

THE STUDY OF THE DOUBLE LAYER AT THE METAL-SOLUTION INTERFACE BY ELECTRO- KINETIC AND ELECTROCHEMICAL METHODS.

By A. FRUMKIN.

Received 18th July, 1939.

1. Elektrokinetic Behaviour of Metals.

There exist a number of experimental methods which allow the study of the double layer at the metal-solution interface. They may be classified as follows :

- (1) Direct measurement of the surface charge (adsorption measurements, charging of a freshly formed surface), or of its variation with the potential (capacity measurements).
- (2) Indirect determination of the surface charge from electrocapillary data.
- (3) Measurement of the total potential difference under non-equilibrium conditions (dropping electrode, overvoltage measurements in dilute solutions).
- (4) Elektrokinetic measurement.
- (5) Contact angle measurement.

As well known, the data obtained by different methods could not be reconciled for a long time ; these discrepancies led to a large extent to a discussion as to the position of the zero point of the charge of metals, and the controversy about the relative value of the zero points of Billitzer and Ostwald-Nernst filled the electrochemical literature during many years.¹ One of the possible causes of such discrepancies has been pointed out by Smoluchovski and Freundlich, who have indicated that the electrokinetic behaviour of metals is determined not by the total potential drop between the metal and the solution, but only by that fraction of it which corresponds to the movable part of the surface layer (ζ potential). Equally important was probably the circumstance that, often, results of measurements carried out by various methods with different metals were compared, without taking into account that the position of the zero point changes with the nature of the latter. Finally, it is necessary to take into account, when comparing electrokinetic data with the results obtained by other methods, the complications in the structure of the double layer, connected with the formation of oxide and hydride films on the surface of the metal.

¹ Billitzer, *Drudés Ann.* II, 1903, 902 ; *Trans. Am. Elektrochem. Soc.*, 1930, 57 ; Palmær, *Z. physikal. Ch.*, 1907, 59, 129 ; Frumkin, *Sov. Phys.*, 1933, 4, 239 ; Freundlich and Mäkel, *Z. Elektrochem.*, 1909, 15, 161.

The discrepancy between the electrokinetic and electrode behaviour of metals which is observed if all the above-mentioned circumstances are left out of account, is so large that colloid chemists used to distinguish sharply the two groups of phenomena; thus, for instance, in their well-known monograph Pauli and Valkó² say: *kann man trotzdem die Nernst'sche Lösungstension für die Ladung der Teilchen verantwortlich machen? Die experimentell festgestellte Unabhängigkeit geht so weit dass wir diese Möglichkeit für äusserst unwahrscheinlich halten müssen.* In reality, however, when electrokinetic and electrochemical measurements are carried out with the same surface and when the behaviour of the system is not complicated by the phenomena of specific adsorption, the determination of the sign of the surface charge by various methods must give coinciding results. This conclusion was confirmed by the investigations of N. Bach and others in this laboratory with activated charcoal, the potential of which was changed gradually from a saturation of its surface with oxygen to a saturation with hydrogen.³ In this case, the sign of the charge and the position of the zero point of the charge of the activated charcoal determined from electrokinetic and adsorption measurements exactly coincided. On the other hand, it can be shown that adsorption measurements give actually a picture of the origin of the total potential drop on a charcoal electrode, for this potential varies over a very wide range according to a linear law, as a function of the charge as determined from adsorption measurements.⁴

I shall consider in more detail the properties of the platinum electrode. Measurements of the adsorption, carried out with platinised platinum at various potentials,⁵ have shown that with a reversible hydrogen potential the platinum surface is negatively charged and adsorbs cations; with the transition to more positive potentials the adsorption of cations, as would be expected, decreases at first and is further replaced by the adsorption of anions. In an acidulated normal solution of Na_2SO_4 , where the specific adsorption of the anions can probably be neglected, the zero point of the charge lies at a potential $\phi = 0.12$ with respect to the normal hydrogen electrode. With further increase of the anode polarisation, the anion adsorption, and consequently the positive surface charge, rises until a certain value is reached (in the solution under consideration about $\phi = 0.7$), the further increase of the potential being accompanied by a decrease of the positive charge, which in not very acid solutions changes its sign once more and becomes negative. This anomalous dependence of the adsorption on the potential (as follows from a comparison

² Pauli and Valkó, *Elektrochemie der Kolloide*, p. 346, 1929.

