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Significance of constants involved
in electrochemical double layers

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22. Significance of Constants Involved in Electrochemical Double Layers

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Introduction

The electrical properties of the phase boundary, which may be summarized under the heading "electrochemical double layer," have been investigated in many ways. First there is the purely *electrochemical* approach. Strictly, one should consider the double layer in any electrochemical experiment in which phase boundaries are involved, that is, in all measurements on galvanic cells either in equilibrium or at finite current. Practically, however, more detailed considerations of the double layer are restricted to the fields of thermionic work functions, overpotentials, polarization currents, membrane potentials, oil-water and air-water potentials, and especially electrocapillarity. Many problems in ion exchange also require consideration of the double layer.

Second, those working in *colloid science* are interested in the electrochemical double layer, because it is now regarded as the direct cause of the stability of hydrophobic colloids [1].² Moreover, the double layer exerts an influence on titration curves of proteins and other hydrophilic colloids; it is at the basis of the electroviscous effect; it explains the formation and dissolution of coacervates and the solubility of globulins. In the physiological field it is related to the permeability of cell membranes.

Finally, *electrokinetic* phenomena which lie between electrochemistry and colloid chemistry and form a striking proof of the extension in space of the double layer should be mentioned. The most important of these, although not the most suitable for interpretation, is *electrophoresis* which has been so significant in the development of protein science.

It is no wonder, therefore, that investigators in such different fields do not always speak the same language. Between naive optimists who take the charge and potential of the double layer for granted and pessimists like Guggenheim [2], who deny the possibility of acquiring any knowledge on the potential difference between two phases or the course of the potential in one phase, almost any point of view can be found.

It is the object of this paper to show that a very sensible middle course can be steered which, recognizing in principle the point of view of the pessimists, escapes its sterility in many practical cases. Our ultimate aim is to obtain a complete description of the structure of the double layer, or what may be called a map of the phase boundary, giving the distribution of nuclei and electrons from which all desirable information could be calculated. Unfortunately, we are still far from this ideal, and must content ourselves with much less detail. Our

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² Figures in brackets indicate the literature references on p. 225.

data are usually restricted to charge and potential difference in the double layer and to its free energy. The interpretation of the relation between charge and potential (or of the capacity of the double layer) adds some information on the structure, especially on the extension of the double layer in space.

It should be realized, however, that the investigator of the double layer is in a rather uneasy position. It has been emphasized many times that potential differences between different phases are as inaccessible as are single ionic activities or diffusion potentials. In passing a suitable test body from one phase to another electrical work $e\Delta\phi$ is always accompanied by chemical work $\Delta\mu$ and the two cannot be separated without arbitrariness. How then is it possible to attribute importance to the potential difference in a double layer? Anticipating our arguments we mention that a double layer potential is only part of a total potential difference between two phases, and although it seems to have the character of a single-phase boundary potential, it is in fact determined as the potential difference of a galvanic cell related to a suitable zero. This can be most easily shown by thermodynamic consideration of a double layer when part of a galvanic cell.

Thermodynamics of the Double Layer [3, 4]

The double layer will be considered as situated at one of the phase boundaries of a galvanic cell. Our considerations will be restricted to situations in which no current flows.

Extension to current carrying cells is possible as a first approximation by assuming that the structure of the double layer is analogous to that at rest, although charge and potential may be modified.

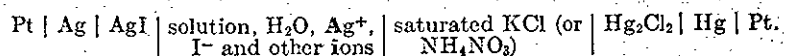
Current-free situations occur with two very different systems, i. e., (a) with a reversible electrode in true thermodynamic equilibrium and (b) with a perfectly polarizable electrode. Experimentally, there is a great difference between (a) and (b) in that with the reversible electrode the emf of the cell is completely determined by the composition of the phases, whereas with the polarizable electrode the potential difference at the cell is a parameter which can be freely changed.

To simplify the discussion we shall choose two examples which, incidentally, are the best investigated cases in this field.

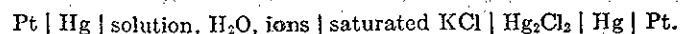
For the reversible double layer, that on AgI will be chosen and for the polarizable one, that on Hg. To incorporate these two double layers in galvanic cells, a second electrode is necessary. It is fundamentally irrelevant whether this second electrode is a reversible type or one connected to the cell by a liquid junction which is supposed to suppress the diffusion potential. For thermodynamic calculations the reversible electrode is more suitable, but in most experiments the liquid junction is used.

The two cells considered are:

a. *Reversible case,*



b. *Polarizable case,*



For simplicity all ions will be assumed to be univalent.

