THE ELECTRICAL DOUBLE LAYER AND THE STABILITY OF LYOPHOBIC COLLOIDS

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I. THE ELECTRICAL DOUBLE LAYER

I. INTRODUCTION

Colloid chemistry has learned to distinguish between two types of colloids. First there are the *lyophobic colloids*, which can be flocculated by comparatively small quantities of electrolytes. It is well known that, between 1880 and 1900, investigations of Schulze (113), Linder and Picton (90), and Hardy (54) introduced the concept that the particles of these sols are prevented from sticking together by electrical repulsing forces. Though an exact picture of the significance of the electrical charge of the particles was desirable, this gave qualitatively a plausible explanation of the "stability" of these colloids. Later experiments showed that there is a close connection between the stability and the so-called electrokinetic phenomena. Perrin (102) and Elissafoff (30) studied the electrosmosis, Burton (20) and Powis (103) the cataphoresis, and Kruyt (78) the streaming potentials. Different electrolytes were shown to influence the electrokinetic potential of a surface in a way that is typical for the electrolyte. The same effects were found when the influence of different electrolytes upon the stability of lyophobic colloids was studied.

On the other hand, there is a second type of colloids, which, according to Kruyt (74), Bungenberg de Jong (17), and others, is influenced electrically by electrolytes in the same way; here, however, the mere reduction of the electrokinetic potential (ζ) by electrolytes does not lead to flocculation, on account of a second stabilizing factor. As this factor is determined by the mutual interaction of the particles and the dispersion medium, these sols are mostly called *lyophilic colloids*.

In this article we deal with the electrical properties of colloids, i.e., we

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will not consider the solvation phenomena. Hence our considerations will be valid for lyophobic colloids mainly, and for lyophilic colloids only in special cases.

In his famous article in Graetz's *Handbuch*, von Smoluchowski (114) has treated the total field of electrokinetic phenomena, of the "ζ-potential" derived from them, and the theory of the electrical double layer (1914). Though his conceptions have been extended in several respects by Gouy (50), Stern (116), Frumkin (45), and others, a complete theory of the ζ-potential, and therefore a satisfactory theory of the stability of (lyophobic) colloids, is still lacking. It is well known that Freundlich (33, 34) tried to explain the action of flocculating electrolytes as a neutralization of the charge of the particles by adsorption. This conception has long been the current one. Comparatively recently (1929), however, the theory has been rejected, partly as a consequence of investigations by Freundlich (41) himself. The incorrectness of this theory demonstrated the increasing need of a fundamental theory for the stability of these colloids, i.e., of an exact picture of the mechanism of the mutual interaction between particles and electrolytes.

Meanwhile the number of colloid chemical facts has increased enormously. Yet there is some doubt whether all these data have been gathered with sufficiently reproducible substances, since in many cases the phenomena seem to be very complicated. An important part of this experimental work is handicapped by the circumstance that there is no leading theory generally accepted by all investigators.

In the laboratory of Kruyt (at Utrecht) an extended investigation, with a small number of well-defined substances, was undertaken. The silver halides were chosen as the chief substances of experimental research, since from earlier experience these compounds were expected to be more reproducible and much less complicated than those generally used previously. Indeed, the capillary electrical and colloid chemical investigations revealed a number of new aspects (74a, 74b).

In the present paper the results of these investigations (partly published in Dutch dissertations of Janssen (64), Julien (65), Cysouw (25), and Verwey (130)) will be discussed, together with work of other scientists which contributed to the recent development of our knowledge. In connection with these investigations, the phenomena of the "adsorption of electrolytes" and of the "stability of (lyophobic) colloids" will be subjected to a new theoretical study. On the basis of this study some general lines of thought will be developed, which, in our opinion, have to be drawn distinctly in all colloid chemical work, in order to give to this field of research its necessary theoretical background.

II. COLLOID ELECTROLYTE OR TWO-PHASE SYSTEM?[2]

The general treatment and the subdivision of our subject may be elucidated by a preliminary remark. The lyophobic colloids constitute a difficult borderline case between two fields studied reasonably well: (1) the molecular disperse system of a solution of an electrolyte, and (2) the two-phase system solid–solution with a single continuous and flat boundary layer. In our study of the laws of colloids both extremities may function as a starting point for our considerations. Then, extending our reasoning to the case of a definite colloidal system as a next approximation, we have to make the necessary corrections.

In the first place we can take colloids as electrolytes, and study them by the well-known methods of electrochemistry. This way is chosen by Zsigmondy (142) and especially by Pauli (100). The charged particles are called "colloid ions," and the ionic spheres of opposite charge around them constitute the so-called "counter-ions." This nomenclature, and the electrochemical study, is advantageous in many respects. It is not sufficient, however. The main problem of colloid chemistry, the stability of the sols, does not come out to advantage in the "electrochemistry of colloids." Its particular difficulty is the asymmetrical character of these "electrolytes." The "valency" of the colloid ion generally amounts to from some thousand to several million unit charges per particle. So the limit laws of Debye-Hückel (27) do not hold any more.

Freundlich (33), Kruyt (74), and others chose the other method, and started from the *flat double layer*. For our purpose, too, this is the only possibility. Only occasionally shall we consider the corrections for a strong curvature of this boundary layer, i.e., for the case when the particles are extremely small. For the present our reasoning will be restricted to systems of low dispersity; hence the number of molecules (ions) in the surface of our particles is assumed to be negligibly small as compared with the total number in these particles.

In the next sections of this paper we shall deal with the electrical double layer and its properties. In Part II our considerations will be applied to the problem of the stability of lyophobic colloids. In Part I we are therefore especially interested in systems where the conditions are much like those in colloidal lyophobic solutions. This is the reason why we restrict ourselves to systems in which one of the phases is a solution of electrolytes.

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[2] *Note added in proof:* Meanwhile a valuable contribution to the problem of this section has been made by a General Discussion on Colloidal Electrolytes held by the Faraday Society (Gurney and Jackson, London, January, 1935). See in particular the papers of Wo. Pauli, H. R. Kruyt, G. S. Hartley, and A. J. Rabinovitch and V. A. Kargin.

As a rule the double layer at gas–solid or gas–liquid interfaces (which is governed by quite different laws) is left out of the discussion.

III. THE STRUCTURE OF THE DOUBLE LAYER

The potential difference between two phases manifests itself in a potential drop in the neighborhood of the boundary layer. In part it is effected by oriented and polarized molecules or (and) ions, i.e., by a shift of electrical charge within one phase. Generally, however, a double layer of free charges contributes also to the potential drop. This double layer consists of two space charges of opposite sign in the surface of both phases. Let us consider, for instance, silver iodide crystal in contact with a dilute solution of electrolytes. When equilibrium is reached, the silver iodide lattice may contain in its surface a number of iodide ions in excess, and the silver iodide thus will be charged negatively. Then, in the immediate neighborhood of the surface, the solution must contain an equal number of cations in excess.

In older pictures of the double layer (e.g., that of Perrin (102)), the latter is assumed to be built up by two "mono-ionic" layers of opposite charges touching each other in the boundary plane. This very simple picture, which obviously neglects the thermal agitation of the ions, is often (but unjustly, according to Janssen (64)) ascribed to von Helmholtz (56). The modern conception has been given by Gouy (1910). (Afterwards similar considerations were held by Chapman (22), Herzfeld (58), and Debye and Hückel (27).) Gouy calculates the partition of the charges in the outer layer on the side of the solution. On account of their kinetic agitation the ions of this layer (in our example the cations) partially escape from the attracting forces of the charge of the surface; on the other hand, some anions will succeed in getting into the first layers. This equilibrium of attracting, repelling, and kinetic forces is calculated by Gouy on the assumption that both ions have negligible dimensions. The number of cations and anions, as a function of the distance from the surface, is then reproduced schematically by figure 1; the shaded surface is a measure of the total charge of the outer layer.

According to this theory the total potential drop caused by the double layer occurs in the outer "diffuse" layer. Moreover, one should expect that the whole outer layer may shift against the surface, e.g., in an electrical field, and thus give rise to electrophoresis, etc. This is contrary to experience. von Smoluchowski (114) has pointed out (1914), and afterwards Freundlich (33) and Gyemant (51) also, that the ζ-potential calculated from electrokinetic measurements is not identical with the total potential drop; both potentials depend on the concentration and the nature of the electrolytes in the solution in a fundamentally different way. The

theory has been improved by Stern (116), who takes into account the size and specific properties of the ions. According to him only part of the ions of the outer layer make themselves free from the attracting surface. Thus the total liquid charge is divided into two parts: the charge of the ions that remain attached to the surface, and a part built up by the free and mobile ions of the diffuse layer. The adhering ions are held by purely electrostatic and by specific forces. In connection with the latter a specific "adsorption potential" is given to each ion. The introduction of the adsorption potentials rather complicates Stern's equations, but in some cases they can be neglected; in which case Stern's picture is an adequate and valuable approximation of the state of affairs in the double layer.

Recently the theory of Gouy has been worked out by Janssen in a somewhat different direction. Janssen (64) argues that the mobility of
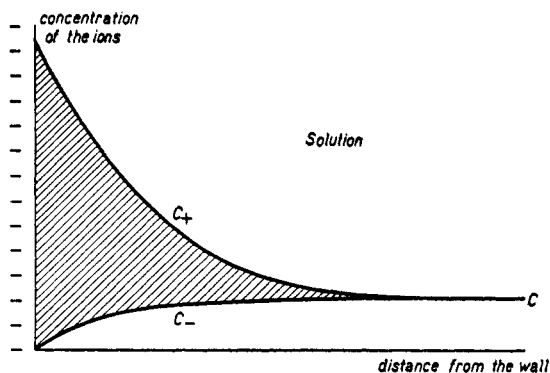

FIG. 1. Distribution of positive and negative ions in the neighborhood of a negative surface ("diffuse layer").

the liquid in the neighborhood of the surface is lowered as a consequence of solvation powers (attraction and orientation of water molecules). He assumes a layer of liquid attached to the surface. This conception may also explain the difference between total potential drop and ζ-potential.

Though von Smoluchowski apparently was not acquainted with Gouy's paper he also assumes an outer charge reaching some distance into the solution. However, according to him the potential drops continuously in both phases, i.e., in our example, part of the total potential occurs in the silver iodide phase. This has been confirmed by calculations by the author (127) from experimental data on the dialyzed silver iodide sol, which is the only case for which sufficient data are as yet available. The result of the calculation is shown schematically in figure 2. The part, ψ, of the total potential drop that falls in the liquid phase is again divided

into two parts: one in the attached layer (Stern-Janssen) and the other in the diffuse layer (Gouy).[3]

The conditions of figure 2, though realized in our case, are only of a simple type. Eventually the slope of the potential may be more complicated, e.g., the potential curve may contain a maximum or minimum, as will be stated later. But even if such complications are neglected for the present, it is an extremely difficult problem to find a relation between the different parts of the total potential drop. Yet this is highly important for colloid chemistry, since the stability of lyophobic sols depends solely or mainly on the ζ-potential of the particles, and this ζ-potential is clearly seen to be connected in a way with the potential drop in other parts of the double layer.

Hence, in order to be able to predict the magnitude of this ζ-potential in a given case, and its variations with the concentration of different
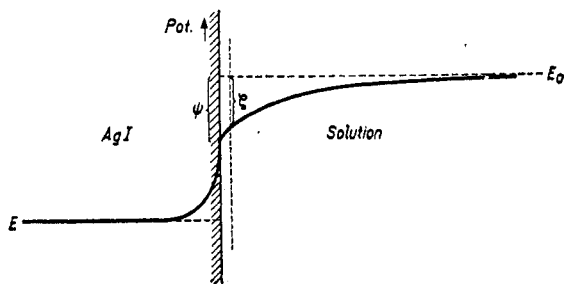

Fig. 2. Curve for the potential, perpendicular to the surface silver iodide–solution, in case of a dialyzed silver iodide sol.

electrolytes, we must study the slope of the potential within the entire double layer. Nevertheless it may be useful, as a simplifying approximation, to consider only the diffuse outer layer, assuming for instance that the charge of this layer (η_2) is constant. It will be shown in Part II that this very simple picture, with the aid of Gouy's theory, already helps us to understand several aspects of the general behavior of lyophobic colloids.

Strictly speaking, the assumption of an electrophoretic charge, which is independent of the concentration of electrolytes, is not correct. This, for instance, is shown in Stern's theory. For rather concentrated solutions only a small fraction of the outer ions will be in the mobile layer ($\eta_1 > > \eta_2$), since a large number of collisions favor a high "adsorption." For extremely small concentrations of the electrolyte, however, the theory of Stern finally becomes practically identical with the picture of Gouy (hence

[3] The corresponding charges will be denoted throughout by η_1 and η_2, respectively.

$\eta_1 < < \eta_2$). Comparing, as usual, the double layer with an electrical condenser, we may state that in concentrated solutions its capacity will not differ much from the capacity of the attached part. For more dilute solutions the mean distance between outer and inner charge increases, since an increasing part of the outer layer is "diffuse." Thus

$$C = \frac{D}{4\pi d}$$

decreases (C = capacity, D = dielectric constant, d = distance between the charges). This is actually seen from Gouy's data on d/D, calculated from the electrocapillary curve of mercury. This quotient (in 10^{-8} cm.) is for two electrolytes as follows:

	1 normal	0.1 normal	0.01 normal
Potassium nitrate	0.393	0.451	0.500
Sodium acetate	0.422	0.467	0.501

From such data we conclude that d/D for the attached layer is of the order 0.4×10^{-8}. The corresponding capacity is about $20\mu F$ per square centimeter. These values are determined by the molecular dimensions and the mean dielectric constant in the double layer. Here some difficulties arise. We must keep in mind that a "dielectric constant" can only be defined distinctly for a volume element which is large in comparison with the size of ions and molecules. Hence we cannot speak of the dielectric constant of the double layer, since this very constant changes there abruptly in a distance of a few molecular dimensions. We can discuss only the electrical polarizability of the ions and molecules present; the average value is determined by the polarizabilities of the constituent ions, of the surface, and of the water molecules in the outer layer. Since the latter are greatly immobilized by the electric fields of the former (hydration), we need to consider practically only the atomic and "optical" polarization and not the orientation polarization, i.e., we must take not the high value $D = 80$ (dielectric constant of pure water), but a value not much larger than 2.

Assuming that the distance of both charges is of the order of 3×10^{-8} cm. (average sum of two ionic radii), we calculate from Gouy's data a "dielectric constant" of the double layer $D = 8$. This is of the expected order of magnitude.

It may be stated here that a general difficulty in the current theory of the double layer is that its special molecular mechanism is generally neglected. Only the partition of charges in a direction perpendicular to the boundary layer is considered; the electric charge is treated mathematically as a continuous one, distributed homogeneously over the surface.

We shall see that actually the conditions often differ considerably from these assumptions. The neglect of all potential gradients along the boundary surface is, to be sure, sometimes allowed, especially in the diffuse outer layer where the time average no longer contains the fine structure of the charges. But in the neighborhood of the boundary layer the discontinuous and possibly irregular distribution of the charges becomes of considerable importance.

The problem we have to deal with is, of course, simple for the double layer between mercury and solution, or between air and solution. Here the ions move freely over the surface, and all points of it are equivalent. It is easy to conclude from the capacity of the double layer calculated above that at the most only a small per cent of the mercury surface is covered with ions.

The phenomena for the system solid–gas are already more complicated. In particular, the boundary layer of solids with a polar lattice (salts) has been studied, e.g., by Langmuir (88), and recently by de Boer (8) and his coworkers. The latter, for instance, examined the adsorption of iodine, cesium, or volatile organic compounds by a thin sublimed layer of calcium fluoride. First they concluded that these layers contained superficially only fluoride ions, thus showing that the surface of the salt layers consists of 111 planes. This statement was confirmed by electron diffraction experiments (Burgers and Dippel (21)). Now on each fluoride ion in the surface, i.e., on each lattice point, maximally one atom of hydrogen, or one-half a molecule of iodine, is adsorbed. A molecule of p-nitrophenol is probably adsorbed on every fourth fluoride ion, but then a second layer of molecules is adsorbed on the first one through weaker forces of the van der Waals type. In the adsorption of cesium atoms the surface is covered by several layers of these atoms. Hence in all cases, though they differ among each other, the adsorption occurs in a definite way at distinct adsorption centers. Optical investigation of slightly covered salt layers (de Boer and Custers (10)) and the study of the sintering process of these sublimed layers (de Boer and Dippel) proved, moreover, that these adsorption centers must be divided into active spots and less active ones; on the former adsorption takes place more easily and with a larger gain of energy. Hence the properties of the lattice are again found to some extent in the adsorbed or double layer.

