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The Double Layer in Electrochemistry[1]

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In every group of phenomena there is some specific feature which leaves its mark on the science dealing with these phenomena. As it seems to me, a specific feature of this kind in the case of electrochemical processes is the existence of the electric double layer at the metal-solution interface. Perhaps I am not quite impartial in this statement, as I, if I may say so, stood at the cradle of the double layer theory, but still I think that there are many elements of truth in it.

There is nothing exceptional in the fact that when two phases come into contact there appears a double layer at the interface. The ions, as any other solute, tend to be distributed between the phases in accordance with the difference in their standard chemical potentials. But, as their large electric charges inhibit the separation of ions in considerable quantities, the distribution equilibrium is secured by attaining a certain difference of electric potentials with a simultaneous formation of a double layer at the interface, which necessitates the transfer of but small quantities of ions from one phase to the other, provided the area of the interface is not very great. The laws governing the value of this equilibrium potential difference were established long ago by Gibbs and Helmholtz; for the form of these laws which is familiar to chemists we are indebted to Nernst and Lewis. The importance of these relationships cannot be overemphasized; however, one must keep in mind that they tell us nothing about the mechanism of the establishment of the potential difference or about the structure of the double layer being formed.

[1] Palladium Medal Address delivered at the Chicago Meeting, May 3, 1960.

At the present time we get our knowledge about the structure of the double layer in the first place from a-c measurements of electrode capacities or by other similar methods. Earlier data which I had to consider when I began to study this problem (more than 40 years ago) were based on measurements of electrocapillary curves, i.e., of the relation between interfacial tension σ and potential difference ϕ. In order to determine from these data the electric properties of the interface, one must use the Lippmann-Helmholtz equation

$$\frac{\partial \sigma}{\partial \phi} = -\epsilon \qquad [1]$$

where ϵ is the charge density on the metal surface.

The application of Eq. [1] to experimental data showed in a number of cases a rather complex relationship between σ and ϕ. The majority of scientists of that time thought that the double layer should behave as a flat condenser, i.e., that ϵ should be proportional to ϕ. They explained the deviations observed by the inaccuracy of Eq. [1], although the latter is strictly deduced from the principles of thermodynamics. Even such an authority in the field of chemical thermodynamics as van Laar held this view. Only the French physicist Gouy found a better approach to the theory of electrocapillarity. But Gouy worked at a provincial university at Nancy which he left but seldom, and his works were little known to scientists interested in physicochemical problems. In any case, when I presented a paper with the experimental confirmation of the correctness of Eq. [1] and some critical remarks on the

theory of van Laar to the "Zeitschrift für physikalische Chemie," it was at first rejected by the Editor.

In this paper the electric charges were determined from the current strength necessary for charging a growing mercury drop, just in the same way as it is often done at the present time, and $\partial\sigma/\partial\phi$ was calculated from electrocapillary curves (1). There still remained a contradiction which could not be removed for a long period of time: the double layer capacities as directly measured by Krüger, Bowden and Rideal, Erdey-Gruz and Kromrey always proved to be much smaller than the capacities calculated from electrocapillary data using Eq. [1] or found from experimental values of ϵ. This discrepancy seemed to be so firmly established that even attempts to give it a theoretical explanation were made. Thus a hypothesis was suggested according to which the capacity measured by means of an alternating current must be exactly equal to one-half the capacity obtained from electrocapillary data (2). However Proskurnin and Frumkin showed in 1935 (3) that the discrepancies observed were caused by a different and much more trivial circumstance, viz., the presence of organic impurities which penetrate the capillary of the capillary electrometer slowly, but easily reach the unprotected surface of a mercury electrode used in capacity measurements. It was found that when such impurities are carefully eliminated both methods of capacity determination give identical results. Overcoming the difficulties connected with capacity measurements in dilute solutions enabled us to find a capacity minimum at the point of zero charge, which was a strong confirmation of the theory of the diffuse double layer (4).

Somewhat later Grahame adapted the a-c method to capacity measurements on a growing mercury drop (5), which permitted the requirements to be lowered in respect to solution purity and to increase the precision of the method.

The demonstration of the correctness of the Lippmann-Helmholtz equation and the development of methods of direct capacity measurements formed a sound basis for the investigation of the structure of the double layer and for the verification of the theory of the double layer on the metal-solution interface. I shall not dwell here on the well-known history of the development of this theory which is associated with the names of Helmholtz, Gouy, and Stern. Considerable advances were made in the post-war period by David Grahame, whose untimely death was a great blow to all his friends and colleagues. By introducing the concept of a difference in the distances of closest approach of anions and cations to the metal surface, Grahame succeeded in giving a satisfactory picture of the relationship between the double layer structure and the concentration of the electrolyte for the case when ions are attracted by coulombic forces only, i.e., when the phenomenon commonly called specific adsorption is absent (6).