Charge and Potential of the Polarizable Double Layer

The notion of *charge* is rather simple in that it is considered to be typical for the phase boundary between Hg and solution that no current can pass through it. By imposing a potential difference between the two Pt electrodes of cell (b) a small amount of electricity passes through the Pt to the Hg and on the other side from the calomel electrode through the liquid junction to the solution. These two amounts of electricity must be equal and of opposite sign and may be considered as the charges of the Hg and solution sides of the double layer, provided we start with an uncharged double layer. The absence of charge on the Hg can be experimentally ascertained, for according to the Lippmann relation it is characterized by a maximum in the interfacial tension of Hg.

The *potential difference* between Hg and solution is, however, not directly assessable. We know the potential difference, E , imposed on the cell, but it is composed of three contributions, i. e., the potential: Hg|solution, saturated KCl|Hg, and the diffusion potential, which cannot be separated from each other without arbitrariness. But when *changes in the potential difference*, dE , are considered, they can be located only at the polarizable interface, Hg|solution, because the potential at the other two interfaces are completely determined by the composition of the phases and these do not change measurably by the passing of the small quantity of electricity necessary to charge the double layer. So, calling the potential difference between Hg and solution, $\Delta\phi$, we have

$$d\Delta\phi = dE. \quad (1)$$

In the zero point of charge there is no double layer, but there may be and probably is a difference in potential between the two phases as a consequence of orientation of dipoles and polarization of surface atoms. Calling this potential difference χ , $\Delta\phi$ may be divided into the unknown χ and a potential difference D , directly connected with the presence of the double layer, thus

$$\Delta\phi = \chi + D \quad (2)$$

This double layer potential D is experimentally assessable according to

$$D = E - E_0. \quad (3)$$

where E_0 is the cell potential at the zero point of charge. From D and the charge density σ , the integral or differential capacity ($C_{\text{int.}}$ and $C_{\text{diff.}}$) of the double layer can be derived according to

$$C_{\text{int.}} = \sigma/D \quad (4)$$

$$C_{\text{diff.}} = \partial\sigma/\partial D = \partial\sigma/\partial E. \quad (5)$$

All this relates to the double layer between Hg and a solution of a given composition. Changing the composition of the solution one finds different relations between σ and D and usually a shift of the zero point of charge. For example, if thio-urea [5] is added to the aqueous solution the Hg must be made more negative to reach the zero point of charge. This shift amounts to 100 mv for 0.01 *N* thio-urea, increases

to a maximum of about 450 mv, and is directly proportional amount of thio-urea adsorbed on the Hg.

With the small amounts of thio-urea involved it is inconceivable that the diffusion potential changes by more than a few millivolts. Consequently the change in E_0 may be considered here as a change in

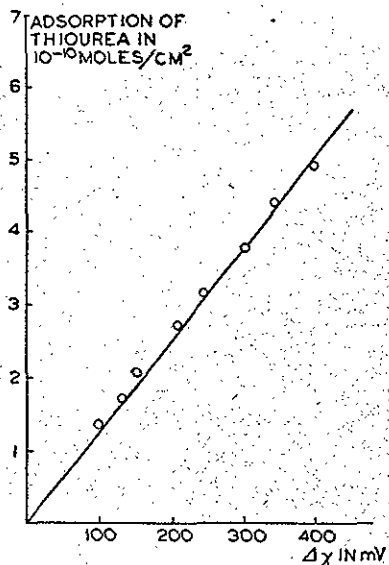


FIGURE 22.1. Adsorption of thio-urea in the zero point of charge plotted against the shift in χ .

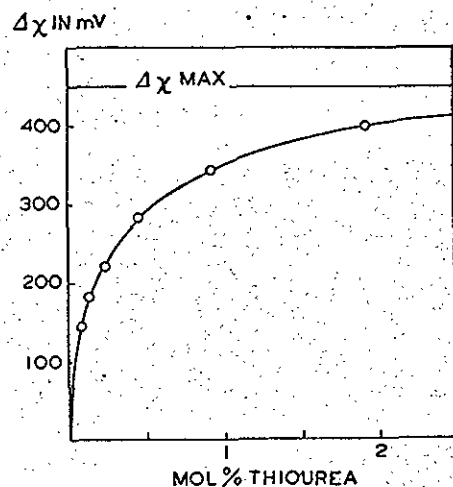


FIGURE 22.2. Shift in χ as a function of the concentration of thio-urea.

the χ potential caused by the oriented adsorption of thio-urea (or by the replacement of oriented water by thio-urea). This is illustrated in figures 22.1 and 22.2.