We were led to similar conclusions by our investigations with the silver iodide sol, although here we deal with a system where water molecules are also present (Verwey and Kruyt (123, 124)).

A first result of this work was that with a dialyzed (negative) silver iodide sol the surface density of the charge is extremely small. We found, for instance, values ten times as small as the charge density (per square

centimeter) for mercury–solution. With the strong "aging" of these sols this value still decreases. A detailed study of these aging phenomena, analytically and with the aid of x-rays, led to the conclusion that on the silver iodide particles the charging iodide ions are present only at certain active spots. All kinds of irregularities, cavities, lattice distortions, etc., of the silver iodide surface may function as such. These preferred places will thus be of the same nature as Smekal's (113a) "Lockerstellen" or H. S. Taylor's (117) active spots on catalysts. It seems that the undisturbed crystal faces do not contribute to the double layer. This is in accordance with modern conceptions of crystal growth (Kossel, Stransky; cf. van Arkel and de Boer (5)). It also explains the abnormally low values of the charge of the double layer per square centimeter of surface.

The aging process therefore consists in the first place of a perfecting of the particles. Immediately after the precipitation the small crystals of silver iodide have a very imperfect lattice with many active spots. Upon aging, such an irregularly formed crystal gradually transforms into a more perfect one, with fewer places that are able to take up iodide ions. Partially also a coarsening of the sols occurs, but with moderate aging this process practically does not yet appear in the case of dialyzed silver iodide sols.

Recently similar aging processes were studied with several other precipitates by Kolthoff, Rosenblum, and Sandell (70, 71, 72), in connection with Kolthoff's investigations of coprecipitation and the physical properties of analytical precipitates. They also found that precipitates of lead sulfate, etc., are subject to enormous changes in their lattice structure during the first period of their existence.

We see therefore that in the case of silver iodide and probably also in other cases the charge is not distributed homogeneously over the surface, and that the double layer is concentrated more and more in a small number of (active) spots. Hence there is actually a strong deviation from the homogeneous and continuous distribution of the charge assumed in the computations of Gouy, Stern, and others.

de Boer and Veenemans (12), in recent investigations regarding the adsorption of the atoms of volatile metals by metal surfaces, have considered the influence of a discontinuous distribution of the charge upon the slope of the potential within the double layer. If the plates of a condenser of infinite surface are charged by two continuous charges, the field at both sides of the condenser is zero (figure 3). If, however, the plates are covered with a number of concrete charges at comparatively large distances from each other (figure 4), only part of the average potential drop occurs between both layers. The discontinuous distribution of the charge is the reason for existence of residual fields outside the condenser.

The actual existence of these residual fields of a double layer of the type of figure 4 has been proved by the experiments of deBoer and Veenemans.

If, moreover, the charges are distributed irregularly over the surface, this factor must *a fortiori* be taken into account. The consequence is that part of the total potential drop must occur *within* the silver iodide
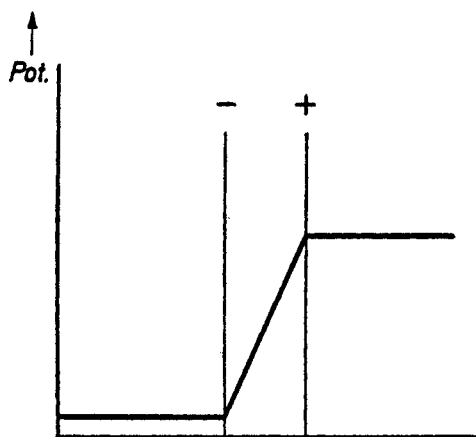

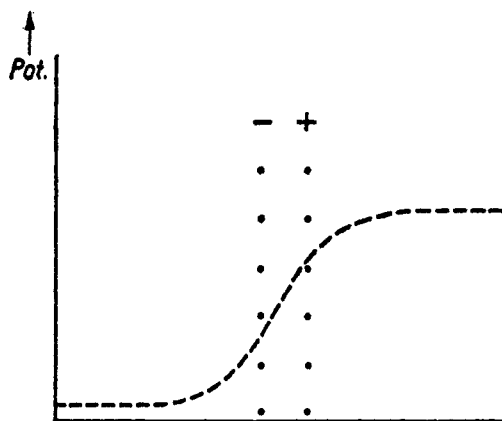FIG. 3. Condenser with continuous charge distribution

FIG. 4. Condenser with discontinuous charges

phase. This is the plausible explanation of the left-hand part of the potential curve of figure 2, calculated by the author from experimental data on the silver iodide sols.

From this we see the importance of a topographical study of the double

layer. In most cases, however, we do not know anything about it. We cannot even account for the extremely high values of the apparent capacity of the double layer found for many sols. We calculated this capacity (126, 130) for arsenic trisulfide, gold, and silver sols, and also for etched silver, from data of Pauli and Valko and of Proskurnin and Frumkin (46). We found values several hundred times larger than the double layer capacity of 1 square centimeter of mercury–solution. The surface density of the charge seems to be much larger even than that of a closely packed layer of ions. In these cases obviously some complication exists. For the same reason there is an unexplained discrepancy between the free charges calculated from the conductivity of the sols and from their electrokinetic potentials, respectively. The first may be found to be about 1000 times as large as the latter. Only in the case of the dialyzed silver iodide sol, where the charge of a particle is extremely small, is this discrepancy not found. This is another argument why the silver halides, in particular, silver iodide, are more simple substances for colloidal research than the usual sols.

IV. THE FORMATION OF THE DOUBLE LAYER

Suppose we bring electrolytically conducting phases in contact with each other, e.g., silver iodide and an aqueous solution of an electrolyte. How, then, is a double layer formed? We assume that the solution has been previously saturated with silver iodide; for this, indeed, a very small amount of silver iodide is sufficient, since the solubility at room temperature is only 10^{-8} equivalent per liter. The concentration of silver and iodide ions may still vary within wide ranges; always, however, the ionic product $c_{Ag^+} \times c_{I^-} = 10^{-16}$.

Both phases contain silver ions, and generally the thermodynamic potentials of these ions are not the same in the silver iodide and in the solution. Hence silver ions will move in one direction, say from the silver iodide to the solution, and cross the boundary layer. Iodide ions move in the opposite direction, since the ionic product in the solution must remain constant. By this transportation of ions the silver iodide phase is going to contain an excessive amount of iodide ions, i.e., the silver iodide is charged negatively. Further transportation will soon be prevented by the charge thus formed. For electrostatic reasons this negative charge, as the equal positive charge in the solution, is localized in the neighborhood of the boundary layer. The potential drop caused by the electrical double layer thus formed occurs in the same region. Thus we may state that the potential difference between silver iodide and solution is determined by a distribution of common ions (silver ions or iodide ions; Lange (82, 87) calls them potential-determining ions) over both phases.

When equilibrium is reached, according to Nernst, van Laar (81), and Haber and Beutner (52a),

$$E = \epsilon + \frac{RT}{F} \ln c_{Ag^+} \tag{1}$$

is valid, or

$$E = \epsilon' - \frac{RT}{F} \ln c_{I^-}$$

So the total potential drop in the double layer, E, depends only on the concentration of the potential-determining ions. However, it is not necessarily true that E is entirely due to a transportation of charges from one phase to the other. For a definite c_{Ag^+} (or c_{I^-}) in the solution such a transportation will not be needed in order to establish an equilibrium; this corresponds to the concentration for which the charge of the ionic double layer is zero. In this "zero point of the charge" the value of E is generally not zero ($E = E_0$). This remaining potential difference E_0 is attributed to the orientation of the water molecules (electric dipoles) in the boundary layer or the mutual polarization of lattice ions, water molecules, etc. Potential differences of this kind can be measured only with difficulty. (χ-potentials, after Lange). Therefore E_0 and thus the absolute value of E is unknown. For our purpose, however, only the changes of E are important. There is some evidence that χ varies only slightly with E (Andauer and Lange (3)). As a first approximation we will assume that there is a simple superposition of the χ-field (in this event equal to E_0) and the field of the double layer. In this ideal case changes of E are entirely supported by a transportation of ions through the boundary layer; the proper potential of the ionic double layer is $E - E_0$.

The formation of the double layer manifests itself as an "adsorption." If silver iodide is charged negatively by a solution of hydriodic acid, a number of iodide ions go from the solution into the surface of the silver iodide. Only an extremely small number of silver ions are transported in the reverse direction, since the concentration of the latter in the hydriodic acid solution is very small and can increase only slightly. Hence the ionic transport is practically unidirectional. The iodide ions adsorbed are accompanied by an equivalent amount of hydrogen ions. These ions remain in the solution phase and constitute the outer charge of the double layer. Hence, as a whole, a certain amount of hydriodic acid is taken from the solution and "adsorbed" by the silver iodide in order to build up the double layer.

At the other side of the zero point of the charge, in a solution with a sufficiently great value for the concentration of silver ions, the formation of a positive double layer takes place in a similar way by the adsorption of, say, silver nitrate.

For a constant capacity of the double layer the amount of iodide ion (silver ion) that is taken up by 1 gram of silver iodide, x, is proportional to $E - E_0$, hence

or

$$\left.\begin{array}{c} x = k_1 + k_2 \log c \\[2mm] \dfrac{\mathrm{d}x}{\mathrm{d}\log c} = \text{constant} \end{array}\right\} \tag{2}$$

These equations will generally hold for any kind of potential-determining electrolytes, hence for the "adsorption" of silver ion by silver, of mercuric ion (Hg_2^{++}) by mercury, of hydroxide ion or hydrogen ion by glass, etc. According to Lange and Berger (82, 84) equation 2 is valid for a precipitate of silver iodide between c_{Ag^+} (or c_{I^-}) = 10^{-9} to 10^{-7}, and they prove the probability of this law for some other cases (see also Lange and Andauer (2)). In our own experiments (125) we have measured the "adsorption" of potassium iodide by dialyzed silver iodide sols, and found that equation 2 actually holds for iodide-ion concentrations up to 10^{-4} equivalent per liter. (In these sols c_{I^-} is about 10^{-7} equivalent per liter.) We were also able to determine the amount of iodide ion that was already present in the double layer of the sols (123, 125), and from this we could estimate by an extrapolation with the aid of equation 2 the value of c_{I^-} for the zero point of the charge ($E = E_0$). We found that the silver iodide of these sols is uncharged when it is in equilibrium with a solution of about 10^{-6} N silver ion (or c_{I^-} = 10^{-10}). The zero point of the charge coincides therefore with the zero point of the electrokinetic potential found earlier by Kruyt and van der Willigen (80) and by Lange and Crane (85). The negative charge of silver iodide in pure water is therefore due to the excess of iodide ion it "adsorbs," and is not caused by a specific adsorption of hydroxide ion as has been generally assumed hitherto. The tendency of the iodide ion to go from the solution into the silver iodide phase is so much greater than that of the silver ions that a 10,000-fold excess of the latter is necessary in order to reach the point where they counterbalance each other.

These data are only valid for the case of our dialyzed silver iodide sols, prepared in a definite way; our sols were electrodialyzed immediately after preparation and then concentrated by "electrodecantation" after Pauli (100a). As the aging process proceeds only very slowly after the removal of the free iodide ion (cf. Part II, section I), the degree of aging of these sols did not vary much. The size of the particles was about $40\,m\mu$. Julien

(65) has found that large crystals of silver iodide (and other halides of silver), e.g. when crystallized from molten silver iodide, cannot be charged electrokinetically positive by even 0.001 N silver nitrate solution. Apparently the zero point of the electrokinetic charge (Julien measured streaming potentials and electrosmosis) and probably also the zero point of the total charge depends chiefly on the nature of the silver iodide; in the dialyzed sols the charge is reversed by 10^{-6} N silver nitrate, but coarse crystals of silver iodide are still negative in 10^{-3} N silver nitrate. Julien also studied the change of the properties of fresh precipitates when they were subjected to an aging and coarsening process in a solution of 0.001 N silver nitrate. In this solution the fresh precipitate of silver bromide is positive, but the charge decreases continually with the time, and after several hours turns negative. With silver iodide the same inversion was observed, but, in accordance with its lower solubility, the change proceeded much more slowly. With better and larger crystals, therefore, the zero point of the charge is shifted considerably to higher silver-ion concentrations, and becomes more and more asymmetrical. The equilibrium of the distribution of the potential-determining ions over silver iodide and solution shifts in such a way that the affinity of the iodide ions for the silver iodide increases continually.[4]

The investigations of Julien may warn us that it is dangerous to apply results gained from macroscopic objects to submicroscopic systems.

Several measurements of "adsorption" of electrolytes do not deal with adsorption in the proper sense, but are in reality measurements of the formation of the double layer by potential-determining electrolytes. Beekley and Taylor (7), for instance, determined the "adsorption" of silver salts by silver iodide. Probably we must explain their data by a definite influence of the size and the polarizability of the anion (in this case the outer ion of the double layer) upon the capacity of the double layer. The experiments of Fajans and Erdey-Grúz (32), too, partly deal with "adsorptions" of the type considered in this section. It must be stressed that this also holds for their qualitative measurements of the "adsorption" of potassium bromide, potassium chloride, and potassium thiocyanate by silver iodide. As silver bromide, etc., forms mixed crystals with silver iodide, the ions Br^-, Cl^-, SCN^- are all potential-determining ions for the case of silver iodide–solution. For these ions will be distributed over both phases. Imre's (61) measurements of the "adsorption" of lead ion (ThB^{++}) by barium sulfate deal with a similar case. His data seem

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[4] *Note added in proof:* Similar phenomena have been observed recently by H. R. Kruyt and R. Ruyssen (Proc. Acad. Sci. Amsterdam **37**, 624 (1934)) in studying the streaming potentials of both large and small crystals of barium sulfate in various solutions.

to indicate that in the first moment the lead ions are distributed over the solution and the surface layer of the barium sulfate crystals; gradually, however, the lead ions diffuse into the barium sulfate lattice, substituting the isomorphous barium ions, until a definite ratio of $Pb^{++}:Ba^{++}$ is reached. Kolthoff (69) also interpreted Imre's results as a formation of mixed crystals.

We found several similar examples in the chemical literature where these phenomena were insufficiently distinguished from real adsorption and other phenomena. But the cases treated above probably prove sufficiently that a better interpretation and a clear insight will be gained only if one takes into account the special rules holding for this type of "adsorption," i.e., the fundamental fact that these potential-determining electrolytes are required for the formation of the double layer.
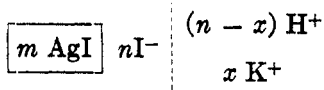
V. EXCHANGE OF COUNTER-IONS

We next examine the interactions between a double layer, once formed, and other (indifferent) electrolytes added to the system. The most general and simple of them is the exchange of counter-ions.

We have, for example, silver iodide negatively charged, which may be written:

$$\boxed{m\ \text{AgI}}\ n\text{I}^- \mid n\text{H}^+$$
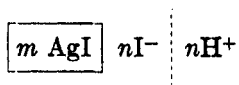
and suppose that an indifferent electrolyte, say potassium nitrate, is added to the solution. Apart from other actions, neglected for the time, part of the potassium ions will penetrate into the outer part of the double layer. Here the positive hydrogen ions are cumulated. These potassium ions, positive ions too, may take the function of supporting the positive space charge from the hydrogen ions, allowing an equivalent amount of the latter to move back into the bulk of the solution. When equilibrium is reached, i.e., when in a sufficiently long time equal amounts of potassium ion enter the double layer and leave it, a quantity, x, of potassium ions has been "adsorbed," but an equal quantity of hydrogen ions has been given back to the solution:

$$\boxed{m\ \text{AgI}}\ n\text{I}^- \mid \begin{matrix} (n-x)\ \text{H}^+ \\ x\ \text{K}^+ \end{matrix}$$

The total concentrations of electrolyte in the double layer and in the solution are not altered; only an exchange of counter-ions has taken place.