³ N. Bach, *Koll. Z.*, 1933, **64**, 153; Pilojan, Krivorutschko and N. Bach, *ibid.*, 287. The results recently obtained by Bennister and King, *J. Chem. Soc.*, 1938, 991, are in contradiction with these conclusions, because according to these authors charcoal activated at 850° in oxygen has a negative electrokinetic potential, in spite of the fact that it adsorbs anions preferentially to cations. It is necessary, however, to bear in mind that, whereas for the charcoals referred to in the papers quoted from our laboratory, it was shown, by specially precise measurements, that the electric potential has identical values at different points of the charcoal surface (Frumkin, Lewina and Zarubina, *Z. physikal. Chem. A*, 1931, **155**, 41), the heating of the charcoal in oxygen produces a very inhomogeneous surface (Bruns, Maximowa and Pos, *Koll. Z.*, 1933, **63**, 290), which can hardly serve for the elucidation of the above relations.

⁴ Bruns, Burstein, Fedotow and Liwschitz, *Acta Physicochim.* 1938, **8**, 47, and especially non-published experiments of Burstein and Kuchinski.

⁵ Slygin, Frumkin and Medwedowsky, *Acta Physicochimica*, 1936, **4**, 911; Frumkin and Slygin, *ibid.*, 1936, **5**, 819; also Verwey and De Boer, *Rec. Trav. Chim. P.B.*, 1936, **55**, 675.

of the adsorption curves with the charging curves of platinised electrodes) is determined by the appearance at sufficiently high positive potentials of an oxide film and by the circumstance that the linkage between the metal and the adsorbed oxygen is of a dipole character, the oxygen being the negative end of the dipole. The appearance of such an orientated layer of dipoles must at a given potential lead, as it is easy to see, to a sharp decrease of the anion adsorption.

In alkaline solutions, the region of the cation adsorption on a surface covered with adsorbed hydrogen passes continuously into a region of cation adsorption on the oxidised surface, without the appearance of the intermediate interval, where anions are adsorbed, because at those potentials at which anion adsorption would take place, the surface in alkali solutions is already oxidised (see ⁵ for greater detail).

The particles of ordinary platinum sols when investigated by electrokinetic methods show a negative charge; as a consequence of the conditions under which they are obtained, the surface of these particles must be oxidised, as was usually assumed by colloid chemists,⁶ corresponding to the last portion of the above-described adsorption curve.

It follows from what has been said that there must exist, in addition to such a negative oxygen sol of platinum, a negative hydrogen sol corresponding to the first region of the adsorption curve, and a positive sol of platinum corresponding to its middle part. These considerations were put forward by the author in the discussion on colloid electrolytes in 1935,⁷ their correctness has been later confirmed experimentally. N. Bach and Balaschowa actually succeeded in obtaining negative "hydrogen" platinum sols,⁸ and, moreover, by careful oxidation of the latter, positive platinum sols also.⁹ The observation of sols does not, however, allow a quantitative determination of the position of the point of zero charge. It has recently been possible to fill up this gap using, with some refinements, the classical method of Billitzer, *i.e.*, by observation of the deflection of a platinised platinum wire in an electric field.¹⁰ Since conducting bodies can be used in electrokinetic measurements only if their surface is completely polarised under the experimental conditions, the choice of a platinised surface instead of a smooth one seems at first sight inadequate; in reality, however, working with a non-platinised surface in a large volume of liquid, one cannot, even with the most careful purification of the electrolyte, avoid poisoning the surface, which leads to a complete vitiation in the course of the curve. Fig. 1 shows the results of these experiments: the abscissæ give the potential of the wire with respect to a normal hydrogen electrode, the ordinates—the deflection under the action of the field in arbitrary units. The positive sign of the deflection corresponds to a positive charge of the surface. The concentration of the electrolytes was about 2×10^{-5} N. As is seen from curves I and II, referring to HCl and H_2SO_4 , the change of electrokinetic potential with the polarisation of the wire corresponds exactly to the adsorption data. In the case of anode polarisation the

⁶ Pennycuik, *J. Chem. Soc.*, 1927, 2600; *Koll. Z.*, 1929, **49**, 407; 1930, **54**, 21; *J. Am. Chem. Soc.*, 1930, **52**, 4621; Pauli and Baczewski, *Monatshefte f. Chemie*, 1936, **69**, 204; Pauli and Schild, *Koll. Z.*, 1936, **72**, 165.

⁷ Frumkin, *Trans. Faraday Soc.*, 1935, **31**, 69.

⁸ N. Bach and Balaschowa, *Acta Physicochimica*, 1935, **3**, 79; N. Bach and Rakow, *ibid.*, 1937, **7**, 85; Zimin and N. Bach, *ibid.*, 1939, **11**.

⁹ Balaschowa and N. Bach, *Acta Physicochimica*, 1937, **7**, 899; *Nature*, 1936, **137**, 617.