Although for changing composition our arguments are not as conclusive as for constant composition, involving as they do an assumption about the diffusion potential, there are many cases like that just cited,

where the shift in E_0 is so large and the concentrations involved so small, that one may confidently identify the change in E_0 with a change in χ potential.

Charge and Potential of the Reversible Double Layer

Next, we shall consider the reversible double layer. The galvanic cell which was indispensable in the polarizable case could be omitted here, because the double layer is not supposed to be influenced by a certain amount of electricity passing through it. We might, therefore, study the double layer of AgI in an aqueous suspension without any electrical attachment whatever. The advantage of using the cell described above lies in underlining the analogy between the two systems considered.

The emf of the AgI cell can as in the case of Hg be divided into several potential jumps; i. e., Ag|AgI, AgI|solution, the diffusion potential, saturated KCl|Hg and Hg|Ag. Of these only the one at the AgI|solution interface and the diffusion potential are variable, and as with the Hg case there are many variations of the total potential which can be ascribed nearly exclusively to variations at the boundary between AgI and solution. When the solution contains a certain amount of electrolytes, say in a concentration of 0.1 N or higher, the concentration of Ag^+ or I^- ions can be changed by several decades without practically influencing the total amount of electrolyte.³ These changes in Ag^+ or I^- ions will therefore not affect the diffusion potential, but the potential difference between AgI and solution will vary according to the Nernst equation. In these circumstances

$$dE = d\Delta\phi = \frac{RT}{F} d \ln a_{\text{Ag}^+} = -\frac{RT}{F} d \ln a_{\text{I}^-}. \quad (6)$$

The notion of *charge* of the double layer on AgI is less obvious than that on Hg. Experimentally we can only determine adsorption of salts on the phase boundary, and it seems artificial to assign one of the ions to the solid phase and the other to the solution. Nevertheless of all the ions present in the solution Ag^+ and I^- take a very special position. Only salts containing Ag^+ or I^- ions can modify the potential difference according to eq (6). They appear to be more strongly adsorbed than other salts. They are the only ions which can be incorporated into or withdrawn from the lattice, and the good reversibility of the AgI electrode proves that this process runs easily. It seems reasonable, therefore, to assume that adsorbed Ag^+ or I^- ions are incorporated in the lattice and that all the other ions remain in the solution phase.

For double layers of the reversible type on other substances, analogous suppositions about the charge should be made. Reversibility means that the transition of the potential determining ions from the lattice to the solution and *vice versa* is unhampered. The charge of the solid phase arises therefore from the adsorption of these ions (e. g., Ag^+ and halide ions on silver halides; OH^- ions, H^+ ions and metal ions on oxides and hydroxides; metal ions and electrons on metals; etc.).

³ The solubility product of AgI is only 10^{-16} .

The charge density of the double layer on AgI is then

$$\sigma = e(\Gamma_{\text{Ag}^+} - \Gamma_{\text{I}^-}), \quad (7)$$

where Γ_{Ag^+} and Γ_{I^-} represent the number of ions adsorbed per square centimeter.

First, this hypothesis defines a *zero point of charge* which can be used as a point of reference for the double layer potential. According to different methods [6, 7] this zero point of charge is found in aqueous solutions at a silver ion concentration of $10^{-5.6} N$, thus rather asymmetrically, as the point of equivalence is at $c_{\text{Ag}^+} = c_{\text{I}^-} = 10^{-8} N$.

Second, adsorption isotherms for Ag^+ or I^- can now be converted with the help of (6) and (7) into relationships between charge density σ and double layer potential D .

