*GENERAL DISCUSSION.**

Professor E. J. Bigwood (*Brussels*) said: Professor Kruyt said that colloids were always to be considered as polymolecular products of aggregation, and that this was the criterion of the colloidal condition. It seems to me that the only fundamental basis for a general definition of colloidal particles must be confined to a question of size of the particles conferring certain physical properties such as slow diffusion, Tyndall effect, non-dialysability . . . etc. . . ., and this, independently of the nature of the chemical constitution of the particle. It would be dangerous to decide that a particle must be necessarily an aggregate whenever it shows evidence of the fact that the particle is large. In the case of proteins for instance, there are substances for which there is no evidence allowing for the assumption that one is dealing with aggregation.

Professor Kruyt said that the electrolytic theory is less fruitful than the surface adsorption theory for further investigation in the study of colloids. It seems to me that this statement is certainly not justified, so far as many lyophilic colloids are concerned. Particularly in the case of proteins, the electrolytic theory has given us a much better insight into their chemical properties.

At the end of his report, Professor Kruyt says that " . . . there is no doubt that its inner layer " (of the electric double layer at the surface of a micelle) " is often built up of ions of the material of the particle itself, or at least by ions which belong homogeneously to the particle. However, another architecture is not only possible, but even always present." I believe there is in my own report, experimental evidence of the fact that, in at least a certain range of p_H values, proteins behave exclusively as electrolytes, even when the protein is in the gel state.

Mr. G. S. Hartley (*London*) expressed his appreciation of Professor Kruyt's having focussed attention so clearly on the two different methods of approach to the electrical properties of colloidal particles—the extrapolation downwards from the properties of matter in bulk and the extrapolation upwards from individual ions. No one could doubt that the two routes, if both could be correctly followed, must lead to the same result. Professor Kruyt preferred the former on the grounds that our knowledge of the latter was too slight, being confined

* On the four preceding papers.

to the behaviour of small ions of low valence. The speaker said that, without wishing to make light of the difficulties in the latter method, he thought that Professor Kruyt had failed to draw attention to a difficulty in the former which seemed to him very great and of fundamental importance.

In extrapolating from the macro-wall downwards we make use of a certain potential function, the ζ-potential, and, since most of the properties in which we are interested can be expressed in terms of it, we are not greatly concerned about the difficulty of relating the charge of the particle with this function. The advantage of the ζ-potential which enables us to make use of it for the desired extrapolation is that it can, for most lyophobic colloids, be assumed independent of the size of the particle. Now this assumption can only be made if the material of the particle remains *in the same physical state* as its size is reduced. In the case of many of the substances which we are accustomed to call colloidal electrolytes this is certainly not true. To take one example: the micelle-forming long-chain salts have a well-defined solubility in water: at the saturation concentration the chemical potential of the salt in the crystalline solid is equal to that in the micellar condition in solution: at concentrations below this the former is obviously the greater: the physical state of aggregation in the micelle is therefore different from that in the solid and it is therefore dangerous to assume that any ζ-potential determined by observation on the solid is of any significance for the behaviour of the micelle. While agreeing with Professor Kruyt that the difficulties in the way of an extension of simple electrolyte ideas to the micellar case were great and at present not surmounted, the speaker thought that the difficulties in the way of extrapolation from the macro-wall downwards in the case of such substances as soaps and dyes was insurmountable, *because a macro-wall in the same physical state as the surface of the micelle could not be obtained.*

Such substances, however, owe their charge to the dissociation of ionogenic groups which are chemically inseparable from the bulk of the particle. It is therefore possible to calculate the charge of the particle from its mass or volume, if the problem of the degree of dissociation of the ionogenic groups can be solved, *because there is a necessary stoichiometric equivalence between mass and maximum possible charge.* In the interpretation of the various measurements which could be made on these substances, the further problem of the distribution of the ions in the double layer or atmosphere had to be attacked. Of the peculiar difficulties of this latter problem the speaker said he was well aware, having discussed them in his own paper, but he wished to point out that they were just as much obstacles to the calculation of the charge from the ζ-potential and it was important to appreciate that the advantage of the ζ-potential method, where applicable, was not that this problem was made easier, but that its solution was in many respects unnecessary.

It was interesting to note that where the ζ-potential method was applicable, *i.e.*, where the material of the particles was in the same physical state in the ultra-micro-particle and the macro-solid, there could be no true thermodynamic equilibrium with regard to this material among the particles of various sizes, so that if the sol were indefinitely stable it could only be because the rate of attainment of equilibrium was indefinitely slow, this being so because the difference of chemical potential between the particles was very small (*i.e.*, the particles still very large in terms of molecular dimensions) or because the material was very insoluble in the molecular disperse condition and the electrical repulsion prevented adhesion of the particles. Colloidal particles could only exist in true thermodynamic equilibrium if the material constituting them was in a different physical state from that in the macro-solid. This was in practice true only for those colloids the charge of whose particles was chemically inseparable from their bulk. Charged colloids therefore divided themselves into two fairly well-defined classes—on the one hand a class where the bulk of the particle is made up of insoluble material in regard to which there is no equilibrium, and whose charge is due chiefly to preferential adsorption of foreign ions : to this class the ζ-potential treatment is applicable but the charge not stoichiometrically related to the mass of the particle—and on the other hand a class in which the particle is made up of a definite ionising compound with regard to which there is true equilibrium and whose charge is due to ionisation of this compound : to this class the ζ-potential treatment is not applicable, but the charge is stoichiometrically related to the mass of the particle : the particles of this class are usually very much smaller than those of the first (a difference emphasised by Freundlich). The speaker would prefer (with McBain and others) to confine the term " colloidal electrolytes " to this latter class, though admittedly on grounds of convenience rather than of etymology.