¹⁰ Balaschowa and Frumkin, *C. R. Acad. Sc. U.R.S.S.*, 1938, **20**, 449.

negative charge decreases, and at $\phi = 0.15 - 0.18$ becomes positive and after reaching at a certain potential a maximum value, begins to decrease, becoming again negative. In alkaline solution (curve IV) also in agreement with the adsorption data, there is no change of sign of the charge of the wire. A similar result is obtained in the case of an electrolyte, which had not been subjected to a special purification (curve III). A change of sign of the charge of the platinum surface was also observed by Kruyt and Oosterman¹¹ in their investigation of the flow potentials in platinum capillaries; this method is, however, connected, apparently, with much larger difficulties than that described here.

It follows from the above data that, under adequately chosen experimental conditions, the results of electrokinetic and of adsorption measurements on platinised platinum are in complete agreement; in particular, both methods yield the same position of the zero point. The origin of the total potential drop on the same electrode can be pictured on the

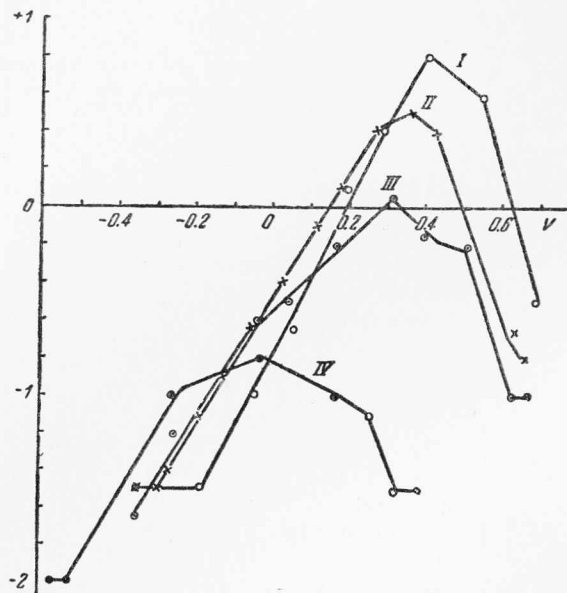


FIG. 1.—Deflection of a platinised platinum wire in an electric field (Balaschowa and Frumkin).

I—HCl, II—H₂SO₄,
III—H₂SO₄ (without special purification),
IV—NaOH.

basis of adsorption and polarisation measurements in a way described in detail in the above quoted papers,⁵ and also in the paper by Frumkin and Slygin.¹²

The behaviour of a silver electrode will be discussed in a forthcoming publication from this laboratory. Special interest attaches to the comparison of the zero point found by electrokinetic and by other methods in the case of mercury. The researches of a number of authors¹³ show that the direction of motion of a drop of mercury in an electric field is actually reversed at a potential which corresponds to the maximum of the electrocapillary curve, i.e. to the zero point of the charge. The observed motions of the mercury drop are produced, however, by surface streamings, connected with a variation of the interfacial tension as a

¹¹ Kruyt and Oosterman, *Koll. Beih.*, 1938, 48, 377.

¹² Frumkin and Slygin, *Acta Physicochimica*, 1936, 5, 819.

¹³ Frumkin, *J. phys. Chem. (russ.)*, 1917, 49, 207; Craxford, *Phil. Mag.* (7), 1933, 16, 268; Craxford, Gatty and McKay, *Phil. Mag.* (7), 1937, 23, 1079.

consequence of the polarisation of the drop, due to the passage of the current; they cannot, therefore, be considered as an electrokinetic phenomenon in the usual sense of this term.¹⁴ This is confirmed in particular by the circumstance that the above agreement is preserved in the presence of capillary active ions, which could not be the case with a true electrokinetic motion. The surface streamings due to a variation of the potential for small polarisations must, on the other hand, always disappear exactly at the maximum of the electrocapillary curve. As has recently been shown, these surface streamings are responsible for the appearance of maxima on current-voltage curves obtained with a dropping mercury electrode.¹⁵

We will not dwell on the quantitative comparison of the ζ -potentials, observed by electrokinetic methods in the case of metallic particles, with the values calculated from the total potential drop with the help of some theory of the double layer. A quantitative theory of electrokinetic phenomena is still beset with too many difficulties in the case of conducting particles; moreover, this question will probably be treated in other communications. It may be possible, however, to determine quantitatively the degree of diffuseness of the double layer on the surface of metals by other methods.