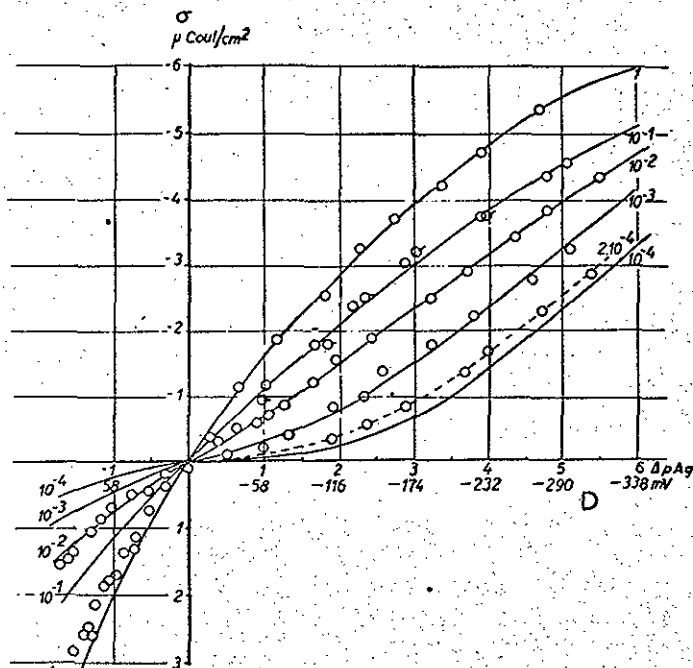


FIGURE 22.3. Adsorption of NaI and AgClO_4 or AgNO_3 on AgI expressed as charge per square centimeter against the double-layer potential D in aqueous solutions. According to eq (3.6) there is a direct relation between D and the p_{Ag} ($= -\log C_{\text{Ag}^+}$) of the solution. E. L. Mackor, Rec. trav. chim. (1952.; J. A. W. Van Laar, thesis, Utrecht).
 O, Points in NaClO_4 solution, \circ , points in 0.1 N in NaNO_3 solution. The drawn curves refer to measurements by J. A. W. Van Laar in KNO_3 - NaNO_3 , 1:7 (Thesis, Utrecht).

For illustration a number of such σ - D relationships are given in figure 22.3.

It should be realized, however, that the choice of eq (7) for the charge density cannot be a universal one. As soon as Ag^+ or I^- play a part in formation of the solution side of the double layer, they will form a part of the analytically determined adsorption Γ , without giving rise to a charge of the AgI. Suppose, for instance, that in the zero point of charge (obtained by a suitable solution of AgNO_3) more AgNO_3 is added to the solution. The surface potential will become

more positive according to (6), silver ions will be adsorbed and charge the surface, but at the same time some silver ions in the solution will be pushed away from the surface by electrostatic forces. Consequently,

$$\sigma > e(\Gamma_{\text{Ag}^+} - \Gamma_{\text{I}^-}). \quad (8)$$

An even more extreme case is formed by a mixture of pure AgI and pure water. We do not have available any means to determine an adsorption in this case, so $\Gamma = 0$ but as the solution contains equivalent amounts of Ag^+ and I^- and the equivalence point and the zero point of charge are not coincident the surface will be charged by I^- ions, which are compensated in the solution by Ag^+ .

Equation (7) as a means of defining the charge density of the surface can therefore be applied only when a sufficient excess of ions is present in the solution so that the part of the Ag^+ or I^- in the solution side of the double layer is negligible. If this is not the case, more detailed knowledge about the structure of the double layer is necessary to determine σ from the analytical adsorption of Ag^+ and I^- ions.

Free Energy of the Double Layer

A phase boundary can be considered to be the seat of a certain amount of free energy and this surface free energy is in part due to the presence of a double layer. When specific adsorption is absent, the free energy G_s of the double layer can be described by the Lippmann relation:

$$\frac{\partial G_s}{\partial D} = -\sigma \quad (9a)$$

or

$$G_s = G_s(\sigma = 0) - \int \sigma dD. \quad (9b)$$

Now it is evident that the free energy of the phase boundary is a completely determined quantity and its value cannot be influenced by uncertainties that may be present in the quantities σ or D . An analysis of the thermodynamics leading to the Lippmann relation is therefore necessary. It leads to the conclusion that for the polarizable interface

$$\frac{\partial G_s}{\partial E_{\text{cell}}} = -\sigma \quad (10)$$

and for the reversible interface

$$\frac{\partial G_s}{\partial \mu_{\text{AgNO}_3}} = -(\Gamma_{\text{Ag}^+} - \Gamma_{\text{I}^-}), \quad (11)$$

where μ_{AgNO_3} is the thermodynamic potential of AgNO_3 . The relations (10) and (11) contain only measurable quantities and are therefore free from the ambiguities mentioned above.

The change in free energy G of the polarizable cell (b) can at constant temperature, pressure and composition be represented by

$$dG = E_{\text{cell}} dQ + G_s d\omega$$

where Q is the charge flowing through the cell, G_s the free energy of the interface per cm^2 and ω the interface between Hg and solution.

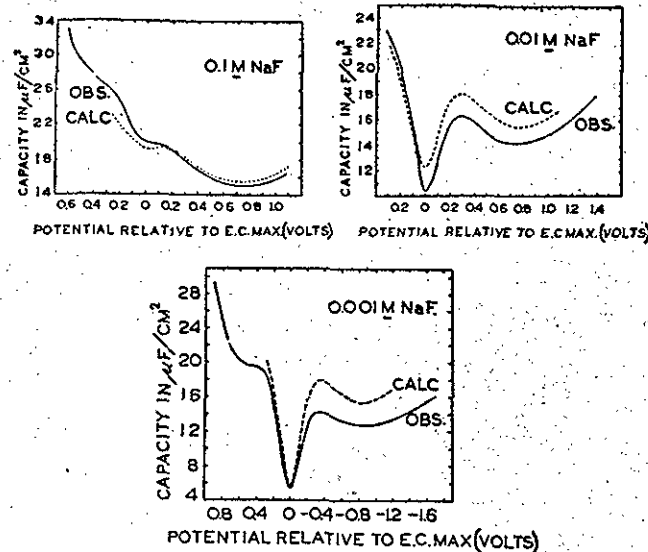


FIGURE 22.4. Differential capacity of the double layer calculated by Grahame. The capacity of the nondiffuse part of the double layer is taken from figure 22.6.