This type of exchange is a general phenomenon, occurring in almost

every case where a solution of an electrolyte is brought in contact with a surface. Always where the counter-ion of the double layer and the equally charged ion of an electrolyte added to the system do not happen to be identical, an exchange occurs. A double layer is always present in a sol (otherwise the sol would not exist) in practically all precipitates, adsorbents, etc. In section IV we have stated that even a thoroughly washed silver iodide precipitate still contains a double layer, hence exchangeable counter-ions. Silver iodide, and presumably silver bromide and other precipitates, when in equilibrium with pure water (Lange and Crane (85) claim 80-fold washing is necessary to reach this) are certainly not "Aequivalenzkörper" (Fajans), for only when the zero point of the charge and the equivalence point in the solution ($c_{Ag^+} = c_{I^-}$, etc.) happen to coincide is the precipitate uncharged. Also charcoal, even when ash-free, contains a double layer. Interesting experiments of Frumkin and coworkers (44) revealed that here hydrogen ion and hydroxide ion are the potential-determining ions. This explains that a "hydrolytic adsorption" was often found (Kolthoff (68) and others), it actually being an exchange.

Historically remarkable is an old study of Whitney and Ober (138), which has been interpreted erroneously by many colloid chemists. These investigators were apparently aware of their observing something else than an "adsorption," when they studied "the composition of the precipitate" obtained after the flocculation of an arsenic trisulfide sol by barium, calcium, strontium, and potassium salts. They stated that the precipitate had a constant composition and were of the opinion that equivalent amounts of barium hydroxide, etc., were coprecipitated. How this "pre-cipitation" of a basic hydroxide could be produced, together with the liberation of the acid, seemed strange to them. As this sol was prepared from arsenious oxide with an excess of hydrogen sulfide, the simple explanation is that in their investigation the following exchange was measured:

$$\boxed{As_2S_3}\ S^{--}\ \big|\ 2H^+ + Ba^{++} \rightarrow \boxed{As_2S_3}\ S^{--}\ \big|\ Ba^{++} + 2H^+$$
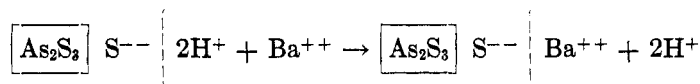
In some cases it had already been observed that an "adsorbed" ion liberated another ion (e.g., Freundlich and Neumann (35)). Michaelis (98) introduced the term "polar adsorption." Mostly, however, exchange of counter-ions was not distinguished from other types of interactions in the double layer, and this often gave rise to strange conclusions and superfluous theories.

A special case of exchange of counter-ions is given by the so-called "base exchange" in permutites, zeolites, clay, etc. However, the amount of

exchangeable ions is here considerably larger. As a consequence of the very peculiar structure of these silicates, studied successfully by F. M. Jaeger (62), W. L. Bragg (14), L. Pauling (101), W. H. Taylor (118), Kelley, Dore, and Brown (66) and others with the aid of x-rays, part of the cations of the *interior* of the crystals are also in free kinetic exchange with a surrounding liquid, and therefore exchangeable by other cations.

Generally the tendency of the ions to substitute another ion diverges considerably. Mostly it is seen that ions of high valence possess a high exchange power. In our silver iodide sols we found the sequence:

$$Ce^{3+} > UO_2^{2+} \gtrsim Pb^{2+} > Ba^{2+} > H^+ > Cs^+ > K^+$$
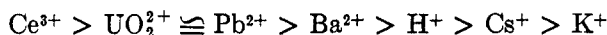
The sequence was studied for several types of clay. Jenny (63), among others, found that it varies somewhat with the nature of the clay.

The exchange of counter-ions follows its own rules. First it is clear that there is a natural maximum of the exchange, equal to the amount of available outer ions of the double layer (T). We will assume that both ions stay, independent of each other, in the double layer. Only their average "time of staying" will vary. Then, for two equally charged ions, the following equation may easily be derived (Verwey (128)):

$$\frac{x_1}{T - x_1} = k \cdot \frac{c_1}{c_2} \tag{3}$$

i.e., the ratio of both ions in the double layer is directly proportional to the ratio in the solution. It is characteristic of the phenomenon that the *ratio* of the concentrations determines the exchange, both ions occurring in the formula being equivalent. If equilibrium is reached, dilution of the system does not cause a shift; the exchange is independent of the dilution.

Exchange isotherms have been measured accurately for permutites only. Most of the experiments were carried out by shaking a sample with a solution containing a cation other than the exchangeable ion of the permutite (say, respectively, 1 and 2). If m grams of the material is used in 1 liter of the solution, c_2 at equilibrium equals the amount mx_1 given back to the solution. (x and T are both given for 1 gram of permutite). Hence, dropping the subscript 1:

$$\frac{x^2}{T - x} = k \cdot \frac{c}{m} \tag{4}$$

Equations 3 and 4 prove to hold roughly for the exchange for clay and permutites. A similar equation has already been derived empirically by Ganssen (47). Deviations are to be expected, for especially in this case

both ions cannot be considered as acting totally independently. In the crowded cavities and canals of the lattice of these silicates the free energy of an ion will actually differ according to the nature of its neighbors. It is difficult to correct equations 3 and 4 for this effect.[5]   Generally, however, a relation

$$\frac{x_1}{T - x_1} = f\left(\frac{c_1}{c_2}\right) \tag{5}$$

is valid. Most equations used in soil chemistry do not satisfy this condition and therefore do not express the characteristic nature of the exchange of counter-ions (for instance, the equations of Wiegner (139), Wiegner-Jenny (140), Vageler (122), and others). Only the equation of Rothmund and Kornfeld (112), an empirical improvement of that of Ganssen, also satisfies equation 5.

When the exchanging ions differ in valence the relation is more complicated. Jenny found that ions of higher valence substitute other ions relatively stronger when added in small quantities.

Summarizing, we may state that exchange of counter-ions, though a general phenomenon, is but little studied as such, and practically only for artificial and natural soils. It is desirable (from a colloid chemical point of view as well, as will be seen in Part II) to examine this type of "adsorption" with the aid of its proper rules. Not a single concentration, but a ratio of concentrations (or an amount of salt added, c/m) determines the exchange; furthermore, the maximal exchange capacity must be known, i.e., the amount of potential-determining electrolyte taken up, or the total charge of the double layer. That the exchange is not a radical change of the double layer but merely a substitution of its outer ions remains characteristic.

VI. THE ADSORPTION OF ELECTROLYTES

We now consider true adsorption phenomena: the accumulation as a whole of an electrolyte in that part of the solution which is nearest to the surface. Negative adsorption may also occur, viz., when the concentration of the electrolyte added becomes smaller in the boundary layer than in the rest of the solution. According to Gibbs (48) an electrolyte lowers the surface tension when it is positively adsorbed; if it raises the surface tension it is negatively adsorbed. This rule can be easily understood.

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[5] *Note added in proof:* This problem has been attacked by A. H. W. Aten, Jr. (Proc. Acad. Sci. Amsterdam **38**, 441 (1935)) by the simple assumptions that the mutual forces between the adsorbed ions are proportional to x_1 and x_2 and that the distribution is a statistical one. For the present case, this treatment is still a rough approximation.

The surface tension is a measure of the (free) energy which is needed to enlarge the total area of the boundary surface; during this process an adsorption energy is gained when there is a positive adsorption. This adsorption energy lowers the required energy, and therefore the surface tension. From the surface energy we can therefore conclude immediately as to the sign of the adsorption. Thus it can be proved that from aqueous solutions most electrolytes are negatively adsorbed at the surface.

We have stated several times that the "adsorption" phenomena described in the previous sections are not adsorptions in the proper sense. This will be clear at once in the case of the exchange of counter-ions. But neither does assimilation of potential-determining electrolytes satisfy Gibbs' definition of adsorption. The difference is that one ion of the potential-determining electrolyte goes from the solution into the other phase, causing there a surface charge, which theoretically might also be effected from within this phase by means of an external electric current. Thus the surface tension is no longer connected directly with the accumulation of electrolyte in the boundary layer, but only indirectly as a consequence of the charge of the double layer thus formed. A real adsorption from a solution is *not* accompanied by a change of the *total* boundary potential drop. Therefore in the case of the "adsorption" of potential-determining electrolytes the surface energy also contains an electrical energy.

Nevertheless, if real adsorption occurs, the situation in the double layer may be seriously complicated. Important conclusions may be deduced from investigations in which the properties of the double layer are examined for the somewhat unusual adsorbents air and mercury.

Generally speaking, an ion in the boundary layer is subjected to two groups of forces: the attraction by the surface and that by the water molecules (hydration). If, for both ions, the latter is stronger, the adsorption will be negative.

It is clear that this case will be realized with the system air–solution. On account of their thermal movement some ions will get into the boundary layer, but the stronger their hydration, the more strongly they will be forced back into the bulk of the liquid. Cations are generally more strongly hydrated than anions; hence the cations especially are held back in the solution, and the ions that reach the boundary will be mainly anions. This means a separation of charges; the boundary layer is charged negatively with respect to the liquid layers further inside. In the outer layers of the solutions there is, therefore, a potential drop, caused by a spontaneous orientation of the (negatively adsorbed) electrolyte. This potential drop has been measured by Frumkin (43) for a large number of electrolytes. For 2 N solutions the values found were (in millivolts):

potassium thiocyanate, -87; ammonium thiocyanate, -87; barium thiocyanate, -87; sodium iodide, -55; potassium iodide, -52; potassium bromide, -16; potassium chloride, -6. It is actually seen that the cations penetrate only slightly into the double layer, for their influence upon the potential drop is negligible. Furthermore there is a distinct "lyotropic" sequence for the anions. Of all ions the thiocyanate ion gives the largest potential, or penetrates into the boundary layer most easily; it lowers the surface tension least, or gives the smallest negative adsorption. It has actually the largest radius, or the lowest hydration.

In the case of mercury–solution the forces from the surface are generally stronger than the hydrating forces. One of the reasons is that the ions induce in the mercury phase a charge of the opposite sign which favors the attraction; this additional force can be calculated by considering it to be due to an opposite charge in the metal, which is the image of the
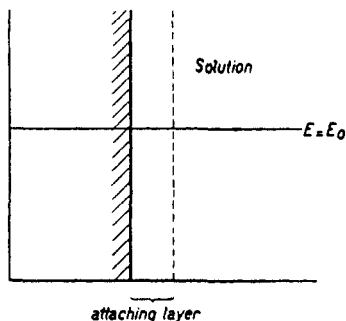

FIG. 5. Potential curve in the zero point of the charge

charge of the ion ("Bildkraft"). Specific forces also play a part. We see, therefore, that most electrolytes are adsorbed positively; a few electrolytes with strongly hydrated anions (arsenates, phosphates, carbonates) raise the surface tension slightly. The potential drop caused by these adsorptions cannot be measured directly in this case, since the total potential drop is only sensitive to the concentration of the mercury ions in the solution. Though the total potential drop of the double layer is therefore not altered by adsorption of an indifferent electrolyte, the potential slope within the double layer may be changed thoroughly by it. We shall have to consider this more in detail.

Suppose we have a surface, e.g., of mercury, in contact with an aqueous solution, and bring on such a potential that the surface is uncharged ($E = E_0$). We now dissolve some potassium iodide in the solution. This electrolyte is adsorbed positively; it accumulates in the boundary layer in such a way that the iodide ions approach the surface more than the

potassium ions.   In other words, mainly iodide ions get into the "attaching" layer of Stern.   This orientation gives rise to the potential drop mentioned above, localized in the outer part of the double layer.   As the total potential drop is kept constant, this local potential drop must be compensated somewhere else.   This occurs through a precipitation of mercury ions upon the surface (or a dissolution of electrons), charging the mercury positively.   The situation before and after the addition of potassium iodide is represented by figures 5, 6a, and 6b.   The slope of the potential as a function of the distance is also indicated qualitatively. Since for our reasoning only that part of E which is due to free charges is important (i.e., the part $E - E_\mathfrak{v}$), in these figures it is assumed for convenience that $E_0 = 0$.   Furthermore we give in figure 6a a situation which is valid only for a non-conducting surface (dielectric); in the case of mercury, however, each ion induces its image (of the opposite sign) in the
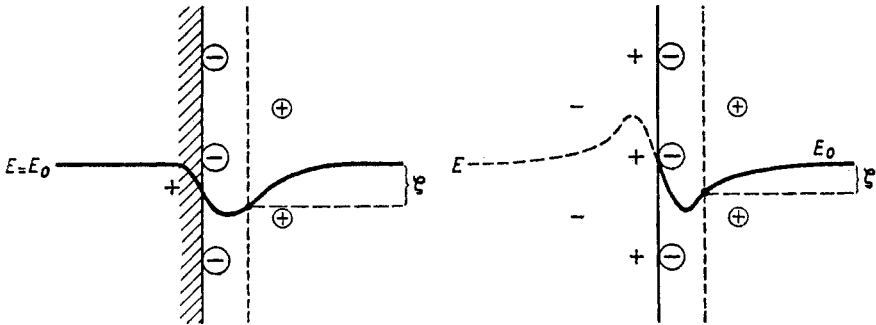

Fig. 6. Potential curve for the adsorption of anions on a previously uncharged surface (a dielectric and a metal respectively).

metal, and this leads to figure 6b.   The potential in the outer layer is not influenced fundamentally by these image powers.   The counter-ions are distributed over the "attaching" and the "diffuse" layer; this detail is omitted in the figures in order to avoid complications.

In the case of figure 5 not only E (or $E - E_0$) is zero, but also $\zeta = 0$. After the addition of potassium iodide, however, ζ will be negative, though the mercury is charged positively, and $E - E_0$ is still zero.

If now E is made more positive, the positive charge of the mercury, but also the adsorption of iodide ion, increases.   The result is given by figure 7 (a and b).

If, however, we wish to reach the new zero point of the charge, we must give to E a more negative value.   This is shown in figure 8.

Thus we see that upon the adsorption of an indifferent electrolyte *a shift of the zero point of the charge* occurs, mostly to more negative values

of E. This shift, and therefore the adsorption, can be measured with the aid of the electrocapillary curve, which represents the surface tension as a function of E. As the surface tension is lowered by a surface charge (the energy necessary for the enlarging of the surface is then partly delivered by the mutual repulsion of the surface charges), the curve has a maximum for $E = E_0$. Gouy (49) and later Frumkin (45) measured the electro-capillary curve of mercury in solutions of several electrolytes. They found for 1 N solutions a shift of the maximum: for potassium sulfide, -420
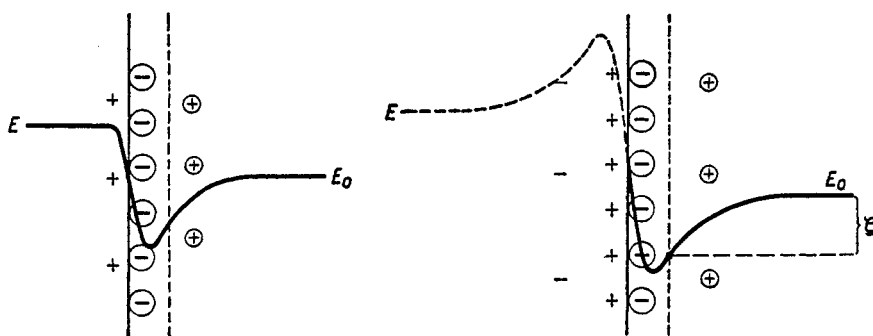

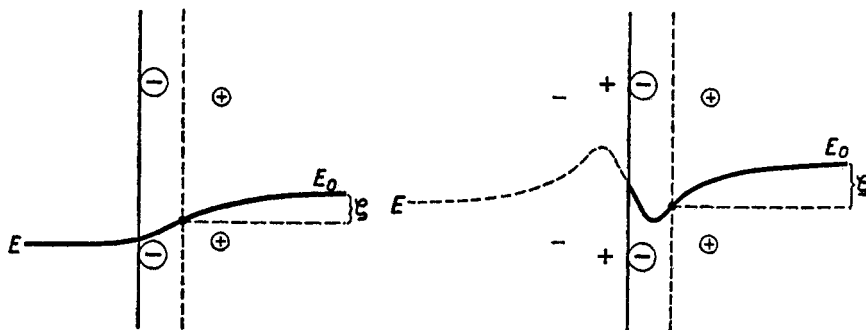FIG. 7. Potential curve for the adsorption of anions on a positive surface

FIG. 8. Potential curve for the adsorption of anions; shifted zero point of the charge.

millivolts; for potassium iodide, -320 millivolts; for potassium thio-cyanate, -220 millivolts; for potassium bromide, -150 millivolts; for potassium chloride, -60 millivolts. In 0.1 N potassium iodide it is -220, in 0.01 N potassium iodide -160 millivolts. Hence the orientation of the adsorbed ions is stronger than at the surface of air, but again the anions are adsorbed primarily. Also we see that the larger or less hydrated anions are adsorbed more strongly, but the sequence is not exactly the same; this is in accordance with the already observed fact that not only

hydrating forces (which determine the lyotropic series) but also the attraction by the mercury govern the adsorption. Hence several other factors play a part, such as polarizability of the ions, eventually the dipole moment and the place of the latter in the molecule, and van der Waals forces (cf. van Arkel and de Boer (5)).