Such an agreement between theory and experiment is somewhat surprising, as the fact that the solution side of the double layer is composed of individual ions was not taken into consideration in the development of the theory, or in other words, the ionic charges were, so to say, smeared parallel to the metal-solution interface. Indeed, the theory developed on this basis cannot account for the experimentally observed dependence of the double layer structure on the concentration in the presence of a marked specific adsorption of anions. On my suggestion Esin and his collaborators (7) and later Ershler (8) attempted to work out a theory of a discrete double layer and to remove these discrepancies. Ershler's concepts recently were developed further by Grahame (9); several papers by Parsons (10) also are concerned with this problem. However, despite the efforts exerted, in my opinion we are not yet in possession of a fairly satisfactory quantitative theory of the double layer in which this discrete structure would be taken into account. Some success in this direction was achieved recently by Levich and Kiryanov (11).

Grahame supposed, following Gouy in this, that inorganic cations, unlike anions, do not display any specific adsorbability on the metal-solution interface; in the case of cations such an adsorbability was ascribed only to large organic cations. The investigations carried out in the past years at the Moscow University showed, however, that this assumption is not quite justified (12). Thus, the adsorbability of the Tl^+ ion on the mercury surface, as seen from Fig. 1, in which the electrocapillary curves for solutions of H_2SO_4 with additions of Tl_2SO_4 are shown, can be compared with that of the Br^- ion. A certain adsorbability also is displayed by the lead ions and a very small, although a clearly detectable one, even by the ions of the alkali metal Cs^+ (13). These phenomena are much more pronounced in the case of cation adsorption on the surface of the solid metal platinum (14). Proving the existence of a specific cation adsorption is, in my opinion, important in connection with the role that the adsorbed atoms (or adions) are supposed to play in the electrodeposition of metals (15-17).

The presence of a double layer at the mercury-solution interface affects a number of its properties, for instance interfacial tension, adhesion between metal and solution, and others. I shall discuss here only one of these properties, viz., mobility in an

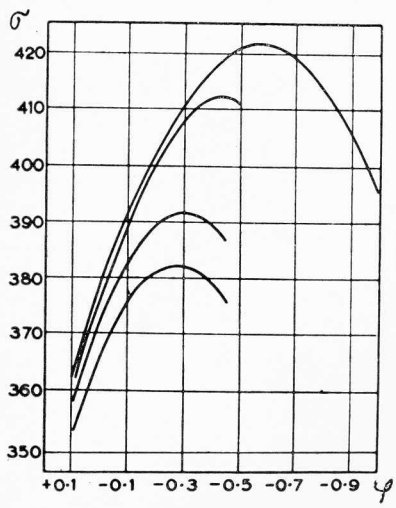

Fig. 1. Electrocapillary curves in N KNO_3 + 0.01N HNO_3 + x N $TlNO_3$ solutions. Curves from top to bottom: x = 0; 0.01; 0.1 and 0.2 (NCE).

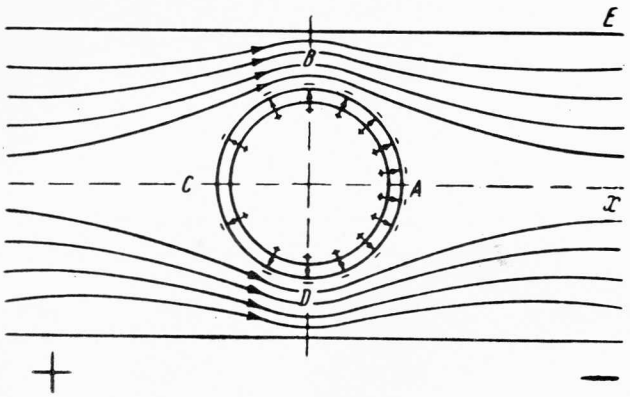

Fig. 2. Schematic picture of the double layer of an ideal polarized positively charged metal drop placed in an external electric field. The arrows show the direction of the lines of force of the field.

electric field. When an electric field is applied, the mercury drop in the electrolyte solution comes into motion. The mechanism of this motion, first observed by Christiansen (18), essentially differs from that of the well-known electrokinetic motion. Its velocity, in the case of identical field tension and solution viscosity for drops having a radius a of the order of 1 mm, may exceed that of electrokinetic motion by five orders of magnitude. The mechanism of these movements is best illustrated by the simple example of an ideal polarized positively charged drop with a Helmholtz double layer. In this case, the distribution of the lines of force of the external electric field in the vicinity of the drop (Fig. 2) is similar to their distribution in the vicinity of an insulator, in other words they are tangential to the drop. Under these conditions the electric field acts on the outer sheet of the double layer, but not on the inner one, as the field tension within the metal is equal to zero due to its high electric conductivity. Thus, the effect of the field on the outer sheet of the double layer is not compensated for (to be more precise, it is compensated by the forces applied at a considerable distance from points B and D to the poles of the drop A and C). Under the influence of these forces the mercury in the drop comes into a vortical motion, as is shown in Fig. 3, and the reactive repulsion from the surrounding medium causes the drop to move along the field lines. The mathematical theory of this motion developed by Levich and myself (19) gives the following expression for the drop velocity v, the field tension at a sufficient distance from the drop being equal to E

$$v = \frac{a \epsilon E}{2\mu + 3\mu^1 + \epsilon^2/\kappa} \qquad [2]$$

where μ and κ denote the viscosity and the electric conductivity of the solution and μ^1 the viscosity of mercury.