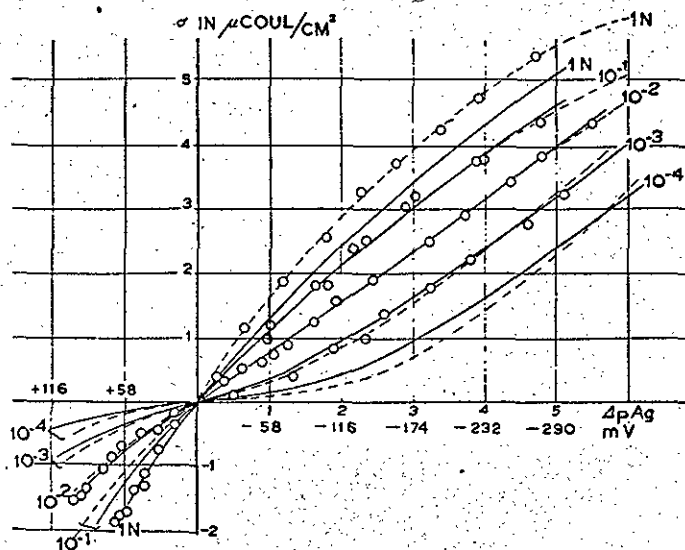


FIGURE 22.5. Comparison of experimental and calculated relations between charge and potential. Capacity of the molecular condenser taken from figure 22.7. Superficial charge σ against double layer potential: -----, experimental: ————, calculated.

Subtracting $d(E_{\text{cell}} \cdot Q)$ from both sides and applying a well-known property of a total differential, we find

$$d(G - E_{\text{cell}} Q) = -Q dE_{\text{cell}} + G_s d\omega$$

$$\left(\frac{\partial G_s}{\partial E_{\text{cell}}}\right)_{\omega} = -\left(\frac{\partial Q}{\partial \omega}\right)_E = -\sigma. \quad (10)$$

The change in free energy of a suspension of AgI in water containing AgNO₃ and of course a slight amount of dissolved AgI can be expressed, neglecting the dissociation of the water which is immaterial to our problem, at constant temperature and pressure by $dG = \mu_{\text{H}_2\text{O}} dn_{\text{H}_2\text{O}} + \mu_{\text{Ag}^+} dn_{\text{Ag}^+} + \mu_{\text{I}^-} dn_{\text{I}^-} + \mu_{\text{NO}_3^-} dn_{\text{NO}_3^-} + G_s d\omega$. Subtracting $d(\mu_{\text{Ag}^+} n_{\text{Ag}^+} + \mu_{\text{I}^-} n_{\text{I}^-} + \mu_{\text{NO}_3^-} n_{\text{NO}_3^-})$ from both sides, applying the condition of electroneutrality, $n_{\text{Ag}^+} = n_{\text{I}^-} + n_{\text{NO}_3^-}$, the condition of saturation with AgI, $\mu_{\text{Ag}^+} + \mu_{\text{I}^-} = \text{const.}$ and the equation $\mu_{\text{Ag}^+} + \mu_{\text{NO}_3^-} = \mu_{\text{AgNO}_3}$ we obtain $d(G - \mu_{\text{Ag}^+} n_{\text{Ag}^+} - \mu_{\text{I}^-} n_{\text{I}^-} - \mu_{\text{NO}_3^-} n_{\text{NO}_3^-} = \mu_{\text{H}_2\text{O}} dn_{\text{H}_2\text{O}} - (n_{\text{Ag}^+} - n_{\text{I}^-}) d\mu_{\text{AgNO}_3} + G_s d\omega$ and consequently

$$\left(\frac{\partial G_s}{\partial \mu_{\text{AgNO}_3}}\right)_{\omega, n_{\text{H}_2\text{O}}} = -\left[\frac{\partial(n_{\text{Ag}^+} - n_{\text{I}^-})}{\partial \omega}\right]_{n_{\text{H}_2\text{O}}, \mu_{\text{AgNO}_3}, \mu_{\text{H}_2\text{O}}} = -(\Gamma_{\text{Ag}^+} - \Gamma_{\text{I}^-}). \quad (11)$$

Interpretation of Charge and Potential of the Double Layer

After having shown how charge and potential of the double layer are obtained it is necessary to indicate how they may be interpreted.

