¹.

Acid	Value of K referred to Al_2Cl_6 as unity	Sp. mol. conductivity when 1 gr. equiv. = 1000 c.c.
Hydrobromic	0.001	2950
Hydriodic		
Hydrochloric		
Nitric		
Sulphuric	0.0006	1935
Oxalic	0.0005	578
Phosphoric	0.00007	230

On the ground of this relation Bödlander² suggested that the aggregating or clumping action of electrolytes might be electrical in nature. This view indeed follows naturally from the assumption that the ions carry static charges. I constructed a table giving the molecular conductivities of Schulze's equicoagulative solutions for colloidal arsenious sulphide. The values for neutral salts stand remarkably close together, so that in this particular case equicoagulative solutions of these salts are those in which the molecule carries approximately the same electric charge. The difficulty which stands in the way of any simple electrical explanation is the fact that the volume density of the electricity in the interior of the water due to the static charges on the ions must vary so widely in equicoagulative solutions. Thus comparing solutions of potassium and aluminium chloride Schulze's figures would give for the volume densities respectively $\frac{\rho}{\rho'} = \pm \frac{300}{1}$.

The coagulative power of electrolytes cannot depend simply on the volume density of electricity in the liquid. For equimolecular solutions the value of this density would, by Faraday's law, be proportional to the valency, and the rapid increase of coagulative power which is observed as the valency rises would be impossible.

I owe to the kindness of Mr Whetham a suggestion which appears to remove this difficulty and, in conjunction with the experimental facts described in this paper, seems to afford a basis for a hypothesis which

¹ *Journ. Chem. Society*, LXVII. p. 63. 1895.

² *Neues Jahrbuch f. Mineralogie*, II. p. 147. 1893.

explains the relation of specific molecular coagulative power to valency. It is as follows.

“The numbers which represent the specific molecular coagulative power for salts of metals of different valency suggest the ratio $R : R'' : R''' = x : x^2 : x^3$ or some similar relation.

Now if we assume that in order to produce a certain state of aggregation of a given group of colloidal particles the presence of a critical amount of charge equal to that on a trivalent ion is necessary, and that no such aggregation occurs in presence of a smaller charge, it will need the conjunction of two divalent and of three univalent ions to produce the same result, for the charge on an ion is proportional to its valency.

In a solution where ions are moving freely, the probability that an ion is at any instant within reach of any fixed point is, putting certainty equal to unity, represented by a fraction proportional to the ratio between the volume occupied by the spheres of influence of the ions to the whole volume of the solution, and may be written as AC , where A is a constant and C the concentration of the solution. The chance that two ions should be present together is the product of their separate chances, that is $(AC)^2$, and the chance that three ions should be in conjunction with the colloidal particle is $(AC)^3$.

If we have three solutions whose ions are trivalent, divalent, and monovalent respectively, the probability that one of the first-named ions should be within its radius of action of a given point is AC_1 , the probability of two of the second kind being within reach together is $A^2C_2^2$, and the probability of three of the third kind being present together is $A^3C_3^3$, the constant being assumed to be the same in each case within the order of accuracy required.

Now in order that these three solutions should have equicoagulative power the frequency with which the necessary conjunctions occur must be the same in the three solutions. We shall then have

$$AC_1 = A^2C_2^2 = A^3C_3^3 = \text{a constant} = B;$$

$$\therefore C_1 = \frac{B}{A}, \quad C_2 = \frac{\sqrt{B}}{A}, \quad C_3 = \frac{\sqrt[3]{B}}{A},$$

or

$$C_1 : C_2 : C_3 = B : \sqrt{B} : \sqrt[3]{B}.$$

Since B is a fraction less than unity, this gives the kind of relation observed, the concentration for trivalent solutions being much smaller than that for an equicoagulative univalent solution.