Dr. E. Valkó (*Ludwigshafen a. Rh*) said : In the discussion, Professor Kruyt raised the question whether the assumption of the ionic structure of the double layer is necessary for the explanation of the ζ-potential. It is true that Helmholtz constructed his theory before the foundation of Arrhenius theory. But this was a defect of birth of his brilliant double layer theory, as clearly proved in an excellent paper by McBain and Mrs. Laing-McBain.[1] Already Smoluchowski [2] had expressed the opinion that progress in the theory of electro-osmotic phenomena is only possible by application of the theory of ions. Indeed, our present knowledge of the structure of matter does not allow us to assume any other mechanism for the transport of matter by electric current than the transport of free ions. Dipoles alone can only be oriented, but not moved, by electric currents. If we renounce the assumption of the ionic structure of the double layer, we renounce any possibility of explaining the electrokinetic phenomena, at least for the moment.

The problem of the origin of the electric charge at the paraffin/water surface is difficult, but I feel sure that the theory of the ionogenic surface compounds will, in this case also, prove true. We can use as a working hypothesis the assumption that there are fatty acids with large molecular weight fixed at the surface which are the carriers of charge. Since they are insoluble in water, they will not be separated from the paraffin mixture by the ordinary purification methods. An amount which is too small to be analytically demonstrable is sufficient to cause the observed streaming potential. This assumption can be tested by application of indirect methods analogous to those used by Pauli.

Dr. F. L. Usher (*Leeds*) said : Professor Kruyt's treatment, in which a very small area of the surface of a spherical particle is considered as a plane surface with a diffuse double layer, raises the interesting question of the possible influence of curvature on the electrical conditions at the interface, since with extremely small particles of equivalent radius

[1] McBain and M. E. Laing-McBain, *Z. physik. Chem.*, **161A**, 279, 1932.
[2] v. Smoluchowski, *Handbuch der Elektrizität*, **2**, 425 (Stuttgart) 1914.

1·5 mμ, even 1 square micron of surface has substantial curvature. Two lines of evidence indicate that either the ζ-potential or the surface density of charge on particles in sols increases as their size decreases. First, so far as is known, the mobility of particles of the same material immersed in the same intermicellar liquid does not vary much with size, whereas according to Henry's analysis the mobility of extremely small particles should be greatly reduced if the surface density of electrification remains constant. Secondly, experiments by Thiessen and others have shown that the stability of gold sols towards electrolytes increases with decreasing size. A similar assumption seems capable of explaining an interesting phenomenon which has recently come to light. The concentrations of potassium, sodium, and lithium ions needed to reduce the potential (or charge) of particles in a gold sol to a given fraction of the initial value are about the same when the radius is greater than 18 mμ. When, however, the radius is 1·3 mμ, between 4 and 5 times as much lithium as potassium is required. Thus sufficiently small particles of a lyophobic substance tend to behave towards these ions as though they were lyophilic, although the explanation may be different in the two cases. In the case of the gold sols I would suggest that the smallest particles have a higher surface density of charge, and that in consequence a greater number of alkali metal ions have to approach each unit area of surface in order to effect a given reduction than with larger particles. If this is so, the greater size of the hydrated lithium ions may lead in the former case to a " crowding " effect which would not be observed with large particles, so that a higher bulk concentration is needed to produce the required result.

Professor A. Frumkin (*Moscow*) said : Professor Kruyt has pointed out that colloidal problems can be attacked from the point of view either of the double layer theory or of the theory of solutions. It appears to me that in applying the double layer theory we must be careful not to push too far the idealisation of the structure of the surface layer. When discussing the relation between the stability of a metal sol and the existence of a double layer on the surface of its particles, colloid chemists refer as a rule to a schematic picture, assuming that there is nothing on the surface of the particles except electric charges of one sign on the metal and of ions of opposite sign, distributed in the solution to a certain depth.

At the present moment it would be difficult to decide the question, whether the existence of a double layer of that kind is sufficient, by itself, to stabilise the sol, since the structure of the surface in most systems which have been hitherto investigated is undoubtedly more complicated. Let us take as an example the surface of a platinum electrode in hydrochloric acid.[3] The relation between the quantity of electricity θ necessary to charge the electrode to a certain potential ϕ is given by the curve drawn on Fig. 1. If we start with the reversible hydrogen potential A, there is first a region of very low capacity AB, where the electrode is covered by a surface hydride or a layer of bound atomic hydrogen. A part of it is ionised and thus causes a negative charge of the surface. In the BC region there is only a normal double layer with positive charges on the platinum surface. In the CD region the surface is covered by an oxide or by more complex compounds containing oxygen and the anion of the acid. The correctness of this picture can be demonstrated by a combination of polarisation measurements with

[3] Frumkin and Šlygin, *C.R. Acad. Sc., U.R.S.S.*, **2**, 176, 1934.