With a double layer on a metal, the charge on the metal side is a surface charge. The charge in the solution, which is carried by ions is a space charge the extension of which is governed by the opposing tendencies of diffusion and electrical attraction. With double layers on other solid substances the charge of the solid phase is usually assumed to be a surface charge although recently Grimley and Mott [18] suggested that this charge may also have the character of a space charge. Whatever the situation near the interface may be, it will be clear that the structure of the double layer far from the interface can be described by using macroscopic properties of the phases as is done in Gouy's [9] and Chapman's [10] theory of the diffuse double layer. The uncertainties about the detailed structure near the phase boundary may be avoided by the conception of the "molecular condenser", introduced by Stern [11]. This molecular condenser also serves to correct for some all too obvious deviations from ideal behavior of the solutes near the interface.

To show the extent the Gouy-Stern theory may explain experimental data, we give a few results obtained by Grahame [12] for the double layer between Hg and solutions of NaF and results obtained by Mackor [13] and the writer for the double layer on AgI. For the first, a comparison is made between measured and calculated capacities of the double layer, in the second experimental and calculated surface charges are shown as a function of the double layer potentials. For both the double layer was represented by a diffuse Gouy-Chapman layer, followed immediately by a molecular condenser. The potential in the diffuse layer was assumed to obey the Poisson-Boltzmann equation

$$\nabla^2 \psi = -\frac{4\pi}{\epsilon} \sum_i n_i z_i e \exp(-z_i e \psi / kT)$$

where ∇^2 is the Laplace operator, ϵ the dielectric constant of the solution, n_i the ionic concentration and z_i the ionic valency. The capacity of the molecular condenser was assumed to be a certain function of the charge of the double layer as shown in the figures 22.6 and 22.7.

Summarizing, one finds that the charge of the double layer and the extra potential difference it superimposes upon the inaccessable potential difference χ existing already between the uncharged phases are known.

Theory explains this extra potential difference by localizing part of it as a diffuse double layer in the solution phase, possibly another

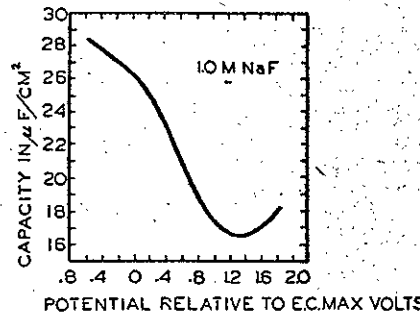


FIGURE 22.6. Differential capacity of molecular condenser on mercury derived from the experimental curve at 1.0 M NaF and used to calculate the capacities at lower concentrations of NaF (see fig. 22.4).

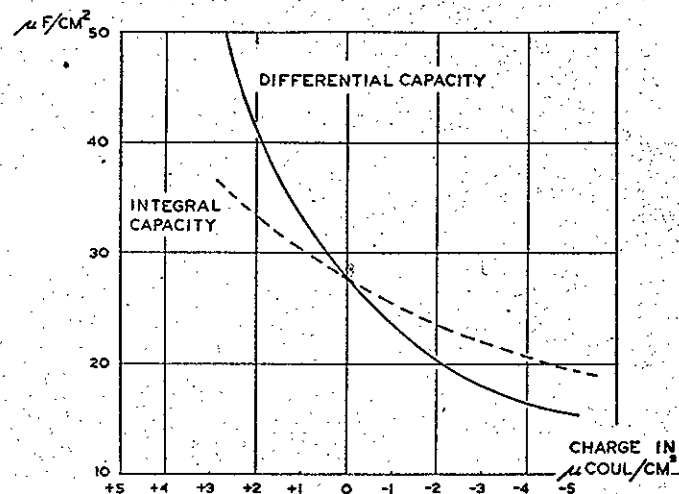


FIGURE 22.7. Capacity of molecular condenser on silver iodide used to calculate the curves of figure 22.5.

part as a diffuse layer in the second phase and a third part somewhere near the phase boundary. For this third part it is assumed only that the potential difference is completely determined by the charge. So both in the empirical and theoretical approach, detailed statements on the potential difference between different phases are avoided as they should be.

Can the χ Potential in Principle be Known?

As there seems to be no direct experiment which can lead to a knowledge of the χ potential, it may be asked whether this notion should not be completely eliminated from our considerations.