Figure 9 gives a number of electrocapillary curves. In the case of adsorption not only does the maximum shift to more negative values of E,
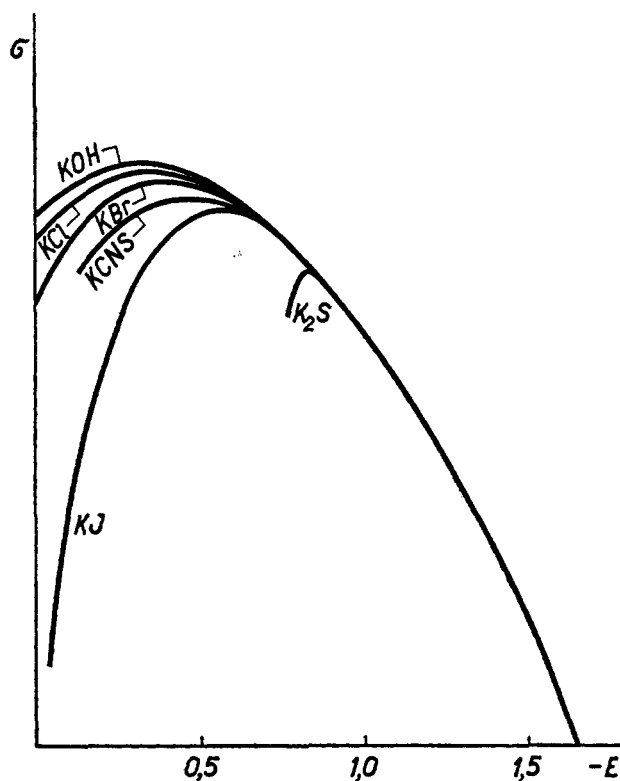
Fig. 9. Electrocapillary curves of various electrolytes (σ = surface tension mercury–solution; E = potential of the mercury).

but the surface tension is also lowered; for a mercury surface that is charged strongly negatively all curves coincide, i.e., the adsorption of the anion is reduced to zero.

From the investigations of Gouy and Frumkin we may conclude that the adsorption of indifferent electrolytes is a rather complicated process. The fact that it is always accompanied by a disturbance of the equilibrium of the distribution of potential-determining electrolytes has often been

overlooked. Inversely, the charge of the surface has a great influence upon the magnitude of the adsorption.

We cannot illustrate these conclusions with direct measurements of the adsorption, since only a small number of reliable investigations of this kind exist. This may seem strange, since a large number of measurements are found in chemical literature. Sometimes, however, these measurements are not very accurate, or they have been carried out with inadequately defined substances. Often they are concerned with true adsorption only in part or perhaps not at all (sections IV, V, and VII). Horovitz and Paneth (59), Fajans (31), Hahn (53), Imre (61) and others tried to give exact "adsorption rules" or "adsorption laws," but their theoretical considerations cannot be accepted, since they do not sufficiently take into account the principles given in these sections, or do not distinguish different phenomena in their interpretation of experimental facts.

Some valuable conclusions can be drawn from an investigation of Miss de Brouckére (15), in which a (positive) adsorption of several electrolytes by barium sulfate was measured with much care. It was affirmed for many cases that the anion and the cation were adsorbed in equivalent amounts. In dilute solutions she found that $\log x$ varies linearly with $\log c$ (x = amount adsorbed, c = concentration of the electrolyte when equilibrium is reached), i.e., Freundlich's isotherm seems to hold good for the adsorption of electrolytes. Again the anion leads the adsorption and for the halides the sequence $I^- > Br^- > Cl^-$ exists.

In the laboratory of Kruyt the adsorption of electrolytes was studied by Janssen (64), using another indirect method. Accurate measurements of the streaming potentials of glass capillaries filled with different electrolytes of varying concentrations were carried out. From the $\zeta-c$ curves thus obtained Janssen calculated the corresponding charges of the diffuse layer with the aid of Gouy's theory. Thus he found that this electrophoretic charge increases strongly upon the addition of bromides, chlorides, etc. Janssen assumes that this charge is directly proportional to the amount of anions adsorbed; this is not quite correct, for it neglects the shift of the equilibrium of the potential-determining ions discussed in this section, but in the present case it may be useful as a first approximation. From his data and from earlier experiments of Kruyt and van der Willigen (78), he finds that again in dilute solutions the adsorption obeys the equation

$$d \log x = k \cdot d \log c$$

For higher concentrations saturation occurs (apparent radius of the ions about 10^{-7} cm.). Similar calculations with about the same result have been published by Abramson and Müller (1) and by Mooney (93). Janssen

has tried to give a theoretical foundation for his results. Starting from Langmuir's well-known adsorption isotherm for neutral molecules he derives the electrical factor which must be added in order to make the equation applicable to the adsorption of electrolytes. Janssen concludes that actually Freundlich's isotherm must hold approximately for this case, and calculates for the constant k_2

$$x = k_1 c^{k_2} \tag{6}$$

the value 2/3. The last conclusion is affirmed by his experiments.

Summarizing, we may state that we have found another characteristic in which the adsorption of indifferent electrolytes differs from the "adsorption" of potential-determining electrolytes; for the latter $dx = k \cdot d \log c$, while for the former $d \log x = k \cdot d \log c$.

VII. EXCHANGE OF LATTICE IONS

Recent investigations of Kolthoff and his coworkers proved that sometimes a lattice ion can also be replaced by ions added to the solution. Kolthoff suggests that many cases of "adsorption" are actually exchanges of this type, as for instance, in the well-known "adsorption indicators" of Fajans-Kolthoff for the titration of silver halides, etc. We need make only a few remarks about this fourth type of "adsorption," since Kolthoff's work on this subject has not been finished and its significance for our theme is not yet clear.[6]

An exchange of lattice ions by an electrolyte solution in contact with the crystals was first stated by Kolthoff and Rosenblum (70); upon the addition of the sodium salt of Ponceau 4R to a suspension of lead sulfate, the dye anions substitute the sulfate ions of the lattice surface. Kolthoff, Rosenblum, von Fischer, and Sandell (71, 73) found several other cases of this exchange "adsorption," including some inorganic ions. A similar exchange has already been observed by de Boer (8) in his experiments on the adsorption of vapor molecules by a salt layer. Alizarin vapor, $C_6H_4(CO)_2C_6H_2(OH)_2$, is adsorbed in a monomolecular layer by calcium fluoride (see section III). Upon heating the adsorbed layer acts chemically with the fluoride ions of the salt, and hydrogen fluoride is liberated. Thus the alizarin ions substitute two fluoride ions of the lattice. At the same time the adsorbed layer changes its color.

To some extent the same principles hold for this exchange as were

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[6] *Note added in proof:* In a paper appearing before long in the Kolloid Zeitschrift, the author has shown recently that this "exchange of lattice ions" is probably not a new type of "adsorption" but might be interpreted as a combination of the phenomena of the preceding sections, effected by a strong adsorbability of one of the ions added.

derived in section V for the exchange of counter-ions. The difference, however, is that one of the ions here is a potential-determining ion. Both ions are therefore not equivalent. On account of the exchange the total potential drop is changed; in the case of the experiments of Kolthoff and Rosenblum, sulfate ion is replaced in the surface, and the concentration of these ions in the solution will thus be increased. The charge of the lead sulfate becomes more negative, and this certainly has some influence upon the exchange.

In all the experiments of Kolthoff the solubility product of the newly formed compound was not reached. It seems therefore as if its "solubility" in a monomolecular layer upon a lattice already present is lower than its solubility as a separate phase. We may therefore describe the phenomenon as a two-dimensional precipitation.

VIII. SUMMARY

We have examined the structure and the origin of the electrical double layer. The influence of added electrolytes was studied. As a whole we met four fundamentally different phenomena generally denoted by the name of adsorption. Only one of them is an adsorption in the proper sense, and it seems desirable to distinguish the others with the aid of more characteristic names, viz., assimilation of potential-determining electrolytes, exchange of counter-ions, and exchange of lattice ions.

In Part II we shall examine the significance of our foregoing considerations for the problems of lyophobic colloid chemistry.

II. THE STABILITY OF LYOPHOBIC COLLOIDS

I. INTRODUCTION

A lyophobic sol can lose its stability in two different ways: (1) by coagulation or (2) by coarsening. Coagulation is the formation of larger agglomerates or "polyons" (Zsigmondy), in which the particles have maintained their individuality. Thus coagulation means that the regular distribution of the particles through the dispersion medium is disturbed without decrease in the degree of dispersion. For this process the ζ-potential is of the utmost importance. Coarsening is a decrease in the degree of dispersion. During this process the smaller particles go into solution and the larger particles grow continually. Coagulation usually occurs in less than a second, whereas coarsening is rather slow. Coarsening will occur if the energy which is gained by a decrease of the total boundary surface (determined by the surface tension) is larger than the electrical energy of the double layer; for this process the total potential drop of the double layer is determinative.

Several authors have tried to calculate the colloidal equilibrium, deter-

mined by the concurrence of electrical and surface energies. Rather complicated and not always correct calculations have been published by Gyemant (52), O. K. Rice (111), March (92), and W. C. M. Lewis (89). It is remarkable to see that each one of them, obviously ignorant of the work of the others, made the same mistake. All of them thought that they calculated the stability with regard to coagulation and used ζ as a physical constant; actually they calculated the stability in the sense of coarsening and tried to determine the degree of dispersion as a function of the properties of the system.

Proof that such calculations must fail is that the condition of equilibrium which is sought does not exist. Colloid chemical experience reveals that a lyophobic sol is never stable in the sense of coarsening and that coarsening always occurs, though in some cases only very slowly. This means, as Kruyt (74) especially has emphasized repeatedly, that *a colloidal system is never a stable system in the thermodynamic sense.* There is no definite degree of dispersion which is more stable than others; the degree of dispersion of a sol depends solely on its method of preparation and further treatment. Obviously the electrical energy of the double layer is not sufficient to stabilize a sol in the sense of coarsening; the most stable state has the smallest total boundary surface, i.e., is coarsely crystalline.

This coarsening process occurs with a velocity that depends largely on the solubility of the disperse phase; apart from this factor it is accelerated, like every other diffusion process, by the elevation of the temperature. Thus the negative sols of silver chloride, silver bromide, and silver iodide, peptized with small quantities of halide, differ strongly in their tenability. Silver chloride, with a comparatively large solubility (in pure water about 10^{-5} equivalent per liter), gives sols which are destroyed in a few days by coarsening. Silver iodide sols, however (solubility 10^{-8}), are tenable during several years. The "stability" of sols of silver bromide and the solubility of silver bromide are intermediate between those two extremes. The coarsening of silver bromide is well known in the process of "ripening" of the photographic "emulsion."

Upon the addition of potassium iodide the solubility of silver iodide increases greatly. According to Hellwig (55) the solubility of silver iodide in 0.33 N potassium iodide is 0.4 $\times$ 10^{-3} equivalent per liter. Therefore the rate of coarsening increases enormously if potassium iodide is added to the sols (Verwey and Kruyt (124)); elevation of the temperature has the same effect.

Coagulation and coarsening of sols are often confused; this may give rise to totally wrong conclusions or theories. This was the case, for instance, in recent work of Basinski (60) and von Weimarn (132). Also Imre's (61) "coagulating precipitates" are rapidly coarsening sols.

Although, strictly speaking, a lyophobic sol is never "stable," we never-theless speak of the "stability" of a sol in terms of its stability toward coagulation (in sense 1). The problem of the stability of lyophobic col-loids is therefore of quite another nature than was supposed by Gyemant, Rice, and March. An exact theoretical treatment of this problem re-quires an estimation of the forces of cohesion and of the forces that prevent cohesion. These mutual attractive forces can be said to act over a distance of only a few molecular dimensions; this we learned, for instance, from the kinetics of flocculation, for which a very valuable theory was developed by von Smoluchowski (115). In this theory it is assumed that the attrac-tive forces are practically active only at the moment when the particles collide; this seems a very good approximation of the real state of affairs. Presumably the attractive forces between the particles are therefore due to the van der Waals forces between the atoms or ions in the surface of the particles. They are thus of the same type as the forces that keep the molecules of a non-polar liquid close together. This type of attraction between two atoms drops rapidly with the increase of the distance $\left(\sim \dfrac{1}{r^6} \right)$.

Generally the particles will have such an irregular habit that, in the floc-culated state, they touch each other only in a few superficial lattice points. Actually, there seems to be only a very loose bond between the particles, for several colloids can easily be peptized again, at least immediately after coagulation. If the flocculated sol is allowed to stand for a longer time, the contact between the particles becomes more intimate. In connection with this, typical aging phenomena (rapidly decreasing adsorbent proper-ties, recrystallization, etc.) are observed with many flaky precipitates (cf., e.g., Freundlich and Haase (37) or Kolthoff (69)). But it is clear that the coarsening process will be accelerated considerably in such flocculated agglomerates; crystal faces can grow together or can be cemented together by molecules (ions) diffusing through the solution and coming from other parts of the crystals. These are all secondary processes in the coagulated state and have no influence upon the flocculation itself, which seems to be a reversible process (cf. also Kruyt and van Arkel (76) or Burton and May Annetts (18)).

Although we do not know exactly which points of the surface will tend preferably to adhere to similar surface spots of other particles, it seems possible, from the considerations mentioned above, to give a rough calcu-lation of the magnitude of the mutual attractive forces between the particles of a given sol. It is much more difficult to give a quantitative computation of the repulsive forces which prevent them from sticking together. We know that these repulsive forces are of an electrical nature. We have seen in Part I that, if a double layer is present, the particles are

surrounded by a partly diffuse outer charge.   If a particle in its Brownian movement approaches another one, their ionic spheres will penetrate into each other, and from this a repulsion results when there is still a discrete distance between the particles.   An exact calculation of this repulsion as a function of the properties of the double layer has never been given.[7]   For the present, we will use the *empirical* fact that a certain "critical" value of the ζ-potential is needed for stability (Powis (103), Kruyt and Briggs (79)), i.e., that a definite potential drop in the diffuse outer layer is required in order to keep the particles far enough from their mutual attraction fields.   If we start from the empirical point of view that the stability is connected intimately with the magnitude of the ζ-potential of the particles, the problem remains, in what way this ζ-potential depends on the structure of the double layer, the nature and the concentration of electrolytes present, etc.   It is this problem that we shall have to examine first in the following sections.

II. PRIMARY STABILITY

Accepting the "stability" of a sol in the restricted sense discussed above, we can still distinguish two types: (1) A sol acquires its *primary stability* by the formation of a double layer which has a sufficiently high ζ-potential. This phenomenon is generally called "peptization."   (2) The stability of a sol once formed is affected by addition of foreign electrolytes.   This is a question of *secondary stability.*

Several concepts of peptization exist.   Sometimes it is believed that the small amount of electrolyte required for the peptization acts chemically with the surface of the particles.   Thus the SnO_3^{--} ion is assumed to be at the inside of the double layer of SnO_2 sol, peptized with potassium hydroxide (Zsigmondy).   The ferric oxide sol is often thought to be charged positively by the dissociation of $FeOCl$ into FeO^+ and Cl^-.   Pauli generally assumes the formation of complex ions of the Werner type in the surface of the particles.   Other investigators believe peptization to be a consequence of a "specific" adsorbability of certain ions (Perrin, Freundlich).

A valuable contribution to the problem of peptization was given by the well-known work of Lottermoser (91), who stated (1907) for the first time that the stability of positive and negative silver iodide sols is governed by the "adsorption" of the proper ions of the precipitate (cf. also Fajans and von Beckerath (31)).

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[7] *Note added in proof:* A very interesting attempt in this direction has been made recently by Levine (Proc. Roy. Soc. London **146**, 597 (1934)), in calculating the sedimentation equilibrium in colloidal suspensions.

However, all these different interpretations, though essentially correct, are restricted to special types of sols and have no general validity for all cases.