adsorption data, as has been discussed elsewhere. The surface of ordinary platinum sols is in a state corresponding to the CD region of the curve. Whether a stable sol with particles carrying only a normal double layer (as in the BC region) can exist is not known; it would be certainly very important to decide this question. N. Bach and N. Balashewa (*Karpow Chemical Institute*) succeeded recently in preparing platinum sols, which correspond to a point of the AB region of the curve. They used the ordinary Bredig method, except that the disintegration of the platinum was carried out in water saturated with hydrogen and after the disintegration hydrogen was bubbled through the solution for a certain time. Adsorption measurements on platinum electrodes show that under these conditions surface oxides should be reduced and a hydride surface obtained. The sols are negatively charged (cataphoretic measurements) through partial ionisation of the surface hydride and appear to be fairly stable; which is rather unexpected from the point of view of the Pauli theory. Their conductivity is practically that of the original water, *i.e.*, $0{\cdot}5 \times 10^{-6}$. It is probable that the formation of the surface hydride is of great importance in the stabilisation of these sols. Adsorption measurements carried out recently by Bruns and Ablesowa [4] have shown that the van der Waals' field of force at the surface of platinum (as judged by its adsorptive power towards ethylene) is enormously decreased through the formation of surface hydride. We may safely assume that in a similar way the saturation with hydrogen of the free valencies on the surface of the platinum particles decreases the attractive forces between two particles and thus helps to stabilise the sol. It is thus impossible to decide from these experiments whether the existence of a double layer would be sufficient to stabilise the sol in the absence of any other stabilising factors. The question could be solved by preparing platinum sols whose surface conditions would correspond to the BC region, but so far our attempts in this direction have not been successful. However, platinised charcoal saturated with hydrogen gives very stable suspensions and, in this case, it appears that the formation of a normal double layer is the only stabilising factor which has to be taken into account.[5]

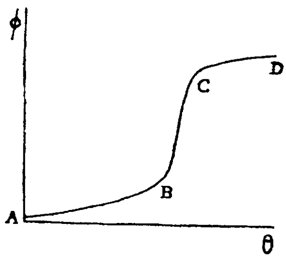

FIG. 1.

Comparing the double layer scheme with the picture of surface compound formation, as given by Pauli, we must bear in mind that the normal structure of the double layer is often complicated by the specific adsorption of anions.[6] The distribution of charges which exists in the double layer in that case is, in many respects, very similar to that assumed by Pauli.

The stabilising action of electric charges on metal sols is usually connected with the ζ-potential, but a non-diffuse double layer, which would not give any ζ-potential must still exert a stabilising action, increasing the binding energy between the particle and the solvent. This is shown, for instance, by the fact that the metals are much better

[4] Bruns and Ablesowa, *Acta physicochimica, U.R.S.S.*, **1**, 90, 1934.
[5] N. Bach, *Koll. Z.*, **64**, 153, 1933; Pilojan, Kriworutschko and N. Bach, *ibid.*, p. 287.
[6] Frumkin, *Physik. Z. Sowjetunion* **4**, 253-259, 1933.

wetted by water at strong polarisations.[7] This effect is a function of the total potential difference and independent of the ζ-potential. The existence could perhaps explain the differences in the stabilising action of ions which give rise to the same electro-kinetic charge mentioned by Professor Kruyt.

There remains but one fact which I should like to point out. All theories of the double layer which have been developed up to now consider the planes parallel to the solution/metal interface as equipotential planes, *i.e.*, they assume that the lines of force are at a right angle to the metal surface. The real distribution of the lines of force must be more or less as shown by Fig. 2 and, especially in the case of polyvalent ions, the properties of the double layer might be very different from those which we should expect on the basis of the idealised theory.[8]

Dr. Karl Söllner (*London*) said: As to the remark of Professor Kruyt about the electrokinetic properties of paraffin and similar substances I would like to point out, with all necessary reserve, that I am rather doubtful, whether we are dealing always in those cases really with the interface water-paraffin or whether gases, most likely in the form of small lenses or layers, play an important rôle. Experiments[9] have shown the great influence of gases upon the formation of emulsions by means of shaking or by applying ultra-sonic waves. In many cases it is quite impossible to obtain emulsions of pure substances in the absence of gases whereas in their presence emulsions are easily formed; in other cases emulsions formed in the presence of gases are much more stable than those obtained in the absence of gas. As far as we can judge now it seems likely, therefore, that gases favour not only the formation but also the stability of emulsions. As mentioned above we think, that this can be explained by the assumption of layers of gas or gas lenses. This phenomenon may be much more common than we know at present.[10] Investigations in this direction are in progress.

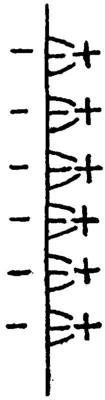

FIG. 2.

Professor H. R. Kruyt (*Utrecht*) said: In the short survey of my paper I mentioned that colloids are polymolecular particles; if not, the word colloid has hardly any sense. To Dr. Bigwood's question whether a *large molecule* is not already a colloid, I should like to state this: Nobody pretends that the colloidal particle of a gold sol, an As_2S_3-, a AgI-, a mastic-sol or an oil emulsion consists of one molecule. With dyestuffs and soaps, where we know exactly the molecular weight, the colloidal properties are ascribed to polymolecular or polyionic aggregations. It is only with proteins and similar compounds, where the chemical molecular weight is dubious, that monomolecular colloidal particles are assumed. This seems arbitrary, the more since we know that mere dehydration of these hydrophilic colloids changes them in hydrophobic ones, which behave exactly as those mentioned above. And as the behaviour of gold sols, etc., can be understood completely by the assumption

[7] Kabanow and Frumkin, Z. *physik. Chem.*, **165A**, 433, 1933; Kabanow, *Koll. Z.*, **65**, 101, 1933.
[8] *Physik. Zeitschr. Sowjetunion*, loc. cit., p. 257.
[9] Rogowski and Söllner, *Z. physik. Chem.*, **157**, 1933.
[10] W. Spring, *Ann. Soc. Geol. Belg.*, **28**, 1901; **29**, 1902; *Bull. Soc. Belg. Geol.*, **17**, 1903; *Bull. Acad. Belg.*, **37**, 790, 1899.

of an electric double layer at a polymolecular wall, there seems to be no reason to look upon the hydrophilic particles in a different way.