2. Electrochemical Methods of Investigating the Structure of the Double Layer.

Starting from the experimentally established fact that the over-voltage η in the discharge of the hydrogen ion on a mercury cathode for a given solution is expressed as a function of the current strength i by Tafel's relation

$$\eta = \frac{2RT}{F} \ln i + \text{constant},$$

and assuming that only those hydrogen ions are discharged, which come into direct contact with the surface of mercury, we easily arrive at the following relation,¹⁶

$$\eta - \psi_1 = \frac{2RT}{F} \ln i - \frac{2RT}{F} \ln [H^+] + \text{constant}. \quad (1)$$

Here ψ_1 denotes the average value of the potential at a distance of one ionic radius from the surface of the metal; in Stern's theory of the double layer¹⁷ this quantity is identified with the electrokinetic (ζ) potential. The correctness of this assumption depends on the idea that the layer of the solvent, which lies nearest to the surface of the metal, is completely held by the latter, while the other layers move with the same viscosity coefficient as inside the liquid. If this assumption is not exactly fulfilled, the error will decrease with increasing dilution of the solution, because at low concentration the variation of the potential with increase of the distance from the surface beyond the limits of the

¹⁴ Christiansen, *Ann. Physik*, (4), 1903, 12, 1072.

¹⁵ Bruns and Frumkin, *Acta physicochimica*, 1934, 1, 232; Bruns, Frumkin, Jofa, Vanjukova and Zolotarewskaja, *ibid.*, 1938, 9, 359; Jofa and Frumkin, *C. R. Acad. Sc. U.R.S.S.*, 1938, 20, 293; Seidel, *Z. angew. Ch.*, 1935, 48, 463; Antweiler, *Z. Elektrochem.*, 1938, 44, 719, 831, 888; Stackelberg, Antweiler and Kieselbach, *ibid.*, 663; Stackelberg, *ibid.*, 1939, 45, 466.

¹⁶ Frumkin, *Z. physikal. Ch. A*, 1933, 164, 121.

¹⁷ Stern, *Z. Elektrochem.*, 1924, 30, 508.

Helmholtz layer proceeds very slowly. With constant values of i and $[H^+]$, equation (1) reduces to

$$\eta = \psi_1 + \text{constant} \quad (1a)$$

This equation enables one to explain the influence on the value of the over-voltage of the specific adsorption of the cations and anions,¹⁸ this question lies, however, outside the scope of the present paper in which we limit ourselves to the simplest case, when such adsorption is not observed. From equation (1a) it is possible to interpret quantitatively the increase of the over-voltage by polyvalent cations, discovered by Herasymenko and Slendyk,¹⁹ as a result of the lowering of the negative value of ψ_1 due to a decrease of the diffuseness of the double layer.²⁰ When polyvalent cations are added to an acid solution the value of η , as can be seen from Fig. 2, increases at first and thereafter reaches a constant limiting value. If the allowable assumption is made that this limiting value of η corresponds to $\psi_1 = 0$, i.e., to a transition of the double layer into a non-diffuse state, then from measurements of the over-voltage one can determine the

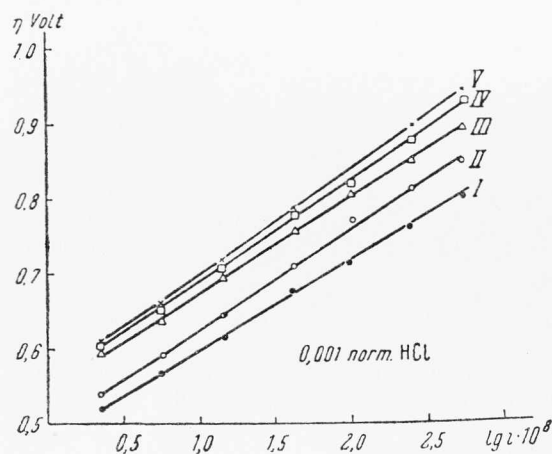


FIG. 2.—Curves for the dependence of over-voltage on the current density in 10^{-3} N. HCl + x LaCl₃ (Levina and Sarinsky).

(I) $x = 0$, (II) $x = 10^{-6}$ N., (III) $x = 10^{-5}$ N., (IV) $x = 10^{-4}$ N., (V) $x = 10^{-3}$ N.

quantity ψ_1 . The values of ψ_1 so found were compared with those calculated from Stern's theory, on the assumption that no specific adsorption took place and that the capacity of the Helmholtz layer was equal to $19 \mu\text{F}/\text{cm}^2$. The results of this calculation are shown in Fig. 3; the dependence of the potential on the concentration is seen to be in satisfactory agreement with Stern's theory, although the experimental values are always smaller in their absolute magnitude than the calculated ones; that is, the double layer has a less diffuse structure than required by Stern's theory.