A more precise conception was given by Kruyt and van der Willigen (80), who tried to extend earlier considerations of Fajans and Mukherjee. They observed that the ζ-potential of different substances can be increased by all kinds of electrolytes (cf. also Mukherjee (94, 95)); but only those ions which "fit" into the lattice of the particles can peptize the substance. Thus silver iodide can be peptized by small amounts of I^-, Br^-, Cl^-, CN^-, SCN^-, but not by NO_3^-, CO_3^{--}, PO_4^{---}, or $Cr_2O_7^{--}$. If certain precautions are taken it can be shown that hydroxide ion also is unable to stabilize a negative silver iodide sol (Verwey and Kruyt (124)).

This rule of Kruyt and van der Willigen has been confirmed for several other sols by Cysouw (25), e.g., for insoluble sulfides, selenides, complex cyanides, etc. Those ions which form isomorphous crystals with the substance to be peptized were always able to give more or less stable sols. A few exceptions, however, were found, e.g., the complex cyanides were peptized by cyanide ion (Kruyt and Cysouw (80a)).

On the basis of our considerations in Part I it is easy to give a full explanation of these regularities and, at the same time, a better formulation of the apparent exceptions. We have stressed the fact that there is a fundamental difference between the building up of the double layer by means of the assimilation of potential-determining electrolytes and the formation of a double layer on account of pure adsorption phenomena. In the latter case there is only an orientation of ions in the solution nearest to the surface, not a separation of charges over two phases. It seems therefore plausible that the building up of a first double layer is required for primary stability. Thus *only potential-determining electrolytes will be able to peptize a substance.* This law actually includes the rule of Kruyt and van der Willigen, since, as we have seen in Part I, section III, all ions that both phases have in common are to be considered as potential-determining ions, and are subjected to an equilibrium of distribution over both phases which causes the formation of the double layer.

The essential fact that only potential-determining ions and not indifferent electrolytes cause primary stability is undoubtedly connected with the fundamentally different behavior with regard to their concentration. The ζ-potential is raised by an increase of the free charge of the double layer (charge η_2; see Part I, section III), but it is lowered by an increase of the concentration of electrolytes in the solution (cf. Part II, section III). If now an increase of the charge is caused by the addition of an electrolyte, it is seen that there are two counteracting tendencies. Those electrolytes will give a high potential to the double layer that are "ad-

sorbed" relatively strongly for the smallest concentrations. The conditions are much more favorable for potential-determining electrolytes; in this case $dx = k \cdot d \log c$ holds; for pure adsorption, however, $d \log x = k' \cdot d \log c$. We can compare, for example, the "adsorption" of potassium iodide by 1 m.^{2} silver iodide (calculated from our measurements on dialyzed silver iodide sols (126), interpolated, and extrapolated to the zero point of the charge $c_{I^-} = 10^{-10}$) and the adsorption of potassium iodide by 1 m.^{2} barium sulfate (calculated from the measurements of Miss de Brouckére (15)):

c	10^{-2}	10^{-3}	10^{-4}	10^{-5}	10^{-6}	10^{-7}	10^{-8}	10^{-9}	10^{-10}
$x(AgI)$		0.56	0.48	0.40	0.32	0.24	0.16	0.08	0.00
$x(BaSO_4)$	0.77	0.25	0.056	0.009					

It is seen that both "adsorptions" occur in quite different concentration regions. The potential-determining electrolyte goes into the double layer when the concentration in the solution is still extremely small, and its lowering influence upon ζ negligible. The indifferent electrolyte, however, is adsorbed to the same extent at very much higher concentrations, where the lowering of the potential is considerable.

The advantage of our conception of primary stability is that it enables a more quantitative treatment of these problems. In a given case the primary stability of a sol is determined wholly by a few physically well-defined magnitudes: *the concentration of its potential-determining ions and the situation of the zero point of the charge.* The author (127) calculated for dialyzed silver iodide sols a total potential drop due to free charges $(E - E_0)$ of about -0.2 volt. We have seen in Part I, section III, that the ζ-potential is only a fraction of this (about one-third), since part of the potential drop occurs in the silver iodide phase and in the "attaching layer" (cf. figure 2). The "critical" value of $E - E_0$, required for primary stability, will thus be almost three times the critical ζ. Usually a value of ± 40 millivolts is given for the latter. From this a critical $E - E_0$ of about 120 millivolts should be expected (for dialyzed silver iodide sol). This agrees very well with the experimental facts, for it is found that a value of $E - E_0$ of about 2×0.058 millivolts is required for stability. A positive silver iodide sol flocculates when its concentration of free silver ions is lowered to about 10^{-4} (e.g., by dialysis); the zero point of the charge is reached at $c_{Ag^+} = 10^{-6}$; a dialyzed negative silver iodide sol ($c_{Ag^+} =$ about 10^{-9}) is stable, but flocculates when its c_{Ag^+} is raised (e.g., by careful titration with very dilute silver nitrate solution) to about 10^{-8}.

If there is sufficient knowledge of the structure and properties of the double layer for a given sol, theoretically it should be possible to predict its primary stability conditions, provided that its particles are large enough

for the approximative use of the theory of the flat double layer.   At present, however, our knowledge is inadequate.   Moreover, we do not even know the situation of the zero point of the charge for most of the sols.

For the present a more qualitative survey will therefore be given, in order to show that our concept may be very useful for the interpretation of peptization.   In any event it is superior to "chemical" or other interpretations.

It is clear that our concept can be easily extended to all colloidal salts. For this case it is very simple to indicate what ions build up the double layer and thus determine the potential drop in it.   For instance, in an arsenic trisulfide sol, prepared with the aid of hydrogen sulfide as a peptizer, the concentration of the free sulfide ion in the sol determines the charge and the potential of the double layer.   The older concepts of peptization were developed mainly for sols of other types, especially the sols of hydrous oxides (Fe_2O_3, Cr_2O_3, Al_2O_3, ThO_2, SnO_2, SiO_2), of silicates (glass, clay, permutite), the noble metals, or carbon.   In all these cases hydrogen ion and hydroxide ion have to be considered as potential-determining ions. The particles of the latter sols either contain water in the bound state, or dissolve hydrogen and oxygen and may thus function as gas electrode. In all these cases the charge and the potential of the double layer are governed by the pH of the sol medium.   Inversely, we may state that only these substances can be peptized by hydrogen ion or hydroxide ion. This is the essential explanation why a silicate is peptized by potassium hydroxide and silver iodide is not.

Obviously the important rôle of hydrogen and hydroxide ions in soil and colloid chemistry is connected with the circumstance that they are frequently potential-determining ions.   The situation of the zero point of the charge seems to be a highly interesting problem for such sols as Fe_2O_3, Al_2O_3, and Cr_2O_3, since they can exist in both the positive and negative state.   Thus a logical distinction between "acidoids" and "basoids" (Michaelis[8]) can be drawn, according to the situation of the zero point of the charge related to pH = 7.   It is remarkable that the positive sols of the hydrous oxides just mentioned show exactly the same reversion of the charge upon their dilution (Lottermoser and Riedel (91a)) as was stated earlier by Kruyt and van der Willigen (80) for the positive silver iodide sol.   These reversions are a consequence of the decrease of the concentration of the potential-determining ions (hydrogen ion, silver ion) by the dilution.

The chemical concept has been accepted especially by Zsigmondy and

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[8] Also the isoelectric point (Michaelis (87)) of albumin and other lyophilic colloids is quite analogous to the zero point of the charge of our lyophobic sols.

his collaborators (142), for instance in their excellent investigation of the
SnO_2 sol. Zsigmondy, however, is apparently well aware of the fact that
the chemical terminology is merely a useful method for the description of
physical phenomena. Indeed, modern concepts of the structure of molec-
ules (van Arkel and de Boer) illustrate that the discrepancy between
chemical and physical theories of the phenomena is quite imaginary.
Whether the negative charge of a hydrated stannic oxide particle is due
to the formation of SnO_3^{--} ions in the surface or is caused by the "adsorp-
tion" of hydroxide ion is fundamentally indistinguishable. In certain
cases the chemical formulations may be handy and advantageous, as in
the work of Zsigmondy, Franz, and Heinz (142); we have to keep in mind,
however, that the SnO_2 sol, as to its secondary stability, forms an excep-
tional case (see section V). For most other sols the advantages of a
chemical formulation of the phenomena are much less obvious. Our
concept is therefore the more general one, and moreover enables a quanti-
tative treatment.

Another field where chemical descriptions of the phenomena may be
substituted successfully by a more exact theory is that of the organic sols
with acid or basic groups in the molecule (mastic, gamboge, congorubin,
etc.). Also the *electric* stabilization factor of most lyophilic colloids must
be governed by regularities similar to those for the primary stability of
silver iodide sol. We cannot deal with these problems here in detail, but
investigations of Tartar (119, 120), Michaelis (96), Janet Daniel (26),
and others yield very interesting support of our views and show clearly
the important rôle of the potential-determining hydrogen ions for the
primary stability of these organic sols (cf. ref. 130).

Finally it seems superfluous to point out that the assumption of a
"specific adsorbability" of certain ions in order to explain peptization can
be dealt with in the same way. The assumption, indeed, as it stands, is
a very inexact formulation, since (as we have seen in Part I) several differ-
ent phenomena are generally included by the term "adsorption." Unsatis-
factory, too, is the use of Coehn's rule to explain the origin of the charge
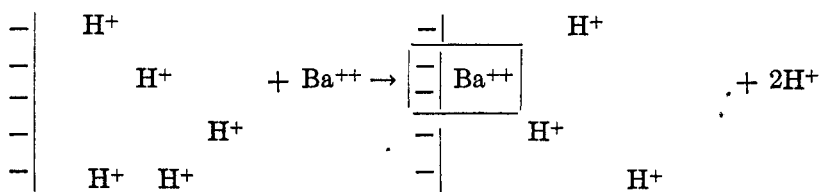(23, 24) (see, for instance, ref. 104).

Summarizing, we state that primary stability (peptization) is governed
by the distribution equilibrium of the potential-determining ions which
are responsible for the formation of the electrical double layer. Peptizing
ions are potential-determining ions. The primary stability of a sol is
thus connected intimately with and might be calculated from the concen-
tration of the free potential-determining ions in the solution and the situ-
ation of the zero point of the charge. The significance of hydrogen ion
and hydroxide ion as potential-determining ions has been discussed for
many sols.

III. SECONDARY STABILITY; THEORIES OF FREUNDLICH AND MÜLLER

We have seen that by the "secondary stability" of a sol is meant its stability once the double layer is formed, with regard to indifferent electrolytes added to it. Schulze (113) and others studied the flocculating values of different electrolytes for several sols. It is well known that characteristic differences between different electrolytes are found if the valence of the ion that is charged oppositely to the colloidal particles is varied. For the flocculation of a negative sol the following is required: 25 to 100 milliequivalents per liter of a 1–1, 1–2, 1–3, etc., valent electrolyte; a few milliequivalents of a 2–1, 2–2, 2–3, etc., valent electrolyte; 0.1 to 1 milliequivalent of a 3–1, 3–2, etc., valent electrolyte. The flocculating values of different cations of the same valence generally do not differ much, and the differences for electrolytes with varying anions are of the same order. The rule of Schulze-Hardy, it is true, has a number of exceptions.

It seemed that both the rule and its exceptions could be explained conclusively by Freundlich's flocculation theory (33, 34). Freundlich and Gann (38) have summarized this theory into four theses. The first two can be formulated as follows: (1) In order to coagulate a sol the particles must be neutralized to a definite point, i.e., a definite amount of the charge must be removed. (The remaining charge, just sufficient to prevent coagulation, is then the "critical" charge.) (2) The neutralization of the particles occurs by the adsorption of oppositely charged ions.

Let us consider a particle of As_2S_3, peptized by hydrogen sulfide. A small amount of barium chloride is added to the sol. According to Freundlich the barium ions are adsorbed, decreasing the charge of the particle:

$$
\begin{array}{l}
-\left|\begin{array}{l} H^+ \\ \quad H^+ \\ \qquad H^+ \\ H^+ \ H^+ \end{array}\right. \quad + Ba^{++} \rightarrow \quad \left|\begin{array}{l} -| \quad H^+ \\ \boxed{\begin{array}{l}-\\-\end{array}\ Ba^{++}} \\ -| \quad H^+ \\ -| \qquad H^+ \end{array}\right. \quad + 2H^+
\end{array}
$$

A number of hydrogen ions, corresponding to the decrease of the charge $(5 - 3 = 2)$, are given back to the solution.

It has already been stated by Freundlich and Neumann (35) that the number of hydrogen ions set free is actually equivalent to the amount of cation "adsorbed." They used organic cations (morphine, new fuchsin) as the "flocculating ions." This equivalence was affirmed by several investigators (Rabinowitch (116) and Weiser (133, 135)) for other sols and electrolytes. Occasionally, it is true, a "supraequivalent" substitu-

tion was believed to occur (Rabinowitch (106, 107)), but Weiser (133, 134) proved the incorrectness of these experiments. Other deviations will be discussed below.

Hence according to Freundlich's theory the "flocculating ions" and the ions already present in the double layer have a different function. The ions penetrating into the double layer are "adsorbed" at the same time, i.e., they go into the immobile part of the outer layer, decreasing the free charge of the particles. Another picture of the "neutralization" of the particles seems impossible. It is clear, however, that a variation of the *total* charge cannot be the general cause of this neutralization; the total charge can change greatly only when the concentration of the potential-determining ions is changed (eventual complications on account of pure adsorption, to be discussed later, will be neglected for the present). Thus the "neutralization" of Freundlich's theory must be considered as a shift from free to immobile charge, an increase of η_1 and a corresponding decrease of η_2 (Part I, section II).

The *second* supposition can be tested comparatively easily. Suppose that we flocculate a sol with different electrolytes, adding a just sufficient amount of each; the charge of the particles must then be decreased by the same constant amount, i.e., the particles have "adsorbed" equivalent amounts of the different oppositely charged ions. We shall see that this test has been applied several times.

In order to give a more detailed explanation of the regularities observed in the flocculation of lyophobic colloids, two other suppositions were added to the former: (3) For the adsorption which effects the neutralization of the particles the usual isotherm is valid. ($x = k \cdot c^p$; k and p are constants, $p < 1$). (4) Calculated in moles the isotherms of different electrolytes coincide, with the exception, however, of a few strongly adsorbable (mostly organic) ions.

With the aid of these suppositions Freundlich was able to give his well-known explanation of the rule of Schulze-Hardy. If we compare, for example, for a negative sol the action of electrolytes with a mono-, di-, and tri-valent cation, their isotherms will be represented, according to supposition 4, by one single curve (figure 10). According to suppositions 1 and 2, the amounts adsorbed in order to reach flocculation should have the ratio $1:1/2:1/3$ (for mono-, di-, and tri-valent cations, respectively) expressed in moles. In figure 10 these amounts are given by a, b, and c. The corresponding concentrations (if the sol is not too concentrated these will equal the flocculating values) must be in the ratio $c_I:c_{II}:c_{III}$. It is seen that, as a consequence of the typical form of the adsorption isotherm, there are actually large differences between the flocculating values of the electrolytes considered.

For a strongly adsorbable cation the isotherm will have a deviating form (curve B), and the flocculating value will thus be abnormally low (for a monovalent ion, e.g., $c_I{}'$).