I accept with full approval Dr. Hartley's graphical representation on the extrapolation of the Debye-Hückel theory to colloids. Moreover, the valency of an ion does not characterise its behaviour entirely: the distance between the charges plays an important rôle,[11] but it is not easy to account for this quantitativety. When studying the influence of neutral salts on the shifting of the p_H with gelatine sols one of my students[12] found that gelatin behaved like a monovalent electrolyte.

When I spoke of two types of ζ potentials I had this in mind: the origin of the double layer, as I mentioned in my paper, may be ascribed either to ions of the material of the wall or to ions, preferentially adsorbed by that wall. The streaming potentials of water pressed through a paraffin tube are very high.[13] An AgBr-capillary shows a potential (the wall being negative) at concentrations of $AgNO_3$, where no doubt the charge of the Br-ions at the periphery (*i.e.*, on the edges of the particle) is compensated.[14] What ions constitute the double layer at paraffin and at the faces of silver halogenide particles? The only explanation would be: adsorbed OH-ions; but this seems not to be probable, as in that case the H-ion would have a very special influence, as it has a special influence on the concentration of the OH-ions. However, there is hardly any difference between a K- and an H-ion on this ζ potential. Moreover, it is interesting that colloidal stability with silver-halogenides is due only to the potential, induced by a double layer of the normal type, originating from ions that determine the total electric potential (*viz.* halide-ions).

The problem arises whether such a ζ potential of the second type is really due to an ionic double layer. The Helmholtz' theory is older than the theory of electrolytic dissociation. However it is difficult to give a satisfactory explanation nowadays, I have thought of orientated water dipoles, but I must acknowledge that this is not clear. Unpolarisable liquids give however no electric kinetic phenomena.

In his introductory paper Freundlich mentions as a special characteristic of colloidal electrolytes their spontaneously going into solution. I wonder whether this must be ascribed directly to a difference in the electric character of the particles or to a difference in solvation. I should not like to emphasise that there is no relation between electric properties and solvation, but it seems to me that the antagonism "ionic micelle or electric double layer" is not analogous to that of "spontaneous dissolution and peptisation by a third component"; it seems that the former is much closer related to "sufficient and insufficient solvation."

In reply to Dr. Söllner: The problem remains the same, whether we have a paraffin-water or an air-water surface, both being themselves absolutely incapable to produce ions.

Mr. G. S. Hartley (*London*) said: Although *as far as the equilibrium properties are concerned* the effect of increasing particle size acts in the reverse direction to the effect of increasing charge and consequently a colloidal electrolyte may, over a limited concentration range, show some resemblance to a uni-uni-valent electrolyte, this will certainly not be true of the *mobility of the particle*. Here, increasing size and increasing

[11] See H. S. Simms, *J. physic. Chem.*, **32**, 1121, 1928.

[12] A. H. W. Aten, Jr., unpublished.

[13] See P. Julien, *Diss.*, Utrecht, 1933, and Ruyssen and Kruyt, *Proc. Roy. Acad. Science, Amsterdam*, 1934.

[14] Where the *Ladungsnullpunkt* is attained; see Verwey's and my papers in *Z. physik. Chem.*, **167**, 1933-34.

charge act together to increase the braking effect of the atmosphere. No similarity to a univalent ion would be found if the change in the mobility of the gelatin ion with concentration of gelatin or salt were measured.

Dr. A. Wassermann (*London*) said: Gross and Halpern [15] and Bjerrum [16] treated the theory of a heat effect in a dielectric medium, and have arrived at a relation between the heat of dilution of an ionic-solution and the electric energy change according to Debye and Hückel.

Nernst [17] and Naudé [18] and Lange [19] and co-workers have measured in the differential-calorimeter the heat of dilution of extremely dilute electrolytes (heat-effects 0·02-2 g.-cal./10 cm.^{3}), and have discussed the degree of dissociation of these electrolytes on the basis of the calculations of Gross, Halpern, and Bjerrum.

In any attempt to apply the Debye-Hückel theory to simple colloidal electrolytes, the degree of dissociation of the colloidal electrolytes and therefore their heat of dilution is of great interest. Changes of the degree of aggregation during the dilution, and other complicating factors, will have to be considered.

Dr. F. Eirich (*Wien*) said: With regard to Dr. Hartley's paper may I call attention to the fact that, in addition to tungstic acid sol, many other colloid acids, *e.g.*, purified gum arabic, gum tragacanth, silicic acid, arsenic sulphide and platinum sol yield curves on conductometric titration, which clearly show the presence of different acid stages. These colloid acids react on neutralisation like crystalloid acids and are similar to these, which are considered as the charging compounds. Thus the anions on the particle surface do not always combine with a polyvalent ion,* but they frequently retain some part of their individual qualities. Consequently it sometimes seems more suitable to consider a colloidal electrolyte as a solution, in which one kind of the ions is not evenly divided, but is found localised in little spots, whereby the concentration of those ions is determined by their distance from each other on the particle. Probably the same division of the *Gegenions* will arise, if one visualises the particle surface as that of a polyvalent ion or as a residue of a certain kind of ions.

