IV. ELECTROCHEMISTRY OF THE DOUBLE LAYER[1]

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§ 1. PROPERTIES OF THE DOUBLE LAYER THAT ARE OF INTEREST TO COLLOID SCIENCE

In chapter II it has been shown that the double layer is responsible for the stability of lyophobic colloids and governs the electrokinetic properties. In order to understand the electrokinetic properties, we shall have to know more or less explicitly the structure of the double layer, that is the location (or mean location) of the charge carriers building up the double layer and the distribution of charge and potential. The stability, on the other hand, asks for a comprehension of the forces, which arise when two or more double layers interact or, what comes to the same thing, of the free energy of a system of double layers.

As the properties of colloidal systems are very sensitive to additions of electrolytes, it will be necessary to investigate the influence of these additions on the double layer.

We shall see then, that many seemingly simple concepts like the charge and the potential of the double layer are in reality much more intricate and can only be defined with a certain approximation.

The double layer itself seems a well defined concept, but as it can only exist in conjunction with two phases with a certain extension, the free energy of the double layer has to be defined as a part of the free energy of that whole system of two phases, and it is not selfevident which part.

On the electrical side the charges are rather easy to visualize, but the potential again leads to difficulties because of the changing composition in the double layer. It is even impossible to estimate the potential difference between two different phases in a strict thermodynamic sense, although a calculation based on model considerations may be useful.

We shall therefore start with the classical result of thermodynamics and gradually build up our picture by paying attention to potentials and charges, relate their distribution in space to more or less elaborate models, and then check our picture on the experimental data that are available.

In this chapter IV we restrict the treatment to single double layers in equilibrium, postponing electrokinetics to chapter V and interaction of double layers to chapter VI.

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[1] The contents of this chapter have been extensively discussed between the author and G. H. JONKER, S. A. TROELSTRA, and E. J. W. VERWEY of *Philips' Research Laboratories*, Eindhoven.

§ 2. THERMODYNAMICS OF ADSORPTION

Consider two phases with a plane contact interface of A cm². The whole system consists of n_1 molecules of kind 1, n_2 molecules of kind 2 etc., but it is impossible to state exactly how many molecules of each kind belong to phase (1), how many to phase (2) and how many, if any, to the surface.

a. Surface tension and surface free energy

The interface is a seat of Gibbs free energy, G_s, which we shall define as the work necessary to enlarge the interface reversibly by 1 cm² at constant temperature and pressure and at constant amount of matter in the system.

$$G_s = \left(\frac{\partial G}{\partial A}\right)_{T,\, p,\, n_1, \ldots n_i, \ldots} \tag{1}$$

When the two phases are liquid or one liquid and one gas, the surface free energy can be measured directly and is numerically equal to the surface tension, γ.

b. Adsorption

In general one or more of the components of the system will be accumulated at the interface or, on the contrary, occur at the interface in smaller concentration than in the rest of the system. In extreme cases the concept of adsorption is rather simple. In the adsorption of a dye from a solution on a fabric the amount adsorbed is defined and may be measured as the amount of solute withdrawn from the solution by the adsorbent. In less extreme cases the definition of adsorption is a matter of careful consideration and as we shall see also of a certain arbitrariness. Consider a two phase system consisting of ether, water and a solute, soluble in both phases. Is there now adsorption of the solute at the interface? And perhaps of ether and water too?

Gibbs [1], the founder of the theories of adsorption, considering this difficulty, saw that adsorption can only be defined relative to one of the components of the system which is considered to be not adsorbed. In detail this idea can be developed in different ways [2] which, however, differ more from a didactic than from an essential point of view.

Applying this idea to the case just mentioned of ether (E), water (W) and a solute (S), we may analyse both phases and determine the concentrations of E, W and S in the two phases. Assuming now that the whole system can be described as two homogeneous phases of masses $M^{(1)}$ and $M^{(2)}$ and a surface layer of mass $M^{(s)}$ the constancy of E, W and S in the whole system leads to three equations

$$\left.\begin{aligned} M^{(1)}\, C_E^{(1)} + M^{(2)}\, C_E^{(2)} + M^{(s)}\, C_E^{(s)} &= M_E \\ M^{(1)}\, C_W^{(1)} + M^{(2)}\, C_W^{(2)} + M^{(s)}\, C_W^{(s)} &= M_W \\ M^{(1)}\, C_S^{(1)} + M^{(2)}\, C_S^{(2)} + M^{(s)}\, C_S^{(s)} &= M_S \end{aligned}\right\} \tag{2}$$

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[1] See *The Scientific Papers of* J. Willard Gibbs, Vol I, London 1906, p. 219ff.

[2] See E. A. Guggenheim and N. K. Adam, *Proc. Roy. Soc.* London, A 139 (1933) 218; J. E. Verschaffelt, *Bull. classe sci Acad. roy. Belg.*, (4) 22 (1936) 373, 390, 402; E. A. Guggenheim, *Trans. Faraday Soc.*, 36 (1940) 397.

In these three equations there are six unknowns, *viz.*, $M(^1)$, $M(^2)$, $M(^s)$ and the three surface concentrations. *Assuming* now — and this is an arbitrary choice — that neither ether nor water are adsorbed so that $C_E(^s) = C_W(^s) = 0$, the equations may be solved for the product $M(^s)C_S(^s)$, which means, that the total mass of the solute in the interface may be calculated. Generally when n components are present, the surface excesses of n-2 components can be calculated. Usually this surface excess is divided by the macroscopic area of the surface leading to the specific surface excess Γ_i.

Usually the choice of the components for which zero adsorption is assumed is not difficult. One takes the major components of the two phases. But when at least one of the two phases is a concentrated solution, the arbitrariness of this assumption is clearly felt.

There is a close relationship between the surface excesses Γ_i and the free energy of the surface G_s. An obvious way to arrive at this relation is to start from the differential of the GIBBS free energy of the whole system

$$dG = -S\,dT + V\,dp + G_s\,dA + \sum_{i=1}^{r} \mu_i\,dn_i \tag{3}$$

In this relation the interface is assumed to be plane which implies equality of pressure throughout both the homogeneous parts of the system. The chemical potentials μ_i are provisionally understood as chemical potentials of uncharged components. (For a consideration of ions as components of the system see § 3 a, p. 119).

A system of r independent components, consisting of two phases has r degrees of freedom, and, in order to describe the system completely, three other variables are necessary to define the extension of the two phases and of the interface. So the r+3 variables of eq. (3) are just sufficient to describe the system.

Several other sets of variables are possible and we will choose one which contains as many intensive variables (T, p, G_s, μ_i) as possible, leaving only three extensive variables to define the total amount of the two phases and the extent of the interface. A suitable choice for the three extensive variables is A, n_1 and n_2, where 1 and 2 are preferably (though not necessarily) major constituents of phase (1) and phase (2). By subtracting $d\,(\sum_{i=3}^{r} \mu_i\,n_i)$ from both sides of eq. (3) this equation is transformed into

$$d\,(G - \sum_{i=3} \mu_i n_i) = -S dT + V dp + G_s dA + \mu_1\,dn_1 + \mu_2\,dn_2 - \sum_{i=3}^{r} n_i\,d\,\mu_i \quad \ldots (4)$$

Using the fact that (4) is a total differential, we can derive immediately the very important GIBBS adsorption equation [1]

$$-\left(\frac{\partial G_s}{\partial \mu_i}\right)_{T,\,p,\,\mu_3\ldots\,\mu_{i-1},\,\mu_{i+1}\ldots\,\mu_r} = \left(\frac{\partial n_i}{\partial A}\right)_{T,\,p,\,n_1,\,n_2\,\mu_1\,\ldots\mu_r} \tag{5}$$

relating the change of interfacial free energy with the chemical potential of one of the

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[1] Formally, eq. (4) demands that in the partial differentiation of G_s with respect to μ_i also A, n_1 and n_2 are kept constant. G_s, however, as an intensive variable, does not depend on these extensive parameters. In the differentiation of n_i with respect to A it is necessary to keep T, p, and (r—2) chemical potentials constant. As the state of the system is however completely determined by r variables, this implies that μ_1 and μ_2 do not change either.

components to the specific surface excess of this component. Indeed the right hand side of eq. (5) represents the amount of component i to be added to the system when the interface is increased by one cm². The comparative arbitrariness of this definition of adsorption is reflected in the requirement of constancy of n_1 and n_2, which implies that these are the two components which are considered to be not adsorbed, in accordance with our more analytical considerations of page 117.

The surface excess as defined by the right hand side of eq. (5) will be denoted [1] as Γ_i

$$\left(\frac{\partial n_i}{\partial A}\right)_{T,\, p,\, n_1,\, n_2,\, \mu_1 \ldots\ldots \mu_r} = \Gamma_i \tag{6}$$

For dilute solutions $\mu_i = \mu_i{}^0 + RT \ln c_i$. In that case the adsorption isotherm (5, 6) may be written

$$\Gamma_i = -\frac{c_i}{RT}\,\frac{\partial G_s}{\partial c_i} \tag{7}$$

expressing (as eq. (5) already does) that a solute which lowers the surface tension is positively adsorbed and one which increases the surface tension is repelled from the surface.

We shall use eq. (5) and (6) frequently in the form (8)

$$(\mathrm{d}G_s)_{T,\,p} = -\sum_{3}^{r} \Gamma_i\,\mathrm{d}\mu_i \tag{8}$$

or its integrated form

$$G_s = G_s(\mu_1{}^\circ, \mu_2{}^\circ, \ldots \mu_r{}^\circ) - \left(\int_{\mu_3{}^\circ}^{\mu_3} \Gamma_3\,\mathrm{d}\mu_3\right)_{\mu_4{}^\circ \ldots \mu_r{}^\circ} - \left(\int_{\mu_4{}^0}^{\mu_4} \Gamma_4\,\mathrm{d}\mu_4\right)_{\mu_3,\, \mu_5{}^\circ \ldots \mu_r{}^\circ} - \text{etc.} \tag{9}$$

The numerical identity of surface tension γ and surface free energy G_s has already been mentioned in § 2 a. The surface pressure p, an important variable in spreading experiments, can be considered as the difference between the surface tension of the solvent and the solution

$$p = \gamma_0 - \gamma$$

and can thus be treated in the same scheme. As excellent monographic presentations of monolayers and spreading experiments exist, they will be treated here only incidentally (See § 7 b, p. 167).

§ 3. ON POTENTIALS IN THE DOUBLE LAYER

Two of the most important ways of treating the electrochemical aspects of surface phenomena are:

a. the application of an external potential difference to a system containing an electrode with a *completely polarizable* interface. In this way the potential difference

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[1] This definition is not exactly the same as the most common convention, introduced by GIBBS and used by many other authors. In this convention the total *volume* of the two phases and the amount of one component are kept constant in the differentiation. This implies, however, that in eq. (5) a $\partial G_s / \partial \mu_i$ is obtained in which the pressure is varied. (See E. A. GUGGENHEIM, *l.c.*).

between this electrode and the solution in which it dips may be altered (within certain limits) at will.

b. the incorporation of the interface in a *completely reversible* galvanic cell of which the E.M.F. may be changed by changing the composition of the phases (or one of them) meeting at the interface.

In this section we shall correlate these potential differences with electrical phenomena at the interface.

a. The completely polarizable electrode

The most extensively studied system of this type is the interface between mercury and an aqueous solution. It may serve as an example for other systems of this kind.

Consider the cell represented schematically in Fig. 1 containing a solution, a mercury electrode (area of interface = A) and a hydrogen electrode saturated with one atmosphere of hydrogen. The hydrogen electrode is assumed to be ideally reversible and of so small surface that its adsorption may be neglected.

The mercury electrode is assumed to be completely polarizable, that is no ions from the solution can be discharged at it (the concentration of Hg_2^{++} ions is negligible). Consequently any charge carried to it by the applied potential difference E remains on the mercury.

Several authors, for instance FRUMKIN[1], have treated the mercury electrode as a reversible one and have explained its polarization as a concentration polarization in the solution. When a negative potential is applied to the mercury, mercury ions are discharged at the surface until their concentration near the interface is so low as to correspond to the applied potential. Anyhow as the concentration of mercury ions is low, this discharge requires only a very small transport of electricity which may be neglected. Given the fact, however, that the mercury electrode may be made 2 volts more negative than the calomel electrode, the concentration of Hg_2^{++} ions would have to vary from about 10^{-20} to 10^{-90} and it seems scarcely real to consider concentrations of less than one atom in the universe as being able to determine a potential jump between two phases, although this kind of treatment may (and indeed must) lead to the correct equation.

The polarizability of the mercury implies, that the potential difference E and the charge on the mercury Q appear as a new set of variables in the thermodynamics of this system. The differential of the GIBBS free energy may now be represented by (compare eq. (3) p. 117).

$$\mathrm{d}G = -S\,\mathrm{d}T + V\,\mathrm{d}p + G_s \mathrm{d}A + \sum_{\alpha} \sum_{i=1}^{r} \eta_i^{\alpha}\,\mathrm{d}n_i^{\alpha} + E\,\mathrm{d}Q \tag{10}$$

where G_s is the free energy per cm² of the interface mercury/solution and η_i^{α} the electrochemical potential of the component i in the phase α.

The electrochemical potential is defined by the relation

$$\eta_i^{\alpha} = \mu_i^{\alpha} + z_i e\,\varphi^{\alpha} \tag{11}$$

in which z_i is the valency of component i and φ^{α} the internal (or GALVANI) potential (see § 3d, p. 124) of phase α.

As there is no complete equilibrium between the phases there might arise some doubt as to the

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[1] A. FRUMKIN, *Z. physik. Chem.*, 103 (1923) 55.

values of η_i in the interface. The complete polarizability of the interface implies, however, that no ions can cross it, so that the attribution of ions to one or the other of the phases is given by the initial conditions.

From analogy with eq. (8) one might immediately write down the value of the differential of G_s

$$dG_s = -\sum_{i=3}^{r} \Gamma_i \, d\,\mu_i - \sigma \, d\, E_{surf} \tag{12}$$

where σ is the charge on the mercury per cm² and E_{surf} the (GALVANI) potential difference between mercury and solution. As eq. (12), however, introduces separate ion activities and a potential difference between two phases which cannot be determined without ambiguity, a complete derivation of eq. (12) is necessary.

In this derivation we will find a precursor of eq. (12), *viz.*, eq. (21) p. 122 where dG_s is expressed in chemical potentials of *salts* and in the *total* potential difference applied to the cell from Fig. 1. This equation remains completely within the realm of thermodynamics, and eq. (12) should then be considered as another way of describing eq. (21) which, although less positive than eq. (21) has the advantage of being easily applicable to models of the interface.

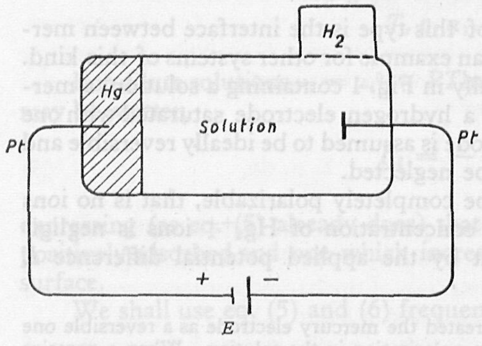

Fig. 1. Cell, containing an interface mercury-solution, which is assumed to be completely polarizable, and a very small completely reversible hydrogen electrode.

As the passage of an amount of electricity Q to the mercury surface implies the discharge of $\frac{Q}{e}$ hydrogen ions on the Pt-electrode the meaning of dn_{H^+} and n_{H^+} has to be considered. These quantities have the meaning of the amount of H^+ — ions introduced into or present in the system, neglecting the electrical process. The *total* amount of hydrogen ions in the solution and its differential are therefore given by

$$\left.\begin{aligned} n^{\text{total}}_{H^+} &= n_{H^+} - \frac{Q}{e} \\ dn^{\text{total}}_{H^+} &= dn_{H^+} - \frac{dQ}{e} \end{aligned}\right\} \tag{13}$$

Moreover the electroneutrality of the whole system demands that

$$\Sigma' z_+ n_+ + n^{\text{total}}_{H^+} + \frac{Q}{e} = \Sigma \, z_- n_- \tag{14}$$

where n_+ represents all the cations except H^+ and n_- the amount of anions.

With the help of eq. (13) and (14) dn_{H^+} can be eliminated from eq. (10):

$$\begin{aligned} dG = -S\,dT + V\,dp + G_s\,dA + \sum_{\substack{\text{neutral}\\ \text{compon.s}}} \mu_i\,dn_i + \Sigma'(\eta_+ - z_+\,\eta_{H^+})\,dn_+ + \\ + \Sigma(\eta_- + z_-\,\eta_{H^+})\,dn_- + E\,dQ \end{aligned} \tag{15}$$

Subtracting from both sides the differential of $\sum\limits_{3}^{r} \mu_i\, n_i$ over neutral components, except $1 =$ water and $2 =$ mercury, and of $\Sigma' (\eta_{+} - z_{+} \eta_{H^+})\, n_{+} + \Sigma (\eta_{-} + z_{-} \eta_{H^+})\, n_{-} + EQ$ one finds

$$\mathrm{d}\,\Big(G - \sum_{3}^{r} \mu_i\, n_i - \Sigma' (\eta_{+} - z_{+} \eta_{H^+})\, n_{+} - \Sigma (\eta_{-} + z_{-} \eta_{H^+})\, n_{-} - EQ\Big) = - S\, \mathrm{d}T +$$

$$+ V\, \mathrm{d}p + G_s\, \mathrm{d}A + \mu_1\, \mathrm{d}n_1 + \mu_2\, \mathrm{d}n_2 - \sum_{3}^{r} n_i\, \mathrm{d}\,\mu_i - \Sigma' n_{+}\, \mathrm{d}\,(\eta_{+} - z_{+}\, \eta_{H^+}) - \Sigma n_{-}\, \mathrm{d}\,(\eta_{-} +$$

$$+ z_{-}\, \eta_{H^+}) - Q\, \mathrm{d}E \tag{16}$$

Now it is possible to combine the electrochemical potentials of the separate ions to the thermodynamic potentials of the salts (or acids or bases), which represent the independent variables of the system by relations of the type

$$\mu_{H_zA} = z_A\, \mu_{H^+} + \mu_A = z_A\, \eta_{H^+} + \eta_A \tag{17}$$

where A is a negative ion.

Eq. (16) becomes then

$$\mathrm{d}\,\Big(G - \sum_{3}^{r} \mu_i\, n_i - \Sigma' (\mu_{+A} - z_{+}\, \mu_{HA})\, n_{+} - \Sigma\, (\mu_{-H})\, n_{-} - EQ\Big) = - S\, \mathrm{d}T + V\, \mathrm{d}p +$$

$$+ G_S\, \mathrm{d}A + \mu_1\, \mathrm{d}n_1 + \mu_2\, \mathrm{d}n_2 - \sum_{3}^{r} n_i\, \mathrm{d}\,\mu_i - \Sigma' n_{+}\, \mathrm{d}\,(\mu_{+A} - z_{+}\, \mu_{HA}) - \Sigma\, n_{-}\, \mathrm{d}\,\mu_{-H} -$$

$$- Q\, \mathrm{d}E \tag{18}$$

in which for convenience A is chosen to be monovalent (not hydroxyl).

As (18) is a complete differential it follows that:

for neutral components
$$\left(\frac{\partial G_S}{\partial \mu_i}\right)_{T,\, p,\, E,\ \text{all } \mu\text{'s except } \mu_1,\, \mu_2,\, \mu_i} = - \left(\frac{\partial n_i}{\partial A}\right)_{T,\, p,\, E,\ \text{all } \mu'\text{s},\, n_1,\, n_2} \tag{19a}$$

for all cations except H+
$$\left(\frac{\partial G_S}{\partial \mu_{+A}}\right)_{T,\, p,\, E,\ \text{all } \mu\text{'s except } \mu_1,\, \mu_2,\, \mu_{+A}} =$$

$$= - \left(\frac{\partial n_{+}}{\partial A}\right)_{T,\, p,\, E,\ \text{all } \mu\text{'s},\, n_1,\, n_2} \tag{19b}$$

for all anions except A
$$\left(\frac{\partial G_S}{\partial \mu_{-H}}\right)_{T,\, p,\, E,\ \text{all } \mu\text{'s except } \mu_1,\, \mu_2,\, \mu_{-H}} =$$

$$= - \left(\frac{\partial n_{-}}{\partial A}\right)_{T,\, p,\, E,\ \text{all } \mu\text{'s},\, ,n_1,\, n_2} \tag{19c}$$

for AH
$$\left(\frac{\partial G_s}{\partial \mu_{AH}}\right)_{T,\, p,\, E,\ \text{all } \mu\text{'s except } \mu_1,\, \mu_2,\, \mu_{AH}} =$$

$$= - \left(\frac{\partial\, (n_A - \Sigma' n_{+}\, z_{+})}{\partial A}\right)_{T,\, p,\, E,\ \text{all } \mu\text{'s},\, n_1,\, n_2} \tag{19d}$$

and finally

$$\left(\frac{\partial G_S}{\partial E}\right)_{T,\, p,\ \text{all } \mu\text{'s}} = - \left(\frac{\partial Q}{\partial A}\right)_{T,\, p,\, E,\ \text{all } \mu\text{'s}\ (n_1,\, n_2)} = - \sigma \tag{20}$$

where σ is the surface charge per cm². This relation (20) is known as the LIPPMANN relation.

At constant temperature and pressure dG_S can be represented by

$$dG_S = -\sum_3^r \Gamma_i d\mu_i - \Sigma' \Gamma_+ \, d\mu_{+A} - \sum_{-A}' \Gamma_- \, d\mu_{-H} -$$

$$-(\Gamma_A - \Sigma' z_+ \Gamma_+)\, d\mu_{AH} - \sigma\, dE \tag{21}$$

in which every Γ is defined by a relation of the kind

$$\Gamma_i = \left(\frac{\partial n_i}{\partial A}\right)_{T,\, p,\, E,\, \mu\text{'s},\, n_1,\, n_2}$$

This eq. (21) is sufficient to describe the capillary electric phenomena at constant T and p, but the confrontation with a model makes it desirable to rewrite it using again the electrochemical potentials of the ions. At the same time we define Γ_{H^+} in such a way that the surface is electroneutral

$$\Sigma' \Gamma_+ z_+ + \Gamma_{H^+} + \frac{\sigma}{e} = \Sigma z_- \Gamma_- \tag{22}$$

We find then

$$dG_S = -\sum_3^r \Gamma_i \, d\mu_i - \underset{\substack{\text{including} \\ H^+}}{\Sigma \Gamma_+ \, d\mu_+} - \Sigma \Gamma_- \, d\mu_- - \sigma\left(\frac{d\mu_{H^+}}{e} + dE\right) \tag{23}$$

As $\frac{d\mu_{H^+}}{e}$ just represents the change of the potential jump at the hydrogen electrode, $\frac{d\mu_{H^+}}{e} + dE$ equals dE_{surface}, the potential change over the surface in consideration. So finally we arrive at the very simple expression

$$dG_S = -\underset{\text{all uncharged and ionic components}}{\sum_3^r \Gamma_i \, d\mu_i} - \sigma\, dE_{\text{surf.}} \tag{24}$$

from which we must however remember that neither dE_{surface}, nor the chemical potentials μ_i are measurable separately although in many cases good estimates can be made.

b. The completely reversible electrode

Also in the case of the reversible electrode we will treat for concreteness a definite example for which we choose the silver — silver iodide electrode. Extension to other cases is then quite simple.

The reversible cell considered is represented in Fig. 2. It is formed by a silver — silver iodide electrode, a solution and a platinum electrode, saturated with hydrogen at one atmosphere. The reversible E.M.F. is given by E.

In contradistinction to the case of the completely polarizable electrode this E.M.F. is not a new variable of the system. It is completely determined by the composition of the phases present.

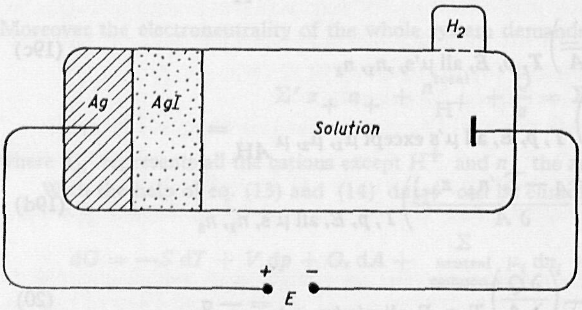

Fig. 2. Reversible cell containing an interface silver iodide -solution. The reversible E.M.F. of the cell is given by E.

At constant temperature and pressure the change in GIBBS free energy of the interface AgI-solution is given by eq. (8) applied to the ionic and neutral components of the system separately

$$(\mathrm{d}G_s)_{T,p} = -\underset{\substack{\text{neutral}\\ \text{components}}}{\sum_3} \Gamma_i\,\mathrm{d}\mu_i - \underset{\substack{\text{ionic}\\ \text{components}}}{\sum} \Gamma_i\,\mathrm{d}\mu_i \tag{25}$$

It is convenient to choose H_2O as the component 1. The choice of component 2 is left open for the moment. On the other hand the differential of the electromotive force of the cell is given by

$$\mathrm{d}E = -\frac{1}{e}\left(\mathrm{d}\eta_{\mathrm{H}^+} + \mathrm{d}\eta_{\mathrm{I}^-}\right) \tag{26}$$

By suitable combination of eq. (25) and (26) and the conditions of electroneutrality the relation between G_s, E and the composition of the solution can be given in a regorous thermodynamic form. We will, instead of doing this, immediately introduce the differential of the potential change over the interface AgI-solution which is equal to

$$\mathrm{d}E_s = -\frac{\mathrm{d}\mu_{\mathrm{I}}}{e} = \frac{\mathrm{d}\mu_{\mathrm{Ag}}}{e} \tag{27}$$

Introducing this relation into (25) we find

$$\mathrm{d}G_s = -\underset{\substack{\text{neutr.}\\ \text{comp.}}}{\sum} \Gamma_i\,\mathrm{d}\mu_i - e\,(\Gamma_{\mathrm{Ag}} - \Gamma_{\mathrm{I}})\,\mathrm{d}E_s - \underset{i \neq \mathrm{I},\,\mathrm{Ag}}{\sum} \Gamma_i\,\mathrm{d}\mu_i \tag{28}$$

When we assume, that the adsorbed silver- and iodide ions are incorporated in the lattice of AgI, whereas all other adsorbed ions belong to the aqueous phase, $e\,(\Gamma_{\mathrm{Ag}} - \Gamma_{\mathrm{I}})$ may be identified with the surface charge σ and eq. (28) transforms into (29) which is identical in form with eq. (24) for the completely polarizable surface

$$\mathrm{d}G_s = -\underset{\substack{\text{all uncharged and ionic com-}\\ \text{ponents except Ag}^+\text{ and I}^-}}{\sum_3^r} \Gamma_i\,\mathrm{d}\mu_i - \sigma\,\mathrm{d}E_s \tag{29}$$

A discussion of the case where part of the adsorbed Ag^+ and I^- ions are present in the aqueous phase will be given in section 4 f. 2, p. 140.

c. The interface oil - water

In a two phase system of an organic liquid ("oil") and an aqueous solution partition of the ionic components between the two phases generally occurs, and adsorption at the interface may be present. If such a system is in thermodynamic equilibrium and two identical reversible electrodes are brought into contact with the two phases no potential difference can be measured between the two electrodes. This is a consequence of the fact that a system in equilibrium can perform no work.

If the two reversible electrodes are not identical a potential difference is present but it is the same as that which would have been measured if the two electrodes had been in contact with the same solution. Consequently this potential difference cannot give any information on the oil-water interface.

Nevertheless with this set up or an equivalent one potential differences have been measured and they have been found to change for instance by the addition of a solute to one of the two phases or by letting a monolayer spread over the interface.

These potential differences must be non-equilibrium phenomena. They are therefore not permanent but decrease in a shorter or longer time to zero[1].

Introduction of the potential concept with respect to the oil-water interface in equilibrium is therefore dependent upon model considerations and we shall return to this matter in § 4 e, p. 137.

d. On double layer potentials

For the description of the potentials, which occur in our problems, we shall mainly follow the distinctions introduced by E. Lange[2].

For each phase one may distinguish (see Fig. 3) the outer or Volta potential, ψ, the inner or Galvani potential, φ, and the surface potential jump, χ, defined by

$$\chi = \varphi - \psi \tag{30}$$

For one phase the potentials φ and ψ are evidently determined by the accidental state of charge of the phase under consideration and as such are not important for physicochemical problems.

The differences of the Volta or the Galvani potentials between two phases in contact, however, are determined by the situation at the interface and it is these differences which enter in all considerations on the electrical state of the interface.

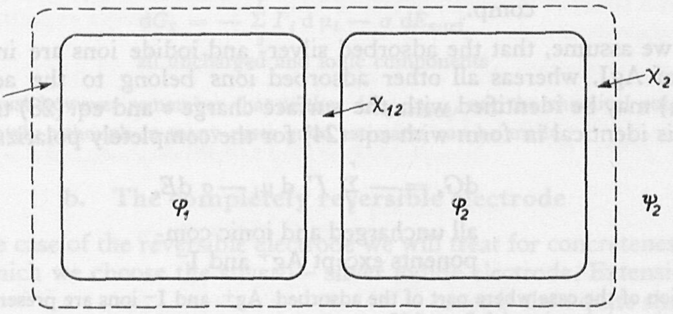

Fig. 3. Volta-potentials, ψ, Galvani-potentials, φ, and surface potential jumps χ in a two phase system.

The Volta potential, being the potential just outside the phase considered, is a well-defined electrical magnitude and can be measured in different ways, for instance by bringing a radioactive probe into the neighbourhood of the phase. By carrying out such a measurement near the surfaces of two phases in contact, the Volta potential difference, $\triangle \psi$, can be determined. As this Volta potential difference is not directly related to

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[1] R. B. Dean, O. Gatty, and E. K. Rideal, *Trans. Faraday Soc.*, 36 (1940) 161. R. B. Dean, *ibidem*, 166.

[2] See for instance E. Lange and F. O. Koenig, *Handbuch der Experimentalphysik*, Vol. 12, part 2, Leipzig 1933, p. 263.

colloidal and interface phenomena, we shall not enter upon details of its measurement or behaviour here. The interested reader is referred to papers by Borelius, Lange [1], *c.s.* where other references are given.

In a less direct way Volta potentials may be important for colloid science. Verwey [2] applied Volta potentials in a discussion of the orientation of water molecules at the surface. The Russian school [3] of electrochemistry recently published results, from which a far going parallelism between Volta potential differences between metals and the points of zero charge of these metals was derived.

The difference between the Galvani potentials of two phases, $\Delta \varphi = \chi_{12}$, on the contrary which seems most interesting for interfacial phenomena, is not accessible to unambiguous measurement, a fact which has been most clearly stated by Guggenheim [4]. For such a measurement it would be necessary to determine the work in bringing a small charge from the bulk of one phase to the other. But the amount of work generally depends very much upon the material carrier of the charge. The work in transporting an electron may be quite different from the work in the transport of an ion. In order to find the work done against the potential difference, the total work in the transport process has to be diminished by the difference in chemical potential $\Delta \mu$ of the transported component. But again these chemical potentials are only defined except for an arbitrary additive constant, and the only thing which can be determined is the difference in electrochemical potential $\Delta \eta$ between the two phases, where the separation into

$$\Delta \eta_i = z_i e \, \Delta \varphi + \Delta \mu_i \tag{31}$$

an electrical and a constitutional part remains arbitrary [5].