Philpot²¹ compared the value of the surface charge as determined by dropping mercury with the value calculated from Stern's theory, assuming the capacity of the Helmholtz layer to be equal to about $23 \mu\text{F}/\text{cm}^2$ for a cationic layer and $55 \mu\text{F}/\text{cm}^2$ for an anionic one and found a fair agreement. The method could be used for solutions as dilute as

¹⁸ Jofa, Kabanow, Kuchinski and Chistyakov, *Acta Physicochimica*, 1939, 10, 317.

¹⁹ Herasymenko and Slendyk, *Z. physikal. Ch., A*, 1930, 149, 123.

²⁰ Levina and Sarinsky, *Acta Physicochimica*, 1937, 7, 485.

²¹ Philpot, *Phil. Mag.* (7), 1932, 13, 775.

0.001 N., and the experimental curves show in the case of dilute solutions a decrease of the capacity in the neighbourhood of the point of zero charge. However, it does not appear possible to determine quantitatively from these data the degree of diffuseness of the double layer with sufficient exactitude.

It seemed desirable to find some way of investigating the structure of the double layer by another independent method. This can be realised by measurements of the capacity of the double layer; but it is just in the case of dilute solutions, which present the greatest interest, that the measurements of the capacity are rendered difficult because of the large resistance of the solution. These difficulties have been overcome quite recently in work carried out at the Karpov Institute by Proskurnin and Worsina,²² who used an alternating current with one period per second and measured the oscillations of the potential directly with the help of a short-period galvanometer. The use of an alternating current with such a low frequency enables one, with an adequate disposition of the electrodes, to carry out capacity measurements at concentrations of the order of 10^{-3} N. and in acids even 10 N.²⁴ The results of these measurements,

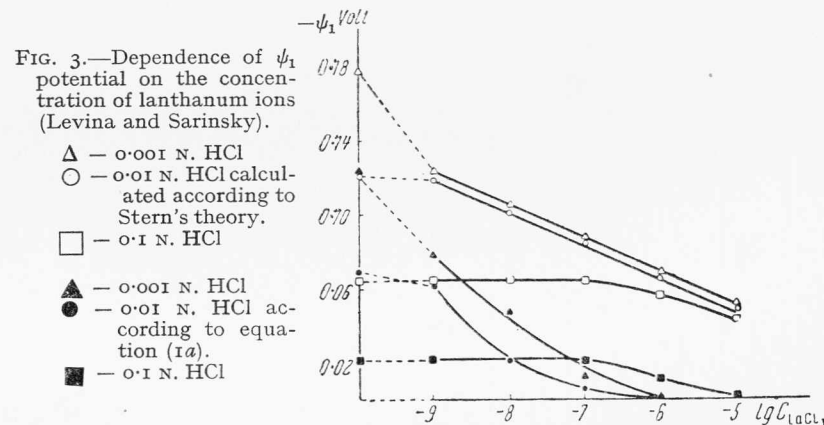


FIG. 3.—Dependence of ψ_1 potential on the concentration of lanthanum ions (Levina and Sarinsky).

Δ — 0.001 N. HCl
 $\circ$ — 0.01 N. HCl calculated according to Stern's theory.
 $\square$ — 0.1 N. HCl
 $\blacktriangle$ — 0.001 N. HCl
 $\bullet$ — 0.01 N. HCl according to equation (1a).
 $\blacksquare$ — 0.1 N. HCl

the precision of which amounts approximately to 5 %, are given in Fig. 4 taken from Worsina's paper. The ordinates give the capacity μF per cm^2 and the abscissa—the potential measured with respect to a normal calomel electrode. It must be kept in mind that the measurements with an alternating current yield directly the value of the differential capacity $d\epsilon/d\phi$, where ϵ is the charge of the mercury surface.

From the theory of Gouy and Stern it follows that the double layer is most diffuse near the point of zero charge. With increase of the absolute value of ϵ , the ions are drawn towards the surface and the double layer passes from a diffuse to a non-diffuse structure. Accordingly, the average thickness of the double layer must have a maximum, and its capacity a minimum, at the point of zero charge. As seen from Fig. 4 the experimental curves display such a minimum neither for 1 N. nor for 0.1 N. KCl. The variation of the capacity in the neighbourhood of the zero point which is connected with a variation of the degree of diffuseness at high concentrations is completely overshadowed by those changes which take place when ions of one sign in the external side of the double layer