Freundlich has tried to prove this theory in different ways. The second, third, and fourth suppositions were subjected to various experimental tests. Suppositions 3 and 4 have been studied mainly in older investigations (34), which do not seem to be very accurate or convincing. The second supposition, however, the equivalence of the amounts adsorbed at the flocculation concentration, seemed to be confirmed by experiments
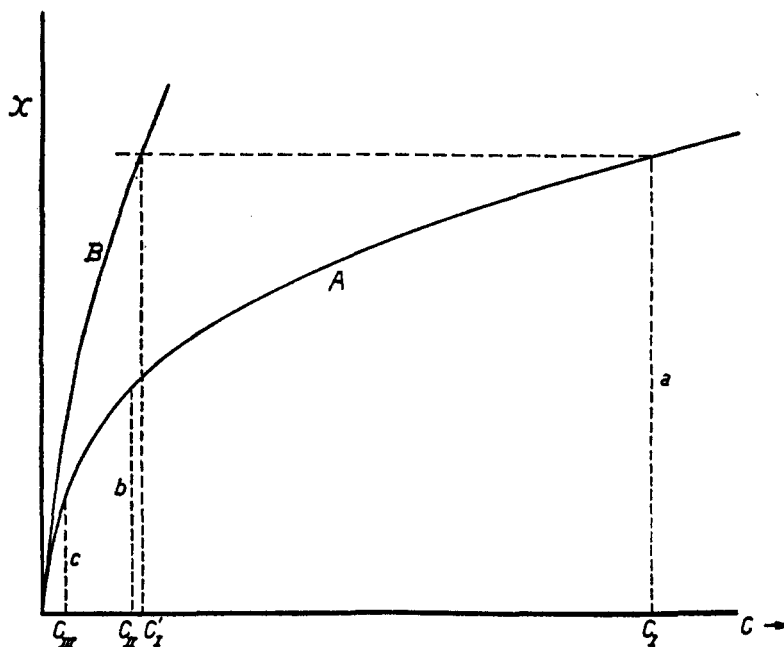

FIG. 10. Explanation of Schulze-Hardy's rule in the old Freundlich theory

with As_2S_3 sol, HgS sol (Freundlich and Schucht (36)), Al_2O_3 sol (Freundlich and Gann (38)), etc. In all these cases more or less equivalent amounts of the oppositely charged ions were carried down by the coagulating particles. For a long time Freundlich's theory was therefore accepted by various colloid chemists.

Several other investigators gathered experimental data, e.g., for Fe_2O_3 sol, which seemed to contradict Freundlich's conceptions. A survey of the discussion on this point is given by Weiser (136) in Alexander's *Colloid Chemistry*. We will not follow it in detail, as Freundlich finally settled it in 1929, admitting the untenability of his theory. Freundlich, Joachim-

son, and Ettisch (41) again measured the "adsorptions" of a large number of cations at the flocculation point of an arsenic trisulfide and a gold sol. This investigation revealed that actually the amounts of cation carried down by the flocculating particles were mostly *not* equivalent. The differences are so considerable, indeed, that Freundlich's negative conclusion seems justified, though there may be some doubt with regard to the analytical accuracy of part of the measurements. In some cases, for instance, the changes of the concentrations of both anions and cations were determined; from these data it seems that the electroneutrality was disturbed, which is obviously impossible. Moreover, Rabinowitch (110) has tried to check Freundlich's investigations, and has stated that the latter's methods were not quite correct. He therefore believes that the negative conclusions of Freundlich, Joachimson, and Ettisch are not sufficiently justified, and thinks that Freundlich's original adsorption theory of the flocculation may still be correct in some respects.

As a result of our own work on the silver iodide sol, to be discussed in more detail in the next section, we came to the conclusion that Freundlich's original theory cannot be maintained as a general theory of flocculation and is only more or less valid for a few special cases.

For the better apprehension of our point of view we must first discuss the flocculation theory of Hans Müller (99), published almost simultaneously with the investigation of Freundlich to which we referred. According to Müller the first assumption of Freundlich's theory is not correct, namely, the assumption that flocculation is due to a decrease of the free charge of the particles. Previously this assumption had been considered to be so obvious that it had been accepted without definite proof.

Müller applied the theory of the diffuse layer of Gouy, Debye, and Hückel, discussed in Part I, and corrected it for the case of the particles being small and of colloidal size, i.e., for a strong curvature of the double layer. With the aid of this theory he calculated from electrophoretic data of Freundlich and Zeh (40) the corresponding charge of the particles. Freundlich and Zeh had measured very accurately the electrophoretic velocity of the particles of an arsenic trisulfide sol and the influence of small quantities of different electrolytes upon it. They varied the charge on the ion, and in order to have ions of a similar nature they used electrolytes with large complex cations. For this case the curves representing ζ as a function of the concentration of the electrolyte have a normal shape, i.e., ζ is lowered gradually at a decreasing rate while c is increasing.

Müller calculated these ζ–c curves for 1–1, 2–1, 3–1, and 4–1 valent electrolytes, assuming that the corresponding charge (i.e., the charge of the diffuse outer layer) was *a constant* throughout the whole concentration region. Then, giving to the particles an average charge of 86 electrons,

he found curves practically coinciding with the experimental curves of Freundlich and Zeh. Thus it is seen that the assumption of a decreasing charge is not necessary in order to explain a lowering of ζ, and consequently a decreasing secondary stability of a sol, when the concentration of electrolytes in the sol is raised. The theory of the diffuse double layer is able to explain the behavior of ζ as a function of c quantitatively, at least for a normal shape of the ζ–c curves. (Abnormal curves, e.g., with a maximum, will be discussed in a following section.)

It is easy to show that the theory of the diffuse layer also gives a very satisfactory explanation of Schulze-Hardy's rule. For this purpose we will avoid Müller's rather difficult mathematical treatment and restrict our reasoning, like Gouy's, to a flat double layer. We thus neglect the influence of the curvature of the double layer, which leads to much more simple formulas. In this case the differential equation, expressing the potential as a function of the concentration, has an exact solution. The approximation introduced by Debye and Hückel for the similar problem of the diffuse ionic sphere around an ion cannot be used for our case, since it holds only for $n\zeta << 25$ millivolts (n = charge of the ion considered, in our case the charge of the particle).

Let φ (z) be the potential at a point (in the solution) that is at a distance z from the attaching layer. Using Poisson's equation, we have:

$$\frac{d^2\varphi}{dz^2} = -\frac{4\pi}{D}\rho$$

The density of the charge, ρ, is determined by the surplus of ions of one sign; if c denotes the concentration of the ions in equivalents per cm.[3], F is the Faraday equivalent:

$$\rho = F(c_+ - c_-)$$

from which, with the aid of Boltzmann's theorem, is easily derived:

$$\left.\begin{array}{l} \dfrac{d^2\varphi}{dz^2} = -\dfrac{4\pi}{D}Fc\left\{e^{\frac{-n_+F\varphi}{RT}} - e^{\frac{+n_-F\varphi}{RT}}\right\} \\[4mm] \text{for } z = 0: \\[2mm] \qquad \varphi = \zeta \text{ and } -\eta_2 = \displaystyle\int_0^\infty \rho dz = \dfrac{D}{4\pi}\left(\dfrac{d\varphi}{dz}\right)_0 \\[4mm] \text{for } z = \infty: \\[2mm] \qquad \varphi = 0 \text{ and } \dfrac{d\varphi}{dz} = 0 \end{array}\right\} \qquad (7)$$

The solution of equation 7 follows by integration, whence:

$$\eta_2 = \sqrt{\frac{DRTc}{2\pi}} \cdot \sqrt{\frac{1}{n_+}\left(e^{\frac{-n_+F\zeta}{RT}} - 1\right) + \frac{1}{n_-}\left(e^{\frac{+n_-F\zeta}{RT}} - 1\right)} \qquad (8)$$

With the aid of this equation we can calculate the amount of an n_+n_--valent electrolyte that is necessary in order to lower the potential of a negative surface to $\zeta = -50$ millivolts. In this calculation we assume, in accordance with Müller, that the charge of the diffuse layer, η_2, is a constant. The choice of -50 millivolts is somewhat arbitrary, but it is selected because under this condition $F\zeta/RT = -2$, and because the value is only slightly larger than the "critical potential" of most sols. Thus we calculate a concentration which will be a measure of the "flocculation value" of the electrolyte. As we do not know the exact value of η_2 we can only calculate the ratio between the various flocculation values. Therefore we choose arbitrarily the "critical" concentration for 1–1 valent electrolytes to be 50 millimoles per liter; the values for other types of electrolytes then follow easily from

$$c\left(\frac{1}{n_+} e^{+2n_+} + \frac{1}{n_-} e^{-2n_-} - \frac{n_+ + n_-}{n_+ n_-}\right) = \text{constant}$$

These values are summarized in the following table:

n_-	$n_+ = 1$	$n_+ = 2$	$n_+ = 3$	$n_+ = 4$
1	50	10.7	2.06	0.38
2	47	10.5	2.06	0.38
3	46	10.4	2.06	0.38
4	46	10.4	2.06	0.38

We see that the characteristic differences between various types of electrolytes, given by Schulze-Hardy's rule, actually result from the calculation. Electrolytes with unequally charged anions have almost the same flocculating action. The ratio between the "flocculation values" thus calculated for electrolytes with a mono-, di-, tri-, and tetra-valent cation is about 125:25:5:1. These concentrations, though expressed in equivalents, actually diverge greatly according to the valence of the ion with a charge opposite to that of the surface. The calculated ratios also correspond approximately to the ratios found experimentally. A strictly quantitative agreement cannot be expected, since we made some neglections and approximations; moreover, the theory still needs a few corrections, which will be discussed in the following sections.

Interchanging n_+ and n_- we can of course use the table for the case of a positively charged surface.

The physical interpretation of these regularities, derived formally from Gouy's theory, can be given easily. As a consequence of the negative charge of the surface, the positive ions in the solution are attracted and accumulated in the neighborhood of the surface and the negative ions are repelled. As we have discussed in Part I, section II, these electrical forces are counteracted by the thermal agitation of the ions, which leads to the picture of the diffuse outer charge. The formation of this positive space charge quite near the surface will be easiest when a large number of ions is available, i.e., when the solution is concentrated. Thus for large concentrations of the electrolytes in the solution, the "thickness" of the diffuse layer is less than for smaller concentrations. We can consider the double layer, as usual, as a condenser, and state that for a decreasing thickness its capacity increases, and for equal charges, its potential is lowered. The influence of the charge of the cations can be explained in a similar way. The higher this charge the more difficult it is to distribute the positive ions over some distance into the solution as a result of the thermal agitation; the smaller therefore is the thickness of the double layer and its ζ-potential.

The anions have the opposite tendency. By entering the outer layer they tend to enlarge the thickness of the diffuse outer charge and to raise the ζ-potential. However, it is only a small quantity that succeeds in reaching these layers. Nearly all of them are repelled by the negative surface, and more strongly so the higher their charge. The above equations indicate that the (integrated) amount of anions in the diffuse outer layer is represented by the second term under the square root in equation 8; this term is small for high values of ζ and n_-. For the case of a 2-2 valent electrolyte, $\zeta = -50$ millivolts; the ratio cation:anion amounts to $(e^4 - 1):(1 - e^4) = 55:1$. The influence of the anions upon the potential is therefore almost negligible.

Obviously unaware of Müller's paper, Audubert (4) has recently tried to calculate ζ-c curves for different types of electrolytes with the aid of the theory of the diffuse layer. His results have a restricted value, since he erroneously used Debye-Hückel's approximation, valid only for $n\zeta < < 25$ millivolts. Yet he also concludes from a comparison of calculated and observed ζ-c curves that, upon the addition of small amounts of electrolytes, the electrophoretic charge is a constant.

In summarizing, we state that the theory of the diffuse layer gives a satisfactory explanation of the secondary stability of lyophobic colloids in several respects. It is not necessary to assume that the particles are "neutralized" by an "adsorption"; on the contrary we can consider this charge, as a first approximation, to be a constant. The lowering of ζ as a result of addition of electrolytes is merely due to a "compression" of

the diffuse outer layer and a subsequent increase of the capacity of this part of the double layer.

Bull and Gortner (16) gave a method to determine the mobile part of the charge of the double layer. They combined measurements of the streaming potential and of the surface conductance, e.g., for cellulose in contact with solutions of different electrolytes. Thus they were able to calculate the variations of ζ and of the charge with varying concentrations. In the concentration region of 10^{-4} to 10^{-3} they found that the ζ-potential, though decreasing normally, is connected with a constant or even a slightly increasing charge.

The first assumption of Freundlich's original flocculation theory is thus definitely invalidated. What, then, was the significance and the function of the ions carried down by the flocculating particles? How can we explain that the amounts of these ions frequently were equivalent, but in other cases not equivalent?

It is clear that these phenomena are not accounted for by Müller's theory. In trying to answer these questions, we will see that this theory needs a few corrections, and in some respects is too simple.

IV. INVESTIGATIONS WITH THE SILVER IODIDE SOL

In our opinion the silver iodide sol had several advantages for a study of the interaction of sol particles and indifferent flocculating electrolytes. The sol is well-defined chemically; the constituents of its double layer are known exactly; and we have seen that we can describe quantitatively the conditions of its primary stability. The aging of these sols has been studied extensively; in dialyzed sols, prepared in the proper way, this aging can be reduced to a minimum. Moreover, the aging and a subsequent change of the total charge of the particles can be controlled easily by the measurement of the free iodide-ion concentration in the sol.

Another favorable condition is that the charge of the particles is so extremely small. A practical disadvantage, however, is that the analytical measurements become much more difficult. The latter drawback could be overcome partly by using strongly concentrated sols (up to 40 per cent). Thus we could avoid difficulties arising eventually from the complication discussed at the end of Part I, section III. We have seen that for several sols there is an unexplained discrepancy between the total charges of the particles found analytically and calculated from the ζ-potential. In the case of the silver iodide sol, this complication seems to be absent.

The dialyzed silver iodide sols, as used in our experiments, contain hydrogen ion as counter-ions of the double layer

$$\boxed{AgI}\ I^- \mid H^+$$
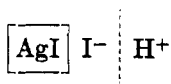
Electrolytes with different cations were added to the sols in varying amounts, and after a definite time the concentration of these cations was measured in the ultrafiltrate or (when complete flocculation had occurred) in the supernatant liquid. Incidentally it was shown that the cations "adsorbed" substituted an equivalent amount of hydrogen ion from the double layer.

We learned from these measurements (Verwey and Kruyt (126)) that sometimes the amount of cation "adsorbed" already reached a maximum for comparatively small concentrations of the ions, and did not increase any more with larger amounts of electrolytes added. Occasionally this maximum was reached for concentrations far below the flocculation region. This maximum proved to be about equivalent to the total amount of hydrogen ion in the double layer; the latter was determined by the electrochemical analysis of the sols after Pauli's methods. The upper limit of the "adsorption" of the cations is therefore determined by the total amount of exchangeable hydrogen ions available.

From this we can conclude that the "adsorption" of cation in all events is not *sufficient* to flocculate the negative sol, for sometimes complete "adsorption" occurs at much lower concentrations than correspond to the flocculation value. In other cases, flocculation occurred long before sufficient electrolyte was added in order to reach the maximum "adsorption." This was found for various kinds of cations if previously a large excess of hydrogen ion was added to the sols.

From our considerations in Part I, section V, it will be perfectly clear that the "adsorption" of cations by the negative particles is a pure exchange of counter-ions. Both exchanging ions play an equivalent part in the phenomenon. The exchange has no relation to the flocculation. Especially a variation of their electrophoretic charge during the exchange does not necessarily occur, in accordance with the opinions of Müller, Audubert, and Bull and Gortner.

In order to be precise in these conclusions we have stated that the phenomenon does not obey the "adsorption isotherm," equation 6 in Part I, section VI, but on the contrary an equation $x = f\left(\dfrac{c}{m}\right)$, which means that it is independent of the dilution. We have seen in Part I, section V, that this is exactly the criterion of an exchange of counter-ions. This proves that the third supposition in Freundlich's original theory is also contrary to the actual state of affairs. Our experiments mentioned above had already proved that the fourth supposition also was wrong for this type of "adsorption."

In Part I, section V, we have reproduced the various exchange tendencies of different cations by a sequence, in which generally the exchange tend-

ency proves to be larger for ions of higher valence. Within a group of ions of the same charge the larger ions exchange more strongly.

Of an ion added to the sol the amount taken up by the particles is thus determined by its position in this sequence, and, since we are dealing with an exchange, by the ratio of the amounts of exchanging and substituted ion. For dialyzed sols, if not too much diluted, the amount of free ions in the sol medium is negligible with regard to the ions present in the double layer. Thus the concentration of the ions, present in the sol as counterions (for silver iodide the hydrogen ions), is proportional to the sol concentration. The flocculation, however, occurs at a definite concentration of the free ions in the sol medium. Thus, for a given sol and a given electrolyte, it depends on the sol concentration how many of the ions added are taken up by the particles at the flocculation point.