Fortunately it often is not necessary to know the value of $\Delta \varphi$ itself, but only the manner in which $\Delta \varphi$ changes when the composition of the phases are (slightly) altered. In that case reliable estimates of the change of $\Delta \mu$ may be made, $\Delta \eta$ can be determined and so the change in $\Delta \varphi$ can be determined. In the subsections 3a and 3b this change in $\Delta \varphi$ has been introduced as the change in interfacial potential dE_s

$$dE_s = d\,(\Delta \varphi) \tag{32}$$

The value of $\Delta \varphi = \chi_{12}$ depends of course on the location of charges in the interface. One may distinguish here polarizations of the interface, orientation of dipoles to which we shall ascribe a part of $\Delta \varphi$ and call it the χ-potential in a restricted sense. Further free charges (ions or electrons) may be displaced, and the part of $\Delta \varphi$ which can be ascribed to these free charges will be distinguished as the double layer potential D.

$$\Delta \varphi = \chi + D \tag{33}$$

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[1] G. Borelius, *Handbuch der Metallphysik*, Vol. I, part 1, Leipzig 1935, p. 451; E. Lange and F. O. Koenig, *l.c.*; M. Andauer and E. Lange, *Z. physik. Chem.*, A 166 (1933) 219. O. Klein and E. Lange, *Z. Elektrochem.*, 44 (1938) 542.

[2] E. J. W. Verwey, *Rec. trav. chim.*, 61 (1940) 564.

[3] T. I. Borisova, B.V. Ershler and A. Frumkin, *J. Phys. Chem. U.S.S.R.*, 22 (1948) 925; *Chem. Abstracts*, 43 (1949) 470; T. I. Borisova and B. V. Ershler, *J. Phys. Chem., U.S.S.R.*, 24 (1950) 337; *Chem. Abstracts*, 44 (1950) 6747.

[4] E. A. Guggenheim, *J. Phys. Chem.*, 33 (1929) 842; 34 (1930) 1540.

[5] It may be remarked here that the E.M.F. of a galvanic cell is equal to the sum of all $\Delta\varphi$'s at the phase boundaries in the cell, which add to a difference in η or φ in the two poles. As these are of the same material $\Delta \mu$ is zero and the difference in φ between two pieces of the same phase is again well determined.

When changes are brought about in the system d $(\triangle \varphi)$ will often be known and the adsorption Γ or the charge density σ at the surface can be determined. A suitable zero point of $\triangle \varphi$ is given by the zero point of charge, that is, by the circumstances where $\sigma = 0$. In that case the double layer potential D is evidently zero, but the value of χ remains unknown.

With the completely polarizable electrode, d$(\triangle \varphi) = dE_s$ *is equal to* dE *(if necessary after a correction for the change in the potential jump at the other electrode), the change in the applied potential.* With the reversible electrode, $\triangle \varphi$ is usually changed by changing the composition of the solution.

In the solid phase (AgI) the electrochemical potentials of the major constituents Ag^+ and I^- are constant whereas the η's of the other constituents are undefined because they are only present in very minute amounts.

In this example $\triangle \varphi$ can be changed by changing the concentration of the Ag^+ and I^- ions in the solution (*potential-determining ions cf.* LANGE and KOENIG, *l.c.*).

According to eq. (31)

$$\triangle \varphi = \frac{\triangle \eta_i - \triangle \mu_i}{z_i e}$$

Now in equilibrium $\triangle \eta_i = 0$. If ideal behaviour of the solution is assumed $\triangle \mu_i$ is dependent upon the concentration of i-ions according to $d \triangle \mu_i = kT \,\mathrm{dln}c_i$, and thus

$$d \triangle \varphi = \frac{kT \,\mathrm{dln}c_i}{z_i e} \tag{34}$$

where d $\triangle \varphi$ is reckoned positively when the solid phase becomes more positive.

In the applications it is often (but not always, see *e.g.*, § 5a, p. 149, 6c, p. 165) assumed that χ does not change when the composition of the solution is not changed too extremely and thus the whole change in potential is located in the double layer potential D.

$$dD \approx dE \text{ (polarizable interface)} \tag{35}$$

$$dD \approx \frac{kT}{z_i e} \,\mathrm{dln}c_i \text{ (reversible interface)} \tag{36}$$

In the following section model theories will be proposed for χ and D.

§ 4. STRUCTURE OF THE DOUBLE LAYER

a. The χ-potential

Although admittedly the potential difference between two phases is not accessible to direct experimental determination, it is important to investigate whether the χ-potential can be approached by model considerations.

In doing this one should realize that in a homogeneous phase the potential fluctuates enormously on an atomic scale. A mean potential may be defined for instance by averaging the charges (nuclear and electronic) over planes parallel to the interface, determining then from simple electrostatics the mean potential far from the interface and calling this quantity the potential of the phase. Generally this potential will not be equal to the potential just outside the phase and the difference between the two, the χ-potential, may now be ascribed to certain definite distributions of the charge in the outermost layers of the phase.

Moreover, when a charged particle (ion or electron) is transferred from the vacuum to the interior of the phase, work has to be done (or is gained) and this work is in principle accessible to measurement for instance in the form of the thermionic work function of metals.

This amount of work can be split into two contributions.

a. The passage through the χ-potential

b. The (short range) interaction with the neighbouring constituents in the bulk of this phase.

This leads to a second method of estimating χ-potentials, namely a calculation of the short range interaction mentioned sub b and a determination of the electronic or ionic work function.

The difference between the two will be equal to the χ-potential.

Both methods for estimating χ-potentials have been applied by VERWEY. Straightforward model considerations have been applied to the case of alkali halide crystals [1]. The results appear to be rather uncertain even with respect to the sign of the χ-potential. Only in the case of LiF and perhaps LiCl are the crystals in all probability more positive than the surrounding vacuum and the potential drop is of the order of magnitude of 1 volt.

The χ-potential at the surface water-vacuum has been calculated by VERWEY [2] from the work function for Na^+, K^+ and Ag^+ions combined with the free energy of hydration in as far as this quantity is determined by the interaction of the ions with their immediate surroundings. The conclusion is that water is about 1/2 volt more negative than vacuum and that consequently in the surface layer the protons of the water molecules are preferentially oriented to the surface. VERWEY has shown that this is in agreement with an ice-like structure of liquid water.

b. The ionic double layer

Apart from the above mentioned calculations on the χ-potential, considerations on the structure of the electrical double layer have been mainly centred around the location of the ionic components. The treatment of the partition of the ions resembles very much the treatment of the ionic atmospheres in the theory of strong electrolytes. Remarkably enough the theoretical treatment of the double layer at a plane interface is older than the theory of DEBYE and HÜCKEL [3], and was first given independently by GOUY [4] and CHAPMAN [5].

In this section we shall mainly consider the double layer at a flat interface. For curved interfaces the treatment is not different in principle, although the mathematical difficulties may be much greater.

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[1] E. J. W. VERWEY, with the collaboration of J. E. ASSCHER, *Rec. trav. chim.*, 65 (1946) 521.

[2] E. J. W. VERWEY, *Rec. trav. chim.*, 61 (1942) 564.

[3] P. DEBYE and E. HÜCKEL, *Physik. Z.*, 24 (1923) 185.

[4] G. GOUY, *J. phys.*, (4) 9 (1910) 457; *Ann. phys.*, (9) 7 (1917) 129.

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

c. Diffuse double layer after GOUY and CHAPMAN

The electrical double layer consists of excess ions (or electrons) present on the solid phase (or on the mercury) and an equivalent amount of ionic charge of opposite sign distributed in the solution phase near the interface.

The charge on the solid ("wall") is treated as a surface charge smeared out uniformly over the surface[1]. The space charge in the solution is considered to be built up by unequal distribution of point-like ions. The solvent is treated as a continuous medium, influencing the double layer only through its dielectric constant.

The COULOMB interaction between the charges present in the system is described by POISSON's equation

$$\triangle \psi = -\frac{4\pi\rho}{\varepsilon} \tag{37}$$

between the potential ψ, which changes from a certain value ψ_0 at the interface to zero in the bulk of the solution, and the charge density, ρ. ε is the dielectric constant[2] $\triangle$ is the LAPLACE operator[3] which in CARTESIAN coordinates is equal to $\partial^2/\partial x^2 + \partial^2/\partial y^2 + \partial^2/\partial z^2$.

The distribution of the ions in the solution is governed by a BOLTZMANN relation expressing that at places of positive potential the negative ions are concentrated and the positive ones are repelled, whereas for places of negative potential the reverse is the case.

$$n_i = n_{io} \exp(-z_i e\, \psi / kT) \tag{38}$$

n_i is the concentration of ions of kind i at a point where the potential is $\psi \cdot n_{io}$ is the concentration in the bulk of the solution. z_i is the valency (sign of the charge included).

The space charge density, ρ, is given by the algebraic sum of the ionic charges per unit volume.

$$\rho = \Sigma\, z_i e n_i \tag{39}$$

By combining equations (37), (38) and (39) a differential equation for the potential ψ as a function of the coordinates is obtained.

$$\triangle \psi = -\frac{4\pi}{\varepsilon} \Sigma\, z_i e n_{io} \exp(-z_i e\, \psi / kT) \tag{40}$$

When only small values of the potential are considered ($z_i e\, \psi / kT < 1$ or $z_i\, \psi <$ 25 mV at room temperature) the exponentials may be expanded and only the first two terms retained.

Remembering, that, on account of the electroneutrality of the solution

$$\Sigma\, z_i e n_{io} = 0 \tag{41}$$

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[1] In § 4 e, p. 137 the case is treated that both charges are space charges.

[2] D. C. GRAHAME, *J. Chem. Phys.*, 18 (1950) 903 showed that although in the double layer the field strength may be so high as to cause dielectric saturation of the solvent (water), its effect upon experimentally measurable properties is negligible. So we may safely reckon ε as a constant.

[3] The same symbol Δ has been used in the preceding sections for a difference. There seems to be no danger of confusion, however, as from the context and the equations themselves it is always evident which of the two possibilities is meant.

the equation arrived at reads

$$\triangle \psi = \varkappa^2 \psi \tag{42}$$

in which

$$\varkappa^2 = \frac{4 \pi e^2 \Sigma n_{io} z_i^2}{\varepsilon kT} \tag{43}$$

This approximate differential equation (42) will in most cases not be suitable to describe colloidal phenomena, because the valencies of positive and negative ions occur in it in a symmetrical way through $\varkappa$, whereas experimentally, for instance in the rule of SCHULZE and HARDY (Ch. II, p. 82) the influence of positive and negative ions is essentially different.

It is, therefore, necessary to return to the complete equation (40) and try to solve it.

In the application to strong electrolytes serious doubt exists whether the application of the complete eq. (40) is permissible because it implies certain internal inconsistencies which have been analyzed most extensively by KIRKWOOD[1]. But CASIMIR[2] extending KIRKWOOD's analysis has shown that these inconsistencies do not arise (remain very small) when the complete eq. (40) is applied to the double layer on a large plane interface or on a large particle if the electrolytic concentrations in the whole system remain so small that in the bulk of the solution the limiting laws of DEBYE and HÜCKEL form a reasonable approximation.

The objection against the use of eq. (38) is that the exponent contains the mean potential while it should contain the potential of the mean force. In other words eq. (38) forgets that when an ion is brought from infinity to another ion the mean distribution of all the ions changes slightly, thus influencing the work done.

In the case of the double layer of colloidal particles there are so many small ions in the double layer that the addition or subtraction of one ion practically does not change the distribution of mean charge or of mean potential.

When two colloidal particles come near to each other the above-mentioned inconsistencies would become serious. The influence of interaction of colloidal particles is however treated separately in Ch. VI and VIII.

We shall now restrict the discussion to an infinitely large plane interface, so that the LAPLACE operator $\triangle$ simplifies to $\frac{d^2}{dx^2}$.

A first integration can then easily be carried out after multiplying both sides of eq. (40) by $2\, d\psi/dx$.

$$2\frac{d\psi}{dx}\cdot\frac{d^2\psi}{dx^2} = -\frac{8\pi}{\varepsilon}\Sigma z_i e n_{io} \exp(-z_i e \psi/kT)\frac{d\psi}{dx}$$

Integration gives

$$\left(\frac{d\psi}{dx}\right)^2 = \frac{8\pi kT}{\varepsilon}\Sigma n_{io}\left[\exp(-z_i e\psi/kT) - 1\right] \tag{44}$$

where the condition that

$$\text{for } x \rightarrow \infty \qquad \psi \rightarrow 0 \text{ and } \frac{d\psi}{dx} \rightarrow 0$$

has been made use of.

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[1] J. G. KIRKWOOD, *J. Chem. Phys.*, 2 (1934) 767; See also H. A. KRAMERS, *Proc. Koninkl. Nederland. Akad. Wetenschap.*, 30 (1927) 145; R. H. FOWLER, *Trans. Faraday Soc.*, 23 (1927) 434; L. ONSAGER, *Physik. Z.*, 28 (1927) 277; *Chem. Revs.*, 13 (1933) 73; R. H. FOWLER and E. A. GUGGENHEIM, *Statistical thermodynamics*, Cambridge 1949, p. 409.

[2] H. B. G. CASIMIR, *Tweede Symposium over sterke electrolyten en over de electrische dubbellaag* Ed. by Sectie voor Kolloidchemie der Ned. Chem. Ver., Utrecht 1944, p. 1.

This equation can be simplified considerably by considering a single binary electrolyte of valency z in the solution. This simplification causes little loss with respect to the explanation of colloidal phenomena, because there the valency of the ion with the same charge as the wall (or particle) is unimportant and so may for convenience be chosen equal to the valency of the counter ions. In that case eq. (44) can be written

$$\frac{d\psi}{dx} = -\sqrt{\frac{8\pi nkT}{\varepsilon}}\left[\exp\left(ze\psi/2kT\right) - \exp\left(-ze\psi/2kT\right)\right] \tag{45}$$

Before carrying out the second integration, we can from eq. (45) establish a relation between the surface charge density, σ, and the surface potential, $\psi_\circ$. The condition of electroneutrality of the total double layer requires that the surface charge is oppositely equal to the total space charge in the solution.

$$\sigma = -\int_0^\infty \rho \, dx \tag{46}$$

By using POISSON's relation, eq. (46) can be integrated as follows

$$\sigma = +\int_0^\infty \frac{\varepsilon}{4\pi}\frac{d^2\psi}{dx^2}\,dx = -\frac{\varepsilon}{4\pi}\left(\frac{d\psi}{dx}\right)_{x=0} \tag{47}$$

Inserting the value for $\frac{d\psi}{dx}$ from eq. (45) we find:

$$\sigma = \sqrt{\frac{\varepsilon\, nkT}{2\pi}}\cdot\left[\exp\left(ze\psi_\circ/2kT\right) - \exp\left(-ze\psi_\circ/2kT\right)\right] \tag{48}$$

When the potential is so small that the exponentials can be expanded, we find

$$\sigma = \sqrt{\frac{\varepsilon\, nkT}{2\pi}}\cdot\frac{ze\psi_\circ}{kT} = \frac{\varepsilon}{4\pi}\sqrt{\frac{8\pi\, nz^2e^2}{\varepsilon\, kT}}\,\psi_\circ = \frac{\varepsilon\varkappa}{4\pi}\,\psi_\circ \tag{49}$$

In this case charge and potential are proportional to each other and the double layer behaves as a flat condenser with a distance $1/\varkappa$ between the two plates.

For the second integration of eq. (45), which leads to an explicit relation between the potential and the coordinate of the double layer, this eq. is written

$$\int_{ze\psi_\circ/2kT}^{ze\psi/2kT} \frac{2d\left(ze\psi/2kT\right)}{\exp\left(\frac{ze\psi}{2kT}\right) - \exp\left(-\frac{ze\psi}{2kT}\right)} = -\int_0^x \sqrt{\frac{8\pi z^2e^2n}{\varepsilon kT}}\,dx = -\int_0^x d(\varkappa x)$$

Integration with the condition $\psi = \psi_0$ for $x = 0$ leads to

$$\varkappa x = \ln\frac{\left(\exp\left(ze\psi/2kT\right)+1\right)\left(\exp\left(ze\psi_\circ/2kT\right)-1\right)}{\left(\exp\left(ze\psi/2kT\right)-1\right)\left(\exp\left(ze\psi_\circ/2kT\right)+1\right)} \tag{50}$$

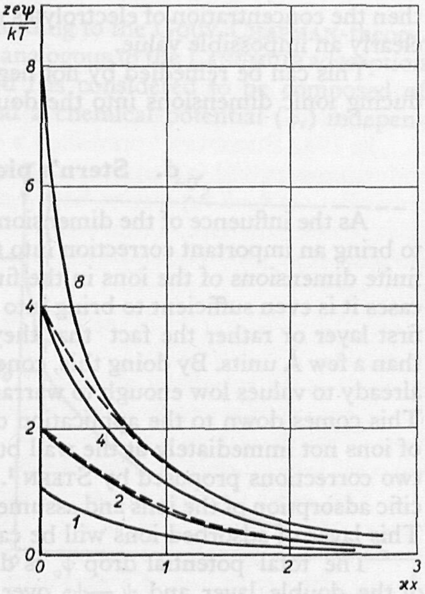

Fig. 4. Electric potential in the double layer according to the theory of GOUY and CHAPMAN. The curves marked 1, 2, 4, 8 are drawn according to the exact eq. (50) for $\frac{ze\psi_0}{kT} = 1, 2, 4$ and 8 resp. The dotted lines follow the approximate equation (51).

This relation, which is illustrated in Fig. 4 for a number of values of $ze\psi/kT$ can be more easily read in the case of small potentials where the exponentials may be expanded. It then simplifies to

$$\varkappa x = \ln \psi_0/\psi \quad \text{or} \quad \psi = \psi_0 e^{-\varkappa x} \tag{51}$$

showing that the potential drops exponentially to zero over a distance of the order of magnitude $1/\varkappa$.

This, and the fact that the equivalent condenser has a thickness, $1/\varkappa$, justifies the custom of saying that "the thickness of the double layer is equal to $1/\varkappa$".

Another useful approximation is obtained for $\frac{ze\psi_0}{kT} \gg 1$ and $\frac{ze\psi}{kT} \ll 1$, that is an approximation valid far away from a surface which is at a high potential. For this case we find

$$\frac{ze\psi}{kT} = 4\gamma e^{-\varkappa x} \tag{52}$$

in which

$$\gamma = \frac{\exp(ze\psi_0/2kT) - 1}{\exp(ze\psi_0/2kT) + 1} \tag{53}$$

One of the properties of the double layer that can be easily tested experimentally is its differential or integral capacity

$$\frac{\partial \sigma}{\partial \psi_0} \quad \text{or} \quad \frac{\sigma}{\psi_0}$$

which can be very easily derived from eq. (48) or (49). For small potentials the differential and integral capacity are both equal to

$$C = \frac{\varepsilon \varkappa}{4\pi}$$

For larger potentials it becomes larger.

At room temperature $\varkappa$ is about $3 \cdot 10^7 z \sqrt{c}$, where c is the concentration in grammoles/litre.

In a 1 N aqueous solution of a monovalent electrolyte the calculated capacity therefore becomes $\frac{3 \cdot 10^7 \cdot 80}{4\pi} = 200\,\mu\,\text{F/cm}^2$. Experimentally the capacities found are more nearly one tenth of this amount. Evidently the picture of the diffuse double layer is too simple. This oversimplification makes itself felt also in another respect. When the solution is not very dilute, say 0.1 N, and the potential at the wall high, say 200 mV., then the concentration of electrolytes near the wall should amount to $0.1\,N \cdot e^8 = 300\,N$; clearly an impossible value.

This can be remedied by not neglecting the ionic dimensions. A method of introducing ionic dimensions into the double layer has been developed by O. STERN.

d. Stern's picture of the double layer

As the influence of the dimensions of the ions is greatest near the wall, it is possible to bring an important correction into the double layer theory by correcting only for the finite dimensions of the ions in the first ionic layers reckoned from the wall. In many cases it is even sufficient to bring into the picture only the dimensions of the ions of the first layer or rather the fact that they cannot approach the wall to a distance smaller than a few Å units. By doing this, concentrations and potentials in the double layer drop already to values low enough to warrant the approximation of the ions as point charges. This comes down to the application of the GOUY-CHAPMAN theory with the first layer of ions not immediately at the wall but at a distance δ away from it. This is one of the two corrections proposed by STERN [1]. STERN further considered the possibility of specific adsorption of the ions and assumed that these ions were also located in the plane δ. This layer of adsorbed ions will be called the STERN layer [2].

The total potential drop ψ_0 is divided into a potential ψ_δ over the diffuse part of the double layer and $\psi_0 - \psi_\delta$ over the molecular condenser. For the diffuse part of the double layer the treatment of the foregoing subsection is taken unchanged except for the fact that the diffuse layer does not reach to the wall but only to a distance δ from it. The molecular condenser has a certain capacity C_m, being the ratio of the charge on the wall σ and the potential difference $\psi_0 - \psi_\delta$

The capacity of the total double layer C_t is then simply found as the equivalent of the capacity of the diffuse layer C_d and that of the molecular condenser C_m placed in series

$$C_t = \frac{C_m\, C_d}{C_m + C_d} \tag{54}$$

As C_m is (nearly) constant but C_d strongly dependent upon electrolyte concentration ($C_d \sim \varkappa$), the partition of the total potential drop in the double layer over its two parts also depends on the amount of electrolyte present. So even when ψ_0, the surface potential, is a constant, ψ_δ, which governs the diffuse double layer, decreases with increasing $\varkappa$, a fact which plays a part both in electrokinetics (chapter V, § 9b, p. 228) and in stability of colloids (chapter VIII, § 4a, p. 311).

In extreme cases, when one of the separate capacities is very much larger than the other, the total capacity is practically equal to the smaller of the two component capacities. So in dilute solutions $C_t \sim C_d$ and in concentrated solutions $C_t \sim C_m$.

The charge on the wall is oppositely equal to the sum of the charges of the diffuse part of the double layer , σ_2, and the charge of the ions in the liquid part of the mole-

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[1] O. STERN, *Z. Elektrochem.*, 30 (1924) 508.

[2] This layer is often called the HELMHOLTZ-layer in honour of the very important theoretical work of HELMHOLTZ on electrokinetics but it does not mean that HELMHOLTZ himself used the picture of a molecular condenser; HELMHOLTZ derived the electrokinetic equations without any special assumption on the structure of the double layer. It was PERRIN, who was the first to schematize the double layer as a simple condenser. *Cf.* chapter V, § 3 a. 1, p. 199.

cular condenser, σ_1. σ_2 is directly related to ψ_δ according to the GOUY-CHAPMAN-theory. For the calculation of σ_1 STERN applies a model analogous to the LANGMUIR adsorption isotherm[1]. The adsorption energy of ions of kind i is considered to be composed of two parts, a purely electrical one $(-z_i\, e\, \psi_\delta)$ and a chemical potential (φ_i) independent of the electrical circumstances.

A schematic picture of the distribution of the potential according to STERN's theory is given in Fig. 5.

The charge σ_1 is given by[2]

$$\sigma_1 = \frac{N_1\, z_+\, e}{1 + \dfrac{N}{n_+ M}\, e^{+\frac{z_+ e\, \psi_\delta + \varphi_+}{kT}}} - \frac{N_1\, z_-\, e}{1 + \dfrac{N}{n_- M}\, e^{-\frac{z_- e\, \psi_\delta - \varphi_-}{kT}}} \qquad (55)$$

where N_1 is the available number of adsorption spots per cm². N is AVOGADRO'S number, and M the molecular weight of the solvent.

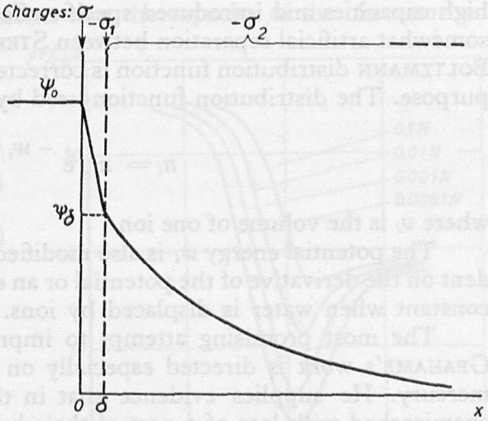

Fig. 5. Schematic representation of the double layer according to the theory of STERN.

A weak point in STERN's theory is the number of available positions in the liquid, which is taken equal to $\frac{N}{M}$ and also the connection between the diffuse double layer and the molecular condenser, as expressed by assuming equality of potential in the innermost part of the diffuse layer and the liquid layer of the molecular condenser. When the molecular condenser is empty $(\sigma_1 = 0)$ then indeed the maximum potential of the GOUY-layer should be ψ_δ. But when the STERN-layer is partly or fully occupied, the distance of closest approach, averaged over the whole surface, of a GOUY-ion to the surface, is larger than δ and consequently the maximum GOUY potential should be smaller than ψ_δ.

In practice very often only one of the terms in the sum of (55) needs to be considered because either the positive or the negative ions are completely expelled from the molecular condenser. Moreover, if the concentration is not very high, the 1 in the denominator may be neglected. This gives a great simplification in calculations using this theory.

As regards the drawbacks of the pure GOUY-CHAPMAN-theory, STERN has indeed indicated the way to overcome them. The non-specificity disappears by the adsorption potentials and by the capacity of the molecular condenser. The impossibly high values of the capacity in GOUY's theory cannot occur in STERN's, as the highest capacity possible here is that of the molecular condenser.

In the original version of STERN'S theory the capacity of the molecular condenser is taken as a constant. In principle of course this capacity will depend upon the specific properties of the ions in the STERN-layer. And especially will be different on both sides of the zero point of charge.

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[1] I. LANGMUIR, *J. Am. Chem. Soc.*, 38 (1916) 2221; 39 (1917) 1885: 40 (1918) 1361.

[2] STERN changes the 1 in the denominator into 2 but his arguments are not very convincing especially not for the simplified case in which either the contribution of the anions or that of the cations can be neglected

In experiments on the electrocapillary curve this effect is quite evident. PHILPOT[1] and FRUMKIN[2]) have given modifications of STERN's theory which take this changing capacity into account, by assuming two different anionic and cationic capacities, and a certain graduel transition between them.

In 1942 BIKERMAN[3] published a different approach which also excluded the very high capacities and introduced specific effects for different ions. In this treatment the somewhat artificial separation between STERN-layer and GOUY-layer is left out, but the BOLTZMANN distribution function is corrected for volume effects, which serves the same purpose. The distribution function used by BIKERMAN is

$$n_i = n_{i_\circ}\, e^{-w_i/kT} \cdot \frac{1 - \Sigma\, n_i\, v_i}{1 - \Sigma\, n_{i_\circ} v_i}$$

where v_i is the volume of one ion.

The potential energy w_i is also modified by including either a dipole energy dependent on the derivative of the potential or an extra term related to the change in dielectric constant when water is displaced by ions.

The most promising attempt to improve STERN's theory is due to GRAHAME[4]. GRAHAME's work is directed especially on the interpretation of the double layer on mercury. He supplies evidence that in the STERN-layer only the anions are really chemisorbed with loss of a part of their hydration shells, whereas the cations remain hydrated and are only attracted to the surface by electrostatic forces. A distinction should therefore be made between what GRAHAME calls the *outer* HELMHOLTZ *plane*, that is the locus of nearest approach of the centres of charge of cations to the wall and the *inner* HELMHOLTZ *plane* that is the locus of the centres of charge of the chemisorbed anions.

The double layer description of GOUY-CHAPMAN may be used from the outer HELMHOLTZ plane on, and this is in principle completely known because the total amount of adsorbed cations is an experimentally determinable quantity. Together with the value of $\varkappa$ this is enough to determine the distribution of charge and potential completely.

The capacity C between the wall and the outer HELMHOLTZ plane (in the absence of chemisorption) is determined by experiment from the eq.

$$C_\circ = \frac{\sigma_{\text{total}}}{\psi_\circ - \psi_{o.H.p.}} \tag{56}$$

This capacity is not a constant but still depends — as GRAHAME assumes — on the surface charge density.

The inner HELMHOLTZ plane may be treated in the same way as in the STERN theory. The number of anions present per cm² in that layer is

$$n_{i.H.p.} = 2\, r\, n_\circ\, e^{-w_{i.H.p.}/kT} \tag{57}$$

where r is the radius of an (unhydrated) anion and $w_{i.H.p.}$ the work to be done in brin-

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[1] J. ST. L. PHILPOT, *Phil. Mag.*, (7) 13 (1932) 775.
[2] A. FRUMKIN, *Trans. Faraday Soc.*, 36 (1940) 117.
[3] J. J. BIKERMAN, *Phil. Mag.*, (7) 33 (1942) 384.
[1] D. C. GRAHAME, *Chem. Revs.*, 41 (1947) 441. (See also this chapter § 5d, p. 156).

ging an ion to the inner HELMHOLTZ plane. The splitting of this work into an electrical and a non-electrical term

$$w_{i.H.p.} = z_i \, e \, \psi_{i.H.p.} - \varphi \tag{58}$$

is usually not without ambiguity. At the zero point of charge, however, $\psi_{i.H.p.} = \psi_0$ and in that case $w_{i.H.p.} = \varphi$.

Moreover GRAHAME gives some arguments that the capacity of the chemisorbed layer — contrary to the capacity of the outer HELMHOLTZ plane — is a constant. With this simplification the whole theory can be completed by the equations

$$C_i = \frac{\sigma_{\text{total}}}{\psi_0 - \psi_{i.H.p.}} \tag{59}$$

and

$$\sigma_{\text{total}} + \sigma_{i.H.p.} + \sigma_{d.l.} = 0 \tag{60}$$

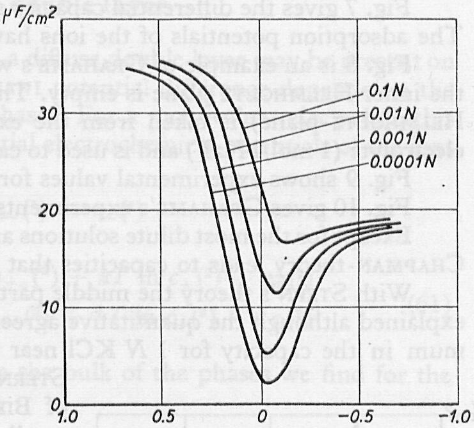

Fig. 7. Differential capacity of the double layer according to STERN's theory. Capacity of the molecular condenser 38 μ F for positive surface and 20 μF for negative surface. (Taken from A. FRUMKIN, *Trans. Faraday Soc.*, 36 (1940) 126).

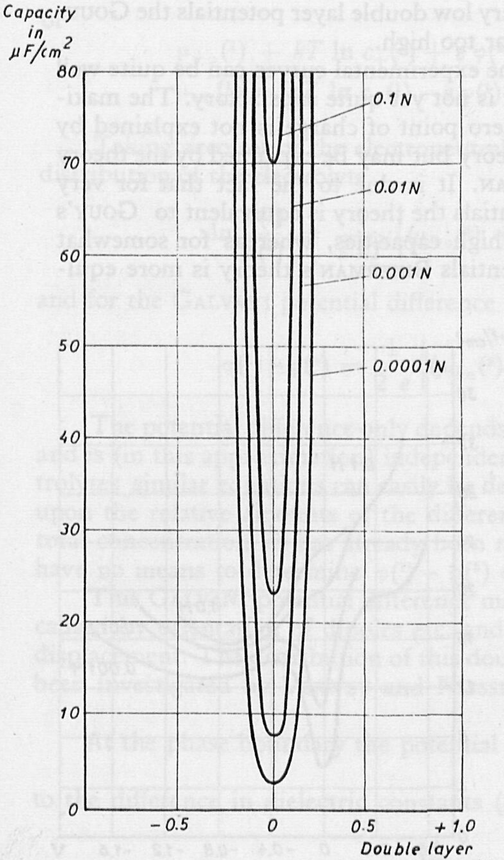

Fig. 6. Differential capacity of double layer according to the GOUY-CHAPMAN theory for monovalent ions.