This result is only approximate; the constants A will not be strictly identical in the three cases; moreover, since the two divalent ions really give a charge greater than that on one trivalent ion the equicoagulative concentration will, in the case of the divalent solution, be less than that deduced above, and it is probable that a nearer approximation to the truth would be given by

$$C_1 : C_2 : C_3 = B : \sqrt[3]{B} : \sqrt[3]{B} = B^3 : B^3 : B.$$

Let us take an example. By choosing a proper value for B , in the case of our first relation 0.0000156, we get $\sqrt[3]{B} = 0.025$, and the ratio $C_1 : C_3 = 1 : 1600$. This gives $\sqrt{B} = 0.00395$, making C_2 proportional to 253, so that we should have

$$R' : R'' : R''' = 1 : 253 : 1600.$$

But by our second relation, if we adjust B to give the 1 : 1600 ratio for $C_1 : C_3$, we must take $B = 0.025$, when B^2 becomes 0.000625 and B^3 0.0000156, so that

$$C_1 : C_2 : C_3 = R' : R'' : R''' = 1 : 40 : 1600,$$

a relation agreeing within the limits of error with that given on p. 299 for chlorides, viz. 1 : 30 : 1650.

It seems likely, therefore, that this hypothesis may explain the relation between valency and coagulative power."

The fact that the proteid molecules can have their electrical characters altered suggests a reflection concerning the classification of colloidal mixtures. It can be based upon the relation to temperature or the relation to electrolytes. The former distinguishes the well-defined groups which form heat reversible, and those which form irreversible or insoluble hydrogels¹. From the latter we get a division into hydrosols in which the power of an electrolyte to effect demobilisation depends upon the basic ion; and hydrosols in which it depends upon the acid ion. In all those cases in which the latter relation has been determined the two methods of classification coincide. The number of cases is however very small. As they are widely scattered in different journals I have brought them together into the following table.

¹ This *Journal*, xxiv. p. 174. 1899.

Substance	Electrical characters	Chemical character	Nature of hydrogel	Prepotent ion
Antimony sulphide	no obs.	acid	insoluble	metal (Schulze)
Arsenic „	negative (Picton and Linder)	acid	insoluble	metal (Schulze)
Cadmium „	no obs.	acid	insoluble	metal (Prost)
Alkali albumen	negative (Hardy)	acid	insoluble	metal (Hardy)
Gelatine	doubtful (Hardy)	?	heat soluble	acid (Pascheles) ¹

Now in this table we see that in those cases in which the metal ion has been shown to be prepotent the colloid particles react to a constant current or to reagents like acid particles. This may be a coincidence, or it may mean that it is the chemical character of the colloidal matter which determines whether the basic or acid ion is prepotent in modifying the spatial relation of the particles in the fluid. The latter view is supported by the following facts. Silicic acid is electro-negative (Picton and Linder) and it is coagulated by salts but not by free acids (Graham). Ferric hydrate is basic and electro-positive (Picton and Linder) and it is coagulated by alkalis but not by acids, with the exception of sulphuric acid. Hydrate of alumina acts both as acid or base, it is coagulated by acids and alkalis as well as by neutral salts. Spring and Lucion² examined the influence of some sulphates and chlorides upon the rate of synæresis (dehydration) of the hydrogel of cupric hydrate. The numbers do not help us however since they differ completely from those found when a hydrosol is used. The figures agree with the common stoichiometrical relation in which the effect is directly proportional to the molecular and ionic concentration.

If we assume that the action of an electrolyte is governed by the chemical nature of the colloid particles, then there is no reason why the two classifications indicated at the beginning of this section should coincide and the reversibility or non-reversibility of the hydrogel remain as the only fundamental difference since it must depend upon a radical difference in the relations of the colloidal solid to the fluid.

The point is of great importance as a guide in the obscure region one is endeavouring to penetrate. In order to throw some light upon it I endeavoured to determine the movement of gelatine in water under the influence of a constant current. If that could be determined then the relation detected by Picton and Linder between the direction of the movement and the acid or basic nature of the substance could be

¹ *Pflüger's Archiv*, LXXI. p. 333. 1898.

² *Zeits. f. anorg. Chem.* II. p. 195. 1892.

applied. The experiments did not give decisive indications. The action of the current is obscured by the remarkable influence it exerts upon the separation of the solution into conjugates. Spherules 2 to 6 μ in diameter with a high gelatine content separate even though the original solution is too dilute to permit of setting. These are repelled from both anode and cathode, so that they aggregate to form a loose jelly in some midway position.

SUMMARY.

Under the influence of a constant current the particles of proteid in a boiled solution of egg-white move with the negative stream if the reaction of the fluid is alkaline; with the positive stream if the reaction is acid. The particles under this directive action of the current aggregate to form a coagulum. The physical characters of the material are discussed, and the action of the current is explained and developed on the lines of Quincke's theory of electric endosmose.