²² Proskurnin and Worsina, *C. R. Acad. Sc. U.R.S.S.*, 1939; Worsina, *ibid.*

are replaced by ions of the other sign.* The curve of a 0.1 N. KCl consists of two nearly horizontal portions which correspond to a double layer formed by anions ($\partial\epsilon/\partial\phi \sim 36$) and by cations ($\partial\epsilon/\partial\phi \sim 19$) and of a linking branch with intermediate values of the capacity; with higher positive or negative values of the charge of the surface an increase of the capacity is observed which is due to a deformation of the ions. This curve gives no indication of a diffuse structure of the double layer; on the curve corresponding to a 0.01 N. solution, however, a weak minimum appears near the point of zero charge, while on the curves corresponding to 0.001 N. and 0.0001 N. solutions this minimum, observed at $\phi = -0.53$ (in excellent agreement with the determination of the position of the point of zero charge from electrocapillary data), becomes very marked. It seemed interesting to compare the results of these measurements with the values of $\partial\epsilon/\partial\phi$, calculated according to Stern's theory. If it be assumed

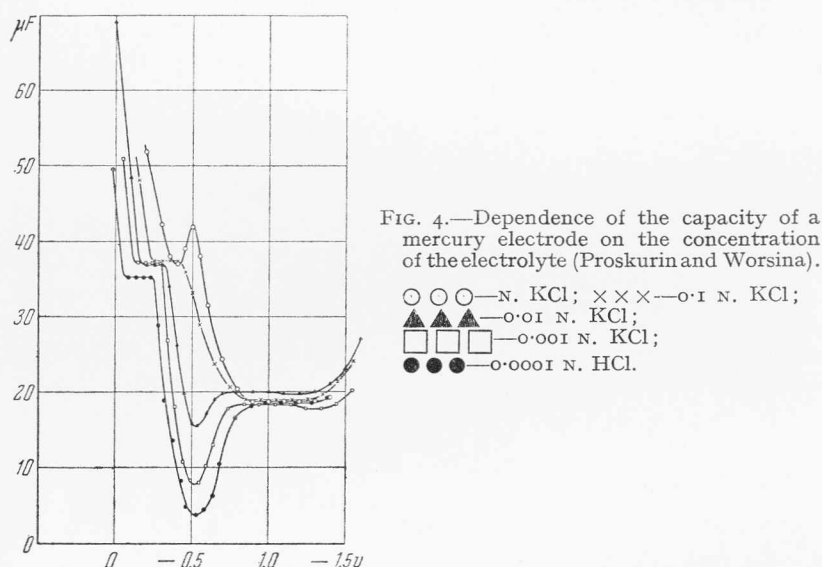


FIG. 4.—Dependence of the capacity of a mercury electrode on the concentration of the electrolyte (Proskurnin and Worsina).

○ ○ ○ — 0.1 N. KCl; × × × — 0.1 N. KCl;
 ▲ ▲ ▲ — 0.01 N. KCl;
 □ □ □ — 0.001 N. KCl;
 ● ● ● — 0.0001 N. HCl.

that the anions are not specifically adsorbed and if the influence of the filling up of the surface on the adsorption be neglected, then identifying the thickness of the Helmholtz layer with the diameter of the water molecule one can put the equations of Stern's theory in the following form:¹⁶

$$\epsilon = K(\phi - \psi_1) = 2cdF \sinh \frac{\psi_1 F}{RT} + 4c\lambda F \sinh \frac{\psi_1 F}{2RT} \quad (2)$$

where d is the diameter of the water molecule (3.1×10^{-8} cm.), λ the thickness of the ionic atmosphere for a uni-univalent electrolyte at a given concentration according to Gouy-Debye, K the capacity of the

* On the curve of 1 N. KCl a small maximum of the quantity $\partial\epsilon/\partial\phi$ is observed, which has already been described.²³ The appearance of this maximum points to a rapid intrusion of the anions into the surface layer near the point of zero charge with a decrease of the cathodic polarisation, connected perhaps with the existence of Van der Waals' forces between the adsorbed anions which decrease their electrostatic repulsion.

²³ Proskurnin and Borissowa, *Acta Physicochimica*, 1936, 4, 819.