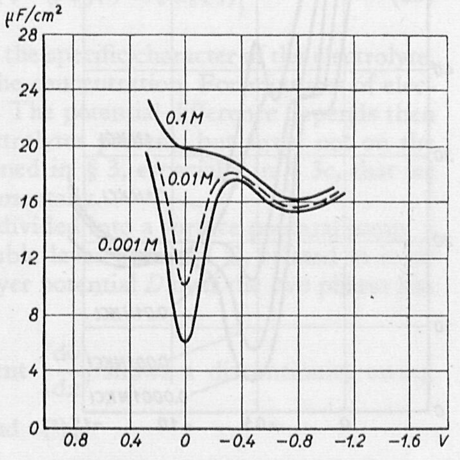

Fig. 8. Differential capacity of double layer calculated by GRAHAME. The curve for 1 *M* NaF from Fig. 10 has served as a basis for calculating the capacity of the molecular condenser.

where $\sigma_{d.l.}$ is the total charge of the diffuse layer. GRAHAME did not give an explicit relation to calculate $\psi_{o.H.p.}$ from $\psi_{i.H.p.}$ in the case that chemisorption is present, but takes the relation from experimental data.

At this stage it may be interesting to compare the capacities of the double layer according to the different theories with the experimental values from the electrocapillary curve.

Fig. 6 gives the differential capacities calculated for the diffuse double layer.

Fig. 7 gives the differential capacity after STERN's theory as modified by FRUMKIN. The adsorption potentials of the ions have been taken zero.

Fig. 8 is an example of GRAHAME's work. Chemisorption is assumed to be absent, the inner HELMHOLTZ plane is empty. The capacity of the molecular condenser (outer HELMHOLTZ plane) is taken from the experiment with the highest concentration of electrolyte (1 mol/l NaF) and is used to calculate the curves for lower concentrations.

Fig. 9 shows experimental values for the mercury electrode in chloride solutions.

Fig. 10 gives GRAHAME's experiments for NaF, to be compared with Fig. 8.

Except for the most dilute solutions and very low double layer potentials the GOUY-CHAPMAN-theory leads to capacities that are far too high.

With STERN's theory the middle part of the experimental curves can be quite well explained although the quantitative agreement is not yet quite satisfactory. The maximum in the capacity for 1 *N* KCl near the zero point of charge is not explained by STERN's theory but may be explained by the theory of BIKERMAN. It is due to the fact that for very small potentials the theory is equivalent to GOUY's leading to high capacities, whereas for somewhat larger potentials BIKERMAN's theory is more equi-

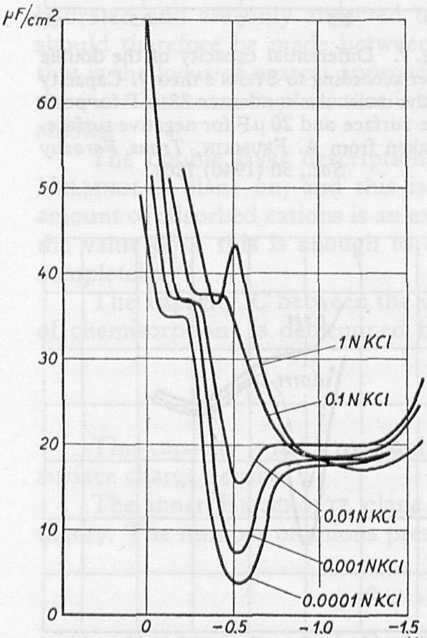

Fig. 9. Double layer capacity at a mercury-water interface after experiments of PROSKURNIN and VORSINA. (Taken from A. FRUMKIN, *Trans. Faraday Soc.*, 36 (1940) 124).

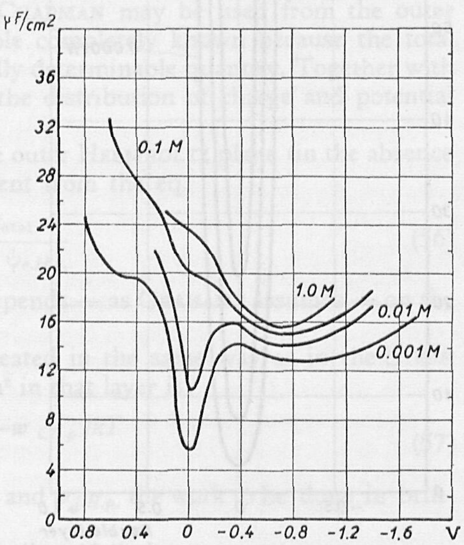

Fig. 10. Differential capacity of double layer between mercury and aqueous solutions of NaF. T = 25° C.

valent to STERN'S. GRAHAME'S approach seems to give a somewhat better accord with experiments than does FRUMKIN'S method, but the differences are not very large.

The high experimental capacities for large positive or negative potentials are not explained by any of the theories.

Further comparison between theory and experiment is given in § 5.

e. Double diffuse double layer

At the interface of two immiscible liquids a diffuse double layer may be present on both sides of the phase boundary. The GALVANI potential difference depends on the unequal distribution of the ions in the two phases. For a monovalent electrolyte this distribution is governed by equality of the partial electrochemical potentials of the ions in the two phases.

$$\eta_+({}^1) = \eta_+({}^2) \text{and } \eta_-({}^1) = \eta_-({}^2)$$

or

$$\begin{aligned} \mu_{+\circ}({}^1) + kT \ln c_+({}^1) + e\,\varphi({}^1) &= \mu_{+\circ}({}^2) + kT \ln c_+({}^2) + e\varphi({}^2) \\ \mu_{-\circ}({}^1) + kT \ln c_-({}^1) - e\,\varphi({}^1) &= \mu_{-\circ}({}^2) + kT \ln c_-({}^2) - e\,\varphi({}^2) \end{aligned} \qquad (61)$$

Taking account of the electroneutrality in the bulk of the phases we find for the distribution of the electrolyte

$$\ln \frac{c({}^1)}{c({}^2)} = \frac{1}{2\,kT} \left\{ (\mu_{+\circ}({}^2) + \mu_{-\circ}({}^2)) - (\mu_{+\circ}({}^1) + \mu_{-\circ}({}^1)) \right\} \qquad (62)$$

and for the GALVANI potential difference

$$\varphi({}^1) - \varphi({}^2) = \frac{1}{2\;e} \left\{ (\mu_{+\circ}({}^2) - \mu_{-\circ}({}^2) - (\mu_{+\circ}({}^1) - (\mu_{-\circ}({}^1)) \right\} \qquad (63)$$

The potential difference only depends upon the specific character of the electrolyte, and is (in this approximation) independent of the concentration. For mixtures of electrolytes similar equations can easily be derived. The potential difference depends then upon the relative amounts of the different electrolytes present, but again not on the total concentration. It has already been mentioned in § 3, especially in § 3c, that we have no means to determine $\varphi({}^1) - \varphi({}^2)$ experimentally.

This GALVANI potential difference may be divided into a surface potential jump χ caused by orientation of dipoles etc. and a double layer potential D, related to ionic displacement. The distribution of this double layer potential D over the two phases has been investigated by VERWEY and NIESSEN [1].

At the phase boundary the potential gradient $\left(\frac{d\psi}{dx}\right)$ shows a discontinuity owing to the difference in dielectric constants ($\varepsilon({}^1)$ and $\varepsilon({}^2)$).

$$\varepsilon({}^1) \quad (\frac{d\psi}{dx}) \, ({}^1) = \varepsilon({}^2) \, (\frac{d\psi}{dx}) \, ({}^2) \qquad (64)$$

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[1] E. J. W. VERWEY and K. F. NIESSEN, *Phil. Mag.*, (7) 28 (1939) 435.

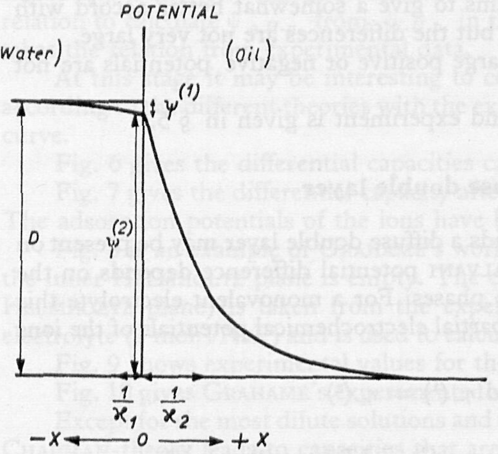

Fig. 11. Distribution of the potential at the interface of two liquid phases for small values of the total double layer potential D

$\varepsilon_1 = 9\,\varepsilon_2 \quad n_1 = 81\,n_2$

Consequently $\varkappa_1 = 3\,\varkappa_2$ and $\psi(^2) = 27\,\psi(^1)$

If both double layers are assumed to be of the GOUY-CHAPMAN-type, eq. (45) may be applied, leading to

$$\sqrt{n(^1)\,\varepsilon(^1)}\,\sinh\frac{z\,e\,\psi(^1)}{2\,kT} = $$

$$= \sqrt{n(^2)\,\varepsilon(^2)}\,\sinh\frac{z\,e\,\psi(^2)}{2\,kT} \qquad (65)$$

where $\psi(^1)$ and $\psi(^2)$ are the potentials on phase (1) and phase (2) and the sum of $\psi(^1)$ and $\psi(^2)$ is equal to D as determined above. See Fig. 11.

The partition of the potential is governed by the quantity

$$\alpha = \frac{n(^1)\,\varepsilon(^1)}{n(^2)\,\varepsilon(^2)} \qquad (66)$$

and as usually the medium with the lower dielectric constant will also have the smaller electrolyte content, the greater part of the potential D will be found in the phase with the smaller dielectric constant. Fig. 12 gives the partition of D as a function of $\log \alpha$ for two different total potentials.

The application of these considerations on the interface between water and an organic liquid (oil) leads to the conclusion that only a weak double layer is present in the water phase, which explains the lack of stability against flocculation of non-stabilized emulsions (*cf.* chapter VIII § 12a, p. 338).

It may be argued that in principle every double layer is of this double diffuse type. In ionic solids the charge on the solid may stretch out over considerable distances in the interior of the solid phase, if departure from the stoichiometric composition by means of interstitial ions or other lattice defects are possible GRIMLEY and MOTT[1] applied this idea to the double layer AgBr-water.

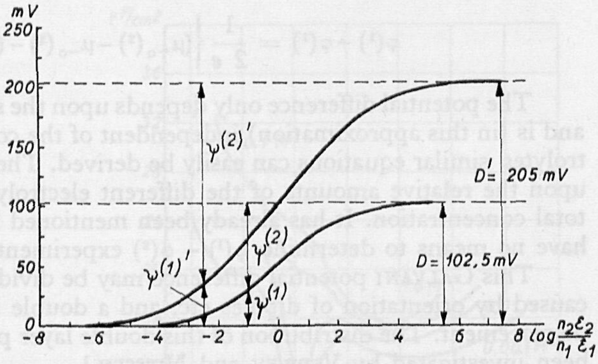

Fig. 12. Distribution of a total potential drop D and D′ of 102.5 and 205 mV resp. over two phases as a function of $\log n(^2)\,\varepsilon(^2)/n(^1)\,\varepsilon(^1) = \log .\alpha$

In the silver bromide the double layer is built up from an unequal distribution of SCHOTTKY defects (vacant anion and cation positions) from which there are about 10^{-17}

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[1] T. B. GRIMLEY and N. F. MOTT, *Discussions Faraday Soc.*, 1947 no. 1, 3.
T. B. GRIMLEY, *Proc. Roy. Soc. London*, A 201 (1950) 40.

per cm^3 in a neutral crystal. The extension of the double layer is then of the order of 10^{-6} cm and already in solutions of $^1/_{5000}$ N a considerable part of the total potential drop is located in the crystal. The introduction of the diffuse layer in the solid phase achieves the same result as the introduction of the STERN correction, *viz.*, a lowering of the potential in the diffuse layer in the solution phase. (See § 4d). A difficulty in this sort of case is the estimation of the number of accessible lattice defects.

Returning to the oil-water double layer we wish to indicate how in the presence of special electrolytes the double layer may acquire again its more one-sided character. If the electrolyte to be distributed contains an amphipolar ion that tends to accumulate at the interface (*e.g.*, a fatty acid ion) and a second ion showing great preference for the water phase, the double layer will be formed of a layer of amphipolar ions at the interface, a diffuse layer in the water phase and, in order to arrive at the necessary value of the total potential, a diffuse layer in the oil phase which however in the case mentioned contains only a very small charge. In the aqueous part of the double layer the potential drop is now much larger than without the presence of the amphipolar ion, which leads to a much greater stability of the corresponding emulsion. (See chapter VIII, § 12, p. 338). A quantitative treatment of this kind of double layer has been given by VERWEY[1].

f. Relation between models and thermodynamic considerations

f. 1. Potential

On a purely thermodynamic basis the electromotive force of a galvanic cell cannot be objectively divided into the three potential jumps at the different phase boundaries. If it is assumed, that separate ion activities (or, what comes to the same thing, diffusion potentials) are known, the dependence of one separate potential jump (E_s) on the ionic composition of the solution becomes accessible, except for an additive constant.

In the models we distinguish the GALVANI-potential difference $\triangle\varphi$ between two phases.

The comparison between theory and experiment is usually carried out by taking E_s and $\triangle\varphi$ equal in the zero point of charge (they are then both equal to the unknown χ-potential), and investigating whether they are also equal in other circumstances. In the comparison it is often (for exceptions see § 5a, p. 149; § 6c p. 165) assumed that χ is independent of the composition of the (dilute) solution, so that practically

$$E_s - E_{s0} = \psi_0 \text{ or } D \tag{67}$$

f. 2. Charge

In the case of the completely polarized (mercury) electrode the charges occurring in the thermodynamical calculations and in the model are identical.

For the completely reversible electrode the surface charge in the model is identified with the charge of the adsorbed potential-determining ions. So in the case of silver iodide

$$\frac{\sigma}{e} = \Gamma_{\mathrm{Ag}} - \Gamma_{\mathrm{I}} \tag{68}$$

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[1] E. J. W. VERWEY, *Proc. Koninkl. Nederland. Akad. Wetenschap.*, 53 (1950) 376.

If the solution contains much foreign electrolyte, this definition of σ is practically correct but if the electrolyte content is low, so that a substantial part of the counter ions is formed by the potential-determining ions themselves, the problem is more complicated because Γ contains the whole surface excess, including the excess in the liquid part of the double layer. For small values of the potential, half of the diffuse charge is formed by a deficiency of ions of the same charge as the surface and the other half by an excess of ions of opposite charge. Considering a silver iodide surface, positively charged in a solution containing only silver nitrate, the solid phase contains an excess of silver ions equal to σ/e but in the liquid there is a deficit of $\sigma/2e$ silver ions. The concentration of I-ions is so small compared to the nitrate concentration that the excess of I-ions in the liquid is negligible. In this case

$$\Gamma_{\mathrm{Ag}} - \Gamma_{\mathrm{I}} = \frac{\sigma}{e} - \frac{\sigma}{2\,e} = \frac{\sigma}{2\,e} \tag{69}$$

A still more extreme case is met with when a solution of AgI in water with no other ions present is considered. As in this case the zero point of charge (*cf.* § 6a, p. 160) and the equivalence point do not coincide, there certainly is a finite surface charge σ. A surface excess however cannot be defined in this case as only two components are present in the system.

In practice these complications do not give rise to many difficulties, as usually the solutions to be measured contain enough foreign electrolyte to make eq. (68) (or an analogous one for other substances) valid.

g. Free energy of the double layer

In § 2, eq. (9) a general relation for the free energy G_s of the interface per cm² has been given in the form

$$G_s = G_s\,(\mu_1{}^\circ, \mu_2{}^\circ \ldots\ldots \mu^\circ{}_r) - \left(\int_{\mu_3{}^\circ}^{\mu_3} \Gamma_3 \mathrm{d}\mu_3\right)_{\mu_4{}^\circ,\, \mu_5{}^\circ \ldots} - \left(\int_{\mu_4{}^\circ}^{\mu_4} \Gamma_4 \mathrm{d}\mu_4\right)_{\mu_3,\, \mu_5{}^\circ \ldots} \text{etc.} \tag{9}$$

In § 3 the case has been treated, where the interface bears an electrical double layer and independent of the way of formation of the double layer (polarizable interface or reversible case) the free energy can be written (see eq. (24) p. 122 and (29) p. 123).

$$G_s = G_s\,(\mu_1{}^\circ, \mu_2{}^\circ \ldots\ldots \mu_r{}^\circ, \sigma = 0) - \left(\int_{\mu_3{}^\circ}^{\mu_3} \Gamma_3 \,\mathrm{d}\mu_3\right)_{\mu_4{}^\circ,\, \mu_5{}^\circ \ldots\ldots,\, \sigma = 0} \ldots$$

$$- \left(\int_{\mu_r{}^\circ}^{\mu_r} \Gamma_r \,\mathrm{d}\mu_r\right)_{\mu_3,\, \mu_4 \ldots\, \mu_{r-1},\ \sigma = 0} - \left(\int_{\sigma = 0}^{\sigma} \sigma \,\mathrm{d}\, E_s\right)_{\mu_3{}^\circ \ldots\, \mu_r{}^\circ} \tag{70}$$

When there is no specific adsorption in the zero point of charge, $G_s\,(\mu_1{}^\circ, \mu_2{}^\circ, \mu_r{}^\circ, \sigma = 0)$ is independent of the special choice of concentrations and eq. (70) may be simplified to

$$G_s = G_s\,(\sigma = 0) - \int_{\sigma = 0}^{\sigma} \sigma \,\mathrm{d}E_s \tag{71}$$

Further assuming — and herewith the model considerations are again introduced — that the χ-potential is independent of the charge density, dE_s is identical with $d\psi_\circ$ and the surface free energy becomes

$$G_s = G_s\,(\sigma = 0, \psi_\circ = 0) - \int_0^{\psi_\circ} \sigma\, d\psi_\circ \qquad (72)$$

The integral in this expression may be called the free energy of the double layer. In two cases the integration leads to a particularly simple result. If the total concentration of electrolytes is high, the capacity of the double layer is practically equal to that of the STERN layer (*cf.* eq. (54)) and may be treated as a constant. (See, however, § 5d, p. 156). For small concentrations of electrolyte and small potentials again the capacity is a constant, now proportional to $\varkappa$. In these two cases

$$G_{\text{double layer}} = -\int_0^{\psi_\circ} \sigma\, d\psi = -{}^1/_2\, \sigma_\circ\, \psi_\circ \qquad (73)$$

For the diffuse double layer the result is somewhat less simple. The relation between σ and ψ has been given in eq. (48), p. 130 and the free energy of the double layer becomes

$$G_{\text{double layer}} = -\sqrt{\frac{\varepsilon\, nkT}{2\,\pi}} \int_0^{\psi_\circ} 2 \sinh \frac{ze\,\psi}{2\,kT}\, d\psi = -\frac{8n\ kT}{\varkappa}\left(\cosh \frac{ze\,\psi_\circ}{2\,kT} - 1\right) \quad (74)$$

A very characteristic feature of the free enthalpy of the double layer is its negative sign, corresponding with the fact that it is spontaneously formed when the surface potential or the concentration of potential-determining ions is changed. This negative sign is of great importance in electrocapillarity (§ 5) and in the stability of hydrophobic colloids (Chapters VI, VII, VIII).

h. Another approach to the free energy of the double layer

There is another way of approach to the free energy of the double layer, which is more convenient for explicit calculations in some cases. (Interaction of two flat double layers, see chapter VI § 3b, p. 252) and which shows clearly the close connection between the activity of strong electrolytes according to DEBYE and HÜCKEL and the free energy of the double layer.

An imaginary charging process, in which the charge of all ions present in the system is gradually increased from zero to the normal value, is used. As, however, the properties of the double layer are not solely determined by the charge of the ions, but also by their preference for one of the two phases present, it will be necessary to consider apart from the change of the charges also a change in thermodynamic potential of the ions. We will give a detailed treatment for the completely reversible case (*cf.* § 3b), the treatment for the polarized electrode (§ 3a) being analogous.

The stage of the charging process is indicated by a parameter λ, varying from 0 to 1. The ionic charges at stage λ are $z_i e \lambda$. The chemical potential of the ions (μ_i) are assumed to be independent of λ in the solution but to be a function of λ later to be defined in the solid phase. The free energy of the double layer can then be described by considering only the excess charges in the double layer as the charging and discharging of the other ions is independent of the presence of the interface.

When at stage λ all ionic charges are increased by an amount $z_i e \mathrm{d}\lambda$, the space charge ρ and the surface charge σ in the double layer increase by $\rho \frac{\mathrm{d}\lambda}{\lambda}$ and $\frac{\sigma\,\mathrm{d}\lambda}{\lambda}$ respectively. Moreover, the chemical potential of the excess ions on the surface is increased by an amount $\frac{\partial \mu_{is}}{\partial \lambda} \mathrm{d}\lambda$ per ion or $\frac{\sigma}{\lambda e} \frac{\partial \mu_{is}}{\partial \lambda} \mathrm{d}\lambda$ for all ions per cm². The total amount of work done at this stage[1] is

$$\mathrm{d}G_s = \int\limits_{\text{volume}} \rho\psi\,\mathrm{d}V \frac{\mathrm{d}\lambda}{\lambda} + \int\limits_{\text{surface}} \sigma\,\psi_\circ\,\mathrm{d}S \frac{\mathrm{d}\lambda}{\lambda} + \int\limits_{\text{surface}} \frac{\sigma}{\lambda e} \frac{\partial \mu_{is}}{\partial \lambda} \mathrm{d}\lambda\,\mathrm{d}S \tag{75}$$

and the free energy of the double layer is found by integrating (75)

$$G_s = G\,(0) + \int_0^1 \frac{\mathrm{d}\lambda}{\lambda} \int_V \rho\psi\mathrm{d}V + \int_0^1 \frac{\mathrm{d}\lambda}{\lambda} \int_S \sigma\,\psi_\circ\,\mathrm{d}S + \int_0^1 \frac{\mathrm{d}\lambda}{\lambda} \frac{\sigma}{e} \frac{\partial \triangle \mu}{\partial \lambda} \int_S \mathrm{d}S \tag{76}$$

in which $G\,(0)$ represents the free energy of the double layer at $\lambda = 0$ and $\triangle\,\mu = \mu_{is} - \mu_{i\ \text{solution}}$, where $\mu_{i\ \text{solution}}$ is independent of λ. As the double layer is always in equilibrium $\triangle\,\mu + \lambda\,e\,\psi_\circ = 0$.

Now the effective integration of (76) completely depends upon the choice made for the dependence of $\triangle\,\mu$ on λ. When $\triangle\,\mu$ is assumed to be zero during the whole charging process, changing only from 0 to the final value when $\lambda = 1$, then the first two integrals are zero and so is $G\,(0)$. The free energy of one cm² of the double layer will then be reduced to the last integral which can be written as

$$G_s = \int_0^1 \frac{\mathrm{d}\lambda}{\lambda} \frac{\sigma}{e} \frac{\partial}{\partial \lambda} (\triangle\,\mu) = \int \frac{\sigma}{\lambda e} \mathrm{d}\,\triangle\,\mu = - \int_0^{\psi_\circ} \sigma\,\mathrm{d}\,\psi_\circ$$

which is the same expression as that found in § 4 g eq. (72) p. 141.

Another convenient way of integration is given by the condition that ψ_0 remains constant. In that case

$$\frac{\partial \triangle\,\mu}{\partial \lambda} = \frac{\partial\,(-\lambda\,e\,\psi_\circ)}{\partial \lambda} = -e\,\psi_\circ$$

and the last two integrals of (76) are cancelled.

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[1] cf. R. H. Fowler, *Statistical Mechanics,* 2nd ed. Cambridge University Press 1936, p.269; L. Onsager, *Chem. Revs.,* 13 (1933) 73; R. M. Fuoss, *J. Chem. Phys.,* 2 (1934) 818, where this method is directly derived from statistical mechanics; For the double layer this relation has been derived by E. J. W. Verwey and J. Th. G. Overbeek, *Theory of the stability of lyophobic colloids,* Amsterdam 1948, p. 56.

Then G_s is found from

$$G_s = G_s\,(0) + \int_0^1 \frac{\mathrm{d}\lambda}{\lambda} \int \rho\ \psi\,\mathrm{d}V \tag{77}$$

where the integration has to be carried out under the condition that ψ_0 has always the same value.

For the infinitely large flat diffuse double layer G_s (0) is zero, and the integral may be evaluated in the following way.

$$G_s = \int_0^1 \frac{\mathrm{d}\,\lambda}{\lambda} \int \rho\psi\ \mathrm{d}V = -\frac{\varepsilon}{4\,\pi} \int_0^1 \frac{\mathrm{d}\,\lambda}{\lambda} \int_0^\infty \psi \frac{\mathrm{d}^2\psi}{\mathrm{d}x^2}\,\mathrm{d}x = \frac{\varepsilon}{4\,\pi} \int_0^1 \frac{\mathrm{d}\,\lambda}{\lambda} \int_{\psi=0}^{\psi=\psi_0} \psi \cdot \mathrm{d}\left(\frac{\mathrm{d}\psi}{\mathrm{d}x}\right)$$

With the value for $\frac{\mathrm{d}\psi}{\mathrm{d}x}$ taken from eq. (45) p. 130, remembering that at stage λ, e has to be replaced by $\lambda\,e$, we find

$$G_s = -\sqrt{\frac{2\,\varepsilon\,n\,kT}{\pi}} \int_0^1 \int_0^{\psi_0} \frac{\psi}{\lambda} \cosh \frac{z\ \lambda\,e\ \psi}{2\,kT} \frac{z\ \lambda\,e}{2\,kT}\,\mathrm{d}\lambda\ \mathrm{d}\psi$$

$$= -\sqrt{\frac{2\,\varepsilon\,n\,kT}{\pi}} \int_0^{\psi_0} \mathrm{d}\,\psi \int_{\lambda=0}^{\lambda=1} \cosh \frac{z\,\lambda\,e\,\psi}{2\,kT}\,\mathrm{d}\,\frac{z\,\lambda\,e\,\psi}{2\,kT} =$$

$$= -\sqrt{\frac{2\,\varepsilon\,n\,kT}{\pi}} \int_0^{\psi_0} \sinh \frac{z\,e\,\psi}{2\,kT}\,\mathrm{d}\psi =$$

$$G_s = -\frac{8\,n\,kT}{\varkappa}\,(\cosh \frac{z\,e\,\psi_0}{2\,kT} - 1) \tag{78}$$

which is the same result as (74) which was calculated by the other method.

An application of this second method of evaluating the free energy of the double layer will be given in chapter VI in the treatment of the interaction of two flat double layers.

For one plane double layer or two parallel plane double layers the mathematical equivalence of the two methods was demonstrated by CASIMIR [1]. LEVINE [2] drew attention to the fact that for the double layer on a curved surface G_s (0) from eq. (77) is different from zero and has to be evaluated separately.

i. The double layer at curved interfaces

So far our considerations have been restricted to flat interfaces. Practically this means that the radius of curvature of the interface is large as compared to the distance

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[1] H. B. G. CASIMIR in E. J. W. VERWEY and J. TH. G. OVERBEEK, *Theory of the stability of lyophobic colloids*, Amsterdam 1948, pp. 60, 63—65.

[2] S. LEVINE, *Phil. Mag.*, (7) 41 (1950) 53.

over which changes of concentration make themselves felt. In colloidal systems this will not always be the case and therefore it is useful to treat some cases of curved double layers. The double layer around spherical particles has been extensively treated[1] and also some data are known on cylindrical particles[2].

i. 1. *Charge and potential in a spherical double layer*

In the approximation for small potentials the distribution of charge and potential around a spherical particle has been given by DEBYE and HÜCKEL[3]

$$\psi = \psi_0 \, a \, \frac{e^{-\varkappa (r-a)}}{r} \tag{79}$$

where a is the radius of the particle and r the distance from its centre.

The charge of the particle Q is related to the surface potential ψ as follows

$$Q = a \varepsilon (1 + \varkappa a) \psi_0 \tag{80}$$

Solutions of the complete POISSON-BOLTZMANN equation (40), p. 128, have been derived by MÜLLER[4] who used a graphical procedure, and by GRONWALL[5] who solved these equations analytically. Unfortunately just in the case when the greatest differences between the treatment for flat double layers and curved ones are to be expected, the objections raised by KIRKWOOD and others (see § 4c p. 129) against the use of the complete eq. (40) gain more and more weight; and therefore it remains doubtful whether extension of the theory to the case of large potentials on spherical double layers, which mathematically is very difficult to handle, is worth this trouble.

Moreover in the spherical double layer with $1/\varkappa$ large compared with the radius of the particle, the distribution of the potential is governed more by the factor $1/r$ in eq. (79) which comes from the spherical extension of the lines of force, than from double layer effects and therefore a slight incorrectness in the treatment of the double layer does not influence the distribution of the potential very much. Table 1 in which the approximate theory of DEBYE and HÜCKEL and the exact solution of eq. (40) by MÜLLER are compared for a case where $1/\varkappa = 5\,a$, illustrates this clearly.

TABLE 1

Illustrating the difference between the approximation of DEBYE and HÜCKEL and the theory of MÜLLER for spherical particles. $\varkappa a = 0.2 \quad z_+ = z_- = z$

$\varkappa r$	$\varkappa (r - a)$	$z e \psi / kT$	
		MÜLLER	DEBIJE and HÜCKEL
0.2	0.0	2.83	2.78
0.5	0.3	0.82^6	0.82^5
1.0	0.8	0.25	0.25

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[1] P. DEBYE and E. HÜCKEL, *Physik. Z.*, 24 (1923) 185; 25 (1924) 97; H. MÜLLER, *Kolloidchem. Beihefte*, 26 (1928) 257; T. H. GRONWALL, *Proc. Nat. Acad. Sci. U.S.*, 13 (1927) 198; T. H. GRONWALL, V. K. LA MER, and K. SANDVED, *Physik. Z.*, 29 (1928) 358; V. K. LA MER, T. H. GRONWALL, and L. J. GREIFF, *J. Phys. Chem.*, 35 (1931) 2245.

[2] G. P. DUBE, *Indian J. Phys.*, 17 (1943) 189; See also S. LEVINE, *Trans. Faraday Soc.*, 47 B (1946) 102.

[3] See footnote 1

[4] See footnote 1

[5] See footnote 1

i. 2. Free energy of the spherical double layer

Estimation of the free energy of spherical double layers by the method outlined in § 4g, that is by evaluation of the integral

$$G = -\int_0^{\psi_\circ} Q \, d\psi \tag{81}$$

is very simple, because for the reasons outlined in § 4i 1 our discussion will be restricted to small potentials where Q and ψ are proportional to each other. Using eq. (80) we find

$$G = -{}^1/_2 \, Q \, \psi_0 = -{}^1/_2 \, a\varepsilon \, (1 + \varkappa \, a) \, \psi_0{}^2 \tag{82}$$

Application of the charging method of DEBYE and HÜCKEL (*cf.* § 4 h) is instructive in this case because the free energy of the double layer does not tend to zero when the ionic charges do so, at least not when the condition of constant surface potential is maintained.