This may be elucidated by figure 11, in which we plotted the amounts of lead ion "adsorbed" against the amounts added to the solution. The "adsorption" was determined (with ThB^{++} as radioactive indicator) for a dialyzed silver iodide sol and for the same sol diluted eleven times. The dotted line gives the curve for the diluted sol again on a scale eleven times larger. All concentrations are in milliequivalents per liter. Actually both curves have exactly the same shape, and nearly coincide. The small difference is due to two effects: in the first place some potential-determining electrolyte (HI) has been given back to the solution on account of the dilution, decreasing the total particle charge to a small amount; moreover the dilution is not exactly elevenfold but somewhat larger, as a consequence of the volume occupied by the silver iodide particles. The flocculation point of the concentrated sol is indicated in figure 11 by $\}$; we see that at this point the exchange is just about quantitative, and the maximum of the exchange is reached. The corresponding point of the curve for the diluted sol, however, represents a concentration of free lead ions which is eleven times smaller, i.e., a lead-ion concentration far below the flocculation region. The latter is given by a line ab, parallel to the straight line $x = y$; all lines of this type connect points of equal concentration of free lead ion.

We have already seen that for other sols the charge, and therefore the concentration of the counter-ions or the exchange capacity (T), is 100 to 1000 or more times as large as it is for silver iodide. In the experiments of Freundlich, Weiser, and Rabinowitch, discussed earlier (Part II, section III) the exchange capacity was therefore mostly larger than in ours, even when they used rather dilute sols. Frequently the case was realized that, at the flocculation point, the maximum of the exchange curve was reached scarcely or not at all. This is the explanation why the amounts "adsorbed" were sometimes equivalent, in other cases not.

Equivalent "adsorption" occurred when the sol concentration and other conditions were such that for all electrolytes the exchange was about complete.

In recent investigations by Weiser and Gray (135) and by Bolam and Bowden (13), carried out respectively with As_2S_3 and Odén sulfur sol, the curves for different electrolytes happen to have such a form that in both cases the investigators concluded that flocculation occurs when the substitution is complete. The theory of Weiser and Gray, developed on the basis of these experiments, is essentially identical with Freundlich's old theory which has already been rejected in the preceding section of this
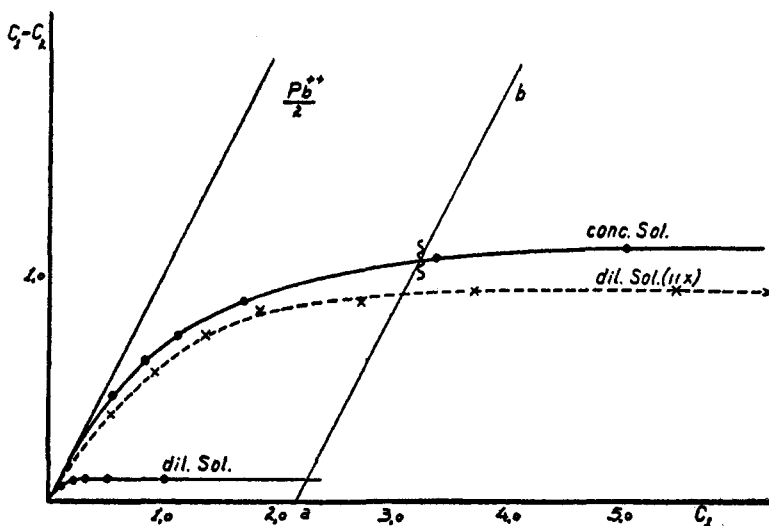

FIG. 11. Exchange isotherms Pb^{++}/H^{+} with silver iodide sol. The curve for the concentrated sol is about the elevenfold multiplication of the curve for the sol diluted eleven times; this is characteristic for an exchange and not for an adsorption.

paper. From the experiments discussed above we have seen that a coincidence of the flocculation region and the point where the exchange is practically complete is not the general case, and therefore only accidental. Thus we may state that the considerations of Weiser and Gray and of Bolam and Bowden are not justified.

Rabinowitch and Kargin (108) have titrated conductometrically an arsenic trisulfide sol with barium chloride solution. A discontinuous change in the curve indicates the point where the hydrogen ion of the double layer has been substituted almost completely by the barium ion added. Rabinowitch and Wassiliev (109) recently stated that the sols to which this amount of barium chloride was added did not coagulate,

even if they were allowed to stand a long time. They conclude that two "phases" of the coagulation exist. Though this conclusion approaches that of ours we cannot quite agree with it. We have seen that the first "phase" of the coagulation, the exchange, is not at all necessary for the flocculation. The exchange may accompany the flocculation but is not essential for it.

V. EXCHANGE OF COUNTER-IONS AND COLLOIDAL BEHAVIOR

The exchange is not important for a general coagulation theory. In a special flocculation theory, however, it can not be neglected.

According to Müller's theory one would expect that all electrolytes of the same type (i.e., with the same values of n_+ and n_-) lower the potential and coagulate in exactly the same way. This is not true, for characteristic differences exist between electrolytes with, for instance, various ions charged oppositely to the sol. Provided that the particles are sufficiently lyophobic (Voet and Balkema (131)), we generally find that the flocculation action of equally charged ions increases with the ionic radius. Thus, for a positive sol $I^- > Br^- > Cl^- > F^-$; for a negative sol $Cs^+ > Rb^+ > K^+ > Na^+ > Li^+$. The H^+ or H_3O^+ ion occupies a special position, and flocculates generally more strongly than Cs^+.

Various explanations have been proposed for these phenomena. In our opinion it is easy to understand this behavior in the following way. The sequence found for the potential-lowering action of equally charged ions is exactly the same as the sequence found for the exchange. Those ions which strongly substitute other ions also have a stronger flocculating action. These phenomena are directly connected with each other. This is clear for an extreme case,—for the exceptions of Schulze's rule. Flocculating an arsenic trisulfide sol with new fuchsin, for instance, we need only an extremely small quantity of these ions. At the same time we can observe that the ion is taken up quantitatively by the double layer. If, however, when the flocculation has been effected, more of the new fuchsin chloride is added, the solution becomes colored immediately (Freundlich and Neumann (35)). Exactly the same has been found by Zsigmondy and Heinz (142) for the coagulation of a negative SnO_2 sol. Some electrolytes, as sodium or potassium salts, give normal values for the flocculation concentration. All polyvalent cations, and also silver ion, are exceptions to Schulze's rule. The amounts needed for coagulation are small, and depend solely on the amount of peptizing electrolyte (KOH) present in the double layer, i.e., they are equivalent to the amount of the peptizing ion. For this case, indeed, a chemical "interpretation" of the coagulation (formation of insoluble stannates, and therefore precipitation) seems to

give a good description of the facts. But we have already stressed the fact that this is an exceptional case (cf. Part II, section II).

In these cases we deal with ions that have a strong attraction toward the surface, and, for that reason, exchange other ions very strongly. In other words, these ions have a very large "adsorption potential" in the sense of Stern (cf. Part I, section III). According to Stern's theory these ions are drawn quantitatively into the "attaching" ionic layer ("Helmholtz layer"). Thus the ions added to the sol completely destroy the diffuse outer layer, and raise the charge η_1 at the cost of η_2. This is actually a kind of "neutralization" of the particles, if one considers that only the electrophoretic charge η_2 is neutralized. For these extreme cases Freundlich's picture of flocculation remains valid, and becomes identical with that of Zsigmondy. But we notice that these pictures are right only when the flocculating ions are "adsorbed" almost quantitatively by the exchange of counter-ions, and the flocculation value is low and about proportional to the amount of peptizing ion (= exchange capacity).

These cases are not of the normal type of flocculation. The transition to the normal case is however a continuous one. The ions of the heavy metals, H_3O^+, and OH^-, frequently occupy an intermediate position. The flocculation values of these ions are mostly considerably smaller than for the equally charged ions with the electronic structure of the inert gases (8- or helium-scale); they are not low enough to "precipitate" the sol particles by an almost complete exchange. Van Arkel and de Boer (5) have already pointed out that these comparatively low flocculation values must be explained by the large polarizabilities of the heavy metal ions and by the dipoles of H_3O^+ and OH^-.

To a smaller extent these specific influences are still present for the ions with a 8-electronic scale. Their polarizabilities, though smaller, vary considerably. We must correct Müller's theory (in which the electrophoretic charge was considered to be independent of the electrolyte and its concentration) in such a way that we take into account the variations of the charge of the diffuse layer. This charge is determined by the distribution of the counter-ions over the diffuse and the "Helmholtz" layer. If we add electrolyte to the sol an exchange of the counter-ions occurs; the composition of the outer layers is changed. Generally there will be a shift of the equilibrium of counter-ion distribution over both layers (independent of changes of this equilibrium by the change of the total electrolyte concentration which are equal for all electrolytes of the same type). Generally speaking the electrophoretic charge (which determines the ζ-potential) is not a constant, but may either increase or decrease.

If the ion added to the sol has a larger adsorption potential (ϕ) than the counter-ion of the double layer, the charge η_2 will always decrease,

intensifying the normal decrease of ζ. In the opposite case the exchange is small, but the ions entering the double layer cause an opposite shift of the charges, increasing the charge η_2. This increase of the electrophoretic charge will perhaps not lead to an initial increase of ζ, for the latter is lowered at the same time by the increased concentration. At any rate the potential will be lowered less than for ions with larger values of ϕ.

The adsorption potential, ϕ, and therefore the exchange is governed, for ions of the simple type, by their polarizability. Since the latter increases considerably in the sequences Li→Cs and F→I, the flocculating action of these ions will increase in the same direction.

In this way we can give plausible explanations for the characteristic variations among various flocculating ions of the same valence.[9]

The exchange of counter-ions is still important for another group of phenomena. It reveals the relation between the flocculation value and the sol concentration. It is clear that the probability of collision and therefore the rate of flocculation will decrease after dilution of the sol. This factor has been discussed by Kruyt and van der Spek (77) and Fodor and Riwlin (42), but its influence upon the change of the flocculation value with varying sol concentration must be small (cf. Weiser and Nicholas (137)). By dilution of the sol the total exchange capacity per liter is diminished. The amount of electrolyte required for flocculation therefore decreases when the ion added flocculates more strongly than the counter-ion of the sol. In the opposite case the flocculation value of the electrolyte will be increased upon the dilution of the sol.

When a dialyzed silver iodide sol is treated with ceric nitrate, the Ce^{3+} is taken up by the particles almost quantitatively until the maximum exchange is reached. A very concentrated dialyzed silver iodide sol, with an exchange capacity of 1.34 milliequivalents per kilogram of sol, required for its flocculation about 1.6 milliequivalents of Ce^{+++}; the flocculation value for a more diluted sol with an exchange capacity of 0.18 milliequivalent was only 0.4 milliequivalent (Verwey and Kruyt (126)). The free concentration of Ce^{+++} was therefore at the moment of flocculation about 0.2 milliequivalent per liter in both cases. For "normal" sols, i.e., for sols with a particle charge some powers of ten times as large as that of silver iodide sol, the exchange capacity is so large that similar effects will already occur in dilute sols. The effect will also increase with the charge of the ion, as generally the exchange tendency is large for ions of high valencies. The experimental facts (see also the work of

[9] *Note added in proof:* In a recent paper H. Jenny and R. F. Reitemeier (J. Phys. Chem. **39**, 593 (1935)) have discussed the relation between ionic exchange and stability of lyophobic colloids in a similar way. Their treatment differs only slightly from ours. In some details we prefer the formulations chosen above.

Burton (19), Freundlich (39), Ghosh and Dhar (29), and Usher (121))
seem to substantiate the above views.

VI. PURE ADSORPTION OF ELECTROLYTES AND COLLOIDAL BEHAVIOR

We have considered the significance of potential-determining electro-
lytes for colloid chemistry and examined the influence of counter-ionic
exchange when indifferent electrolytes are added to a sol. In our previous
review we have, however, neglected the pure adsorption of electrolytes.
For several sols, especially for the silver iodide sol, this was perfectly
allowable. That the phenomena were found to be rather simple for this
sol was probably partly due to the circumstance that silver iodide does
not adsorb foreign electrolytes (Beekley and Taylor (7)). Actually we
found no indication of pure adsorption and observed only an equivalent
ionic exchange. The analytical results of Freundlich, Joachimson, and
Ettisch, discussed in a previous section (Part II, section III), prove,
however, that in the case of the arsenic trisulfide sol and gold sol, the
phenomena are complicated by a pure adsorption of the electrolytes.

The available data seem to be insufficient to discuss this problem in
detail, especially in connection with the stability and other properties of
the sol. However, we can give some general points of view which have
to be considered fully in order to have a better understanding of these
rather complicated phenomena.

Let us consider, for example, the double layer of arsenic trisulfide sol:

$$\boxed{As_2S_3}\ S^{--} \mid 2H^+$$
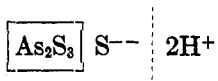
An electrolyte is added, say potassium chloride, which is indifferent since
it does not change the total potential of the double layer. In the first
place an exchange of some hydrogen ion by potassium ion occurs; we
have seen that this does not change the double layer fundamentally.
Moreover, the potassium chloride is adsorbed, and we will assume that
in this process the chloride ion is the leading ion. Thus there will be an
orientation of charges in the outer layer of the double layer, and this will
cause a transportation of S^{--} ions to the solution (cf. Part I, section VI),
as a consequence of the shift of the zero point of surface charge.
The concentration of S^{--} in the sol medium is increased, and the total
potential of the double layer becomes more negative. The potential slope
in the double layer and therefore ζ is changed in a rather complicated way.

From the work of Kruyt, Janssen, and others, discussed in Part I,
section VI, we learn that a strong adsorption of anions by a negative sol
leads to a maximum in the ζ–c curve. Such a maximum is always an

indication that adsorption occurs.   The same is true for electrolytes which are able to reverse the charge of a sol ("irregular series"); for instance, it is a well-known fact that a negative gold sol can be charged positively by Th^{++++}.   Here apparently the cations go into the "attaching" layer so strongly that their total charge surpasses that of the gold particles. The compensating charge of the diffuse layer then becomes negative.   We have therefore the case of figure 7, with the opposite signs only.   A more quantitative treatment of these phenomena meets with serious difficulties. Moreover, the discontinuity of the changes (Part I, section III) may be here of considerable importance (see the discussion of Frumkin (44, pp. 255–6).

VII. SUMMARY

In Part I we have studied the properties of the electrical double layer and the "adsorption" of electrolytes.   In Part II we have tried to apply our theoretical considerations to the problems of the stability of lyophobic colloids.   The general relationships for this "stability" have been discussed, both from the thermodynamic and the kinetic point of view.   The conditions for primary stability (peptization) and secondary stability (coagulation) have been studied especially.   These phenomena are not "stabilities" in the absolute sense and must be clearly distinguished from "coarsening" of the sol particles.   A concept of general validity has been given of the fundamental significance of the potential-determining electrolytes for the primary stability.   With the aid of this principle, the theory of peptization has been discussed.   An extensive survey of the theory of coagulation has been given, including the original theory of Freundlich and more modern concepts on the basis of the theory of the double layer. We have tried to indicate the limitations of these theories and to arrive at a synthesis.   The corrections that are still necessary (in order to take into account the exchange of counter-ions and the pure adsorption of electrolytes) have also been discussed briefly.

REFERENCES

(1) ABRAMSON, H. A., AND MÜLLER, H.: Proc. Am. Phys. Soc. **7**, 11 (1932).
(2) ANDAUER, M., AND LANGE, E.: Z. physik. Chem. **156A**, 241 (1931).
(3) ANDAUER, M., AND LANGE, E.: Z. physik. Chem. **166A**, 219 (1933).
(4) AUDUBERT, R.: J. chim. phys. **30**, 89 (1933).

(5) VAN ARKEL, A. E. AND DE BOER, J. H.: Chemische Bindung. S. Hirzel, Leipzig (1931). Also in French translation, considerably revised, to appear before long (Serie: Le livre scientifique, Paris).

(6) BASINSKI, A.: Kolloid Beihefte **36**, 258–349 (1932).

(7) BEEKLEY, J. S., AND TAYLOR, H. S.: J. Phys. Chem. **29**, 942 (1925).

(8) DE BOER, J. H.: Z. physik. Chem. **14B**, 149, 457; **15B**, 281, 300; **16B**, 397; **17B**, 161 (1932).

(9) DE BOER, J. H., AND DIPPEL, C. J.: Z. physik. Chem. **21B**, 198, 278 (1933); **25B**, 399 (1934).

(10) DE BOER, J. H., AND CUSTERS, J. F. H.: Z. physik. Chem. **21B**, 208 (1933); **25B**, 225, 238 (1934).

(11) DE BOER, J. H., AND LEHR, J. J.: Z. physik. Chem. **22B**, 423 (1933); **24B**, 98 (1934).