The present writer answers this question in the negative. In the first place, to avoid speaking of a potential difference between phases would force us to clumsy and unnecessary circumlocutions. Moreover, although we do not yet possess the means of determining the χ potential it is a well defined quantity. If we were better able to handle the wave equation it would be possible to solve the problem of the distribution of particles and charges in the region of the phase boundary and hence the average potential at every point of space should be determined.

Although in each phase this average potential is a very variable function of phase, it could be averaged over large enough regions of the phase and thereby give a value for the potential of the phase.

Electrokinetics and the ζ Potential

A different method of attack on the problem of double layer is found in electrokinetic experiments, wherein shearing motions of the double layer along the phase boundary are studied. This subject, which of necessity is concerned with irreversible processes, is more difficult than the equilibrium situation. Even if we disregard the possible influence of the roughness of the phase boundary [14], the uncertainty about values of viscosity and dielectric constant in the double layer introduces uncertainties in interpretations of electrokinetic effects.

The basic equation for electro-osmotic velocity along a plane wall formulates the equality of the force on the electric charge and the viscous drag of the liquid:

$$\frac{d^2v}{dz^2} = -\rho E = \frac{\epsilon}{4\pi} \frac{d^2\psi}{dz^2} E, \quad (12)$$

where z is the coordinate perpendicular to the phase boundary, v the velocity of the liquid, ψ the potential in the double layer and E the field strength along the phase boundary.

Usually the viscosity and the dielectric constant are considered to be constant up to a plane, where shearing just begins to be possible. Integration of eq (12) leads then to the Helmholtz-Smoluchowski equation:

$$\frac{v}{E} = \frac{\epsilon \zeta}{4\pi \eta}, \quad (13)$$

where v is the velocity of the liquid far from the phase boundary and ζ the potential at the plane of shear, the potential of the liquid far from the phase boundary being taken as zero.

When one drops the hypothesis of the constancy of ϵ and η the integration leads to

$$\frac{v}{E} = \frac{1}{4\pi} \int \frac{\epsilon}{\eta} d\psi. \quad (14)$$

Guggenheim [15] has remarked that it would be more natural to calculate $\int \epsilon d\psi$ or $\frac{1}{2}\pi \int \epsilon d\psi$ from electrokinetic experiments than to calculate ζ . However, when one doubts the constancy of ϵ , it seems consistent to doubt that of η as well and therefore turn to eq (14).

This equation, although correct, is rather unfruitful. It gives only some information on the zero point of charge, for, whatever the values

of ϵ and η , the integral in (14) is zero when $d\psi=0$, which implies zero charge of the double layer.

For double layers which are not extremely compact, that is for double layers in dilute solutions, the assumption of constant ϵ and η over the major part of the double layer seems justified. In these cases the ζ -potential may not only be calculated from (13), but it may be interpreted as the potential drop over a large part of the double layer in the solution. It is therefore reasonable to compare ζ with the total potential of the double layer and to expect ζ to be somewhat (or much) smaller than D . Such a comparison would become almost meaningless when electrokinetics are expressed through

$$\int \epsilon d\psi \text{ or } \int (\epsilon/\eta) d\psi.$$

Unfortunately the cases where D and ζ have both been determined on one and the same object are very rare and as far as modern accurate

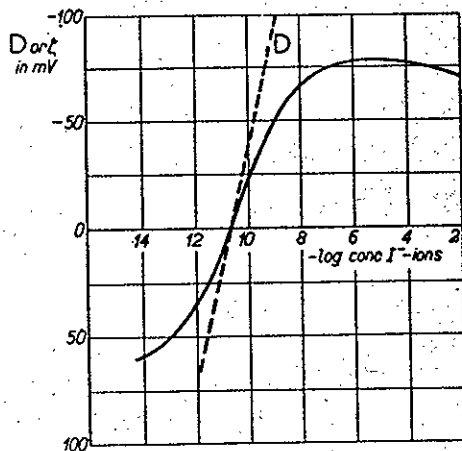


FIGURE 22.8. D and ζ of silver iodide against the logarithm of the I^- ion concentration in the solution.

work is concerned nearly restricted to some experiments on glass by Rutgers [16] and on AgI by Troelstra [17].

From experiments by Troelstra we derive figure 22.8, in which it is seen that the zero point of charge and that of electrokinetic motion coincide and that, at least near this zero, ζ seems to be a nearly constant fraction of D . For higher potentials it is difficult to derive reliable values of ζ from the electrophoretic velocity [18] although one would expect that with D continuously rising ζ would rise less and less because at high potentials the double layer gets more compressed and for the greater part in regions with high viscosity.