Eq. (77) may be written for a sphere of radius a

$$G_s = G_s \, (\lambda = 0) + \int_0^1 \frac{d\lambda}{\lambda} \int_a^\infty \rho \, \psi \, 4 \, \pi \, r^2 \, dr \tag{83}$$

The free energy for $\lambda = 0$ is determined as

$$G_s \, (\lambda = 0) = -\left[\int_0^{\psi_\circ} Q \, d\psi \right]_{\lambda = 0} = -{}^1/_2 \, Q_{\lambda = 0} \, \psi_{\circ \, \lambda = 0}. \tag{84}$$

When $\lambda = 0$ all ionic interaction has disappeared and so Q (0) is simply given by

$$Q \, (0) = \varepsilon \, a \, \psi_\circ \tag{85}$$

from which follows that

$$G_s \, (\lambda = 0) = -{}^1/_2 \, \varepsilon a \, \psi^2_\circ \tag{86}$$

The integration of the second term of eq. (83) is carried out as follows

$$\int_0^1 \frac{d\lambda}{\lambda} \int_a^\infty \rho \, \psi \, 4 \, \pi \, r^2 \, dr = \int_0^1 \frac{d\lambda}{\lambda} \int_a^\infty - \frac{\varepsilon}{4 \, \pi} \, \psi \triangle \psi \, 4 \, \pi \, r^2 \, dr =$$

$$= -\int_0^1 \frac{d\lambda}{\lambda} \int_a^\infty \varepsilon \, \lambda^2 \, \varkappa^2 \, \psi^2 \, r^2 \, dr = -\, \varepsilon \, \varkappa^2 \, a^2 \, \psi_\circ{}^2 \int_0^1 d\lambda \int_\lambda^\infty e^{-2 \, \lambda \, \varkappa \, (r - a)} \, dr =$$

$$= -\frac{\varepsilon \, \varkappa \, a^2 \, \psi_\circ{}^2}{2} \int_0^1 d\lambda = -\frac{\varepsilon \, \varkappa \, a^2 \, \psi_\circ{}^2}{2} \tag{87}$$

Taking (86) and (87) together we find for the free energy of the double layer around a spherical particle

$$G_s = -\frac{\varepsilon \, a \, \psi_\circ{}^2}{2} - \frac{\varepsilon \, \varkappa \, a^2 \, \psi_\circ{}^2}{2} = -\frac{\varepsilon \, a}{2} \, (1 + \varkappa \, a) \, \psi_\circ{}^2 \tag{88}$$

which has also been derived by direct integration of $- Q \, d \, \psi$ (eq. 81, 82).

i. 3. *Cylindrical double layer*

The diffuse double layer around cylindrical particles has been treated by DUBE [1] for the case of small potentials. The relation between charge and potential can be expressed by means of BESSEL functions. The same relation has been derived by GORIN [2].

§ 5. THE ELECTROCAPILLARY CURVE AND RELATED EXPERIMENTS AS AN EXAMPLE OF THE COMPLETELY POLARIZABLE INTERFACE

The interface between mercury and an aqueous solution is a very favourable case for studying the properties of the electrical double layer. By measuring the surface tension the free energy of the double layer is directly accessible. The potential difference between the two phases can be altered within wide limits by applying an external potential difference. From the relation between surface tension and potential the charge and the capacity of the double layer can be derived by differentiation (see § 3, eq. (20), § 4, p. 131). Moreover, these two magnitudes can also be directly determined by experiment. So it is not to be wondered at that our best and most extensive data on the double layer are coming from the mercury water interface.

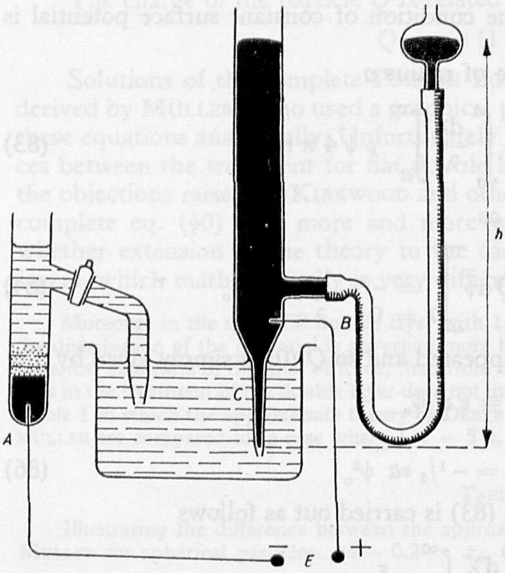

Fig. 13. Capillary electrometer after LIPPMANN. The polarizing tension E is applied between a calomel electrode A and a mercury electrode B. The interface between mercury and solution is situated in a narrow, slightly conical capillary C. The surface tension is measured by determining the height h for which the meniscus is at a certain point in C.

a. The electrocapillary curve

The first determinations of the relations between surface tension and polarizing potential are due to LIPPMANN [3], whose experimental set-up is shown in Fig. 13 and is still in use without many alterations.

Some authors [4] used more complicated forms of apparatus, others made use of completely different methods for the determination of the surface tension (drop weight [5], form of a sessile drop [6]) but they seem to be less accurate and not so easy to handle as the classical capillary electrometer.

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[1] G. P. DUBE, *Indian J. Phys.*, 17 (1943) 189.

[2] M. H. GORIN in H. A. ABRAMSON, L. S. MOYER, and M. H. GORIN, *Electrophoresis of proteins*, New York 1942, p. 126.

[3] G. LIPPMANN, *Ann. Physik*, 149 (1873) 546; *Ann. chim. et phys.*, (5) 5 (1875) 494, 12 (1877) 265; *Wied. Ann.*, 11 (1880) 316.

[4] F. O. KOENIG, *Z. physik. Chem.*, A 154 (1931) 454; L. A. HANSEN and J.W. WILLIAMS, *J. Phys. Chem.*, 39 (1935) 439.

[5] G. KUCERA, *Ann. Physik.*, 11 (1903) 529, 698; S. R. CRAXFORD and H. A. C. MC KAY, *J. Phys. Chem.*, 39 (1935) 545.

[6] G. GOUY, *Ann. phys.*, 6 (1916) 5.

In a very narrow, slightly conical, capillary C an interface between mercury and an aqueous solution is kept at a chosen place by applying a suitable pressure, h, when a given polarizing tension E has been set up between the mercury (B) and the calomel electrode (A). The *interfacial tension can be determined from the height h and the* diameter of the capillary at the chosen place. The general type of relation between the interfacial tension and the polarizing potential E is shown in Fig. 14. A roughly parabolic curve is found. At the *electrocapillary maximum* the charge on the mercury is zero, for $\partial G_s/\partial E = 0$ at that point and $\partial G_s/\partial E = -\sigma$ (see eq. (20) p. 121). On the *rising branch* the mercury bears a positive charge and on the descending branch a negative one. The measurements are limited at the cathodic side by the discharge of hydrogen (when the overvoltage of hydrogen on mercury is surpassed) and at the anodic side by oxidation of the mercury surfave giving rise to unreproducible layers which hamper the motion of the meniscus.

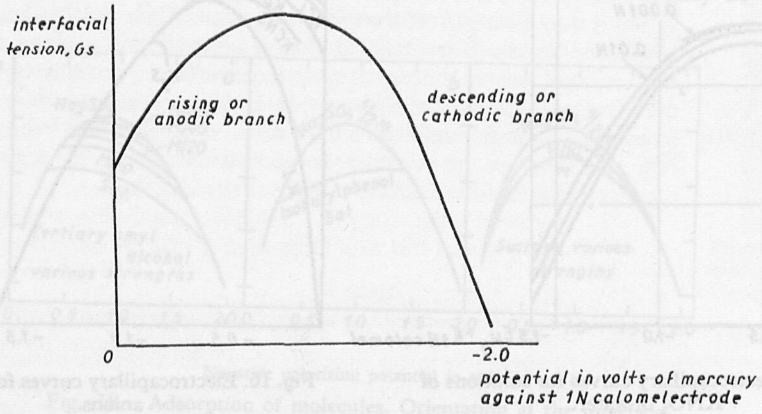

Fig. 14. General form of electrocapillary curve.

In order to obtain reliable results the apparatus and the chemicals must be very thoroughly cleaned. *E.g.*, PROSKURNIN and FRUMKIN[1] have shown, how, by touching the mercury surface with a piece of picein (usually considered to be a very inactive wax) the shape of the electrocapillary curve is profoundly altered. This is one of the principal reasons why many earlier measurements on electrocapillary phenomena can now no longer be regarded as being trustworthy. The second reason is, that for the interpretation of electrocapillary curves in the form of models *two differentiations* have to be carried out, which is only possible when the original data are extremely accurate.

The first differentation $\partial G_s/\partial E$ gives the charge of the mercury, the second differential $\partial^2 G_s/\partial E^2$ the capacity (differential capacity) of the double layer and it is this last property which is most easily accessible to model considerations. If the capacity of the double layer were a constant, the electrocapillary curve would be exactly parabolic and thus it is the width of the parabola which informs us on the mean value of the capacity, and the deviations from the parabolic form reflect the non-constancy of the capacity. The absolute height of the curve is relatively unimportant for double

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[1] M. PROSKURNIN and A. FRUMKIN, *Trans. Faraday Soc.*, 31 (1935) 110.

layer considerations. The relative situation of curves for different solutions again is important as the derivative $(\partial G_s/\partial \mu_i)_E$ gives information on the amount of the component i adsorbed. (Eq. (19) p. 121).

Fig 15 [1] shows electrocapillary curves of different solutions of KNO_3. The downward displacement of the curves for more concentrated solutions ($\partial G_s/\partial \mu_i$ negative) indicates a positive adsorption of this salt even at the electrocapillary maximum that is in the absence of charge on the mercury. The maximum is displaced slightly to more cathodic polarization indicating a relative negativation of the mercury surface which might tentatively be interpreted as a primary adsorption of the anions followed by electrostatic attraction of the potassium ion. (see also the remarks on GRAHAME's modification of the theory of STERN, § 4d p. 134).

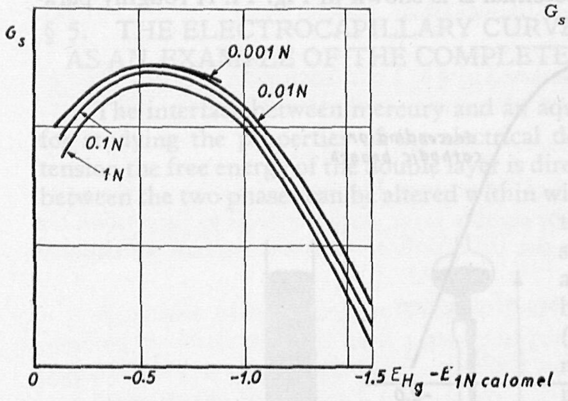

Fig. 15. Electrocapillary curves for solutions of KNO_3 in water.

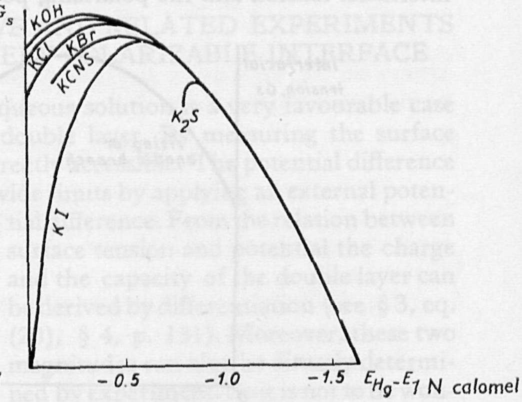

Fig. 16. Electrocapillary curves for different anions.

The preponderance of the anions in the adsorption comes out much more clearly when one compares electrocapillary curves for different salts as given in Fig. 16 [1].

Various potassium salts all show the same cathodic branch of the electrocapillary curve. Here the anions are repelled electrostatically from the surface and only the adsorption of the cation plays a role. In the anodic branches however, large differences are found and especially the more highly polarizable anions are strongly adsorbed, depressing thereby the surface tension and displacing the maximum to lower values at more negative potentials.

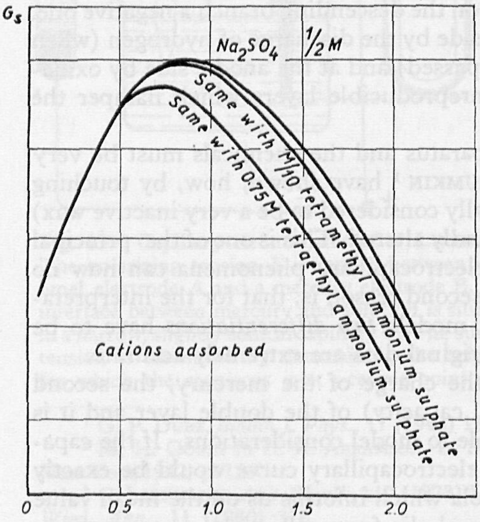

Fig. 17. Adsorption of cations.

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[1] Taken from A. FRUMKIN, *Ergeb. exakt. Naturw*, 7 (1928) 235.

Curves for different inorganic cations are nearly coincident, indicating almost complete absence of specific adsorption of the cations. More strongly adsorbable organic cations, however, depress the cathodic branch of the curve as is demonstrated by Fig. 17[1].

The addition of non-ionic organic substances often results in a more or less symmetric truncation of the electrocapillary curve. See Fig. 18[1].

In the central part of the curves the surface tension is strongly depressed indicating a pronounced adsorption. From the displacement of the maximum it may be inferred that amyl alcohol turns its positive pole to the mercury, *iso*butylphenol its negative pole, whereas the adsorption of sucrose does not introduce a dipole moment on the interface.

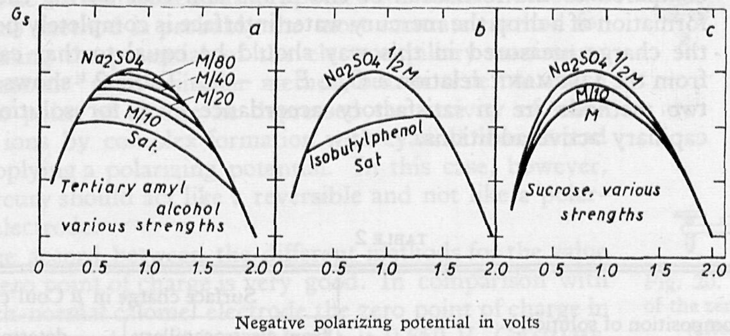

Fig. 18. Adsorption of molecules. Orientation at the interface. Expulsion of adsorbed molecules by high charge of the surface.

At large positive or negative polarizations the electric field strength close to the interface gets higher and under these circumstances the counter ions and the highly polar water molecules are drawn more strongly to the interface thereby expelling the adsorbed less-polar molecules.

For a quantitative theory of this phenomenon see Butler[2] and Frumkin[3].

A final remark[4] might be made on the potential E, which plays a rôle in the differentiations mentioned in this section. It follows from the theory given in § 3 that the potential with respect to which the interfacial tension has to be differentiated in order to get the surface charge, and which has to be held constant in the differentiation with respect to μ_i (eqs. (19)) is the externally applied potential difference (E in Fig. 1 p. 120) and not the less well defined "potential difference between the two phases".

b. Direct determinations of the surface charge

The surface charge σ, which can be calculated by differentiation of the electrocapillary curve, can also be determined directly. For this purpose Frumkin[5] used the

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[1] From N. K. Adam, *The physics and chemistry of surfaces*, 3rd ed. Oxford 1941, p. 341.

[2] J. A. V. Butler, *Proc. Roy. Soc., London*, A 122 (1929) 399. See also J. A. V. Butler, *Electrocapillarity*, London 1940, p. 82.

[3] A. Frumkin, *Z. Physik*, 35 (1926) 792.

[4] See D. C. Grahame, *Chem. Revs.*, 41 (1947) 458; also W. Schottky, *Thermodynamik*, Berlin 1929, p. 121—122.

[5] A. Frumkin, *Z. physik. Chem.*, 103 (1923) 55.

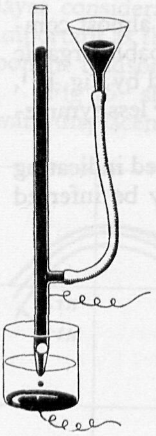

Fig. 19. Determination of the surface charge.

simple set-up sketched in Fig. 19. The mercury flows drop by drop from the capillary tip and the drops unite with the pool of mercury on the bottom of the vessel. Each drop represents a certain new surface, and thus needs a certain amount of charge, when the potential difference between the mercury in the capillary and that in the pool is kept constant. This charge can be measured as a current flowing *e.g.*, from the capillary to the pool when the capillary is negatively polarized. When it may be assumed that the formation of the double layer is rapid compared to the formation of the drops and that during the time of formation of a drop the mercury water interface is completely polarized, the charge measured in this way should be equal to that calculated from the LIPPMANN relation $\partial\, G_s/\partial\, E = -\sigma$. Table 2[1] shows that the two methods are in satisfactory accordance even for solutions with capillary active additions.

TABLE 2

Composition of solution		Surface charge in μ Coul/cm^2	
		from electrocapillary curve	determined directly
1 N NaCl	saturated with Hg_2Cl_2	50	47
1 N KOH	,, ,, HgO	21	17
1 N H_2SO_4	,, ,, Hg_2SO_4	39	39
1 N KNO_3 + 0.01 N KI	,, ,, Hg_2I_2	86	90
1 N KOH + ether	,, ,, HgO	— 1.5	— 1.3

SCHOFIELD[2], using a very elegant method to determine the charge set free (in the form of Hg_2^{++} ions) when mercury drops unite with a pool of mercury, could confirm and extend FRUMKIN's results.

More recently PHILPOT[3] carried out measurements of the charge of the interface mercury-sodium chloride or hydrochloric acid solution, which are in very good accord with CRAXFORD's[4] determinations of the electrocapillary curve for the same solutions.

Similar experiments have been carried out by GRAHAME[5].

By suitable polarization of the mercury flowing from the capillary the zero point of charge may be determined[6]. In that case no current flows in the outer circuit.

Another way of determining the potential of zero charge, that is the potential of the electrocapillary maximum has been suggested by HELMHOLTZ[7] and is based upon the fact that an *isolated* mass of mercury automatically comes to the potential of zero charge when the interface with the solution is sufficiently enlarged. Indeed if the

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[1] From A. FRUMKIN, *Erg. exakt. Naturw.*, 7 (1928) 235.
[2] R. K. SCHOFIELD, *Phil. Mag.*, (7) 1 (1926) 641.
[3] J. ST. L. PHILPOT, *Phil. Mag.*, (7) 13 (1932) 775.
[4] S. R. CRAXFORD, *Dissert.*, Oxford 1936, cited from *Trans. Faraday Soc.*, 36 (1940) 85.
[5] D. C. GRAHAME, *J. Am. Chem. Soc.*, 63 (1941) 1207 esp. p. 1212.
[6] H. PELLAT, *Compt. Rend.*, 104 (1887) 1099.
[7] H. VON HELMHOLTZ, *Wiss. Abhandl. physik. tech. Reichsanstalt*, 1 (1879) 925.

interface is completely polarizable, its charge is constant and by enlarging the interface the charge density can be made arbitrarily small. The method is usually carried out by letting a fine jet of mercury flow into the solution. Where the mercury jet hits the solution, it is divided into many small droplets, thereby enormously enlarging the surface. (See Fig. 20).

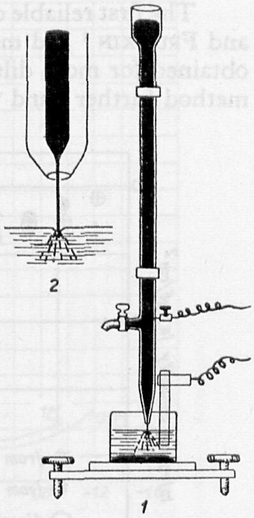

Fig. 20. Determination of the zero point of charge (after PASCHEN).

The method has been applied by PASCHEN [1], SMITH and MOSS [2], ERDEY-GRUZ and SZARVAS [3] and GRAHAME, LARSEN, and POTH [4]. The last mentioned authors point out that for dilute solutions this method is probably the most accurate method for determining the potential of the electrocapillary maximum.

PALMAER [5] used a similar method but in order to reach the zero point of charge he depressed the activity of mercurous ions by complex formation with cyanide ions instead of by applying a polarizing potential. In this case, however, the mercury should act like a reversible and not like a polarizable electrode.

The accord between the different methods for the value of the zero point of charge is very good. In comparison with the tenth-normal calomel electrode the zero point of charge in one tenth normal potassium chloride is 0.559 V. GRAHAME, LARSEN, and POTH (*l.c.*) give a list of the values found by different authors with different methods which we repeat here without details: *0.5590*, *0.559*, *0.560*, *0.5595*, 0.556, 0.553, 0.57, 0.573.

c. Direct determination of the capacity

As the capacity of the double layer is the quantity most easily compared with model considerations on the structure of the double layer, a direct determination of this capacity seems a very attractive method of investigation. In principle the measurement is very simple. The cell containing the mercury-solution interface forms one arm of a capacitance bridge, constructed in such a way that a variable d.c. potential can be applied to the cell. The measurement of the capacity which is in series with the resistance of the cell, is carried out by a small a.c. potential in the bridge. The frequency used is rather low (1000 cycles per second or lower). Its actual value does not — within limits — influence the results obtained [6]. The a.c. potential on the double layer is of the order of a few millivolts. As in all electrocapillary work mercury, solution and the glasswork should be scrupulously clean, exempt from capillary active impurities and well deaerated. In earlier work [7] these conditions have not always been observed with the result that the measured capacities were much too low.

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[1] F. PASCHEN, *Ann. Physik*, 43 (1891) 568; 41 (1890) 42, 177.

[2] S. W. J. SMITH and H. MOSS, *Phil. Mag.*, (6) 15 (1908) 478.

[3] T. ERDEY-GRUZ and P. SZARVAS, *Z. physik. Chem.*, A 177 (1936) 277.

[4] D. C. GRAHAME, R. P. LARSEN, and M. A. POTH, *J. Am. Chem. Soc.*, 71 (1949) 2978.

[5] W. PALMAER, *Z. physik. Chem.*, 25 (1898) 265; 28 (1899) 257; 36 (1901) 664; 59 (1907) 129.

[6] D. C. GRAHAME, *J. Am. Chem. Soc.*, 68 (1946) 301.

[7] F. KRÜGER, *Z. physik. Chem.*, 45 (1903) 1; *Ann. Physik*, (4) 21 (1906) 701; T. ERDEY-GRUZ and G. G. KROMREY, *Z. physik. Chem.*, A 157 (1931) 213. The measurements by F. P. BOWDEN and E. K. RIDEAL, *Proc. Roy. Soc. London*, A 120 (1928) 59 on the charge necessary to polarize the surface to a certain potential (*cf* § 5b) also led to values of the capacity which were 3 or 4 times too low.

The first reliable determinations of the capacity have been reported by Proskurnin and Frumkin [1] and more recently by using very low frequencies, data have also been obtained for more dilute (10^{-3} and 10^{-4} N) solutions [2]. Grahame developed the same method further [3] and was able to obtain results with an accuracy [4] of 0.1 to 1 percent in the capacity. By integrating these results twice the electrocapillary curve is found again, but with an accuracy which has probably never been reached in the direct determination of surface tension vs. potential.

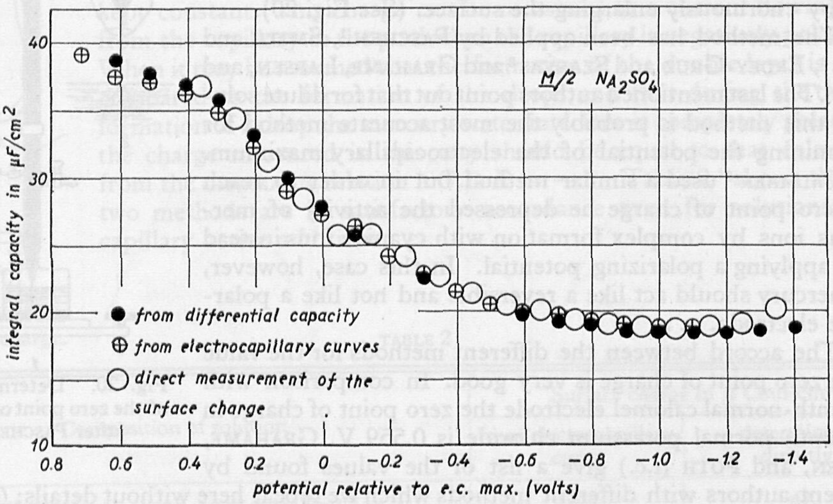

Fig. 21.

The concordance between the three different methods is very satisfactory as is illustrated in Fig. 21, where the integral capacity of the double layer mercury $\frac{M}{2}$ Na_2SO_4 is determined

a. from the electrocapillary curve (Gouy)
b. from measurement of the surface charge (Grahame)
c. from determination of the differential capacity (Grahame) and application of eq. (89)

$$K = \frac{\sigma}{\psi_\circ} = \frac{1}{\psi_\circ}\int_0^{\psi_\circ} c\, d\psi \tag{89}$$

in which c is the differential and K the integral capacity.

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[1] M. Proskurnin and A. Frumkin, *Trans. Faraday Soc.*, 31 (1935) 110; *Acta Physicochim. U.R.S.S.*, 4 (1936) 825; T. Borissova and M. Proskurnin, *Acta Physicochim. U.R.S.S.*, 4 (1936) 819.

[2] M. Proskurnin and M. A. Vorsina, *Compt. rend. acad. sci. U.R.S.S.*, 24 (1939) 915; M. A. Vorsina and A. Frumkin, *ibidem*, p. 918; M. A. Vorsina and A. Frumkin, *Acta Physicochim. U.R.S.S.*, 18 (1943) 242.

[3] D. C. Grahame, *J. Am. Chem. Soc.*, 63 (1941) 1207; 68 (1946) 301; See also *Chem. Revs.*, 41 (1947) 441.

[4] D. C. Grahame, *J. Am. Chem. Soc.*, 71 (1949) 2975.

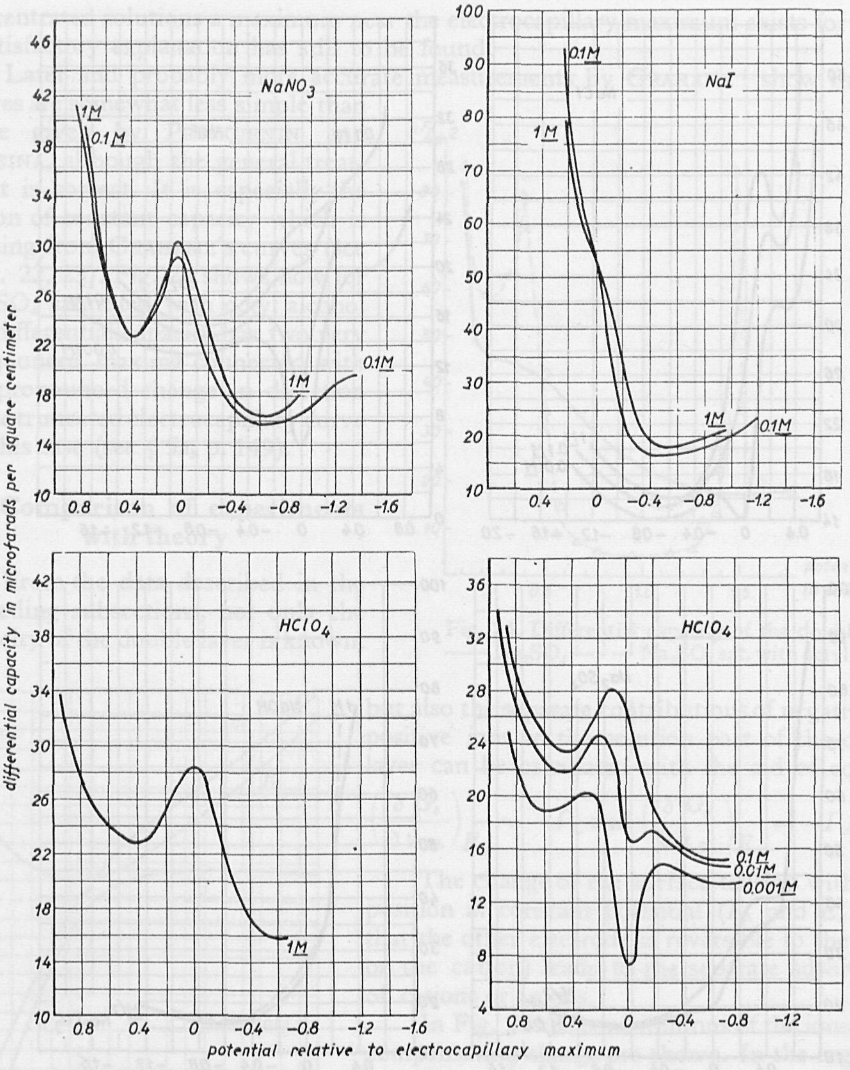

Fig. 22. Differential capacity of the electrical double layer between mercury and aqueous solutions of the salts named. T = 25°C.

In Figs. 9, 22, 23, 24 we give a few examples of the differential capacity measured directly.

Fig. 9 gives measurements by Proskurnin and Vorsina [1] on KCl of different concentrations and a very dilute solution of HCl. The curves suggest strongly that both in cathodic and in anodic polarization a constant value of the capacity is reached which

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[1] M. Proskurnin and M. A. Vorsina, *Compt. rend. acad. sci. U.R.S.S.*, 24 (1939) 915; M. A. Vorsina and A. Frumkin, *ibidem*, p. 918.

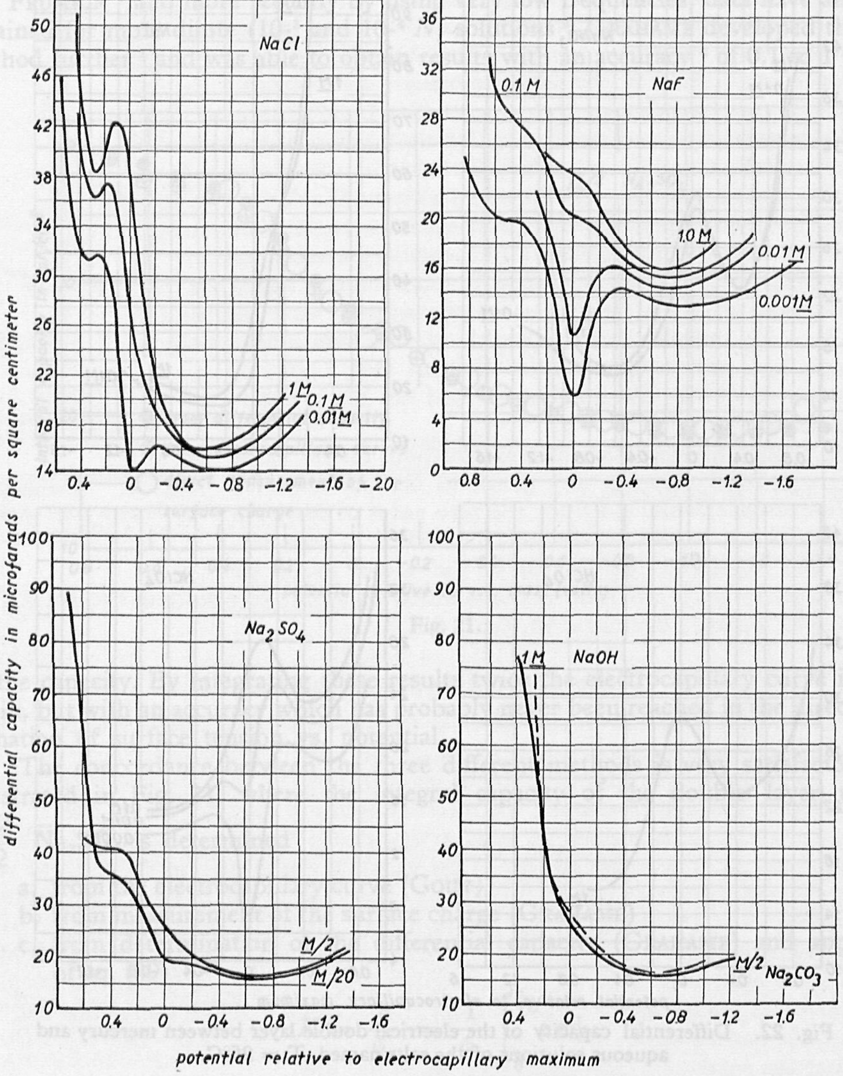

Fig. 23. Differential capacity of the electrical double layer between mercury and aqueous solutions of the salts named. T = 25°C.

might be interpreted as the capacity of the cationic and anionic STERN layer resp. At very high anodic or cathodic polarization the capacity becomes very large probably owing to non-ideal polarizability of the interface. In the middle part of the curves, near the electrocapillary maximum, the capacity falls to a low value especially for dilute solutions. This is easily explained by the development of a diffuse GOUY layer (*cf.* Fig. 7). For concentrated solutions a maximum near the electrocapillary maximum exists for which a satisfactory explanation has still to be found.