Professor Wo. Ostwald (*Leipzig*) said: Dr. Henry of Manchester published some years ago a very interesting development of the theory of the electrical double layer, which has not been mentioned in our discussion so far. In this theory Henry applies the fundamental conceptions of the Debye-Hückel theory of electrolytes itself to develop the structure and the properties of the double layer of any surfaces, *e.g.*, also of macroscopical ones. We find here a very interesting bridge between the theoretical treatment of highly dispersed charged particles such as common ions and micro- or macroscopical charged surfaces, and a very general way to consider both from the same point of view.

Dr. Ph. Gross (*Wien*) said: I agree with Professor Kruyt and Dr. Hartley in saying that generally speaking one should not apply the principle of ionic strength to colloidal electrolytes. In certain cases, however, it may be useful to describe the state of solutions of colloidal electrolytes by comparing them with real strong electrolytes in a manner which I now should like to discuss.

[15] *Physik. Z.*, **26**, 403, 1925.
[16] *Z. physik. Chem.*, **119**, 145, 1926; *Trans. Faraday. Soc.*, **23**, 445, 1927. *Cf.* also Lange and Meixner, *Physik. Z.*, **30**, 670, 1929.
[17] *Z. physik. Chem.*, **135**, 237, 1928. [18] *Ibid.*, **135**, 209, 1928.
[19] *Fortschritte Chemie, Physik., physik. Chem.*, Bd. 19, Heft 6.
* The theory of adsorption does not allow a gradual neutralisation.

As an example of a colloidal electrolyte I choose an aqueous sodium hydrosilicate ($NaHSiO_3$) solution. The measurements of the depression of freezing-points and of the conductivity I use here are taken from various authors.

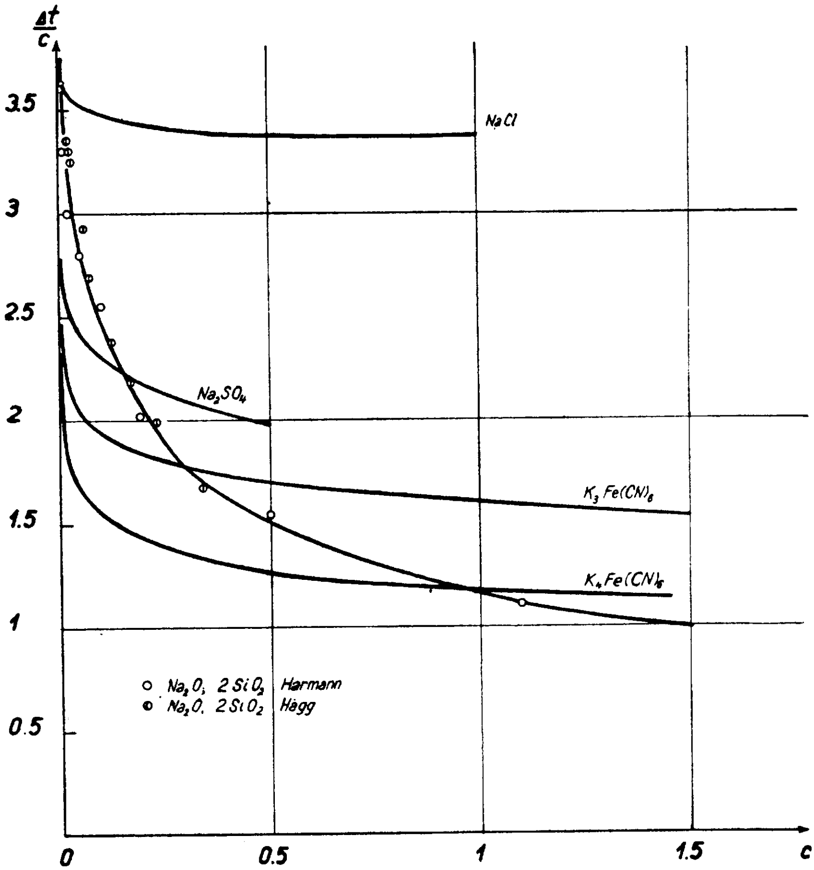

FIG. 1. c = Equivalents/Litre.

Fig. 1 shows the curves if the molecular freezing-point depression $\left(\frac{\Delta t}{c}\right)$ is plotted against the concentration (c):

(1) of a uni-univalent electrolyte, sodium chloride ($NaCl$),
(2) of a uni-divalent electrolyte, sodium sulphate (Na_2SO_4),
(3) of a uni-trivalent electrolyte, potassium ferricyanide ($K_3Fe(CN)_6$),
(4) of a uni-tetravalent electrolyte, potassium ferrocyanide ($K_4Fe(CN)_6$),
(5) of a sodium hydrosilicate solution ($NaHSiO_3$).

We see that the curve of $NaHSiO_3$ cuts the other four curves at different concentrations. We may assume that the association of the $HSiO_3$ ions leads to colloidal particles which have, at those concentrations, the same electrical charges as the ions of the respective electrolyte. The degree of association thus obtained is, of course, a rather rough mean value.

In doing the same with measurements of conductivity there arises a certain difficulty. We cannot state with any certainty the various mobilities of the different colloidal particles. I have for the moment neglected this difficulty, which I think will have to be overcome by a more thorough treatment.

In Fig. 2 the coefficient of conductivity (*f*) of strong electrolytes of the different valency types and of $NaHSiO_3$ is plotted against the concentration (*c*). We find that the points of intersection of the $NaHSiO_3$ curve with the other curves are found within the same range of concentrations as in the first picture (Fig. 1) respectively.