non-diffuse layer, and c the concentration expressed in g. eq. per cm.³ The first term of the right hand part of equation (2) expresses, as is well known, the charge of the non-diffuse, and the second one that of the diffuse portion of the double layer. Equation (2) cannot, however, be used for the calculation of $\partial\epsilon/\partial\phi$ or for comparison of the value obtained with the experimental data within the whole accessible potential range, since it implies the constancy of the quantity K for all values of ϕ , whereas, in reality the values of K for a positively and negatively charged surface are certainly different. I have, therefore, attempted, as it has already been done by Philpot, to modify equation (2) by introducing two values for the capacity of the Helmholtz layer K_1 and K_2 , corresponding to a double layer formed by anions and by cations respectively. Under such conditions the quantity K in equation (2) must be treated as a variable, depending on the concentration of the anions and of the cations in the Helmholtz layer. Since these concentrations are proportional to $\exp. \frac{\psi_1 F}{RT}$ and to $\exp. \left(\frac{-\psi_1 F}{RT} \right)$ respectively, it is natural to define the quantity K by the equation

$$K = \frac{K_1 \exp. \frac{\psi_1 F}{RT} + K_2 \exp. \left(\frac{-\psi_1 F}{RT} \right)}{\exp. \frac{\psi_1 F}{RT} + \exp. \left(\frac{-\psi_1 F}{RT} \right)} \quad (3)$$

The physical meaning of equation (3) is that of a Helmholtz layer consisting of two parallel condensers charged to the same potential $\phi - \psi_1$. Philpot uses another method of linking both branches of the curve which apparently does not correspond to a definite physical picture. If this value of K is substituted in equation (2) then the following relations are readily obtained:

$$\phi = \psi_1 + \frac{2cdF}{K} \sinh \frac{\psi_1 F}{RT} + \frac{4c\lambda F}{K} \sinh \frac{\psi_1 F}{2RT} \quad (4)$$

$$\frac{\partial\epsilon}{\partial\phi} = KA \left\{ A + K - \frac{1}{2} (K_1 - K_2) \frac{(\phi - \psi_1) F}{RT} \cosh^{-2} \frac{\psi_1 F}{RT} \right\} \quad (5)$$

where
$$A = \frac{2cF^2}{RT} \left(d \cosh \frac{\psi_1 F}{RT} + \lambda \cosh \frac{\psi_1 F}{2RT} \right).$$

From the equations (4), (5) and (3) it is easy to plot a curve which gives the value of the capacity $\partial\epsilon/\partial\phi$ as a function of ϕ . In this way the curves of Fig. 5 were calculated for concentrations varying from 0.1 to 0.0001 N. with $K_1 = 38$ and $K_2 = 20 \mu F/cm.^2$ (the abscissae are reckoned from the point of zero charge). As seen from a comparison of Figs. 4 and 5 the general disposition and the shape of the curves calculated from Stern's theory is very similar to that of the experimental curves. The calculated values of the capacity lie, however, much lower than the observed ones; thus, the smallest observed value of the capacity for a 0.0001 N. solution is equal to 3.9, whereas calculation from equation (5) yields $\partial\epsilon/\partial\phi = 2.15$, and according to Gouy's theory of the diffuse layer $2.36 \mu F$ per cm.². This confirms the conclusion derived from overvoltage data, according to which the real double layer is less diffuse than would be expected theoretically. This discrepancy points to the existence of specific (*i.e.*, independent of the charge), attractive forces between the surface of the metal and the ions. This adsorption effect cannot, however, be identical

with that which is observed at higher concentrations. In fact an excessive capacity is observed on both sides of the point of zero charge, *i.e.*, the above interaction must be ascribed both to cations and anions, whereas, as is well known from electrocapillary data the inorganic cations display at higher concentrations a negative and not a positive adsorption.²⁴ We are thus forced to the assumption that we have to do here with an attraction which, at very small distances, is replaced by repulsion. It is possible that at large distances the image forces postulated by Gurney²⁵ come into play, but that, for some hitherto unknown reason, they are not observed when the ions are in a close vicinity to the surface of the mercury electrode. We thus see that the deviations from Stern's theory observed experimentally cannot be removed by the introduction of a specific adsorption potential for the ions in the form advanced by the author of this theory. We cannot therefore directly use Stern's theory for the calculation of ψ_1 -potentials in which we are particularly interested. These values can, however, be obtained from the experimental values of the capacity if one assumption of Stern's theory only

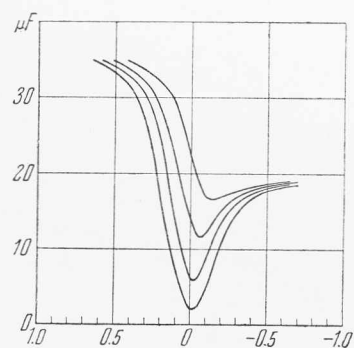


FIG. 5.—Dependence of the capacity on the concentration of the electrolyte according to Stern's theory. (0.1, 0.01, 0.001 and 0.0001 N. solutions.)