Later and probably more accurate measurements by GRAHAME[1] show that the curves are somewhat less simple than those given by PROSKURNIN and VORSINA, although the general treatment is correct. It is especially the region of constant capacity which is missing from GRAHAME's curves (see Figs. 22, 23). Fig. 24 shows how for Na_2SO_4 saturated with octyl alcohol the differential capacity has two very pronounced maxima connected with the pronounced change in direction of the truncated electrocapillary curve for this case (see § 5a, p. 149).

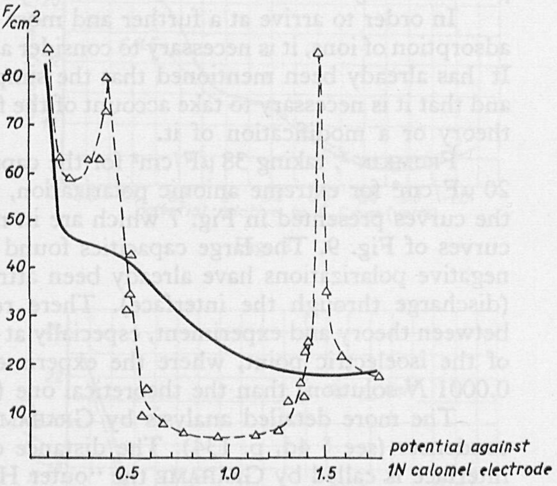

Fig. 24. Differential capacity of the double layer. ——— Na_2SO_4 — — — Na_2SO_4 sat. with octyl alcohol.

d. Comparison of experiments with theory

From the data described in the preceding subsections, not only the capacity of the double layer is known, but also the separate contributions of negative and positive ions to the solution part of the double layer can be calculated with the aid of eq. (19)

$$\left(\frac{\partial G_s}{\partial \mu_{CA}}\right)_{E_A} = -\Gamma_C \text{ and } \left(\frac{\partial G_s}{\partial \mu_{CA}}\right)_{E_C} = -\Gamma_A \quad (19)$$

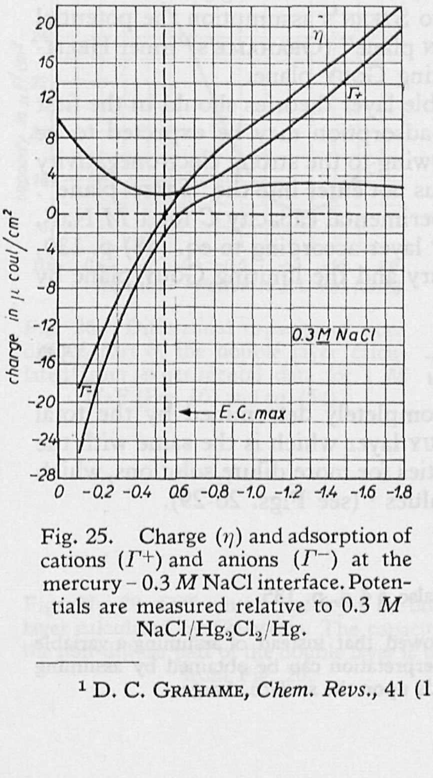

Fig. 25. Charge (η) and adsorption of cations (Γ^+) and anions (Γ^-) at the mercury - 0.3 M NaCl interface. Potentials are measured relative to 0.3 M $NaCl/Hg_2Cl_2/Hg$.

The change of the surface tension with composition at constant potential (E_A and E_C mean that the other electrode is reversible to the anion or the cation) leads to the separate adsorptions of cations or anions.

In Fig. 25 the contributions of the ions to the compensating charge are shown. In the region of high negative charge on the mercury, this charge is for the greater part compensated by cations and for a small, almost constant part by desorption of anions. With positive polarization again a large part of the positive charge is compensated by anions but there remains a positive cation adsorption, which even increases with increasing positive potential. The most simple inference seems that there is a rather strong non-electrostatic anion

[1] D. C. GRAHAME, *Chem. Revs.*, 41 (1947) 441 esp. p. 462, 463.

adsorption but that specific cation adsorption is probably absent. The increased specific anionic adsorption is attributed by GRAHAME[1] to the strengthening of the supposed covalent bond between the Cl^- ions and the mercury in the presence of positive charge.

In order to arrive at a further and more quantitative interpretation of charge and adsorption of ions, it is necessary to consider a rather detailed model of the double layer. It has already been mentioned that the simple GOUY picture leads to inconsistencies and that it is necessary to take account of the finite dimensions of the ions by the STERN theory or a modification of it.

FRUMKIN[2], taking 38 μF/cm^2 for the capacity at extreme positive polarization and 20 μF/cm^2 for extreme anionic polarization, finds for solutions from 0.1 to 0.0001 N the curves presented in Fig. 7 which are in not too bad accord with the experimental curves of Fig. 9. The large capacities found experimentally for extreme positive and negative polarizations have already been attributed to the non-ideality of the system (discharge through the interface). There remains, however, a certain discrepancy between theory and experiment, especially at low concentrations in the neighbourhood of the isoelectric point, where the experimental capacity is higher (3.9 μF/cm^2 for 0.0001 N solution) than the theoretical one (2.15 μF/cm^2).

The more detailed analysis by GRAHAME[3] distinguishes *two* kinds of molecular condenser (see § 4d, p. 134). The distance of closest approach of the cations to the interface is called by GRAHAME the "outer HELMHOLTZ plane". We wish to introduce the name "limiting GOUY plane" thereby expressing the fact that up to this plane the double layer may be treated completely according to the diffuse double layer theory.

The anions, however, according to indications, are more strongly adsorbed and closer to the mercury. This implies that contrary to STERN's assumption the potential in the plane of anions which we shall call the "STERN plane" (GRAHAME's "inner HELMHOLTZ plane") is not the same as that in the limiting GOUY plane.

GRAHAME therefore suggests that a test of double layer theories should in the first place be directed to a case, where specific anion-adsorption may be expected to be absent, that is practically to the case of fluorides. Owing to the strong electronegativity of the F^- ion this ion will not be dehydrated and thus not enter into the "STERN plane".

In order to carry out this test he takes the experimental capacity C for 1 M NaF, calculates the capacity $C_d = d\sigma / d\psi_\delta$ of the GOUY layer according to eq. (48) p. 130, and evaluates the capacity C_m between the mercury and the limiting GOUY plane by eq. (54) p. 132.

$$\frac{1}{C} = \frac{1}{C_m} + \frac{1}{C_d} \tag{54}$$

Assuming further that the capacity C_m is completely determined by the total charge of the mercury (or by the charge of the GOUY layer which is the same with the sign reversed) he can then calculate the total capacities for more dilute solutions, which really are in good accord with the experimental values[4] (see Figs. 26-29).

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[1] D. C. GRAHAME, *Chem. Revs.*, 41 (1947) 441.

[2] A. FRUMKIN, *Trans. Faraday Soc.*, 36 (1940) 117. See also § 4 d, p. 135.

[3] D. C. GRAHAME, *Chem. Revs.*, 41 (1947) 441.

[4] E. L. MACKOR, *Rec. trav. chim.* 70 (1951) 763, showed that instead of assuming a variable capacity C_m of the molecular condenser, an equivalent interpretation can be obtained by assuming a constant capacity and a variable χ-potential which depends upon the surface charge.

e. Specific adsorption of anions

It is possible to extend these considerations to the case where anionic adsorption is present (*e.g.*, chloride).

From the cation adsorption Γ_+, which is completely localized in the GOUY layer, the whole structure of the GOUY layer may be derived including the adsorption of anions in the GOUY layer. On the other hand the total adsorption of anions (Γ_-) is available from experiments and by taking the difference, the amount of anions in the STERN plane is found. This amount (n_s per cm²) can be explained by a simple BOLTZMANN factor (eq. (57) p. 134).

$$n_s = 2\,r\,n_0\,e^{-w_s/kT} \qquad (57)$$

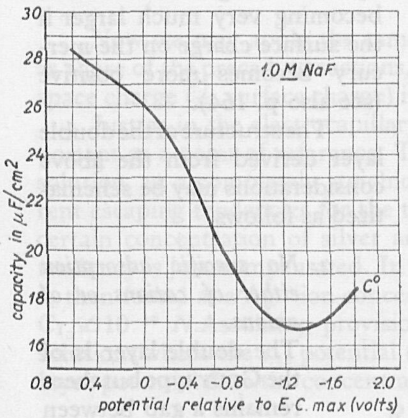

Fig. 26. Differential capacity of non-diffuse part of the double layer calculated from experimental data for 1 *M* NaF (Fig. 10) and eq. (54).

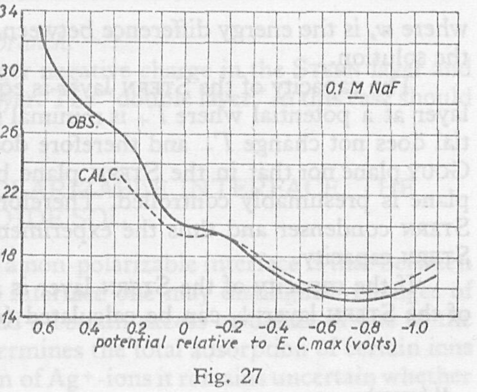

Fig. 27

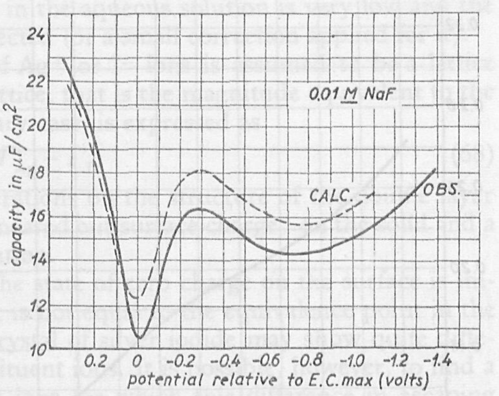

Fig. 28

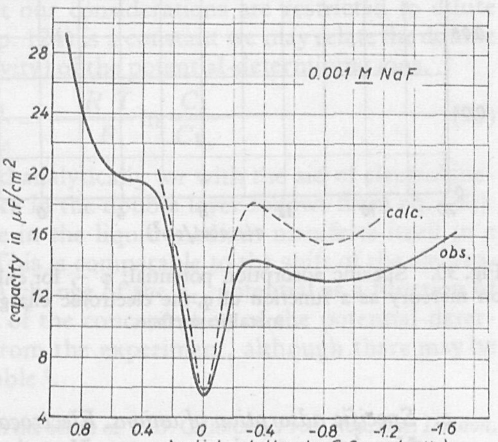

Fig. 29

Figs. 27—29. Differential capacity of the double layer calculated by GRAHAME. The capacity of the non-diffuse part of the double layer is taken from Fig. 26.

where w_s is the energy difference between an ion in the Stern layer and in the bulk of the solution.

The capacity of the Stern layer is equal to the differential capacity of the double layer at a potential where Γ_+ is minimal (see Fig. 25) because there a change of potential does not change Γ_+ and therefore does not change the potential in the limiting Gouy plane nor that in the Stern plane by which the potential in the limiting Gouy plane is presumably controlled. Therefore the whole change of potential is over the Stern condenser and thus the experimental capatciy at this potential is equal to the Stern capacity.

If the capacity of the Stern layer is assumed to be a constant, then the potential of the Stern layer ψ_s can be calculated (eq. (59) p. 135) and w_s can be split into an electrostatic part $(z_i e\psi_s)$ and an adsorption potential φ_i (eq. (58).) Fig. 30 shows the adsorption potential of Cl$^-$ ions calculated in this way by Grahame.

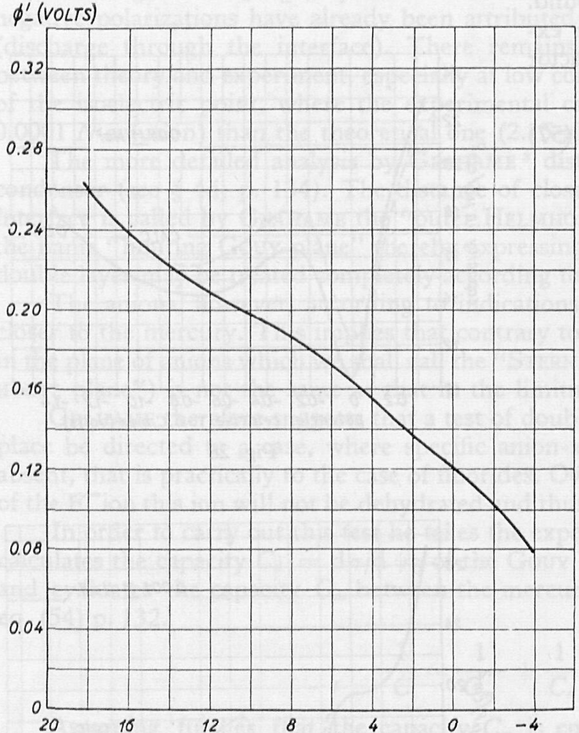

Fig. 30. Specific adsorption potential, $\varphi'-$, for chloride ion on mercury as a function of q, the electronic charge on the metallic surface.

The most important conclusion is that the adsorption potential is strongly dependent upon the charge on the surface, becoming very much larger if the surface charge on the mercury becomes more positive (see also p. 164).

The structure of the double layer derived from the above considerations may be schematized as follows

a. No specific adsorption either of cations or of anions.

The double layer is of the Gouy type but there remains a gap between the charge on the mercury and the first ions present in the double layer.

b. Specific adsorption of anions. Cathodic branch.

The double layer is of the same type as under *a.*

c. Specific adsorption of anions. Electrocapillary maximum.

No charge on the mercury. Negative charge in the Stern layer and a Gouy layer with positive charge.

d. Specific adsorption of anions. Anodic branch.

Positive charge on the mercury. Larger negative charge in the STERN layer and again a positive charge in the GOUY layer. The "double layer" in this case should more rightly be called triple layer.

§ 6. THE COMPLETELY NON-POLARIZABLE INTERFACE. THE SILVER IODIDE SOL

A good and well investigated example of a non-polarizable interface is that between silver iodide and aqueous solutions. At this interface one may distinguish changes of ionic concentrations in the aqueous layer and a certain excess or defect of one of the kinds of lattice ions. Experimentally one determines the total adsorption of certain ions (cf § 2, p. 116) and thus at a certain adsorption of Ag^+-ions it remains uncertain whether this is an adsorption in the lattice or in the liquid layer (§ 4 f. 2, p. 139). Usually, however, the concentration of Ag^+ or I^- ions in the aqueous solution is very low and the adsorption in the liquid layer may be neglected (or a small correction applied for it).

With this restriction the adsorption of Ag^+ or I^- ions is assumed to be a lattice adsorption and the excess charge of the lattice, that is the magnitude equivalent to the charge of the mercury in the electrocapillary case, is expressed as

$$\sigma = e\,(\Gamma_{Ag} - \Gamma_{I}) \qquad (68)$$

Now we may apply the same considerations on the structure of the double layer as those of the preceding sections, *viz.*, a smeared out surface charge[1] on the solid and a space charge (+ surface charge) in the solution.

Just as in the electrocapillary curve the state of zero charge on the surface is important as a point of reference. This point is not equal to the equivalence point in the solution as a completely stoichiometric crystal of silver iodide may show quite different escaping tendencies for the two constituent ions. It is possible, however, to find a certain concentration of silver and iodide ions for which this difference in escaping tendency is just compensated. In very dilute aqueous solutions the point of zero charge is then found at a Ag^+ ion concentration of $C_{Ag_0} \backsimeq 10^{-6}N$ and an I^-ion concentration $C_{I_0} \backsimeq 10^{-10}\ N$. Assuming provisionally that our considerations are restricted to dilute solutions where the χ_{12} potential (cf § 3 d, p. 124) is a constant we may relate the double layer potential D to the concentration (activity) of the potential-determining ions.

$$D = \frac{R\,T}{F} \ln \frac{C_{Ag}}{C_{Ag_0}} = -\frac{R\,T}{F} \ln \frac{C_I}{C_{I_0}} \qquad (90)$$

The zero point of charge is determined analytically (or with the aid of electrokinetics, *cf.* chapter V). The potential difference in the double layer follows from eq. (90). A change of the χ_{12} potential by a change in the liquid medium manifests itself in a displacement of the zero point of charge. This is comparable to the shift of the electrocapillary maximum in the mercury case. A change of the χ_{12} potential as a function of the surface potential, that is as a function of the concentration of the potential-determining ions, cannot be derived directly from the experiment, although there may be other indications making such a shift probable[2].

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[1] Although this excess may be a space charge in the sense of T. B. GRIMLEY, *Proc. Roy. Soc. London*, A 201 (1950) 40 (see § 4 e, p. 138), we shall usually consider it as a surface charge. In many considerations the difference is not essential.

[2] E. L. MACKOR, *Rec. trav. chim.*, 70 (1951) 763.

a. Determinations of the zero point of charge

The first — not very accurate — determination of the zero point of charge of silver iodide in water has been given by FRUMKIN and OBRUTSCHOWA[1]. They concluded from the *maximum* of adsorption of caprylic and hexylic acid to AgI that the zero point of charge was near the point of equivalence ($C_{\mathrm{Ag}^+} = C_{\mathrm{I}^-} = 10^{-8}$).

LANGE and BERGER[2] drew the same conclusion ($c_{\mathrm{Ag}_0^+} \cong 10^{-8}$) from titration curves.

A more accurate determination has been carried out by VERWEY and KRUYT[3]. Using a concentrated, well dialyzed silver iodide sol, they determined the change in adsorption of I-ions with the activity of the I-ions in the solution and found the following simple relation.

$$\Gamma_{\mathrm{I}^-} = k \log a_{\mathrm{I}^-} + \text{const.} \tag{91}$$

As the double layer potential D depends linearly on log a_{I}, eq. (91) seems to indicate that the double layer has a constant capacity.

As the total charge of the sol was known by a potentiometric determination of the counter ions (H^+ions) relation (91) can be extrapolated to $\Gamma_{\mathrm{I}^-} = 0$, that is to the zero point of charge. This was found at a $\mathrm{p_I} = 10$ or a $\mathrm{p_{Ag}} = 6$[4], thus clearly shifted to the silver side.

From the greater stability of the negative AgI sol as compared to the positive one, KRUYT and VAN DER WILLIGEN[5] had also concluded that the zero point of charge was situated asymmetrically. By measurements of electrophoresis[6] and electro-osmosis[7] nearly the same zero point has been found.

NAGEL[8], using an *abrasion electrode* in which periodically the surface of a silver iodide electrode is scratched away, also found a zero point of charge near $\mathrm{p_{Ag}} = 6$. This method, which for solid substances should be equivalent to the direct determination of the charge with the dropping mercury electrode (see § 5 b, p. 149), seems to be difficult to handle and has often led to false or uncontrollable conclusions. For literature, see NAGEL, *l.c.*

Special attention to the zero point of charge has been given by KOLTHOFF and LINGANE[9] and by VAN LAAR[10]. They applied different methods which lead to concordant values for the zero point of charge. The methods used were:

a. Mixing of very accurately measured quantities of $\mathrm{AgNO_3}$ and KI and measuring of the resulting $\mathrm{p_{Ag}}$. Only in the zero point of charge did the measured $\mathrm{p_{Ag}}$ coincide with the calculated one.

b. *Ageing* of the sol or suspension resulting in a decrease of the adsorbing surface. Only in the zero point of charge is no I^- or Ag^+ liberated.

c. Determination of I^- and Ag^+ adsorption isotherms at several concentrations

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[1] A. FRUMKIN and A. OBRUTSCHOWA, *Biochem. Z.*, 182 (1927) 220.

[2] E. LANGE and R. BERGER, *Z. Elektrochem.*, 36 (1930) 171, 980.

[3] E. J. W. VERWEY and H. R. KRUYT, *Z. physik. Chem.*, A 167 (1934) 149.

[4] $\mathrm{p_I} = -\log a_{\mathrm{I}^-}$, $\mathrm{p_{Ag}} = -\log a_{\mathrm{Ag}^+}$.

[5] H. R. KRUYT and P. C. VAN DER WILLIGEN, *Z. physik. Chem.*, A 139 (1928) 53.

[6] H. R. KRUYT and P. C. VAN DER WILLIGEN, *l.c.*

[7] E. LANGE and P. W. CRANE, *Z. physik. Chem.*, A 141 (1929) 225.

[8] K. NAGEL, *Sitz. ber. physik. med. Sozietät Erlangen*, 72 (1940/41) 127.

[9] I. M. KOLTHOFF and J. J. LINGANE, *J. Am. Chem. Soc.*, 58 (1936) 1528.

[10] J. A. W. VAN LAAR, unpublished.

of indifferent electrolytes. The capacity of the double layer is changed, the adsorption will be different except in the zero point of charge.

d. A charged suspension does influence the diffusion potential between two electrolyte solutions, an uncharged suspension does not do so (suspension effect, see § 10 p. 187).

Table 3 gives a survey of the results obtained by the different methods from which Van Laar deduces a most probable value of the zero point of charge.

TABLE 3

Determinations of the zero point of charge of AgI in water

Method	Author	p_{Ag} of zero charge
Stability of sol	Kruyt and Van Der Willigen	< 8
Electrophoresis	Kruyt and Van Der Willigen	5 — 5.4
Electro-osmosis	Lange and Crane	5.4
Adsorption of capillary active molecules	Frumkin and Obrutschowa	8
Abrasion electrode	Nagel	6
I^- adsorption and counter ion concentration	Verwey and Kruyt	6
$a\,KI + b\,AgNO_3 \rightarrow a\,AgI + a\,KNO_3 + (b - a)\,AgNO_3$ titration	Lange and Berger	∼8
	Kolthoff and Lingane	5.85
Ageing of interface	Kolthoff and Lingane	6.05
	Van Laar	5.50
I^- and Ag^+ adsorption with more or less indifferent electrolytes	De Bruyn	5.6
	Van Laar	5.52
Suspension effect	Van Laar	5.6
Best value	Van Laar	5.52

The zero point of charge is remarkably indifferent to electrolytes. By KNO_3 it is not shifted in concentrations up to 0.01 *M* and only a few millivolts by 1 *M* KNO_3. Polyvalent ions and typically capillary active ions do shift the zero point of charge (Van Laar, *l.c.*).

b. Adsorption isotherms

Lange and Berger[1] established empirically that in many cases, including that of silver iodide, the adsorption of potential-determining ions obeys the equation

$$\Delta \Gamma = k\, \Delta \ln c \tag{92}$$

As

$$\Delta E = \frac{RT}{zF}\, \Delta \ln c \tag{93}$$

eq. (92) would imply that the capacity of the double layer is a constant.

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[1] E. Lange and R. Berger, *Z. Elektrochem.* 36 (1930) 171.

Earlier experiments[1] are in rather good accord with eq. (92), but later, more accurate experiments with silver iodide showed that the adsorption isotherm is less simple, consequently the capacity of the double layer is not a constant.

The difficulties in getting reliable results in this field are at least twofold. In the first place, the adsorbing interface is prepared by chemical reaction between relatively large amounts of material, and the sol or precipitate must then be very thoroughly dialyzed or washed with great quantities of water before it is suitable for the experiments. Even very small amounts of impurities[2] may accumulate at the interface and in this way impair the reliability of the results.

A second difficulty is found in the sol-concentration effect discovered by De Bruyn[3], which may radically disfigure potential measurements made in colloidal

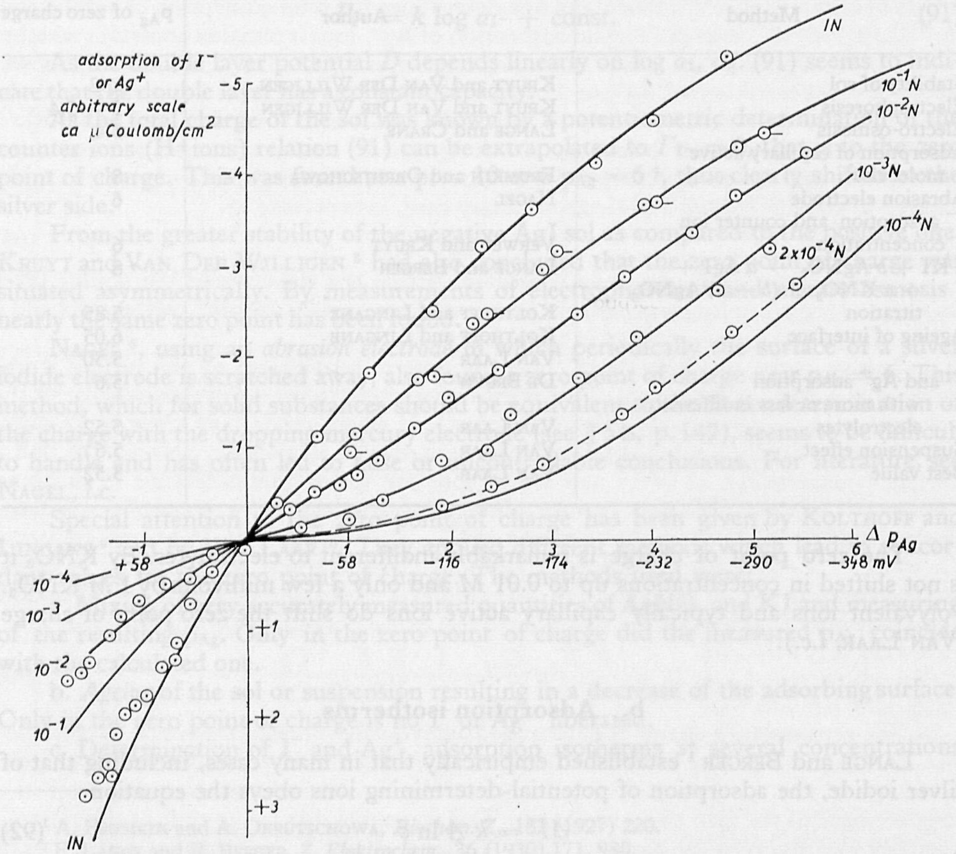

Fig. 31. Adsorption of potential-determining ions to AgI for different concentrations of electrolytes. Drawn curves KNO_3–$NaNO_3$ 7 : 1 (Van Laar) ⊙ $NaClO_4$ (Mackor) ⊙-$NaNO_3$ (Mackor).

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[1] E. Lange and R. Berger, *l.c.*; E. J. W. Verwey and H. R. Kruyt, *Z. physik. Chem.*, A 167 (1933) 149; A. Kellermann and E. Lange, *Kolloid-Z.*, 81 (1937) 88, a review in which more literature is cited. See also *ibidem*, 88 (1939) 341.

[2] See H. De Bruyn and J. Th. G. Overbeek, *Kolloid-Z.*, 84 (1938) 186.

[3] H. De Bruyn, *Thesis*, Utrecht 1938; *Rec. trav. chim.*, 61 (1942) 12.

systems and which in the case of AgI-sols may lead to a completely false estimate of the electrometrically determined C_I or C_{Ag}. For further details of this effect, see § 10 of this chapter, p. 184.

Adsorption of I^- or Ag^+ ions to AgI sol or suspension particles have been determined for several different conditions. For an easy interpretation those experiments are preferred, in which the ionic strength is kept constant for each adsorption isotherm, as has been realized in the investigations by Van Laar [1] and by Mackor [2].

Van Laar used a mixture of KNO_3 and $NaNO_3$ as electrolyte. Mackor did a few experiments with $NaNO_3$ and a complete series with $NaClO_4$. The results for the different electrolytes coincide as well as the experimental accuracy allows. In Fig. 31 the results of Mackor are given together with those of Van Laar. The two ordinate scales have been adjusted (the adsorbing surfaces are not known and are probably not equal) to the best possible fit.

It will be shown on page 164 how an estimate of the absolute value of the ordinate scale could be made.

De Bruyn [3], who has done similar experiments, established that the specific influence of cations is very small. Adsorption isotherms for monovalent ions (K, Na) are indistinguishable. So are those of bivalent ones (Mg, Ba, Zn, Pb). A mutual comparison of monovalent and bivalent ions is difficult owing to their different influence on the ionic strength and on the diffuse part of the double layer.

Beekley and Taylor [4], on the contrary, find a very pronounced specific influence of the anions. Their curves (Fig. 32) cannot be compared to those of Fig. 31 because no indifferent electrolyte was present and the ionic strength thus was not constant. These results have been confirmed by Kellermann and Lange [5].

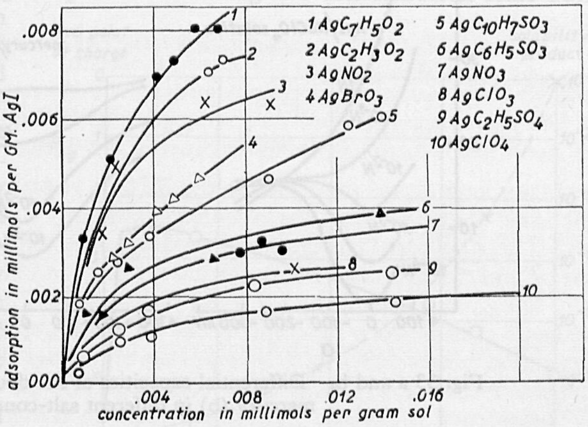

Fig. 32. Specific influence of anions on the adsorption by AgI

De Bruyn [3] also determined adsorption isotherms for different salt contents. His results differ from those of Van Laar and Mackor in that for high electrolyte concentrations (> 0.1 *N* for monovalent ions, > 0.001 *N* for bi- and poly-valent ions) he always found the same practically linear adsorption isotherm which would point to a constant capacity of the molecular condenser. It is not certain, however, that the complications of the sol concentration effect (§ 10, p. 184) have been sufficiently avoided in his experiments.

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[1] J. A. W. Van Laar, *unpublished*

[2] E. L. Mackor, *Rec. trav. chim.*, 70 (1951) 763.

[3] H. De Bruyn, *Rec. trav. chim.*, 61 (1942) 21; *Thesis*, Utrecht 1938.

[4] J. S. Beekley and H. S. Taylor, *J. Phys. Chem.*, 29 (1925) 942.

[5] A. Kellermann and E. Lange, *Kolloid-Z.*, 88 (1939) 341.

For a further interpretation of the adsorption curves of Fig. 31 and for a comparison with the results on the mercury surface it is necessary to derive the differential capacity of the double layer by differentiation of the adsorption (charge) with respect to the double layer potential. The capacities obtained are given in Fig. 33a and the capacities of the double layer on mercury against NaF solutions in Fig. 33b. The two sets of curves resemble each other very much especially for dilute solutions. As in these solutions the diffuse parts of the double layer are preponderant and there is every reason to expect that the diffuse double layers will be identical for the two cases, the adsorption scale in Fig. 31 and therewith the capacity scale in Fig. 33 have so been adjusted that the capacities for 0.001 *N* solutions at the zero point of charge are identical.