(12) DE BOER, J. H., AND VEENEMANS, C. F.: Physica **1**, 573, 953, 960 (1934).

(13) BOLAM, TH. R., AND BOWDEN, G.: J. Chem. Soc. **1932**, 2684.

(14) BRAGG, W. L.: Z. Krist. **74**, 237 (1930).

(15) DE BROUCKÉRE, L.: J. chim. phys. **25**, 605 (1928); **26**, 250 (1929); **27**, 543 (1930).

(16) BULL, H. B., AND GORTNER, R. A.: J. Phys. Chem. **35**, 309 (1931).

(17) BUNGENBERG DE JONG, H. G.: Rec. trav. chim. **42**, 437 (1923); **43**, 35 (1924).

(18) BURTON, E. F., AND ANNETTS, MAY: J. Phys. Chem. **35**, 48 (1931).

(19) BURTON, E. F., AND BISHOP, E.: J. Phys. Chem. **24**, 701 (1920).
BURTON, E. F., AND McINNES, E. D.: J. Phys. Chem. **25**, 517 (1921).

(20) BURTON, E. F.: Phil. Mag. [6] **11**, 440 (1906).

(21) BURGERS, W. G., AND DIPPEL, C. J.: Physica **1**, 549 (1934).

(22) CHAPMAN, D. L.: Phil. Mag. [6] **25**, 475 (1913).

(23) COEHN, A.: Wied. Ann. **64**, 217 (1898).

(24) COEHN, A., AND RAYDT, U.: Ann. Physik [4] **30**, 777 (1909).

(25) CYSOUW, H. A.: Dissertation, Utrecht, 1934.

(26) DANIEL, JANET: J. Gen. Physiol. **16**, 547 (1933).

(27) DEBYE, P., AND HÜCKEL, E.: Physik. Z. **24**, 185, 305 (1923).
DEBYE, P.: Trans. Faraday Soc. **23**, 334 (1927).

(28) DEBYE, P., AND HÜCKEL, E.: Physik. Z. **25**, 49 (1924).

(29) DHAR, D. R., AND GHOSH, S.: J. Phys. Chem. **31**, 187, 649 (1927).

(30) ELISSAFOFF, V.: Z. physik. Chem. **79**, 385 (1912).

(31) FAJANS, K., AND VON BECKERATH: Z. physik. Chem. **97**, 478 (1921).

(32) FAJANS, K., AND ERDEY-GRÚZ, T.: Z. physik. Chem. **158A**, 97–151 (1932).

(33) FREUNDLICH, H.: Kapillarchemie, 4th edition, with J. Bikerman. Akademische Verlagsgesellschaft, Leipzig (1930).

(34) FREUNDLICH, H.: Kolloid-Z. **1**, 321 (1907); Z. physik. Chem. **73**, 385 (1910).

(35) FREUNDLICH, H., AND NEUMANN, W.: Z. physik. Chem. **67**, 538 (1909).

(36) FREUNDLICH, H., AND SCHUCHT, H.: Z. physik. Chem. **85**, 641 (1913).

(37) FREUNDLICH, H., AND HAASE, E.: Z. physik. Chem. **89**, 417 (1915).

(38) FREUNDLICH, H., AND GANN, J. A.: Kolloidchem. Beihefte **8**, 127 (1916).

(39) FREUNDLICH, H., AND LOENING, E.: Kolloidchem. Beihefte **16**, 1 (1922).

(40) FREUNDLICH, H., AND ZEH, P.: Z. physik. Chem. **114**, 65 (1924).

(41) FREUNDLICH, H., JOACHIMSON, K., AND ETTISCH, E.: Z. physik. Chem. **141A**, 249 (1929).

(42) FODOR, E., AND RIWLIN, R.: Kolloid-Z. **44**, 69 (1928).

(43) FRUMKIN, A.: Z. physik. Chem. **109**, 34 (1924).

(44) FRUMKIN, A.: Sow. Phys. **4**, 239 (1933).

(45) FRUMKIN, A.: Ergebnisse der exakten Naturwissenschaften **7**, 235 (1928).

(46) FRUMKIN, A., AND PROSKURNIN, M.: Z. physik. Chem. **155A**, 29 (1932).
(47) GANSSEN, R.: Centr. Mineral. Geol. **1913**, 699, 728.
(48) GIBBS, J. W.: Thermodynamics. Longmans, Green and Co., London and New York (1906).
(49) GOUY, G.: Ann. chim. phys. [7] **29**, 145–241 (1903).   *
(50) GOUY, G.: J. phys. [4] **9**, 457 (1910); Ann. Physik. [9] **7**, 129 (1917).
(51) GYEMANT, A.: Z. Physik **17**, 190 (1923).
(52) GYEMANT, A.: Kolloidphysik. F. Vieweg and Son, Braunschweig (1925).
(52a) HABER, F., AND BEUTNER, R.: Ann. Physik [4] **26**, 947 (1908).
(53) HAHN, O., AND IMRE, L.: Z. physik. Chem. **144A**, 161 (1929).
(54) HARDY, W. D.: Z. physik. Chem. **33**, 385 (1900).
(55) HELLWIG, K.: Z. anorg. allgem. Chem. **25**, 180 (1900).
(56) HELMHOLTZ, W.: Pogg. Ann. **89**, 211 (1853); Wied. Ann., N. F., **7**, 339 (1879).
(57) HENRY, D. C.: Proc. Roy. Soc. London **133A**, 106 (1931).
(58) HERZFELD, K. F.: Physik. Z. **21**, 28, 61 (1920).
(59) HOROVITZ, K., AND PANETH, F.: Z. physik. Chem. **89**, 513 (1915).
(60) HÜCKEL, E.: Physik. Z. **25**, 204 (1924).
(61) IMRE, L.: Z. physik. Chem. **146A**, 41 (1930); **153A**, 127, 262 (1931); **164A**, 327, 343, 364 (1933); Z. Elektrochem. **38**, 534 (1932).
(62) JAEGER, F. M.: Trans. Faraday Soc. **25**, 320 (1929).
    JAEGER, F. M., WESTENBRINK, H. G. K., AND VAN MELLE, F. A.: Proc. Acad. Sci. Amsterdam **30**, 249 (1927); **32**, 167 (1929).
(63) JENNY, H.: Kolloidchem. Beihefte **23**, 428 (1928); J. Phys. Chem. **36**, 2217 (1932).
(64) JANSSEN, L. W.: Sow. Phys. **4**, 322 (1933); Dissertation, Utrecht, 1933.
(65) JULIEN, P. F. J. A.: Dissertation, Utrecht, 1933.
(66) KELLEY, W. P., DORE, W. H., AND BROWN, S. M.: Soil Science **31**, 25 (1931).
(67) KING, J. F., AND PINE, P. R.: J. Phys. Chem. **37**, 851 (1933).
(68) KOLTHOFF, I. M.: Rec. trav. chim. **46**, 549 (1927).
(69) KOLTHOFF, I. M.: J. Phys. Chem. **36**, 860 (1932); Chem. Weekblad **29**, 332, 362 (1932).
(70) KOLTHOFF, I. M., AND ROSENBLUM, CH.: J. Am. Chem. Soc. **55**, 2656, 2665 (1933).
(71) KOLTHOFF, I. M., AND SANDELL, E. B.: J. Am. Chem. Soc. **55**, 2170 (1933).
(72) KOLTHOFF, I. M., AND ROSENBLUM, CH.: Phys. Rev. **45**, 341 (1934).
(73) KOLTHOFF, I. M., VON FISCHER, W., AND ROSENBLUM, CH.: J. Am. Chem. Soc. **56**, 832 (1934).
(74) KRUYT, H. R.: Colloids, 2nd edition. Wiley and Sons, New York (1930).
(74a) KRUYT, H. R.: Sow. Phys. **4**, 295 (1933).
(74b) KRUYT, H. R.: Bull. soc. chim. Belg. **43**, 559–96 (1934).
(75) KRUYT, H. R.: in Alexander's Colloid Chemistry, Vol. I, pp. 305–22. D. Van Nostrand Co., New York (1926).
(76) KRUYT, H. R., AND VAN ARKEL, A. E.: Kolloid-Z. **32**, 29 (1923).
(77) KRUYT, H. R., AND VAN DER SPEK, J.: Kolloid-Z. **25**, 1 (1919).
(78) KRUYT, H. R.: Kolloid-Z. **22**, 81 (1918).
    KRUYT, H. R., AND VAN DER WILLIGEN, P. C.: Kolloid-Z. **45**, 307 (1928).
(79) KRUYT, H. R., AND BRIGGS, D. R.: Proc. Acad. Sci. Amsterdam **32**, 384 (1929).
(80) KRUYT, H. R., AND VAN DER WILLIGEN, P. C.: Z. physik. Chem. **139**, 53 (1928).
(80a) KRUYT, H. R., AND CYSOUW, H. A.: Z. physik. Chem. **172A**, 49, 56 (1935).
(81) VAN LAAR, J. J.: Lehrbuch der theoretischen Elektrochemie, (1907).
(82) LANGE, E., AND BERGER, R.: Z. Elektrochem. **36**, 171 (1930).

(83) LANGE, E., AND BERGER, R.: Z. Elektrochem. **36**, 980 (1930).

(84) LANGE, E., AND BERGER, R.: Z. physik. Chem. **147A**, 470 (1930).

(85) LANGE, E., AND CRANE, P. W.: Z. physik. Chem. **141A**, 225 (1929).

(86) LANGE, E., AND MISCENKO, P. W.: Z. physik. Chem. **149A**, 1–42 (1930).

(87) LANGE, E.: Handbuch der Experimentalphysik, Vol. XII, **2**, p. 265.
    Akademische Verlagsgesellschaft, Leipzig (1934).

(88) LANGMUIR, I.: J. Am. Chem. Soc. **38**, 2221 (1916); **40**, 1361 (1918); Phys. Rev.
    6, 79 (1915); **8**, 149 (1916).

(89) LEWIS, W. C. M.: Trans. Faraday Soc. **28**, 597 (1932).

(90) LINDER, S. E., AND PICTON, H.: J. Chem. Soc. **67**, 148 (1892); **67**, 62 (1895); **71**,
    568 (1897).

(91) LOTTERMOSER, A.: Z. physik. Chem. **60**, 451 (1907); Kolloid-Z. (Erg.-Bd.) **36**,
    230 (1925).

(91a) LOTTERMOSER, A., AND RIEDEL, W.: Kolloid-Z. **51**, 30 (1930).

(92) MARCH, A.: Kolloid-Z. **45**, 97 (1928).

(93) MOONEY, M. M.: J. Phys. Chem. **35**, 331 (1931).

(94) MUKHERJEE, J. N., AND KUNDU, P. W.: J. Indian Chem. Soc. **3**, 335 (1926).

(95) MUKHERJEE, J. N., BASU, J. K., AND MUKHERJEE, A.: J. Indian Chem. Soc. **4**,
    459 (1927).

(96) MICHAELIS, L., TIMENEZ-DIAZ, C., AND HIRABAYASHI, N.: Kolloid-Z. **29**, 184
    (1921); **30**, 209 (1922).

(97) MICHAELIS, L.: Die Wasserstoffionen Konzentration. J. Springer (1914).

(98) MICHAELIS, L., AND RONA, P.: Biochem. Z. **97**, 57 (1919).

(99) MÜLLER, H.: Kolloidchem. Beihefte **26**, 257 (1928).

(100) PAULI, Wo, AND VALKÓ, E.: Elektrochemie der Kolloide. J. Springer, Wien
     (1929).

(100a) PAULI, Wo.: Naturwissenschaften **30**, 555 (1932).

(101) PAULING, L.: Z. Krist. **74**, 213 (1930); Proc. Nat. Acad. Sci. **16**, 453 (1930).

(102) PERRIN, J.: J. chim. phys. **2**, 601 (1904); **3**, 50 (1905).

(103) POWIS, F.: Z. physik. Chem. **89**, 91, 189 (1915).

(104) PRAUSNITZ, P. H.: Kolloid-Z. **51**, 359 (1930).

(105) RABINOWITCH, A. J.: Z. physik. Chem. **116**, 97 (1925).

(106) RABINOWITCH, A. J., AND KARGIN, V. A.: Z. physik. Chem. **133**, 203 (1928).

(107) RABINOWITCH, A. J., AND FODIMANN, E.: Z. physik. Chem. **159A**, 403 (1932).

(108) RABINOWITCH, A. J., AND KARGIN, V. A.: Z. physik. Chem. **143A**, 21 (1929).

(109) RABINOWITCH, A. J., AND WASSILIEV, D. TH.: Kolloid-Z. **60**, 268 (1932).

(110) RABINOWITCH, A. J.: Sow. Phys. **4**, 304 (1933).

(111) RICE, O. K.: J. Phys. Chem. **30**, 189, 1348, 1660 (1926).

(112) ROTHMUND, V., AND KORNFELD, G.: Z. anorg. allgem. Chem. **103**, 129 (1918);
     108, 215 (1919).

(113) SCHULZE, H.: J. prakt. Chem. [2] **25**, 431 (1882); **27**, 320 (1883).

(113a) SMEKAL, A.: Z. angew. Chem. **42**, 489 (1929).

(114) VON SMOLUCHOWSKI, M.: Graetz' Handbuch der Elektrizität und des Mag-
     netismus **2**, 366 (1914).

(115) VON SMOLUCHOWSKI, M.: Physik. Z. **17**, 557, 583 (1916); Z. physik. Chem. **92**,
     129 (1918).

(116) STERN, O.: Z. Elektrochem. **30**, 508 (1924).

(117) TAYLOR, H. S.: Proc. Roy. Soc. London **108**, 105 (1925).

(118) TAYLOR, W. H.: Z. Krist. **74**, 1 (1930).

(119) TARTAR, H. V., AND GAILEY, Z. J.: J. Am. Chem. Soc. **44**, 2212 (1922).

(120) TARTAR, H. V., AND DRAVES, C. J.: J. Phys. Chem. **30**, 763 (1926).

(121) USHER, F.: Trans. Faraday Soc. **21**, 406 (1925).

(122) VAGELER, P.: Der Kationen- und Wasseraushalt des Mineralbodens. S. Hirzel, Leipzig (1932).

(123) VERWEY, E. J. W.: Proc. Acad. Sci. Amsterdam **36**, 225 (1933).

(124) VERWEY, E. J. W., AND KRUYT, H. R.: Z. physik. Chem. **167A**, 137 (1933).

(125) VERWEY, E. J. W., AND KRUYT, H. R.: Z. physik. Chem. **167A**, 149 (1933).

(126) VERWEY, E. J. W., AND KRUYT, H. R.: Z. physik. Chem. **167A**, 312 (1934).

(127) VERWEY, E. J. W.: Rec. trav. chim. **53**, 933 (1934).

(128) VERWEY, E. J. W.: Chem. Weekblad **31**, 789 (1934).

(129) VERWEY, E. J. W.: Natuurwetenschappelijk Tijdschrift **7**, 89 (1934).

(130) VERWEY, E. J. W.: Dissertation, Utrecht, 1934.

(131) VOET, A., AND BALKEMA, F.: Rec. trav. chim. **52**, 371 (1933).

(132) VON WEIMARN, P. P.: Repts. Imp. Ind. Research Inst. Osaka Japan **12**, 5, pp. 1-148 (1931).

(133) WEISER, H. B.: J. Phys. Chem. **35**, 1, 1368 (1931).

(134) WEISER, H. B., AND GRAY, G. R.: J. Phys. Chem. **36**, 2178 (1932).

(135) WEISER, H. B., AND GRAY, G. R.: J. Phys. Chem. **36**, 2796 (1932).

(136) WEISER, H. B.: in J. Alexander's Colloid Chemistry, Vol. I, p. 600. D. Van Nostrand Co., New York (1926).

(137) WEISER, H. B., AND NICHOLAS, O.: J. Phys. Chem. **25**, 742 (1921).

(138) WHITNEY, W. R., AND OBER, J. E.: J. Am. Chem. Soc. **23**, 842 (1901).

(139) WIEGNER, G.: Kolloid-Z. **36A**, Zsigmondy Festschrift, pp. 341-69 (1925).

(140) WIEGNER, G., AND JENNY, H.: Kolloid-Z. **42**, 268 (1927).

(141) VAN DER WILLIGEN, P. C.: Dissertation, Utrecht, 1927.

(142) ZSIGMONDY, G.: Kolloidchemie. Otto Spamer, Leipzig (1920).