Turning to the theoretical interpretation of the structure of the double layer, one would expect ζ to resemble especially that part of D that, according to theory, is located in the liquid phase. Until now such comparisons have met with little success probably because adequate experimental material is lacking. It would be very much worth while to try to fill this gap in our knowledge.

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Discussion

DR. J. O'M. BOCKRIS, Imperial College of Science and Technology, London, England: I should like to congratulate Prof. Overbeek on his attitude towards this subject, because he is less pessimistic than some workers. Lange has also tried to make a more rational approach to the definition of potentials at a metal-solution interface. It is now possible to calculate the dielectric constant of the solution as a function of potential, and taking these revised values into account makes quite appreciable differences to the calculated charge in the diffuse layer.

DR. J. TH. G. OVERBEEK: I think you refer to the new calculation by Grahame.

DR. BOCKRIS: I am referring primarily to some calculations we have been doing recently (Bockris et al, Trans. Faraday Soc. **47**, 756 (1951).

DR. OVERBEEK: Well, of course it might affect the innermost parts of the double layer.

DR. BOCKRIS: The dielectric constant in the Helmholtz layer turns out to be a good way off the minimum saturation value, expect at very high electrode potentials. In the diffuse layer, the mean dielectric constant may be as low as 45.

DR. G. SCATCHARD, Mass. Institute of Technology, Cambridge, Mass.: Were you saying χ is independent of the $AgNO_3$ concentration?

DR. OVERBEEK: That was the χ between the $AgNO_3$ solution and the gas phase above the $AgNO_3$, and it was only dependent upon the $AgNO_3$ when its concentration came in the neighborhood of 1 eq/liter.

DR. SCATCHARD: What is the order of magnitude of conductance of AgI?

DR. OVERBEEK: These measurements are done on suspensions of fairly small particles. It may be they are less regularly formed than larger pieces and that their conductance is larger. We find, for

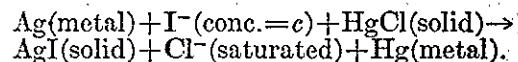
in magnitude, that the order of magnitude is 10^{-6} ohm⁻¹ cm⁻¹, perhaps somewhat lower. We know this is the order of magnitude because we have special difficulties in doing electrokinetic measurements on AgI, which indicate a conductance of the same order as that of distilled water. We cannot make a direct measurement of the conductance without treating the AgI so that it is not a representative sample.

DR. T. SHEDLOVSKY, Rockefeller Institute for Medical Research, New York, N. Y.: The AgI is not on the electrode as a continuous film?

DR. OVERBEEK: No, you can only determine the absorption of the AgI when the surface is very large. We use AgI as a fine suspension or as a colloidal solution. It is for simplicity that I have drawn the AgI to be present on the electrode but for the whole thermodynamics of the cell it is not essential for the AgI to be attached to the Ag electrode.

DR. SHEDLOVSKY: What is affecting the potential of the Ag electrode, absorption of the Ag or of the iodide?

DR. OVERBEEK: We can argue that the potential difference of the cell when it is reversible depends upon the cell reaction which apart from the process at the liquid junction is given by,



The emf of this cell changes only with changes of the concentration of I⁻ ions. The potential difference between Ag and AgI, both being solid substances with a given chemical composition, is constant. If I measure potential differences between Ag and Hg, I know that, apart from a constant, it is equal to the potential difference between Ag electrode and the solution, and consequently apart from another constant, to the potential difference between AgI and the solution. One can picture that most easily. That is what I have done on the blackboard by just interposing AgI between the Ag and the solution, but it is not necessary for the kind of measurement we have done. I think the simplification is not essential.

DR. SHEDLOVSKY: Isn't the function of AgI simply to fix the Ag ion activity and so make it an iodide electrode?

DR. OVERBEEK: I quite agree with you there; yes.

DR. J. V. PETROCELLI, The Patent Button Co., Waterbury, Conn.: As I see it, at present, we have a fairly good picture of the double layer at the Hg metal electrode. How are we going to picture, kinetically, the Ag electrode? In other words, Hg has these ions absorbed very close to it. Now, if you have a piece of Ag in the solution, what do you have on the surface, solid particles of AgI or Ag ions?

DR. OVERBEEK: You mean the silver electrode I have used in my experiment?

DR. PETROCELLI: Yes. Can the mechanisms you have described be applied to the metal? When we are talking about the double layer, we would like to see a picture of the orientation of the ions and their position on the metal also.

DR. OVERBEEK: I have tried to make not a picture of the double layer on the silver but on the silver iodide. The silver electrode only comes in as a means to bring electric charges in the form of Ag⁺ ions to or from the solution.