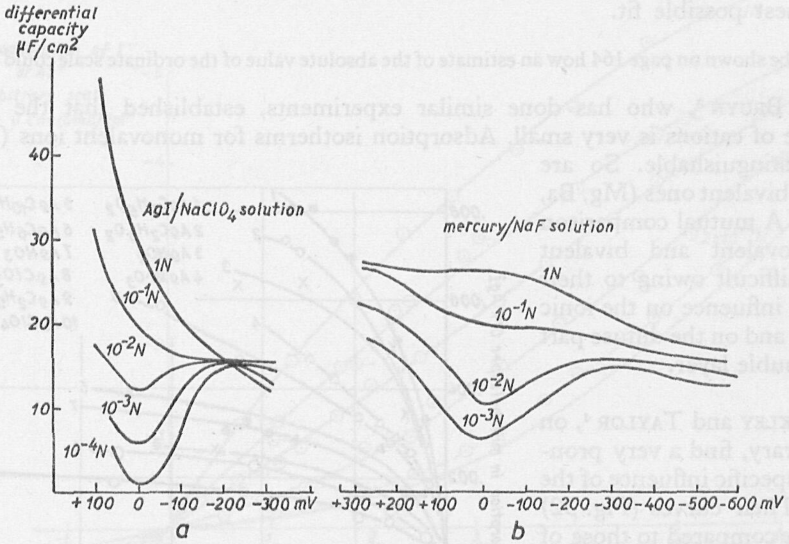

Fig. 33 a and b. Differential capacities of the double layer on AgI (a) and on mercury (b) in different salt-concentrations.

The measurements on AgI in dilute solutions can then evidently be explained in exactly the same way as those on the mercury water interface. For the more concentrated solutions there are two evident deviations.

In the first place there is the striking increase in the capacity on the silver side of the zero point of charge. Here the explanation is probably a pronounced specific adsorption of the anions which is in agreement with the strong spreading between the curves for different anions (Fig. 32). One would expect that this adsorption makes itself still felt in the zero point of charge. In that case there would be a diffuse double layer present at the zero point of charge which could be detected by electrokinetic measurements. Such measurements have not yet been reported.

In the second place we notice a decrease of the capacity especially for the 1 *N* solution at high negative charges, reflecting the curvature of the 1 *N* curve (and to a lesser extent the 0.1 *N* curve) of Fig. 31 to the potential axis. A satisfactory explanation of this fact has not yet been given.

c. Influence of non-electrolytes on the charging curves

According to § 3d, p. 126, the potential difference between two phases in equilibrium is related to the chemical potentials of the potential-determining ions by the eq.

$$\triangle \varphi = \frac{1}{z_i e} \triangle \mu_i \tag{94}$$

In the zero point of charge there is no double layer due to inhomogeneous partition of ions and $\triangle \varphi = \chi_{12}$. Introducing the concentration dependence of the chemical potential in the solution, we may transform (94) into

$$\chi_{12} - \frac{1}{z_i e} \triangle \mu_i^o = \frac{RT}{z_i e} \ln c_i^o \tag{95}$$

where $\triangle \mu_i^o$ is the difference in standard chemical potentials of the i-ions between the two phases and c_i^o the concentration (activity, if necessary) at the zero point of charge. It is clear that a zero point of charge may be shifted along the concentration scale both by a change in χ or by a change in the standard chemical potentials.

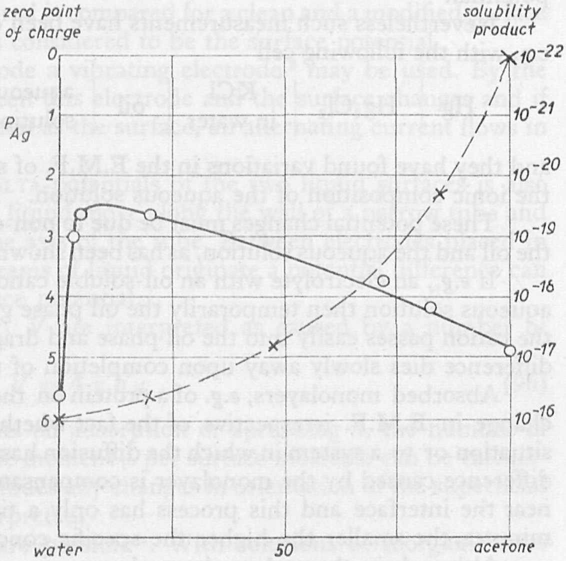

Fig. 34. The change in the zero point of charge (full curve) and the solubility product (dotted curve) of AgI by addition of acetone.

This is clearly demonstrated in an investigation by Mackor[1] on the influence of acetone on the AgI-water interface. He determined the zero point of charge by electro-kinetic measurement and found a considerable shift as represented in Fig. 34. Especially small quantities of acetone shift the zero point of charge to the silver side, larger quantities shift it more gradually. The first shift is probably connected with an oriented adsorption of acetone which changes the χ_{12} potential by about 250 mV, the later gradual shift with the change in chemical potential of the ions which manifests itself also in the change of the solubility product.

The differential capacities in acetone and in acetone-water mixtures are smaller than in water ($\sim 5\ \mu F/cm^2$ for pure acetone) which may be brought into relation with the greater dimensions of the acetone molecule and its smaller dielectric constant.

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[1] E. L. Mackor, *Rec. trav. chim.*, 70 (1951) 747.

§ 7. THE INTERFACES OIL-WATER AND AIR-WATER

a. The interface between oil and water

In principle the interface between two immiscible liquids seems to be an attractive object for investigation, especially if one remembers the successes obtained on the mercury-water interface. Practically the situation at the oil-water interface is much less simple and the experimental material available is rather restricted. The interface is not completely polarizable, like the mercury-water one. If we go to the other extreme of a completely reversible interface, then the situation is less favourable than in the case AgI-water. In the latter case the chemical potentials of the Ag^+ and I^- ions in the solid phase are constant, but they can be varied at will in the aqueous phase. In the oil-water case the chemical potential of any added substance is a variable in both phases, and the two variations are coupled in such a way that a potential measurement with two reversible electrodes in the two phases does not tell us anything about the properties of the surface, as has been argued in § 3c, p. 123 and § 4e, p. 137. When instead of reversible electrodes salt bridges are used, the same argument can be given. Although in this case it is quite possible that a potential difference exists between the electrodes connected to the salt bridges, this potential difference gives no information on the interfacial potential.

Nevertheless such measurements have been done by BEUTNER [1] c.a. and by BAUR [2] c.a. with the following cell

$$\mathrm{Hg}\;\Big|\;\mathrm{Hg_2Cl_2}\;\Big|\;\begin{array}{c}\mathrm{KCl}\\ \text{in water}\end{array}\;\Big|\;\text{oil}\;\Big|\;\begin{array}{c}\text{aqueous}\\ \text{solution}\end{array}\;\Big|\;\begin{array}{c}\mathrm{KCl}\\ \text{in water}\end{array}\;\Big|\;\mathrm{Hg_2Cl_2}\;\Big|\;\mathrm{Hg}$$

and they have found variations in the E.M.F. of several hundred millivolt by changing the ionic composition of the aqueous solution.

These potential changes must be due to non-establishment of equilibrium between the oil and the aqueous solution, as has been shown clearly by DEAN, GATTY and RIDEAL [3].

If *e.g.*, an electrolyte with an oil-soluble cation like methylene blue is added to the aqueous solution then temporarily the oil phase gets a more positive potential, because the cation passes easily into the oil phase and drags the anion behind it. This potential difference dies slowly away upon completion of the diffusion process.

Absorbed monolayers, *e.g.* of a protein on the interface give only a very transient change in E.M.F. irrespective of the fact whether they are applied to an equilibrium situation or to a system in which the diffusion has not yet come to an end. The potential difference caused by the monolayer is compensated by a slight rearrangement of ions near the interface and this process has only a time of relaxation of the order of a few minutes, the smaller the higher the specific conductance of the oil phase.

Although in themselves these phenomena are interesting and may be important in the explanation of potential differences in living organisms (BEUTNER, BAUR) and in the stability of emulsions, the available data are still so scarce and badly defined that anything more than this qualitative discussion would seem premature.

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[1] R. BEUTNER, *Z. Elektrochem.*, 19 (1913) 319, 467; *Z. physik. Chem.*, 87 (1914) 385; *Protoplasma*, 19 (1933) 370.

[2] E. BAUR, *Z. Elektrochem.*, 19 (1913) 590; *Rec. trav. chim.*, 42 (1923) 656; E. BAUR and E. ALLEMAN, *Z. Elektrochem.*, 32 (1926) 547.

[3] R. B. DEAN, O. GATTY, and E. K. RIDEAL, *Trans. Faraday Soc.*, 36 (1940) 161; R. B. DEAN, *ibidem*, p. 166.

b. The air-water interface

An equilibrium based on a distribution of potential determining ions is not possible between air and water through lack of ions in the air phase. A double layer, however, may be present at this interphase. As usual, an absolute value of the potential difference over this double layer cannot be determined (for a calculation see § 4a, p. 127) but it is possible to measure how this potential difference changes when the structure of the surface layer is changed by adsorption.

The experimental methods used can all be considered as a comparison of the VOLTA-potentials, just outside a clean and a modified surface, under the assumption that the difference in composition of the bulk-liquids, is so small that the GALVANI-potentials are equal (see Fig. 3, p. 124). Consequently the surface potentials are χ-potentials or rather differences in χ-potentials, where χ of the clean surface is taken arbitrarily zero.

In the most extensively used method[1] the potential is determined between a calomel electrode connected through a salt bridge to the solution and a second electrode in the air just above the solution. This second electrode contains a radioactive preparation, which, by its ionizing radiation, makes the air gap conducting enough to allow a measurement.

The potential difference so measured is compared for a clean and a modified surface and the difference between the two is considered to be the surface potential.

Instead of the radioactive electrode a vibrating electrode[2] may be used. By the change of distance the capacity between this electrode and the surface changes and if the electrode is not at the same potential as the surface, an alternating current flows in the circuit.

A direct comparison[3] of the VOLTA-potentials of the two liquid surfaces is also possible by letting a thin sheet of one liquid move along the wall of a narrow tube and a thin jet of the other liquid along the axis of the tube. Between electrodes placed in the reservoirs from which the two streams of liquid originate a potential difference can then be measured equal to the surface potential.

Often these surface potentials $\triangle V$ are interpreted as caused by a number of dipoles in the surface layer

$$\triangle V = 4\,\pi\, n\, \mu \tag{96}$$

If, for instance, from experiments on adsorption or spreading n, the number of molecules per cm² is known, the dipole moment μ per surface molecule can be calculated. Evidently this dipole moment includes any changes in orientation of the superficial water layer and thus is not easily interpreted.

Nevertheless some conclusions are possible[4]. With solutions of inorganic salts the outer surface is made (slightly) more negative. This would mean, that the anions are somewhat closer to the surface than the cations, the negative potential being in the order $F < Cl < Br < I < CNS$. This reminds one of the situation in electrocapillary work (§ 5d, p. 156), where indications have been found that the anions come closer to

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[1] J. GUYOT, *Ann. phys.*, 2 (1924) 506; A. FRUMKIN, *Z. physik. Chem.*, 116 (1925) 485.

[2] A. VOLTA, *Ann. chim. et phys.*, 40 (1801) 225; J. GUYOT, *l.c.*; H. G. YAMINS and W. A. ZISMAN, *J. Chem. Phys.*, 1 (1933) 656; E. F. PORTER, *J. Am. Chem. Soc.*, 59 (1937) 1883.

[3] F. B. KENRICK, *Z. physik. Chem.*, 19 (1896) 625; A. FRUMKIN, *Z. physik. Chem.*, 109 (1924) 34; 111 (1924) 190; 123 (1926) 321.

[4] A. FRUMKIN, *l.c.*

the interface because they are more easily dehydrated. The strongly hydrated F$^-$ion does not get easily to the surface, not more easily than a normal cation, with the consequence that fluorides show very small surface potentials.

On the other hand many (undissociated) organic substances make the surface more positive, probably because usually the apolar part, which will be driven out of the water, is positive with respect to the more hydrophilic polar part.

A curious case is that of the fatty acids. In the undissociated form they make the surface more positive. The dissociated soaps, however, make the surface more negative. Going from air to water we first pass the positive hydrocarbon chain, then the negative COO$^-$ group and finally the positive part of a diffuse double layer.

That this double layer is at least partly of the diffuse type, is made very probable by the experiments of J. J. HERMANS[1] who found electro-osmotic displacements along the air water interface, which are in good accord with the above cited measurements on the total potential. HERMANS finds, *e.g.*, that the water surface in clean water moves to the cathode and thus is positively charged. Addition of salts (NaCl, Na_2SO_4, $CaCl_2$, Na_3PO_4) leads to a reversal of charge at a concentration of the order of 10^{-3} *N*. On the other hand fatty acids, which make the total potential more positive, increase the electro-osmotic movement to the cathode.

For more details on these air-water potentials especially in the case of spread monolayers, see the excellent book by ADAM[2].

§ 8. DOUBLE LAYERS ON OTHER SYSTEMS[3] (NOT TREATED IN § 5, 6, 7)

a. Platinum, activated carbon, platinized carbon

The complicated behaviour of the interfaces Pt/H_2O and C/H_2O has been unravelled by a long series of investigations. The most important contributions have been given by BARTELL and MILLER[4], FRUMKIN[5] and his school, KRUYT and DE KADT[6], KOLTHOFF[7], VERWEY and DE BOER[8].

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[1] J. J. HERMANS, *Rec. trav. chim.*, 60 (1941) 747.

[2] N. K. ADAM, *The physics and chemistry of surfaces*, Oxford 1944.

[3] A. KELLERMANN and E. LANGE, *Kolloid-Z.*, 81 (1937) 88; 90 (1940) 89.

[4] F. E. BARTELL and E. J. MILLER, *J. Am. Chem. Soc.*, 44 (1922) 1866; 45 (1923) 1106; *J. Phys. Chem.*, 28 (1924) 992; E. J. MILLER, *J. Am. Chem. Soc.*, 46 (1924) 1150; 47 (1925) 1270.

[5] *Carbon*

B. BRUNS and A. FRUMKIN, *Z. physik. Chem.*, A 141 (1929) 141; 147 (1930) 125; R. BURSTEIN and A. FRUMKIN, *ibidem*, A 141 (1929) 158; R. BURSTEIN, A. FRUMKIN, D. LAWROWSKAJA, *ibidem*, 150 (1930) 421; A. FRUMKIN, *Kolloid-Z.*, 51 (1930) 123; N. BACH and A. ZIMIN, *Acta Physicochim. U.R.S.S.*, 7 (1937) 451; B. BRUNS, R. BURSTEIN, N. FEDOTOW, M. LIWSCHITZ, *ibidem*, 8 (1938) 47; S. PETROV, R. BURSTEIN, P. KISELEVA, *Acta Physicochim. U.R.S.S.*, 9 (1939) 59.

Platinum

N. BACH and N. BALASHOVA, *Acta Physicochim. U.R.S.S.*, 3 (1935) 79; 7 (1937) 899; *Nature*, 137 (1936) 716; A. FRUMKIN, *Trans. Faraday Soc.*, 31 (1935) 69; B. V. ERSHLER and M. PROSKURNIN, *Acta Physicochim. U.R.S.S.*, 6 (1937) 195; B. V. ERSHLER, *ibidem*, 7 (1937) 327; B. V. ERSHLER, G. DEBORIN and A. FRUMKIN, *ibidem*, 8 (1938) 565; N. BALASCHOVA and A. FRUMKIN, *Compt. rend. acad. sci. U.R.S.S.*, 20 (1938) 449; B. V. ERHSLER and A. FRUMKIN, *Trans. Faraday Soc.*, 35 (1939) 464; A. FRUMKIN, *ibidem*, 36 (1940) 117.

[6] H. R. KRUYT, and G. S. DE KADT, *Kolloid-Z.*, 47 (1929) 44; *Kolloidchem. Beihefte*, 32 (1931) 249; H. R. KRUYT and T. KRUYT, *Proc. Koninkl. Nederland. Akad. Wetenschap.*, 38 (1935) 570.

[7] I. M. KOLTHOFF, *Z. Elektrochem.*, 33 (1927) 497; *Rec. trav. chim.*, 46 (1927) 552; *J. Am. Chem. Soc.*, 54 (1932) 4476; I. M. KOLTHOFF and T. KAMEDA, *J. Am. Chem. Soc.*, 51 (1929) 2888.

[8] E. J. W. VERWEY and J. H. DE BOER, *Rec. trav. chim.*, 55 (1936) 681.

The conclusions from the work by these authors is that carbon, platinum and probably also gold behave as gas (hydrogen or oxygen) electrodes. Hydrogen and hydroxyl ions may consequently be considered as the potential-determining ions.

One of the big difficulties in this investigation has been that under oxidizing conditions surface oxides are formed, which strongly influence the χ-potential. Moreover the reversible oxygen potential is seldom reached, which makes quantitative predictions still more difficult.

When the carbon or platinum surface is prepared under exclusion of oxygen and the interface with water investigated in a hydrogen atmosphere, the zero point of charge is found in both cases near pH = 0. For (slightly platinized) carbon [1] PETROV, BURSTEIN, and KISELEVA (*l.c.*) find —0.027 V with respect to the normal hydrogen electrode as the zero point of charge. For platinum [2] it is + 0.12 V. This means that in a hydrogen atmosphere carbon is positively charged below pH = 0.5 and negatively at higher pH. Platinum in hydrogen is negatively charged at any accessible pH. When the hydrogen atmosphere is replaced by oxygen, the reversible potential increases by 1.23 volt or in other words it is necessary to make the pH 1.23 : 0.058 = 21 higher in order to arrive again at the zero point of charge [3].

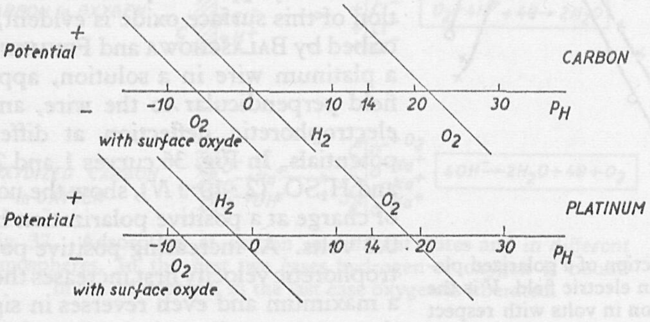

Fig. 35. Sketch of double layer potential as a function of p_H and atmosphere. The curve for the reversible potential of carbon in oxygen is given. In fact the reversible potential is not reached and the zero point of charge lies at $p_H \backsim 14$ instead of at $p_H \backsim 21$. (See B. BRUNS, R. BURSTEIN, N. FEDOTOW, and M. LIWSCHITZ, *Acta physicochimica U.R.S.S.*, 8 (1938) 56).

It is assumed here, that the χ-potential remains unaltered. This implies, of course, that the amounts of adsorbed hydrogen or oxygen remain low and that the potential-determining process is a transition of electrons between the metal and the redox system (H^+/H_2 or OH^-/O_2) in the solution.

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[1] See also B. BRUNS, R. BURSTEIN, N. FEDOTOW, and M. LIWSCHITZ, *Acta Physicochim. U.R.S.S.*, 8 (1938) 47.

[2] A. FRUMKIN, *Trans. Faraday Soc.*, 36 (1940) 117; A. SLYGIN, A. FRUMKIN, and W. MEDWEDOWSKY, *Acta Physicochim. U.R.S.S.*, 4 (1936) 911; A. FRUMKIN and A. SLYGIN, *ibidem*, 5 (1936) 819; B. BRUNS, R. BURSTEIN, N. FEDOTOW, and M. LIWSCHITZ (*l.c.*), indicate a value of + 0.24 for platinum.

[3] In fact the reversible potential is not reached. The zero point of charge is found near pH = 14 instead of near pH = 21. See B. BRUNS, R. BURSTEIN, N. FEDOTOW, and M. LIWSCHITZ, *Acta Physicochim. U.R.S.S.*, 8 (1938) 56.

Consequently in oxygen at any accessible pH, C and Pt are positively charged. However, in an oxidizing atmosphere platinum is soon covered by a chemically bound oxide layer. With carbon this oxide layer is only very slowly formed at room temperature, but it can be formed by heating the carbon in oxygen at about 400° C. Now this oxide layer causes an extra χ-potential at the interface which may easily reach a value[1] of more than one volt and which turns its negative side to the liquid. This shifts the zero point of charge again to very low values of the pH and consequently the surface charge again becomes negative. This behaviour is represented schematically in Fig. 35.

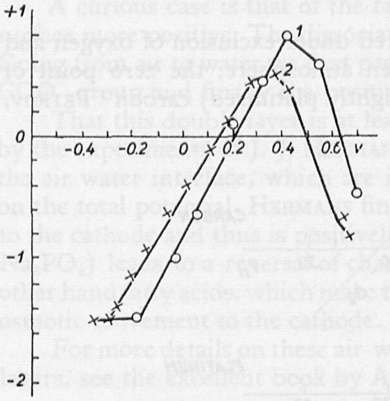

Fig. 36. Deflection of a polarized platinum wire in an electric field. *V* is the polarizing tension in volts with respect to the normal hydrogen electrode. 1 HCl $2 \cdot 10^{-5}$ *N*; 2 H_2SO_4 $2 \cdot 10^{-5}$ *N*

A very typical experiment in which the formation of this surface oxide is evident, has been described by BALASCHOWA and FRUMKIN[2]. They placed a platinum wire in a solution, applied an electric field perpendicular to the wire, and measured its electrophoretic deflection at different polarizing potentials. In Fig. 36 curves 1 and 2, valid for HCl and H_2SO_4 ($2 \cdot 10^{-5}$ *N*), show the normal zero point of charge at a positive polarization between 0.1 and 0.2 volts. At increasing positive potential the electrophoretic velocity first increases then goes through a maximum and even reverses in sign. This means that at an anodic polarization of somewhat more than 0.4 volt the formation of the platinum oxide layer will start.

Experiments[3] with platinum sols in hydrogen and oxygen atmospheres fully confirmed this point of view.

The phenomena with charcoal have often been investigated with the help of adsorption measurements. It was found then that carbon heated to about 1000° C in hydrogen or vacuum adsorbed bases even from neutral salts (hydrolytic adsorption). Acids were only adsorbed at very high concentrations.

When at room temperature oxygen was admitted instead of hydrogen, adsorption of acids was found. Carbon which had been heated in oxygen at 300° or 400° C, adsorbed both bases and acids[4]. The explanation is simple in the light of Fig. 35 and Fig. 37. Pure carbon in hydrogen must be negatively charged (see Fig. 35). It takes the electrons necessary for this charge from OH^- ions. The discharged ions form water with hydrogen. Sodium ions are the counter ions. For the other situations the explanation is similar.

Theoretically the oxidized carbon should only adsorb bases. In practice both acids and bases are adsorbed. This is because oxidized carbon never has a uniform surface. In the oxidation process at 300°—400°, there are always moments in which a new carbon surface is set free and so in the surface oxidized places are intermingled with the pure carbon surface.

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[1] E. J. W. VERWEY and J. H. DE BOER, *l.c.*,

[2] N. BALASCHOWA and A. FRUMKIN, *Compt. rend. Acad. Sci. U.R.S.S.*, 20 (1938) 449.

[3] N. BACH and N. BALASCHOWA, *l.c.*

[4] H. R. KRUYT and T. KRUYT, *Proc. Koninkl. Nederland. Akad. Wetenschap.*, 38 (1935) 570.

From the reaction equations in Fig. 37 it follows that together with the adsorption of acids or bases a certain amount of hydrogen or oxygen is bound or liberated. This was confirmed in the experiments of BRUNS, FRUMKIN and others [1].

Adsorption isotherms as a function of pH have been determined by BRUNS, BURSTEIN, FEDOTOW and LIWSCHITZ [2]. In the presence of 0.5 molar solutions of NaCl, Na_2SO_4 or NaI the adsorbed quantity of base on platinized carbon in H_2 is linearly dependent on the pH of the solution, except at very low pH where also a difference between the different curves can be seen (Fig. 38). These curves imply that the double layer capacity on negative carbon is constant, independent of the anion, except at very low potentials where the capacity increases due to specific adsorption of the anions in the order $I^- \gg Cl^- > SO_4^{--}$. The adsorption curves on carbon in an oxygen atmosphere are still rather difficult to explain [3]. This carbon, which is positively charged [4] shows a very pronounced spreading in the adsorption of anions [5] which reminds us of the behaviour of the Hg and the AgI surfaces in this respect.

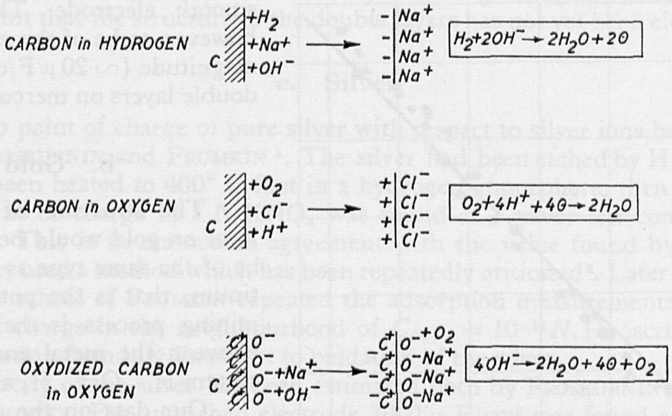

Fig. 37. Adsorption at carbon in different states and in different atmospheres. In the first two cases hydrogen or oxygen is bound in the adsorption, in the last case oxygen is liberated.

The order of adsorption found by KOLTHOFF is

$$CNS^- > I^- > NO_3^- > IO_3^- > Br^- \approx Cl^- \approx ClO_4^- \gg SO_4^{--}$$

For the platinum surface measurements of adsorption or capacity are available on platinized surfaces [6]. The general trend of the capacity is a very high capacity near the hydrogen discharge potential and near the reversible oxygen potential. Between these

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[1] B. BRUNS and A. FRUMKIN, *Z. physik. Chem.*, A 147 (1930) 125; R. BURSTEIN, A. FRUMKIN, and D. LAWROWSKAYA, *ibidem*, A 150 (1930) 421; B. BRUNS and A. PILOJAN, *ibidem*, A 155 (1931) 77.

[2] B. BRUNS, R. BURSTEIN, N. FEDOTOW, and M. LIWSCHITZ, *Acta Physicochim. U.R.S.S.*, 8 (1938) 47; B. RRUNS, see A. FRUMKIN, *Kolloid-Z.*, 51 (1930) 126; B. BRUNS and A. FRUMKIN, *Z. physik. Chem.*, A 141 (1929) 141.

[3] B. BRUNS, R. BURSTEIN, N. FEDOTOW, and M. LIWSCHITZ, *l.c.*

[4] H. R. KRUYT and G. S. DE KADT, *l.c.*

[5] I. M. KOLTHOFF, *Z. Elektrochem.*, 33 (1927) 497; *Rec. trav. chim.*, 46 (1927) 549.

[6] A. FRUMKIN and A. SLYGIN, *Acta Physicochim. U.R.S.S.*, 4 (1936) 911.

two extremes a region of low capacity due to pure double layer phenomena is present. **Ershler**[1] succeeded in measuring the capacity of bright platinum electrodes and found in principle the same behaviour as with platinized electrodes. The capacities in the double layer were still difficult to evaluate exactly, due to a certain lack of reversibility in the experiments with the smooth electrode. They seemed, however, to be of the same order of magnitude (∼ 20 μ F/cm²) as in the double layers on mercury or AgI.

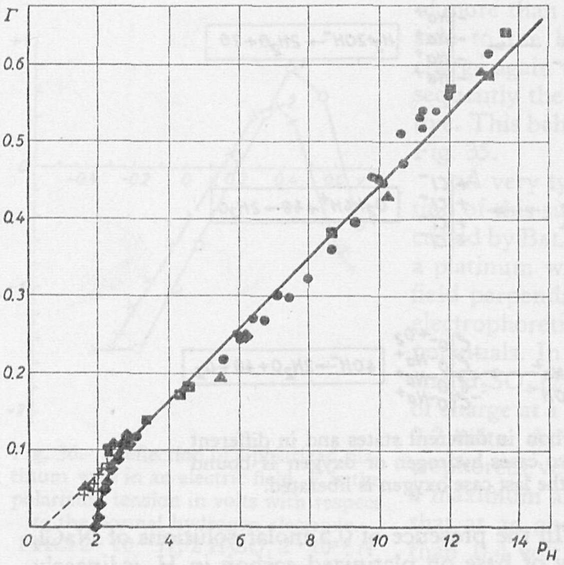

Fig. 38. Adsorption at platinized carbon in hydrogen atmosphere as a function of p_H.
● ■ ▲ = Na_2SO_4, + = NaCl, ◆ = NaI.

b. Gold

The structure of the double layer on gold would be expected to be of the same type as that on platinum, that is the potential-determining process is the equilibrium between the metal and the redox system H^+, OH^-, H_2 and O_2.

Our data on the double layer on gold are exclusively derived from experiments on gold sols and their stability, and there this strict electrochemical point of view has scarcely been taken into consideration. Investigations on the structure of the double layer of gold have been made especially by **Pauli**[2] and his school. **Pauli** reaches the conclusion, that the ionic part of the double layer is built up from $(AuCl_2)^-$ or $(AuClOH)^-$ ions adsorbed to the particles and positive counter ions. The argumentation is completely different from that used in the foregoing subsection and the two methods of approach are difficult to compare. **Pauli**'s experiments usually start with very pure concentrated sols prepared by electrodialysis and electrodecantation[3] (see chapter II, § 3, p. 72).

The chemical structure of the double layer is determined by chemical analysis often after coagulation of the sol. Usually **Pauli** finds a very large number of charges per cm² of surface of the sol, which in the language of the previous sections would mean an extremely high capacity.

However, **Wintgen** and **Hacker**[4] could show that in electrodecantation probably

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[1] B. V. **Ershler**, *Acta Physicochim. U.R.S.S.*, 7 (1937) 327; B. V. **Erhsler** and M. **Proskurnin**, *ibidem*, 6 (1937) 195.

[2] W. **Pauli**, *Trans. Faraday Soc.*, 31 (1935) 11; W. **Pauli**, E. **Russer**, and E. **Brunner**, *Kolloid-Z.*, 72 (1934) 26.

[3] This powerful method of purification and concentration of sols was introduced by W. **Pauli**, *Naturwissenschaften*, 30 (1932) 555. See also H. **De Bruyn** and S. A. **Troelstra**, *Kolloid-Z.*, 84 (1938) 192.

[4] R. **Wintgen** and W. **Hacker**, *Kolloid-Z.*, 61 (1932) 335; confirmed by S. A. **Troelstra** for I^- ions in the AgI-sol, *Thesis*, Utrecht 1941, p. 25.

also non-colloidal electrolytes are concentrated in the bottom-layer (sol-layer) so that perhaps the major part of the intermicellar electrolytes is erroneously considered as constituting the double layer.

From the author's point of view the situation at this moment is that the chloro-complexes may be involved in the double layer (strong chemisorption) and stability of gold sols, but that the structure of the double layers has not yet been elucidated.

c. Silver

The zero point of charge of pure silver with respect to silver ions has been determined by PROSKURNIN and FRUMKIN [1]. The silver had been etched by HNO_3 and after that, it had been heated to 400° C first in a hydrogen atmosphere, then in a vacuum. The zero point of charge in 1 N KNO_3 was found at a silver ion concentration of $1.5 \cdot 10^{-5}$ N. This is in reasonable agreement with the value found by BENNEWITZ [2] who, however, used a method which has been repeatedly criticized[3]. Later VESELOVSKY [4], also from the school of FRUMKIN repeated the adsorption measurements and found a zero point of charge in the neighbourhood of $C_{Ag^+} = 10^{-13} N$. He ascribes the higher Ag^+ concentration found by FRUMKIN to oxidation of the silver.