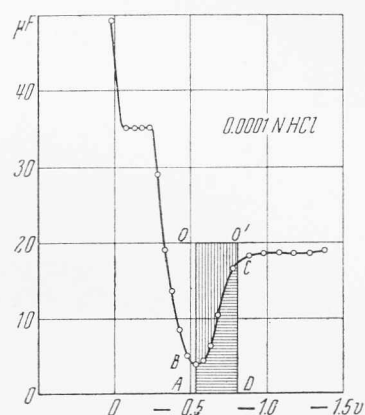


FIG. 6.—Calculation of the ψ_1 potential from the experimental data of the electrode capacity.

is preserved, namely, that the Helmholtz double layer has a constant capacity. This assumption which, as has been pointed out above, does not hold for the entire curve is certainly valid for a part of it, corresponding to not too large and not too small negative charges of the surface (Helmholtz layer with undeformed cations), because in this range the experimental values of $\partial\epsilon/\partial\phi$ at higher concentrations as seen from Fig. 4, actually show a satisfactory constancy. In dilute solutions it is thus possible to apply to this part of the curve the first equation of Stern's theory

$$\epsilon = K(\phi - \psi_1) \quad (6)$$

the derivation of which does not imply any assumptions beyond that of the constancy of the capacity in the Helmholtz layer. Inasmuch as the measurements of the capacity in dilute solutions enable one to find the value of the potential corresponding to $\epsilon = 0$ and the quantity $\partial\epsilon/\partial\phi$, we can thus find the value of ϵ for any ϕ ; it is determined by the area

ABCD (Fig. 6). If AO is equal to K , then the area BOO'C divided by K gives, according to equation (6), the quantity ψ_1 . This simple graphical calculation of the quantity ψ_1 implies the knowledge of the quantity K , which can be found from the experimental curve for $\partial\epsilon/\partial\phi$ as the limit to which this quantity tends with increase of ϕ . With that precision of the measurements which has been realised hitherto, the quantity K can be determined but approximately; the determination of the ψ_1 -potential by the method described becomes therefore inexact as soon as the observed values of $\partial\epsilon/\partial\phi$ do not vary much with the potential. In that part of the curve where the value of $\partial\epsilon/\partial\phi$ is still markedly lower as compared with its limiting value, a certain degree of arbitrariness in the choice of the value K hardly influences the result of the calculation of ψ_1 . Thus at 0.001 N. and $\phi = -0.73$ (0.2 from the point of zero charge on the cathode side) the above method of calculation yields $\psi_1 = -0.067$ with $K = 20$ and $\psi_1 = -0.06$ with $K = 19$. According to Stern's theory at this value of the potential with $K = 20$, we should have $\psi_1 = -0.11$. It seemed very interesting to compare these values of ψ_1 with those obtained from equation (1a) from overvoltage data. Unfortunately, the value $\phi = -0.73$ at $c = 0.001$ N. corresponds to a value of η equal to 0.28 only, whereas the measurements of Levina and Sarinsky²⁰ begin with $\eta = 0.52$, and our calculations of ψ_1 are no longer reliable for more negative values of ϕ . If the overvoltage curves obtained by Levina and Sarinsky are extrapolated to $\eta = 0.28$ then, by comparison of the overvoltages observed in pure HCl and in the presence of an excess of LaCl_3 , one gets $\psi_1 = -0.06$, in good agreement with the results of capacity measurements. We give in Table I a few more values obtained for ψ_1 from (6) for 0.0001 N. HCl, assuming $K = 20$, and the corresponding values calculated according to Stern's theory. The potentials are reckoned not with respect to the normal electrode but from the point of zero charge.

TABLE I.
(10^{-4} N. HCl. $K = 20$.)

	ψ_1 According to Equation (6).	ψ_1 According to Stern's Theory.
-0.1	-0.076	-0.085
-0.2	-0.123	-0.147
-0.3	-0.141	-0.177

The coincidence of the results of the determination of the value of ψ_1 according to the capacity curves and to the overvoltage, although not yet tested on a sufficiently large experimental material, forces us to consider these values of ψ_1 as sufficiently reliable. The values of the ζ -potential given in the literature and obtained from electrokinetic data, usually lie somewhat lower than the values ψ_1 calculated by us; this could be explained by the insufficient exactness of the assumptions underlying the theory of electrokinetic phenomena; the values obtained recently for glass by Rutgers, Verlende and Moorkens,²⁶ with due account for the surface conductivity are, however, very close to those given here.

Moskau, The Karpow Chemical Institute.

²⁶ Rutgers, Verlende and Moorkens, *Proc. Kon. Ak. Wet. Amsterdam*, 1938, 41, 763.

²⁴ Frumkin, *Sov. Phys.*, 1933, 4, 364.

²⁵ Gurney, *Proc. Roy. Soc., A*, 1931, 134, 144.