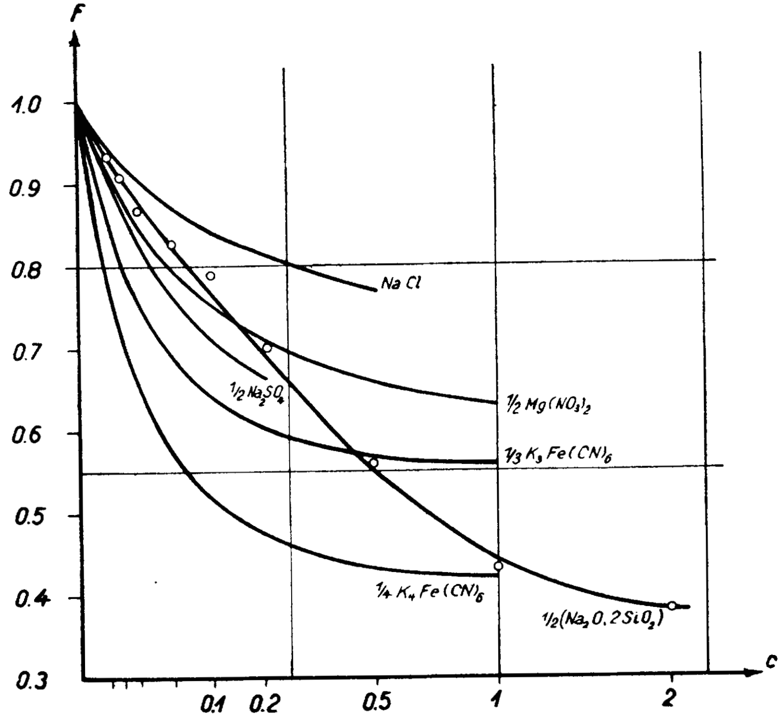

FIG. 2. c = Equivalents/Litre.

The whole method, of course, needs a little more justification. To this end, for instance, measurements of the activity coefficient of the sodium ion would be very useful.

Dr. Conmar Robinson (*London*) said: Professor Rabinovitch points out the difficulties met with in attempting to apply a theory of colloid electrolytes to lyophobic colloids, as is done by Pauli. Nevertheless he concludes, in the last paragraph of the summary of his paper, that it is desirable to build up such a theory (" but attempts have to be made to build it up ").

If by applying a theory of colloidal electrolytes to lyophobic colloids he means explaining all the properties of lyophobic colloids by methods analogous to those used to explain the properties of colloidal electrolytes such as soaps, dyes and proteins, I feel he is here suggesting that we attempt the impossible. There is a difference between these two classes of colloids which is more fundamental than any of the differences which have been stressed by Professor Rabinovitch. This difference has already been mentioned by Professor Freundlich in his introduction and is as follows: On the one hand we have dyes, soaps and proteins, substances which dissociate into ions or ion aggregates on being dissolved—here all the substance is determining the colloidal properties —and on the other hand colloids such as gold sols which possess a central core which plays no direct part in many of the colloidal properties of the solution, these colloidal properties being to a very large extent determined by small amounts of " foreign " electrolytes, which are bound to the core of (*e.g.*) gold. All the colloidal properties of both these classes will never be explained by the same theories. But in solving a particular problem it may be useful to treat any charged colloid as a colloidal electrolyte. For instance, this was done by Mr. Hartley and myself [20] in explaining the high diffusion of starch obtained by Bruins. A similar treatment could have been used to explain the diffusion coefficient of any charged colloid, but it does not follow that because we used such a treatment we necessarily consider starch to be a colloidal electrolyte or that all its colloidal properties can be explained by an extrapolation of our knowledge of ordinary electrolytes.

Professor A. J. Rabinovitch, in reply, said: I completely agree with Mr. C. Robinson that there are serious doubts as to the possibility of constructing a full theory of colloidal electrolytes capable of explaining the behaviour of lyophobic colloids. I think that in this respect the colloids may be divided into two different classes, in accordance with Freundlich's classification, only a part of lyophilic colloids being typical colloidal electrolytes.

However, attempts may be made to build up a general theory, treating all the colloids from one point of view, as has been done in the interesting paper by Hartley. Unfortunately, any theory of electrolytes as applied to lyophobic colloids is very difficult to verify experimentally on real colloidal systems, the colloidal part of the system playing a very small rôle in comparison with the electrolyte contents.

Dr. E. Valkó (*Ludwigshafen a/Rh.*) said: I should like to discuss some points in the interesting paper of Professor Rabinovitch, in the name of Professor Pauli and myself.

Professor Rabinovitch quoted our answer to Mukherjee. In this we referred to the well-known chapter in the history of the electrochemistry of colloids where, on the basis of misinterpretation or of erroneous methods, research workers were mislead to assume that the fundamental laws of solutions are not applicable to these systems.

The one case was the interpretation of the osmotic behaviour of proteins. Here the influence of membrane potential was not taken into account. The other case was the measurement of steam tension and of the boiling-point of soap solutions with the aid of an insufficient method.

In the first case the theory established by Donnan, in the second case the new exact measurements carried out by McBain, showed that the denial of the fundamental principles was hasty. Our answer to Mukherjee contained also, however, a series of detailed arguments against his conclusions.

Professor Rabinovitch doubts whether potentiometric measurement can give a value for the activity of the *Gegenions*. His criticism of the

[20] *Proc. Roy. Soc.*, **134A**, 20, 1931.

work of Pauli and co-workers fails, however, just as his criticism of the work of Wiegner and Pallmann. His picture of the ideal colloid ignores completely the fact that the electric double layer is, even on the motionless surface, diffuse and not rigid. Our ideal colloid solution has the following properties :—

(1) It is diluted.