The capacity of the silver has been estimated both by PROSKURNIN and FRUMKIN and by VESELOVSKY. For an etched electrode 7000 μ F/cm² was found and even for a smooth electrode the minimum capacity (in 0.1 N KNO_3) was 100 μ F/cm², suggesting either a pronounced roughness of the "smooth" electrode or contribution to the capacity of other phenomena than the formation of the double layer.

With a metal, which, like silver, is not very precious, extra care should be exercized in the interpretations because it is not a priori known which of the two possible potential-determining mechanisms (Ag/Ag^+ or O_2/OH^-) is the actual one. The electrode potential of Ag/1 N Ag^+ is + 0.80 V and that of the oxygen electrode (1 atm) at pH = 7 has practically the same value. Consequently at lower silver ion concentrations, higher oxygen pressures or lower pH silver may be oxidized, thus changing the composition of the system.

In an investigation on the stability of silver sols KRUYT and VAN NOUHUYS [5] conclude that independently of the atmosphere (oxygen, however, not rigorously excluded) the silver is covered by a layer of argentate ions (AgO^-). This would be indistinguishable from the presence of a surface oxide combined with free electrons or a desorption of Ag^+. One gets the impression that both the silver ion and the pH (OH^-ion) are potential-determining but the situation is not made clear. A zero point of charge has not been found.

d. Silver halides

After the extensive treatment of silver iodide in § 6, p. 159 we may be very brief about the other silver halides. They have been much less extensively investigated and the results obtained only differ from those for AgI in a quantitative sense.

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[1] M. PROSKURNIN and A. FRUMKIN, *Z. physik. Chem.*, A 155 (1931) 29.
[2] K. BENNEWITZ, *Z. physik. Chem.*, 124 (1926) 115.
[3] E. LANGE and R. BERGER, *Z. Elektrochem.*, 36 (1930) 980; M. PROSKURNIN and A. FRUMKIN, *l.c.*
[4] V. I. VESELOVSKY, *Acta Physicochim. U.R.S.S.*, 11 (1939) 815.
[5] H. R. KRUYT and H. L. VAN NOUHUYS, *Kolloid-Z.*, 92 (1940) 325.

LOTTERMOSER and PETERSEN [1] determined the adsorption of potential-determining ions for AgCl, AgBr, AgCNS. Their measurements have been recalculated by KELLERMANN and LANGE [2].

BASINSKI [3] carried out a more complete investigation on concentrated silver bromide sols. The zero point of charge was situated slightly asymmetrically at a Br^- ion concentration of $2\text{–}4 \cdot 10^{-7}$ *N* and a Ag^+ ion concentration of $1\text{–}2 \cdot 10^{-6}$ *N*. The adsorption isotherms resemble those of the AgI sols. The capacity of the double layer is of the order of 10 μF. This value is rather uncertain owing to the difficulty of the estimation of the total interface of the sol particles.

JONKER [4] determined the zero point of charge for AgCl from the stability of AgCl sols at $p_{Ag} \backsim 4$.

For further information on the silver halides see also chapter V, Electrokinetic *phenomena*, § 9 *b*. 3, p. 231.

e. Lead salts

Lead salts have formed a favourite object of investigation because the adsorption of the potential-determining lead ions can easily be followed by the method of radioactive indicators (ThB). The first investigations in this direction were from PANETH and VORWERK [5]. Later the method was applied by IMRE [6] and by KOLTHOFF [7]. The latter also applied several other methods of adsorption measurement on $PbSO_4$.

PANETH and IMRE report adsorption of Pb^{++} to the insoluble salts of Pb. KOLTHOFF and ROSENBLUM [7] only find an exchange between the solution and the Pb^{++} ions in the surface but no measurable adsorption.

In very fresh precipitates of $PbSO_4$, KOLTHOFF [7] and collaborators find not only a rapid exchange with the surface ions but also the Pb^{++} in the interior of the crystals is freely exchanged against the ions in the solution.

Zero points of charge do not seem to have been determined. The adsorption measurements by PANETH and IMRE have been recalculated by KELLERMANN and LANGE [8] who found in all cases investigated a constant capacity of the double layer, usually for a change in the Pb^{++} concentration over a factor 10 or 10^2, that is equivalent to a change in potential of only 30 or 60 mV. The salts investigated are $PbSO_4$ (rather extensively), $PbCrO_4$, PbI_2, $PbBr_2$, $PbCl_2$.

f. Barium sulphate

Adsorption phenomena at $BaSO_4$ have been repeatedly investigated particularly by KOLTHOFF and his collaborators and by Miss DE BROUCKÈRE. A rather sharp controversy [9] between these two investigators has occurred on the existence of true "equi-

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[1] A. LOTTERMOSER and W. PETERSEN, *Z. physik. Chem.*, 133 (1928) 69.
[2] A. KELLERMANN and E. LANGE, *Kolloid-Z.*, 81 (1937) 88.
[3] A. BASINSKI, *Rec. trav. chim.*, 59 (1940) 331; 60 (1941) 267.
[4] G. H. JONKER, *Thesis*, Utrecht 1943, p. 40.
[5] F. PANETH and H. VORWERK, *Z. physik. Chem.*, 101 (1922) 445.
[6] L. IMRE, *Z. physik. Chem.*, A 171 (1934) 239; A 177 (1936) 409; *Trans. Faraday Soc.*, 33 (1937) 571.
[7] I. M. KOLTHOFF and CH. ROSENBLUM, *J. Am. Chem. Soc.*, 55 (1933) 2656.
[8] A. KELLERMANN and E. LANGE, *Kolloid-Z.*, 81 (1937) 88.
[9] I. M. KOLTHOFF, *Chem. Weekblad*, 31 (1934) 244; 33 (1936) 321; I. M. KOLTHOFF and A. H. BUSHEY, *ibidem*, 36 (1939) 51; *Bull. soc. chim. Belg.*, 47 (1938) 689; L. DE BROUCKÈRE, *Chem. Weekblad*, 33 (1936) 104; *Bull. soc. chim. Belg.*, 47 (1938) 702.

valent" adsorption of non-potential-determining salts and on the magnitude of the surface of the barium sulphate which according to KOLTHOFF is of the order of 1 m^2/gram and according to Miss DE BROUCKÈRE about 60 m^2/gram.

KOLTHOFF and MC NEVIN [1] determined among other things the adsorption of Ba^{++} and Pb^{++} on $BaSO_4$, which they found negligible except when the solvent was 50% ethanol instead of water. In all media the exchange between ions in the solution and those in the surface was evident.

Adsorptions were determined of $Ba(BrO_3)_2$, $Ba(NO_3)_2$, $Ba(ClO_4)_2$, $BaCl_2$, $BaBr_2$, BaI_2, $Ba(CNS)_2$, $(HCOO)_2Ba$. In none of these cases was the capacity of the double layer a constant. The adsorption could be described by the adsorption isotherm of FREUNDLICH. Translated, this means that the capacity at higher concentrations of Ba^{++} becomes relatively larger, which is qualitatively in accord with a GOUY-type of double layer firstly because for higher potentials the capacity should be larger, and secondly because by addition of the salts the ionic concentration increases, which also increases the capacity of a diffuse double layer.

Apart from the adsorption of potential-determining ions and the exchange adsorption of counter ions (see § 9) examples of equivalent adsorption of non-potential-determining electrolyte have been reported.

Miss DE BROUCKÈRE [2] finds adsorptions for many chlorides, the adsorption being roughly proportional to the concentration. KOLTHOFF and MCNEVIN (*l.c.*) mention a similar adsorption of $KBrO_3$ and $CaOHBrO_3$ from 50% ethanol.

Electrokinetic measurements on $BaSO_4$ also lead to the conclusion that Ba^{++} and SO_4^{--} are the potential-determining ions. The zero point of charge seems to be dependent upon the age and origin of the specimen used [3].

g. Iron oxide

TROELSTRA [4] investigated the adsorption on a hydrophobic sol of iron oxide. This had been prepared by heating a normal hydrated iron oxide sol to 150°—160°C in an autoclave. The particles are then transformed into pure hematite [5] (α Fe_2O_3). The sol has an acid reaction and the particles are positively charged with Cl^- as gegenions. If the pH is increased, a zero point of charge is reached at about pH = 8. The adsorption phenomena are, however, rather complicated probably owing to the presence of complexes like FeOCl etc.

§ 9. ION EXCHANGE

Only in the simplest cases is the double layer built up from the ions of a single salt. In this section we shall consider the distribution of ions when two or more salts are present. If the double layer structure is accurately known, this distribution is not difficult to work out. But in many cases when details of double layer structure are lacking,

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[1] I. M. KOLTHOFF and W. M. MC NEVIN, *J. Am. Chem. Soc.*, 58 (1936) 1543.

[2] L. DE BROUCKÈRE, *J. chim. phys.*, 25 (1928) 605; 26 (1929) 250; 27 (1930) 543; *Thèse*, Paris 1932; *Ann. chim.*, 19 (1933) 79; *Bull. soc. chim. Belgique*, 45 (1936) 353.

[3] H. R. KRUYT and R. RUYSSEN, *Proc. Koninkl. Nederland. Akad. Wetenschap.*, 37 (1934) 624; A. S. BUCHANAN and E. HEYMANN, *Nature*, 161 (1948) 648, 691; *J. Colloid Sci.*, 4 (1949) 137, 151, 157; R. RUYSSEN and R. LOOS, *Nature*, 162 (1948) 741; See also chapter V § 9b. 3, p. 231.

[4] S. A. TROELSTRA, *Thesis*, Utrecht 1941.

[5] A. VON BUZAGH, *Kolloid-Z.*, 66 (1934) 129; 78 (1937) 284.

one remains nevertheless interested in the ion exchange and asks for a simple description of this phenomenon. This is especially true in technical applications of ion exchanges, when often the exchanged ions are not only situated in a double layer but are more or less uniformly distributed throughout the whole mass of the exchanger. We shall not, however, treat the exchange of true lattice partners, that has been extensively studied by KOLTHOFF [1].

This exchange of lattice ions is usually only present to any considerable extent in very young precipitates. Therefore equilibrium phenomena are not easily observed here and in the kinetics, there is only a remote connection with the problems of exchange in double layers.

Historically ion exchange is important because for a long time the stability of hydrophobic colloids was considered to be determined by the amount of adsorption of the flocculating ion [2]. It was only after the accurate adsorption experiments of FREUNDLICH, JOACHIMSOHN, and ETTISCH [3] and the exchange experiments of VERWEY and KRUYT [4], that FREUNDLICH's original theory of the stability could definitely be considered to be disproved.

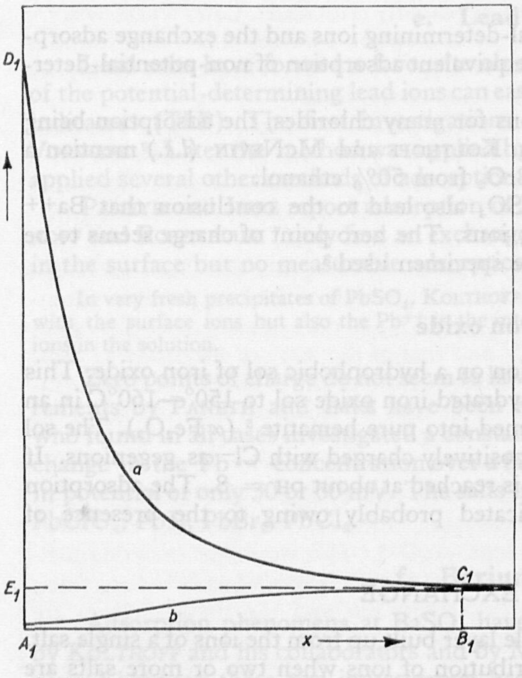

Fig. 39. Concentration of positive (a) and negative (b) ions in the double layer at a negative plane wall.

a. Ion exchange in the diffuse double layer

From a theoretical point of view the simplest case of ion exchange is that for a pure diffuse (GOUY) double layer, where all specificity of the ions, except their valency can be neglected. If for instance negatively charged particles are present in a solution containing two different kinds of monovalent cations, the concentration ratio of these ions at any point of the double layer should be the same as their concentration ratio in the bulk of the liquid and the ion exchange is given by the simple law

$$\frac{x_1}{x_2} = \frac{c_1}{c_2} \qquad (97)$$

when x_1 and x_2 are the amount of the ions 1 and 2 in the double layer, c_1 and c_2 their concentrations in the bulk of the liquid.

When one of the counter ions is monovalent and the other divalent, the ion exchange will be greatly shifted in the direction of the divalent ion which will be very preponderently accumulated in places of negative potential.

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[1] I. M. KOLTHOFF and CH. ROSENBLUM, *Phys. Rev.*, 45 (1934) 341; 47 (1935) 631; *J. Am. Chem. Soc.*, 56 (1934) 1264, 1658; 57 (1935) 597, 607, 2573, 2577; 58 (1936) 116, 121.

[2] H. FREUNDLICH, *Z. physik. Chem.*, 74 (1910) 385.

[3] H. FREUNDLICH, K. JOACHIMSOHN, and G. ETTISCH, *Z. physik. Chem.*, A 141 (1929) 249.

[4] E. J. W. VERWEY and H. R. KRUYT, *Z. physik. Chem.*, A 167 (1934) 312.

VAN OS [1] has worked this problem out. In the first place it must be decided, which part of the ions belongs to the double layer and which part to the intermicellar liquid. Fig. 39 gives the distribution of positive and negative ions near a plane wall of negative charge. Two choices for the "ions belonging to the double layer" present themselves.

One possibility is to take the ions corresponding to the surface $A_1C_1D_1$, that are the excess counter ions, just compensating the surface charge.

The other choice would be the surface $E_1C_1D_1$, being the surplus of counter ions above the bulk concentration.

Translating these choices into adsorption language (Γ, see § 2, p. 118) the first possibility means that the adsorption is related to the ions bearing the same charge as the wall, which are thus considered to have zero adsorption. In the second choice the solvent is taken as the reference substance.

Although customarily adsorptions are referred to the solvent, in ion exchange the other choice is the usual one, because in this way an amount of charge equivalent to the surface charge is considered as exchangeable and this choice is in line with the normal analytical procedures.

In discussing ion exchange between monovalent and divalent ions VAN OS considers a diffuse double layer at a negatively charged plane wall in equilibrium with a solution

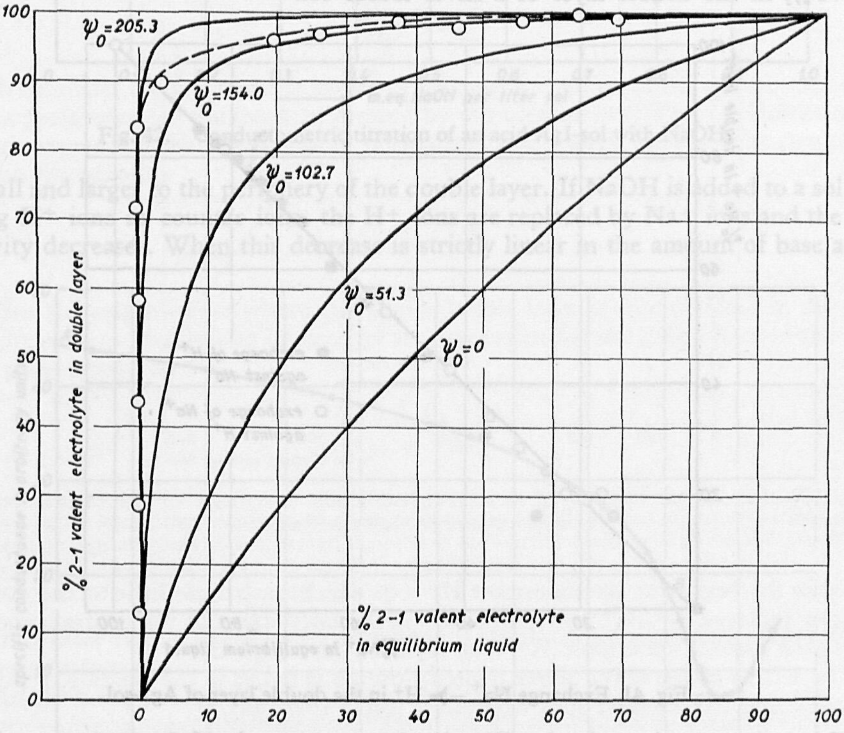

Fig. 40. Exchange of monovalent for divalent electrolyte as a function of the composition of the solution and of the surface potential ψ_0 in mV.
Circles describe exchange of HNO_3 against $Ba(NO_3)_2$ in a silver iodide sol.

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[1] G. A. J. VAN OS, *Thesis*, Utrecht 1943.

containing two different salts 1 and 2 of molar concentrations n_1 and n_-. The first salt is dissociated in 1 positive and 1 negative ion (both monovalent), the second salt in 1 divalent positive and 2 monovalent negative ions.

The excess of charge of the first cation over the first anion at a place where the potential is equal to ψ is given by

$$n_1F \left\{ \exp\left(-e\psi/_{kT}\right) - \exp\left(e\psi/_{kT}\right) \right\} \tag{98}$$

and the excess of charge for the second salt by

$$n_2F \left\{ 2\exp\left(-2e\psi/_{kT}\right) - 2\exp\left(+e\psi/_{kT}\right) \right\} \tag{99}$$

The ratio of the two excesses is found by integrating expression (98) and (99) over the whole double layer. Skipping the calculations we immediately give the result in Fig. 40. The exchange proves to depend only upon the surface potential and upon the concentration ratio in the solution, not upon the absolute values of the concentrations. Especially for high potentials the distribution is very onesided with the divalent ions in the double layer. Between the curves for $\psi_\circ = 205.3$ mV. and $\psi_\circ = 154.0$ mV. experimental points are inserted, found by VAN OS[1] for the exchange of HNO_3 against $Ba(NO_3)_2$ in the double layer of a silver iodide sol.

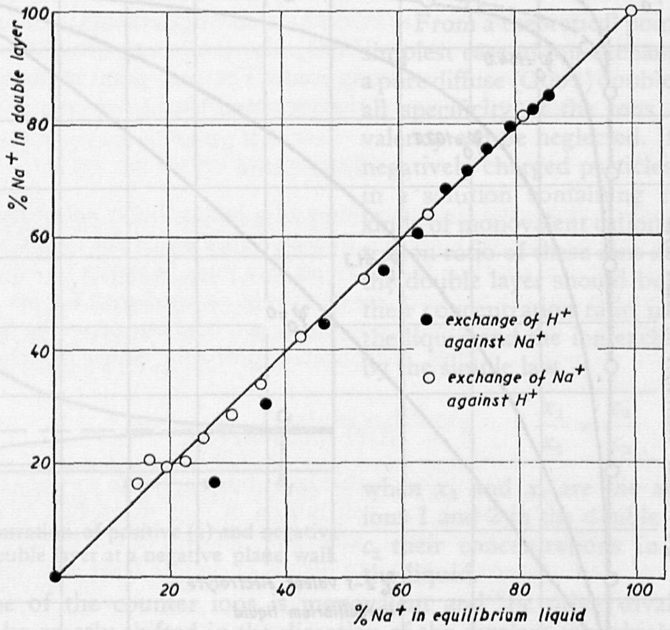

Fig. 41. Exchange $Na^+ \longrightarrow H^+$ in the double layer of AgI-sol.

From the same investigation Fig. 41 gives an example of the exchange of Na^+ against H^+ ions in the double layer of AgI. The linearity is very convincing.

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[1] For the technique used, see also Ch. V., § 13, p. 240.

A somewhat more indirect example is found in the conductometric titration of counter ions in sols. It will be shown in Ch. V, § 13, p. 238 that the counter ions give a contribution to the conductivity of the sol. This contribution is small for the ions near the wall and larger to the periphery of the double layer. If NaOH is added to a sol containing H+ ions as counter ions, the H+ ions are replaced by Na+ ions and the conductivity decreases. When this decrease is strictly linear in the amount of base added

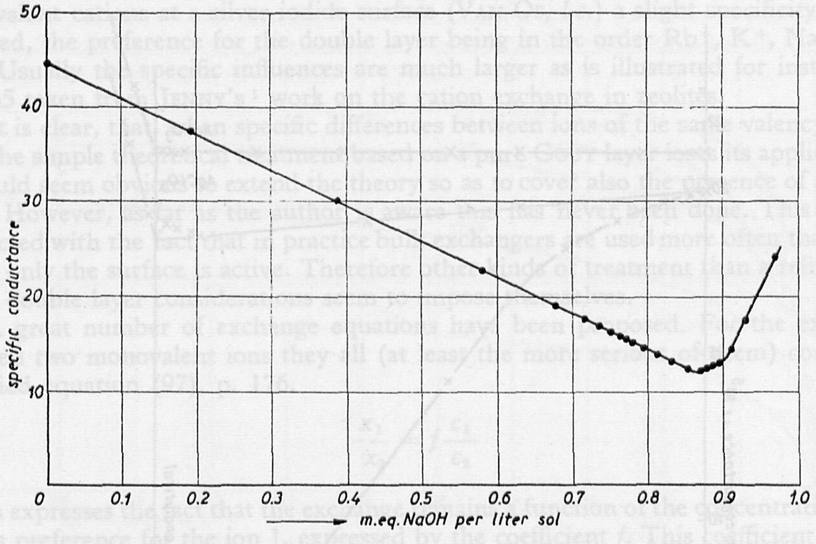

Fig. 42. Conductometric titration of an acid AgI-sol with NaOH.

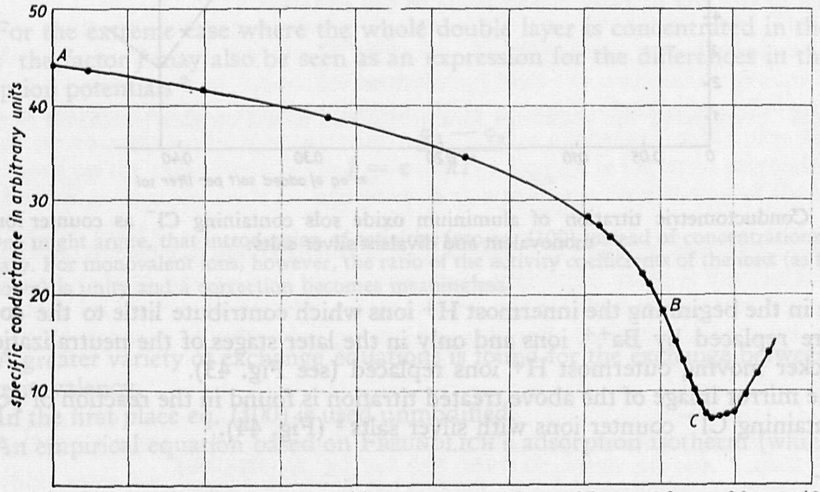

Fig. 43. Conductometric titration of an acid AgI-sol with Ba $(OH)_2$.

this proves that the Na^+ and H^+ ions are completely equivalent in the double layer. With the AgI-sol the titration line is indeed straight[1]. See Fig. 42.

If the titration is performed with $Ba(OH)_2$, however, the titration line is curved,

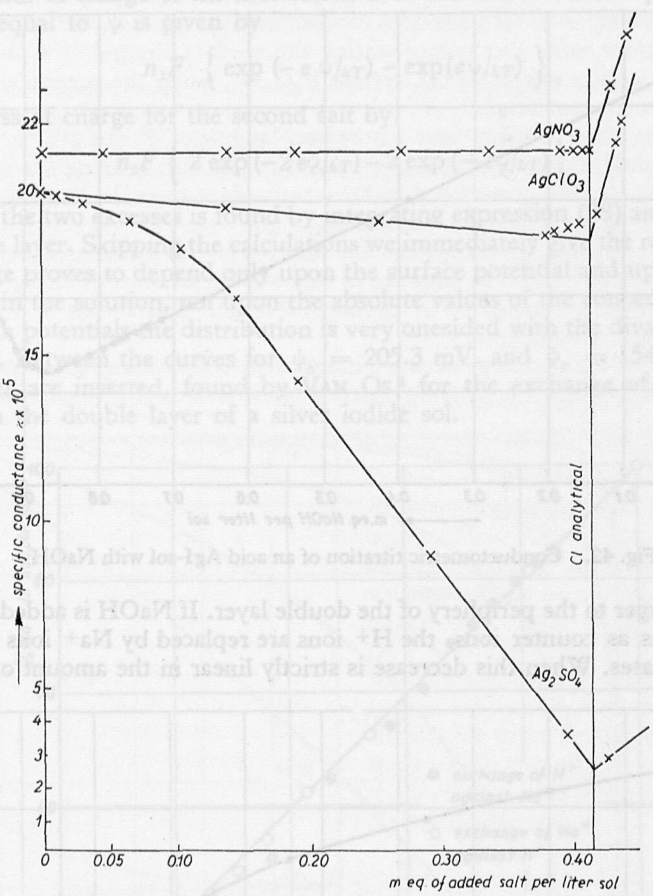

Fig. 44. Conductometric titration of aluminium oxide sols containing Cl^- as counter ions with monovalent and divalent silver salts.

because in the beginning the innermost H^+ ions which contribute little to the conductivity are replaced by Ba^{++} ions and only in the later stages of the neutralization are the quicker moving outermost H^+ ions replaced (see Fig. 43).

The mirror image of the above treated titration is found in the reaction of positive sols containing Cl counter ions with silver salts[2] (Fig. 44).

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[1] E. J. W. Verwey and H. R. Kruyt, *Z. physik. Chem.*, A 167 (1933) 149; H. De Bruyn and J. Th. G. Overbeek, *Kolloid-Z.*, 84 (1938) 186; G. A. J. Van Os, *Thesis*, Utrecht 1943.

[2] W. Pauli, *Trans. Faraday Soc.*, 31 (1935) 11.

b. Specific influences in ion exchange

In most cases of ion exchange, specific influences play a much more prominent part than in the cases treated in the foregoing subsection. Even in the exchange of monovalent cations at a silver iodide surface (VAN OS, *l.c.*) a slight specificity can be detected, the preference for the double layer being in the order Rb^+, K^+, Na^+, Li^+, H^+. Usually the specific influences are much larger as is illustrated for instance in Fig. 45 taken from JENNY's[1] work on the cation exchange in zeolites.

It is clear, that, when specific differences between ions of the same valency play a role, the simple theoretical treatment based on a pure GOUY layer loses its applicability. It would seem obvious to extend the theory so as to cover also the presence of a STERN layer. However, as far as the author is aware this has never been done. This may be connected with the fact that in practice bulk exchangers are used more often than those where only the surface is active. Therefore other kinds of treatment than a refinement of the double layer considerations seem to impose themselves.

A great number of exchange equations have been proposed. For the exchange between two monovalent ions they all (at least the more serious of them) come to a modified equation (97), p. 176.

$$\frac{x_1}{x_2} = f\frac{c_1}{c_2} \tag{100}$$

which expresses the fact that the exchange remains a function of the concentration ratio with a preference for the ion 1, expressed by the coefficient f. This coefficient may be seen as expressing the differences in normalized free energy between the two sorts of ions on the adsorber

$$f = e^{\frac{\mu_1 - \mu_2}{kT}} \tag{101}$$

For the extreme case where the whole double layer is concentrated in the STERN layer, the factor f may also be seen as an expression for the differences in the STERN adsorption potentials[2]

$$f = e^{\frac{\varphi_1 - \varphi_2}{kT}}$$

One might argue, that introduction of activities into eq. (100) instead of concentrations might be necessary. For monovalent ions, however, the ratio of the activity coefficients of the ions (as far as they are known) is unity and a correction becomes meaningless.

A greater variety of exchange equations is found for the exchange between ions of different valency.

In the first place eq. (100) is used unmodified.

An empirical equation based on FREUNDLICH's adsorption isotherm (which by the

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[1] H. JENNY, *J. Phys. Chem.*, 36 (1932) 2217.

[2] E. J. W. VERWEY, *Thesis*, Utrecht 1934, p. 27.

way has nothing to do with ion exchange) of the following form (eq. 102) has been given by Rothmund and Kornfeld[1].

$$\frac{x_1}{x_2} = f\left(\frac{c_1}{c_2}\right)^{1/p} \tag{102}$$

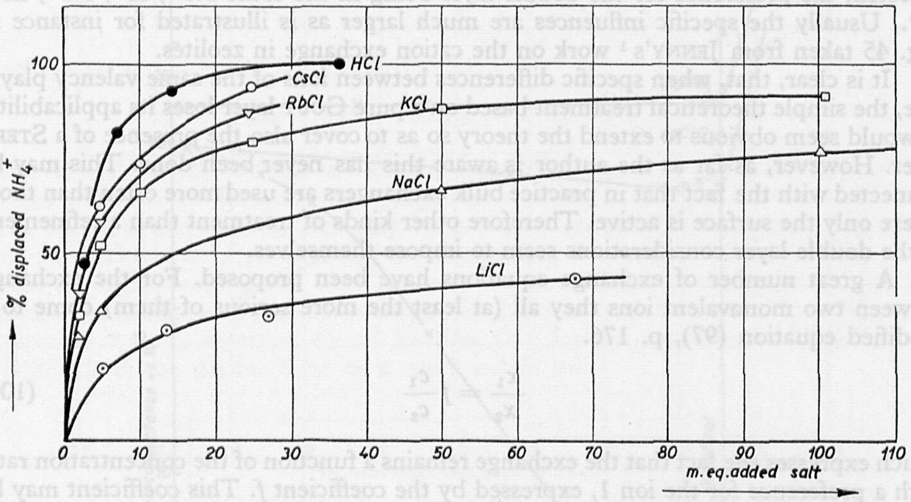

Fig. 45. Exchange of counter ions of a NH_4^+ permutite against other monovalent ions.

If the exchange equilibrium is written in the form (X is the exchanger)

$$Me^{++}_{sol} + 2\,Me^{+}X \rightleftarrows 2\,Me^{+}_{sol} + Me^{++}X_2$$

application of the law of mass action leads to the equation[2]

$$\frac{(x_{Me^+})^2}{x_{Me^{++}}} = f\,\frac{(c_{Me^+})^2}{(c_{Me^{++}})} \tag{103}$$

Gapon[3] considered the exchange kinetically and based on this treatment derived eq. (104)

$$\frac{x_{Me^+}}{x_{Me^{++}}} = f\,\frac{c_{Me^+}}{(c_{Me^{++}})^{1/2}} \tag{104}$$

In the treatments for the exchange of ions of different valency the applications of activity coefficients is more important than when only ions of one valency are considered. Several treatments both for the activity in the solution phase and for that in the exchanger have been proposed. For this subject we may refer to monographic treatments of ion exchange[4].

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[1] V. Rothmund and G. Kornfeld, *Z. anorg. u. allgem. Chem.*, 103 (1918) 129; 108 (1919) 215.

[2] H. W. Kerr, *J. Am. Soc. Agron.*, 20 (1928) 309; *Soil Sci.*, 26 (1928) 384.

[3] E. N. Gapon, *J. Gen. Chem. U.S.S.R.*, 3 (1933) 144.

[4] F. C. Nachod, *Ion exchange, Theory and application*. New York 1949. R. J. Mijers, *Advances in Colloid Science I*, New York 1942. A series of papers by various authors connected with the Plutonium project, *J. Am. Chem. Soc.*, 69 (1947) 2796, 2881.

There is neither a clear cut experimental decision, nor are the theoretical derivations sound enough to choose one out of the above equations.

Especially for the more homogeneous exchangers perhaps eq. (103) or one of its modifications which takes activities into account is the most promising.

BOYD, SCHUBERT and ADAMSON [1] found relation (103) valid for a sulphonic acid resin and could express the affinities of different ions for the exchanger in the form of standard free energies of the reaction equation

$$\mathrm{Me^+ + HX \rightleftarrows H^+ + MeX}. \text{ See Table 4.}$$

STANDARD FREE ENERGIES FOR THE REACTION $\mathrm{Me^+ + HX \rightleftarrows MeX + H^+}$

TABLE 4

Ion	$-\triangle F^\circ$ cal/mol.
H^+	0
Li^+	−60
Na^+	320
NH_4^+	410
K^+	530
Rb^+	615
Cs^+	860
Ba^{++}	1380
Y^{+++}	1830
La^{+++}	2110

c. Role of pH

In many exchanging processes the pH plays an exceptional role. This may be correlated with the fact that the H^+ ions can be considered as potential-determining ions for the exchanger or in another terminology that the exchanging groups are weak acids or bases (COOH, aluminosilicates, NH_2 groups). Only when the exchanging groups are strongly acidic it is reasonable to compare exchanges of H^+ ions with other metal ions on the same basis. With weak acids or bases it is better to correlate first the total exchange capacity with pH and then on this basis the distribution of the ions over the available places.

In Fig. 45 (p. 182) the strong exchanging power of the H^+ ion may be understood in this way.

d. Application

The applications of ion exchanges are very numerous. Before 1935 the usual exchangers were aluminosilicates and zeolites (clays, synthetic aluminosilicates) which by their extended surface, but especially by their possibility of exchanging throughout the whole mass had a large exchanging capacity.

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[1] G. E. BOYD, J. SCHUBERT, and A. W. ADAMSON, *J. Am. Chem. Soc.*, 69 (1947) 2828.

ADAMS and HOLMES [1] discovered that resins of the phenol or polyphenol formaldehyde type were suitable as exchangers. They also prepared the first anion exchangers on the basis of polyamine formaldehyde resins.

Another suitable exchanger was found in sulphonated coal [2] which had the advantage of containing a strongly acidic group as bearer of the exchange properties, so that the influence of the pH on the exchange capacity was relatively unimportant.

Nowadays all sorts of exchanging groups are incorporated into synthetic resins, resulting in exchangers of nearly all desired properties. Only a really good strongly basic anion exchanger is still lacking.

One of the oldest applications of ionic exchange is softening of drinking-water and boiler water by exchanging Ca^{++} against Na^{+} ions. When the exchanger is saturated with Ca^{++} it is regenerated by letting a concentrated NaCl solution percolate through it.

A more advanced form of water treatment is the complete deionizing of water by applying first an acid-treated cation exchanger, which takes up all the cations and leaves only the acids. When this water is then percolated through an anion exchanger the acid is removed by the reaction

$$—NH_2 + H^+X^- \rightarrow —NH_3^+X^-$$

In this way it is possible to prepare water which may replace distilled water at a much cheaper price than by distillation. Additional processes have been elaborated to remove the SiO_2 which normally passes both cation and anion exchanger.

Another important place of ion exchange is in the separation of difficultly separable cations, like the rare earths and the transuranium elements. An important feature of the ion exchange process in this respect is that it can be easily controlled from a distance and is therefore very suitable for the treatment of "hot" materials from the uraniumpile.

Several applications of ion exchange are also found in analytical chemistry but as they have no place in a treatise on colloid science the reader is referred to the monographic treatments mentioned in footnote 4 on p. 182.

§ 10. POTENTIAL MEASUREMENTS IN COLLOIDAL SYSTEMS PALLMANN EFFECT, SOL CONCENTRATION EFFECT

In many investigations on colloidal systems potential measurements are used as a tool to determine ionic concentrations. Most extensive use has been made of the pH, but there also many cases when p_{Ag}, p_{Cl}, p_{SO_4} have been determined. The interpretation of the measurements for colloidal systems proves to be much more difficult than for simple ionic systems. Especially the use of salt bridges, necessary to determine (approximately) single ion activities, gives rise to complications and has even led to completely false conclusions.

Fundamentally the difficulty is this: what is the pH (or p_X) of a sol? Is it the pH of the intermicellar liquid or should it be understood as a property of the suspension as a whole? A simple experiment shows that two different results of the pH determination are possible. If a sol or suspension is in equilibrium with a particle-free solution

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[1] C. A. ADAMS and E. L. HOLMES, *J. Soc. Chem. Ind.*, 54 (1935) 1—6 T.

[2] P. SMIT, U.S. Patent 2.191063 (Feb. 20 1940), 2.205235 (June 25 1940); O. LIEBKNECHT, U.S. Patent 2.191060 (Feb. 20 1940), 2.206007 (June 25 1940).

(by dialysis or sedimentation) then a pH determination may be done in four different ways. The hydrogen electrode may be situated in the suspension or in the equilibrium liquid. The salt bridge also may be brought into contact with either of two systems.

The place of the hydrogen (or other reversible) electrode is without influence on the potential measured. This is necessarily so. For if two hydrogen electrodes in contact with the sol and the equilibrium solution would show a potential difference, work might be gained from a system in thermodynamic equilibrium, which is contrary to the Second Law.

The place of the salt bridge does make a difference, however. Usually the electrode connected to the salt bridge shows a lower potential when the salt bridge is in contact with the suspension than when it is in contact with the equilibrium solution, at least if the suspension is negatively charged. For a positive suspension the effect is in the reverse direction.

This effect has been described and extensively investigated by PALLMANN and WIEGNER [1], who determined the pH in suspensions of clays and similar materials. DE BRUYN [2] found the same effect (which he called sol-concentration effect) in the determination of the pI of concentrated negatively charged AgI-sols.

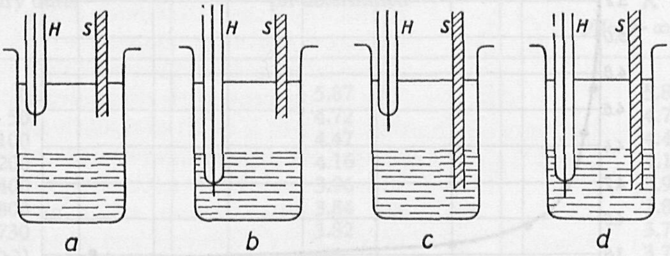

Fig. 46. Four different methods of determining the pH of a sol or suspension. H is a hydrogen electrode, S is a salt bridge, connecting the system to a calomel electrode.
The systems a and b are equivalent and measure the pH of the equilibrium liquid. The systems c and d give an E.M.F. which can be alternatively interpreted as "the pH of the suspension" or as the pH of the equilibrium liquid disfigured by sol concentration effect or PALLMANN effect.

LOOSJES [3] could produce a change in E.M.F. analogous to the sol concentration and the PALLMANN effect by placing a liquid junction alternatively in a capillary and in a wide tube.

Qualitatively these effects are easy to understand. A rigorous quantitative treatment is still lacking, although especially LOOSJES made an attempt in this direction.

Let us first consider a liquid junction between a concentrated KCl solution and a dilute solution in a wide tube. The equality of the mobilities of Cl^- and K^+ implies a negligible diffusion potential between the two solutions. The concentrated KCl solution

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[1] H. PALLMANN, *Kolloidchem. Beihefte*, 30 (1930) 334; G. WIEGNER and H. PALLMANN, *Z. Pflanzenernähr. Düngung Bodenk.*, A 16 (1930) 1; G. WIEGNER, *Kolloid-Z.*, 51 (1930) 49.
[2] H. DE BRUYN, *Thesis*, Utrecht 1938; *Rec. trav. chim.*, 61 (1942) 12.
[3] R. LOOSJES, *Thesis*, Utrecht 1942.

has nearly the same potential as the other dilute one. Now consider a same junction but in a narrow capillary where a considerable part of the cross section is the carrier of the double layer and consequently in the dilute solution has a more negative potential than the bulk of this solution (the capillary wall is considered to be negatively charged). Now the concentrated KCl solution will try to assume the same potential as the dilute solution everywhere in the cross section of contact. This implies that in the concentrated solution the potential is more negative near the wall than in the middle of the capillary. Clearly this is not a stable situation and a current will flow perpendicular to the cross section of the capillary until the concentrated solution has everywhere the same potential. This potential will be somewhere between the potential of the wall and that in the middle of the capillary, in any case *more negative* than in the case where the double layer had no influence.

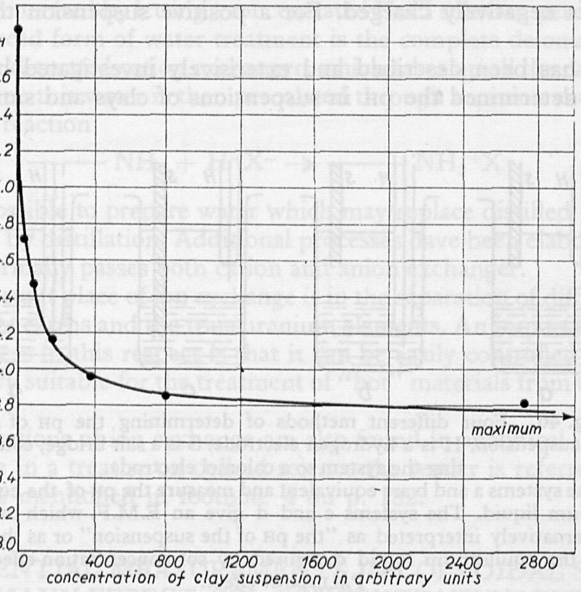

Fig. 47. Relation between "pH" measured with salt bridge in the suspension and concentration of suspension.
.... measurements by PALLMANN
——— calculated with eq. (106).

Generally speaking, the salt bridge will not indicate the potential of the equilibrium solution but a potential nearer to that of the wall (capillary effect) or of the particles (PALLMANN effect, sol concentration effect).

LOOSJES (*l.c.*) has worked this picture out in a very schematized way and deduced the following equation for the PALLMANN and sol concentration effect

$$(E_{c_s} - E_{c_s \to \infty})(c_s + K) = (E_{c_s = 0} - E_{c_s \to \infty})K \qquad (105)$$

where the E's are the E.M.F.'s measured between a calomel electrode connected to the sol through a salt bridge and a reversible electrode in the sol. c_s is the sol concentration in arbitrary units. The constants K and $E_{c_s \to \infty}$ have to be determined from a series of measurements of the potentials at different dilutions of the sol, the dilution being made with the equilibrium liquid. As the E.M.F.'s are linearly dependent upon the pH or pX an equivalent expression is

$$(\mathrm{pH}_{c_s} - \mathrm{pH}_{c_s \to \infty})\,(c_s + K) = (\mathrm{pH}_{c_s = 0} - \mathrm{pH}_{c_s \to \infty})\,K \qquad (106)$$

LOOSJES recalculated data from PALLMANN [1] on hydrogen clay where the pH of the equilibrium liquid was 5.87. The values of the calculated pH for different concentrations compare very favourably with the measured values (Table 5, Fig. 47)

TABLE 5

pH OF HYDROGEN CLAY IN DIFFERENT DILUTIONS

c_s in arbitrary units	pH determined	pH calculated with eq. (106) $K = 45$, $\mathrm{pH}_{cs \to \infty} = 3.74$
0	5.87	5.87
50	4.72	4.75
100	4.47	4.40
200	4.16	4.13
400	3.96	3.96
800	3.84	3.85
2730	3.82	3.77
(∞)	—	3.74

Other data of PALLMANN, a series of experiments of LOOSJES himself and the sol concentration effect by DE BRUYN are equally well described.

From the data of Table 5 and other similar data it is clear that the sol concentration effect is by no means a small correction. The difference in pH for the infinitely dilute and a concentrated solution amounts to 2 units of pH, equivalent to more than 100 mV. in the potential.

VAN LAAR [2] used the sol concentration effect in order to determine the zero point of charge of AgI. He determined the $\mathrm{p_{Ag}}$ for which there was no difference in E.M.F. between a salt bridge in a silver iodide suspension and a salt bridge in the equilibrium solution. At this $\mathrm{p_{Ag}}$ there is no diffuse double layer and when specific adsorption is absent the zero point of charge is reached. See also § 6a, p. 161.

In concluding this section we want to emphasize that when ion activities are to be determined by E.M.F. measurement in a sol or suspension extrapolation to infinite dilution of the sol or suspension is necessary in order to obtain the activity of the equilibrium liquid. A direct interpretation of an E.M.F. measurement in a concentrated sol is not possible at the moment.

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[1] H. PALLMANN, *Kolloidchem. Beihefte*, 30 (1930) 334.

[2] J. A. W. VAN LAAR, *unpublished.*

§ 11. THE DONNAN EQUILIBRIUM

When two solutions are separated by a membrane which is impermeable to at least one of the ionic species (usually a colloidal component) present in one of the solutions an unequal distribution for the other ionic species, to which the membrane is permeable results. At the equilibrium reached the two solutions show a difference in pressure and if two calomel electrodes are connected to the solutions by means of salt bridges an E.M.F. is found to be present. These equilibria were described for the first time and explained by DONNAN [1] and are usually indicated as DONNAN equilibria.

a. Relation between DONNAN equilibrium and sol-concentration effect

There is a very close relation between the DONNAN potential and the sol-concentration effect treated in the foregoing section.

In Fig. 48 we sketched a suspension and its equilibrium liquid separated by a membrane. In both the solutions a reversible electrode, H (for instance a hydrogen electrode) and a salt bridge, S, with a calomel electrode are inserted. The DONNAN potential is measured between the two salt bridges. The sol-concentration effect is usually given as the difference in E.M.F. of the galvanic cells with the sol and the equilibrium liquid. As the two reversible electrodes have necessarily the same potential, the sol-concentration effect and the DONNAN potential are identical, and what is true for one of them is as true for the other. We have treated the two effects separately, because the sol-concentration effect is often met in cases where one would not be inclined to think of a DONNAN equilibrium. On the other hand the DONNAN equilibria include more than the DONNAN potential alone.

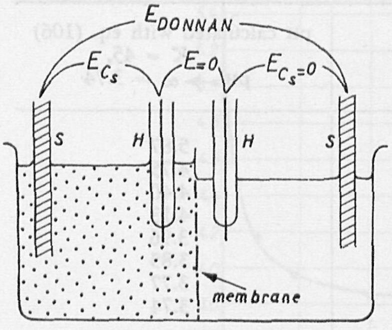

Fig. 48. Sol concentration effect ($E_{cs} - E_{cs} = 0$) is equal to DONNAN potential.

b. DONNAN equilibrium for ideal solutions

The original theory of DONNAN assumes ideal behaviour for both the solutions. Later the theory has been refined by DONNAN himself and by others to include non-ideal behaviour. We will for simplicity first treat the DONNAN equilibrium for ideal solutions.

Consider a system given schematically in Fig. 49 and consisting of two phases separated by a membrane permeable to the solvent S and the ions A^- and M^+ but impermeable to the (colloidal) n-valent ion C. In each of the solutions the mol fractions are denoted by x, the pressures by p, and the potentials [2] by ψ. The two solutions are denoted by indices I and II.

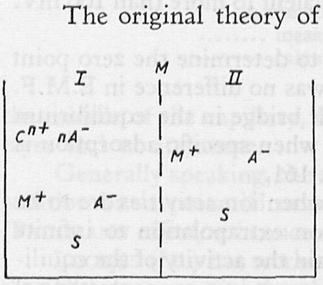

Fig. 49. DONNAN equilibrium.

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[1] F. G. DONNAN and A. B. HARRIS, *J. Chem. Soc.*, 99 (1911) 1554; F. G. DONNAN, *Z. Elektrochem.*, 17 (1911) 572; *Chem. Revs.*, 1 (1924) 73.

[2] Provisionally we assume the potential of a phase to be directly measurable by means of a salt bridge.

The conditions for equilibrium are

$$\mu^{\mathrm{I}}_{+} = \mu^{\mathrm{II}}_{+} ; \mu^{\mathrm{I}}_{-} = \mu^{\mathrm{II}}_{-} ; \mu^{\mathrm{I}}_{s} = \mu^{\mathrm{II}}_{s} \tag{107}$$

By using the approximations for ideal behaviour we convert these eq. into

$$RT \ln x^{\mathrm{I}}_{+} + p^{\mathrm{I}} V_{+} + F\,\psi^{\mathrm{I}} = RT \ln x^{\mathrm{II}}_{+} + p^{\mathrm{II}} V_{+} + F\,\psi^{\mathrm{II}} \tag{108}$$

$$RT \ln x^{\mathrm{I}}_{-} + p^{\mathrm{I}} V_{-} - F\,\psi^{\mathrm{I}} = RT \ln x^{\mathrm{II}}_{-} + p^{\mathrm{II}} V_{-} - F\,\psi^{\mathrm{II}} \tag{109}$$

$$RT \ln x^{\mathrm{I}}_{s} + p^{\mathrm{I}} V_{s} = RT \ln x^{\mathrm{II}}_{s} + p^{\mathrm{II}} V_{s} \tag{110}$$

By adding the first two equations we derive after neglecting the pV term, which is small,

$$x^{\mathrm{I}}_{+} x^{\mathrm{I}}_{-} = x^{\mathrm{II}}_{+} x^{\mathrm{II}}_{-} \tag{111}$$

which eq. with the expressions for electroneutrality

$$n x^{\mathrm{I}}_{c} + x^{\mathrm{I}}_{+} = x^{\mathrm{I}}_{-} \text{ and } x^{\mathrm{II}}_{+} = x^{\mathrm{II}}_{-} = x^{\mathrm{II}} \tag{112}$$

describes the distribution of the ions over the two phases.

From the eq. (108) and (109) separately we find two expressions for the potential difference between the two phases (again neglecting the pV terms):

$$\psi^{\mathrm{I}} - \psi^{\mathrm{II}} = \frac{RT}{F} \ln \frac{x^{\mathrm{II}}_{+}}{x^{\mathrm{I}}_{+}} = \frac{RT}{F} \ln \frac{x^{\mathrm{I}}_{-}}{x^{\mathrm{II}}_{-}} \tag{113}$$

and finally the osmotic pressure is derived from eq. (110)

$$p^{\mathrm{I}} - p^{\mathrm{II}} = \frac{RT}{V_s} \ln \frac{x^{\mathrm{II}}_{s}}{x^{\mathrm{I}}_{s}} = \frac{RT}{V_s} \ln \frac{1 - x^{\mathrm{II}}_{+} - x^{\mathrm{II}}_{-}}{1 - x^{\mathrm{I}}_{+} - x^{\mathrm{I}}_{-} - x^{\mathrm{I}}_{c}} \tag{114}$$

For small colloid concentrations the following approximations are useful.

The electrolyte distribution can be expressed as the difference between the concentrations of counter ions in the two phases which is found from eq. (111) and (112)

$$x^{\mathrm{II}}_{+} - x^{\mathrm{I}}_{+} = x^{\mathrm{II}}_{+} - \sqrt{(x^{\mathrm{II}}_{+})^2 + \frac{n^2\,(x^{\mathrm{I}}_{c})^2}{4}} + \frac{n x^{\mathrm{I}}_{c}}{2} = \frac{n x^{\mathrm{I}}_{c}}{2} \left(1 - \frac{n x^{\mathrm{I}}_{c}}{4 x^{\mathrm{II}}}\right) \tag{115}$$

$$x^{\mathrm{II}}_{-} - x^{\mathrm{I}}_{-} = -\frac{n x^{\mathrm{I}}_{c}}{2} \left(1 + \frac{n x^{\mathrm{I}}_{c}}{4 x^{\mathrm{II}}}\right) \tag{116}$$

For small colloid concentrations the excess of charge on the colloidal ions is compensated by a (nearly) equal contribution from the counter ions and a defect of ions of the same charge.

In the same approximation the membrane potential $\psi^{\mathrm{I}} - \psi^{\mathrm{II}}$ is equal to

$$\psi^{\mathrm{I}} - \psi^{\mathrm{II}} = \frac{RT}{F} \frac{n x^{\mathrm{I}}_{c}}{2 x^{\mathrm{II}}} \tag{117}$$

and the osmotic pressure to

$$p^{\mathrm{I}} - p^{\mathrm{II}} = \frac{RT}{V_s} \frac{x_c^{\mathrm{I}} + \frac{n^2 (x_c^{\mathrm{I}})^2}{4\, x^{\mathrm{II}}}}{1 - 2x^{\mathrm{II}}} = RT\, c_c \left(1 + \frac{n^2}{4} \frac{c_c}{c^{\mathrm{II}}}\right) \tag{118}$$

where the c's are concentrations in mols per cm³ solvent.

The first term may be considered to arise from the colloid particles themselves, the second term from the unequal distribution of the electrolyte.

The DONNAN equilibrium is seen to be a mighty instrument of characterization of a colloid. The osmotic pressure for great dilution of the colloid ($c_c \ll c^{\mathrm{II}}$) gives the molar concentration, and thus leads to the molecular weight[1]. The first higher term in the osmotic pressure and the first terms in the membrane potential and the distribution of ions all contain n, the valency (or charge) of the colloidal particle, which can thus be determined in a completely independent way.

In the applications it is however rarely possible to apply the DONNAN theory for ideal systems, at least if more than qualitative results are wanted. From the eq. (115, 116, 117 and 118) it is possible to determine the charge on the colloid in three independent ways. This means, that two relations between the three phenomena (distr. of ions, membrane potential, osmotic pressure) should exist. Now usually, when the osmotic pressure is calculated either from analytical data or from the membrane potential it is found to be too low (HAMMARSTEN effect[2]). This clearly indicates the need for a more exact treatment of the DONNAN equilibrium, in the first place the introduction of activity coefficients.

c. Non-ideal solutions

A very striking example of the influence of non-ideality of the solutions on the DONNAN equilibrium is the system $KCl - K_4Fe(CN)_6$ where the membrane is permeable to K^+ and Cl^- but impermeable to $Fe(CN)_6{}^{4-}$. It has been investigated by DONNAN and ALLMAND[3] and by KAMEYAMA[4]. The experimental data have been treated by HÜCKEL[5] who could explain the results by introducing mean activity coefficients according to the theory of DEBYE and HÜCKEL. KAMEYAMA had also reached a satisfactory interpretation with the help of activity coefficients after LEWIS.

In the case of real colloidal solutions the problem is more difficult because presumably the activity coefficients are less simply related to the concentrations than in the case of simple electrolytes.

For non-ideal solutions the conditions (111, 112, 113, 114) are modified as follows by the introduction of activity coefficients.

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[1] As n may be very large it is often necessary to go to very low colloid concentrations, or better, to use large concentrations of electrolyte before the osmotic pressure is a pure measure of the colloid concentration.

[2] E. and H. HAMMARSTEN, *Arkiv Kemi Mineral. Geol.*, 8 (1923) 1; H. HAMMARSTEN, *Biochem. Z.*, 147 (1924) 481.

[3] F. G. DONNAN and A. J. ALLMAND, *J. Chem. Soc.*, 105 (1914) 1941.

[4] N. KAMEYAMA, *Phil. Mag.*, 50 (1925) 849.

[5] E. HÜCKEL, *Kolloid-Z.* (*Zsigmondy Festschrift*), 36 (1925) 204.

$$f_+^{\mathrm{I}}x_+^{\mathrm{I}} \cdot f_-^{\mathrm{I}}x_-^{\mathrm{I}} = f_+^{\mathrm{II}}x_+^{\mathrm{II}} \cdot f_-^{\mathrm{II}}x_-^{\mathrm{II}} = \left(f_\pm^{\mathrm{I}}\right)^2 x_+^{\mathrm{I}}x_-^{\mathrm{I}} = \left(f_\pm^{\mathrm{II}}\right)^2 x_+^{\mathrm{II}}x_-^{\mathrm{II}} \tag{119}$$

$$nx_c^{\mathrm{I}} + x_+^{\mathrm{I}} = x_-^{\mathrm{I}} \text{ and } x_+^{\mathrm{II}} = x_-^{\mathrm{II}} = x^{\mathrm{II}} \tag{120}$$

$$\psi^{\mathrm{I}} - \psi^{\mathrm{II}} = \frac{RT}{F} \ln \frac{f_+^{\mathrm{II}}x_+^{\mathrm{II}}}{f_+^{\mathrm{I}}x_+^{\mathrm{I}}} = \frac{RT}{F} \ln \frac{f_-^{\mathrm{I}}x_-^{\mathrm{I}}}{f_-^{\mathrm{II}}x_-^{\mathrm{II}}} \tag{121}$$

and

$$p^{\mathrm{I}} - p^{\mathrm{II}} = g \frac{RT}{V_s} \ln \frac{1 - x_+^{\mathrm{II}} - x_-^{\mathrm{II}}}{1 - x_+^{\mathrm{I}} - x_-^{\mathrm{I}} - x_c^{\mathrm{I}}} \tag{122}$$

Now if we adhere strictly to the conception (see § 3d, p. 125) that a potential difference between different phases cannot be determined eq. (121) has no practical significance. Eq. (119) can be used to determine f_+ in the colloidal system when the analytical data are available and f_+ in the colloid-free solution has been determined. Likewise the osmotic coefficient g can be determined from eq. (122) if all other quantities (notably the molar fraction of the colloid) are known. But as there is no simple relation between $f_\pm$ and g in this case, that would mean nearly the end of all practical application of the DONNAN equilibrium.

Only in the case where the concentration of electrolyte is very large compared with the equivalent concentration of the colloidal ion does the osmotic pressure remain a measure for the molar concentrations of the colloid and can then be used to estimate the molecular weight.

$$p^{\mathrm{I}} - p^{\mathrm{II}} = RTc_c \tag{123}$$

ADAIR [1] goes one step further to utilize eq. (121) as well, by assuming that when the colloid concentration is low the activity coefficients in the two solutions may, as a good approximation, be taken as equal. Moreover he assumes that insertion of two identical salt bridges in the two solutions gives a means of determining the potential difference $\psi^{\mathrm{I}} - \psi^{\mathrm{II}}$. Eq. (121) which then simplifies again to eq. (117) gives then a possibility of determining the valency n of the colloidal particle and when n has been determined in this way it can be inserted into eq. (118) to determine the correction to the osmotic pressure, so permitting the osmotic contribution of the colloidal particles to be determined when still a measurable contribution of the ions is present.

KLAARENBEEK [2] has criticised especially the assumptions made about the activity coefficients and he has shown that for the DONNAN equilibrium of gum arabic, these hypotheses do not lead to an acceptable interpretation. He attacks the problem from a different point of view.

Summarizing, the DONNAN equilibrium consists of:

α. Different salt concentrations in the colloidal solution and in the equilibrium liquid.

β. An excess osmotic pressure.

γ. A potential difference measurable with salt bridges.

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[1] G. S. ADAIR and M. E. ADAIR, *Trans. Faraday Soc.*, 36 (1940) 23; 31 (1935) 130; G. S. ADAIR, *ibidem*, 33 (1937) 524; See also F. G. DONNAN and E. A. GUGGENHEIM, *Z. physik. Chem.*, A 162 (1932) 346; F. G. DONNAN, *ibidem*, A 168 (1934) 369.

[2] F. W. KLAARENBEEK, *Thesis*, Utrecht 1946.

α. In the double layers of a colloidal solution there is a defect of ions of the same sign as the colloid and an excess of ions of opposite sign. This explains the distribution of the electrolyte.

β. When two double layers approach each other to such a distance that a substantial interaction is present, they will repel each other (see chapter VI, p. 245). This explains the excess osmotic pressure.

γ. In a sol the potential of the liquid is not a constant, but fluctuates between zero and the surface potential $\psi_\circ$. With salt bridges a kind of average of this potential is measured (sol concentration effect = DONNAN potential).

KLAARENBEEK has applied these ideas to the DONNAN equilibrium using the model of flat double layers of the GOUY-CHAPMAN-type, and obtained rather satisfactory results, which were in better agreement with the experimental data than the classical DONNAN theory even when the latter has been corrected for activity coefficient.

The distribution of ions can be described as the expulsion of a certain amount of ions of the same sign as the colloid. In the classical DONNAN theory and also in the case of equal activity coefficients in the two solutions (ADAIR) the expulsion for a small amount of colloid is just equal to half the equivalent concentration of the colloid (see eq. 116). For a flat double layer on a negatively charged wall

$$\frac{\text{Defect of negative ions}}{\text{Total double layer charge}} = \frac{-\int_0^{\psi_\circ} \left(e^{\frac{e\psi}{kT}} - 1\right) \frac{dx}{d\psi}\, d\psi}{\int_0^{\psi_\circ} \left(e^{\frac{-e\psi}{kT}} - e^{\frac{e\psi}{kT}}\right) \frac{dx}{d\psi}\, d\psi}$$

$$= - \frac{e^{\frac{e\psi_\circ}{2kT}} - 1}{e^{-\frac{e\psi_\circ}{2kT}} - e^{\frac{e\psi_\circ}{2kT}}} \tag{124}$$

For small values of the double layer potential $\psi_\circ$ this quotient is equal to $^1/_2$ but for large negative values of $\psi_\circ$ the quotient is smaller *even in the limit of low sol concentration.*

Experimentally KLAARENBEEK finds the following values for dilute gum arabic with KBr as electrolyte.

TABLE 6

DONNAN EQUILIBRIUM OF GUM ARABIC

Conc. K Br. in equilibr. liquid	$\frac{\text{Defect of Br}^-}{\text{Equiv. conc. of gum arabic}}$	Calculated surface potential in mV
0.001 *N*	0.11	— 102
0.01 *N*	0.19	— 71
0.1 *N*	0.32	— 37
1 *N*	0.50	∾ 0

For higher colloid concentrations the expulsion of Br^--ions becomes relatively smaller, which is in agreement with the expectation for interacting double layers. Calculating the amount of interaction of the double layers from the measured osmotic pressure, KLAARENBEEK finds a good agreement between the calculated and determined defects of Br^--ions also for the higher colloid concentrations.

In Fig. 50 we give an example for 0.001 *N* K Br and gum arabic concentrations up to 0.014 *N*.

By this method both the analytical features of the DONNAN equilibrium and the osmotic pressure find a reasonable interpretation.

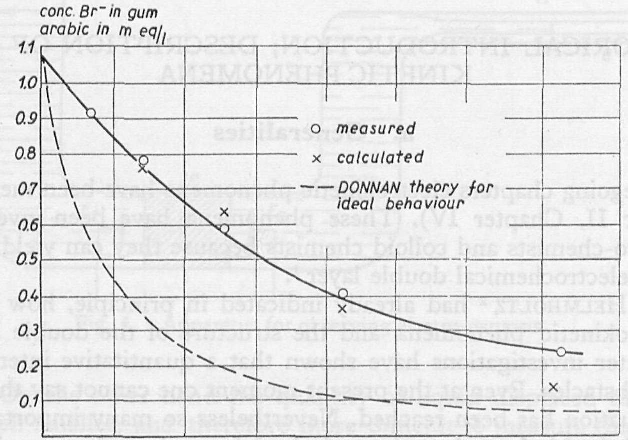

Fig. 50. Measured and calculated values of the Br^- ion concentrations in a gum arabic solution, which is in equilibrium with a KBr solution of 1.076 *m* eq/1.

The fact that usually the measured membrane potential is higher than the calculated one (HAMMARSTERN effect, p. 190) shows a close parallelism to the ideas of LOOSJES (see § 10, p. 185) on the sol concentration effect. Indeed the potential measured by a salt bridge will be the average potential in the liquid phase, or even nearer than this to the wall potential, whereas the osmotic pressure and the distribution of the ions is governed by the potential halfway between two interacting particles.

It would certainly be important to apply KLAARENBEEK's ideas to more examples of the DONNAN equilibrium and see whether they are generally applicable.