(2) The charge density or electric potential on the surface of the colloid particle is small.

In such a system all the *Gegenions* are free and therefore the activity coefficient is equal to unity. The potentiometric measurement gives the value for the concentration of the *Gegenions*.

In the real colloid system these conditions are not fulfilled. Therefore the activity coefficient is smaller than unity. The potentiometric effect of the *Gegenions* is less than their concentration. Since Pauli (as well as Wiegner) based his work on this assumption, his interpretations are perfectly sound and correct. The situation is just the same as in the solutions of ordinary electrolytes.

Finally, I cannot agree with Professor Rabinovitch's view that the fact has generally been neglected that the charging ions are, in regard to the likelihood of combination, in equilibrium with the surface of colloid particles. Pauli and I have dealt with this equilibrium in detail. Only in those systems which are thoroughly purified, preferably by electrodialysis, is this equilibrium so established that the fraction of free charging ions is comparatively small. With the electric current the free ions must be driven out. In other systems the free-charging ions were carefully taken into account by us.

Professor A. J. Rabinovitch, in reply, said : Dr. Valkó has not pointed to the considerations of other authors as to the equilibrium of ions between the particles and the intermicellar liquid in order to emphasise the particular importance which the present authors ascribe to this factor.

With regard to the second point of Dr. Valkó's criticism, there is a profound discrepancy between the views of the school of Pauli and that of the author, and no agreement can be attained on this point at present. We still believe that our point of view has been sufficiently clearly exposed in the thermodynamical argument in our paper (p. 5), and no serious objections have been raised against it.

Dr. H. Neurath (*Wien*) said : In his paper Professor Rabinovitch calls attention to the fact that the determination of the p_H in iron-oxide sols, by means of the hydrogen electrode, as carried out by Pauli and Matula,[21] leads to wrong results, owing to the poisoning of the electrode by Fe ions. Hence all calculations of the charge (*Kolloidaequivalent*) are inexact.

I desire to point out that these authors, at the time, realised these difficulties, and therefore they compared the measurements of the p_H in the sol with those in the filtrate flocculated with potassium chloride. Both measurements agreed almost exactly. As it was shown in later papers,[22, 23] the activity of hydrogen ions in iron oxide sols can be determined exactly, if the sol is set free from iron ions by thorough electrodialysis. We can ignore, however, all these doubts if we deal, for

[21] W. Pauli and J. Matula, *Koll. Z.*, **21**, 49, 1917.
[22] Winnifred L. McClatchie, *J. physical Chem.*, **36**, 2087, 1932.
[23] H. Neurath and W. Pauli, *Z. physik. Chemie*, **163**, 351, 1933.

example, with an aluminium oxide- or a thorium oxide sol, [24, 25, 26] with which the possibility of an oxidation-reduction potential is excluded.

I wish to emphasise that all these investigations are carried out with sols, of which the concentration and the activity of all types of ions were exactly known.

Professor A. J. Rabinovitch, in reply, said : Our measurements of p_H-values of ferric oxide sols made with different electrodes (Pt-H_2, quinhydrone, glass electrode) have decidedly shown that the Fe_2O_3-sols are acid. This could not be stated by Pauli and Matula because the Pt-H_2-electrode is poisoned in ferric oxide colloidal solutions.

It is easy to understand that Pauli and Matula found very high p_H-values (near to neutrality) in the filtrates after coagulation of ferric oxide sols by electrolytes or in corresponding ultrafiltrates. As previously found by the authors, electrolyte coagulation is accompanied in this case by an increase of p_H-values, owing to the change of hydrolysis conditions. If the filtrate after coagulation was nearly neutral, the sol itself must have been acid.

Dr. E. Valkó (*Ludwigshafen a/Rh.*) said : In connection with the very interesting remarks by Professor Frumkin, I should like to stress the fact, that the difficulties in applying the theory of the diffuse double layer especially to the question of the capacity are often due rather to the inner component of the double layer than to its outer diffuse part. Only the latter is the object of the theory of Gouy and of Debye-Hückel. I have the impression that the complications in the structure of the double layer lie chiefly in the composition of the inner part. It is a question of the formation of complex compounds at the surfaces, the nature of which is in many cases recognised by Pauli.

Dr. F. Eirich (*Wien*) said: Professor Rabinovitch emphasised some consequences of his reflections on coagulation. But the two possibilities of the coagulation described are not sufficient to explain a great deal of important experimental work. I will only give one characteristical example: which is already contained in Pauli's paper. I refer to the flocculation results of very well-defined gold sols, prepared by electrical dispersion in purest diluted hydrochloric acid or sodium hydroxide. If to these acid sols a caustic is added (or vice versa to the alkaline sol an acid) they show a peculiar behaviour. Their stability is gradually diminished as they are more and more neutralised, then flocculation occurs at a still very small concentration and later, on greater additions of HCl or HBr only a new range of stability follows' leading to a new flocculation at high concentration. Any coagulation theory assuming a building of insoluble compounds or specific adsorption is too schematic to explain either our irregular and irreversible flocculation series and, at the same time, the still more remarkable difference between the effects of different kinds of acid, which difference disappears (in the presence of the anions known to form complexes with gold. All these facts can, however, be well explained from the electrochemical point of view as an exchange of chlorine with hydroxyl ion in the interior of the complexes on the surface of the gold particles, which causes coagulation or electrical charge. Therefore these variations and complications seem to be more readily explained chemically by means of the well-known ionic or complexionic reactions, without any assumption of special adsorption.

[24] W. Pauli and E. Schmidt, *Z. physik. Chemie,* **129,** 199, 1927.
[25] F. Muttoné and W. Pauli, *Koll. Z.,* **57,** 312, 1931.
[26] W. Pauli and A. Peters, *Z. physik. Chemie,* **135,** 1, 1928.

Professor A. J. Rabinovitch said, in reply : It is quite probable that we have not enumerated in our paper all the possible cases of coagulation. This was not our purpose. A full theory of this process does not exist at the present time.

Anyhow, there is not a very great discrepancy between our views in the case cited by Dr. Eirich. He emphasises the importance of processes in the inner part of the double layer, treating them from a chemical point of view. In our paper we also emphasise the importance of the inner part of the double layer, in considering the adsorption of *both* ions of the stabilising electrolyte, *i.e.*, of *Nebenionen*.

Professor Wo. Ostwald (*partly communicated*) : The discussion between Professor Kruyt and Mr. Hartley as to whether colloids with electrical conductivity are better treated from the standpoint of electrical surface phenomena or from the standpoint of the ionic theory is a partial resurrection of the discussion held thirty years ago on the question, whether colloids are better treated as heterogeneous or as homogeneous systems. The latter question is hardly discussed any more now. The introduction of the conception of " dispersed systems," including macroscopic suspensions as well as molecular dispersed solutions, closed this discussion. This conception meant an outspoken and conscientious *emancipation* from the classical ideas of heterogeneous and homogeneous systems, based upon the fact (to quote J. Perrin) that " even the most fruitful scientific conceptions lose their fruitfulness and even their meaning if they are applied to phenomena which lie outside the experimental field for which these conceptions have originally been made for." Colloid particles are not phases according to Gibbs' own definition, because the amount of energy and entropy located in their surfaces is *not* to be neglected when compared with the amount of energy and entropy located in the interior of the particle. Nor do gold sols, for example, obey the laws of Faraday for normal ions, the masses transferred in cataphoresis not being proportional to the number of elementary charges, and the masses not being in equivalent proportions to each other, if different sols are compared. Of course it seems *a priori* possible, empirically as well as theoretically, to extrapolate from both points of views, as Mr. Hartley points out. This has been tried over and over again. But the overwhelming evidence goes to show firstly that the experimental transition-curves very frequently show maxima or minima in the region of colloidal dimensions, so that extrapolation is somewhat dangerous ; and secondly, that enlargements or modifications of the classical theories for colloidal systems tend to become extraordinary complicated and correspondingly diffuse. Instances are at hand.

The safest way seems to treat colloidal systems—generally as well as in regard to their electro-chemistry—as essentially *new* systems. It is an error to believe that the phenomenological or functional stage of colloid science can be passed over or that it is already finished. We do not even know, for instance, the general shape of such a simple function as conductivity—dilution for the different types of conducting colloids, and Mr. Robinson's graph of this function for benzo-purpurine is a very pretty instance of this colloidal specificity shown even by a colloid that is very closely related to common electrolytes. This point of view, the theoretically unbiassed collection and description first of the fundamental experimental functions in colloids, is what is indicated by the use of the word " *Eigengesetzlichkeiten* " of colloids by Mukherjee and by myself. You may call this point of view a very modest one. We think modesty in this case to be especially progressive.

Dr. Ph. Gross (*Wien*) said: In connection with one of the remarks of Professor Kruyt I would refer to a paper by Scatchard and Kirkwood.* This paper deals theoretically with the interaction between common ions and ions, the charged groups of which are widely separated from each other. The problem is treated according to outlines quite similar to the treatment originated by Debye and Hückel, but the results are rather different.

Dr. F. Fairbrother (*Manchester*) said: There exists a potential between the solid and liquid phases of a melting solid or a freezing liquid. This was first observed by Faraday [27] in the case of ice and water, and has also been shown to exist in the case of a number of organic compounds.[28] It is difficult to imagine an ordinary ionogenic mechanism in these circumstances.

Dr. A. H. Hughes (*Cambridge*) said: A possible source of the high negative electrokinetic potential obtained with paraffins against water is the presence of minute traces of long-chain fatty acids. A quantity of such material as small as 10^{-7} gm. per sq. cm. present as an oriented monolayer at an oil-water interface may produce a potential difference due to partially ionised carboxyl groups of from 2-300 millivolts.

Professor W. C. M. Lewis (*Liverpool*) recalled the findings of E. Jones [29] in connection with the effect of vigorous stirring upon the magnitude of the ζ potential difference. If the colloidal particles (gold sol) have had their ζ value reduced to zero by suitable addition of electrolyte, the effect of stirring is to hasten the rate of aggregation of the individual particles as one would expect purely on a collision frequency basis. On the other hand, if the electrolyte concentration is insufficient to reduce ζ to zero, the effect of stirring is actually to slow down the rate of aggregation. This can be explained on the basis of a mobile outer portion in the double layer, the removal of which effectively increases ζ. The results seem therefore to demand the actual existence of a double layer, of the Gouy-Stern type in general.

* G. Scatchard and J. G. Kirkwood, *Physik. Z.*, **33**, 297, 1932, see also J. G. Kirkwood, *J. Chem. Physics*, **2**, 351, 1934.

[27] Faraday, *Experimental Researches*, **2**, No. 2131, 122.

[28] Fairbrother and Wormwell, *J. Chem. Soc.*, 1991, 1928.

[29] *Trans. Faraday Soc.*, **27**, 51, 1931.