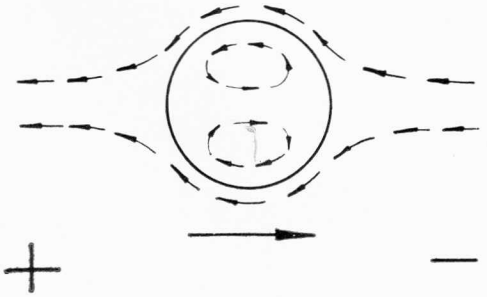

Fig. 3. Motion of a positively charged mercury drop in an electrolyte solution under the action of the electric field. The small arrows show the direction of the motion of the solution and mercury at any point, the big arrow, the direction of the motion of the drop as a whole.

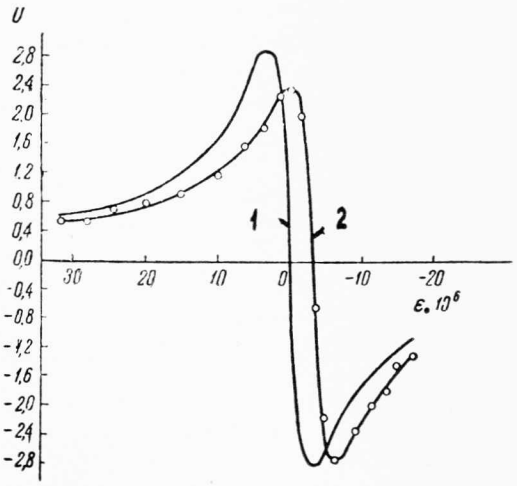

Fig. 4. Relationship between the mobility of mercury drops in a 0.02N KBr solution in glycerol and the charge density ϵ; $\kappa = 1.9 \times 10^{-5}$; $\mu = 2.8$. 1, Computed from Eq. [2]; 2, experimental data. μ in cm/sec v; ϵ in coulomb/cm^2.

Equation [2] was verified on mercury drops falling in a viscous glycerol solution and deflected by a horizontal electric field; definite electric charges were imparted to the drops before they broke off from the capillary (20). As seen from Fig. 4, the theoretical calculations are confirmed by experiments; the slight shift of the experimental curve is caused by the presence of oxygen traces which gradually made ϵ somewhat more positive (it is very difficult to remove oxygen completely from the viscous solution). For small values of ϵ, Eq. [2] gives mobility values of the same order as those which would be found in the case of a sphere having a free charge with the density ϵ. At first sight, this seems surprising, as the charge of the metal side of the double layer is completely compensated by the charges with an opposite sign which are located in the ionic sheet of the double layer. However, as I have already mentioned, a compensation of charges does not lead to a compensation of forces. With increase of ϵ, v increases, reaching a maximum at

$$\epsilon = \kappa^{1/2}(2\mu + 3\mu^1)^{1/2} \qquad [3]$$

and then decreases. This can be accounted for by the fact that the transfer of charges by the moving mercury surface results in an electric field directed opposite to the impressed field and diminishing its effect (this has not been taken into account in plotting Fig. 4, which therefore holds true only for small values of ϵ). A similar inhibiting effect is also observed in the case of a drop moving under the action of forces of a different nature, e.g., gravity, which results in a somewhat unexpected relationship between the velocity of the falling drop and its

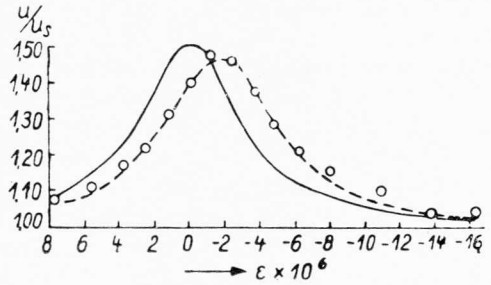

Fig. 5. Ratio of the rate of fall of a mercury drop in a glycerol solution saturated with Na_2SO_4 to that calculated by Stokes formula as a function of the charge density ϵ; $\kappa = 8.1 \times 10^{-6}$, $\mu = 7.2$. Solid curve, calculated values; circles, experimental data.

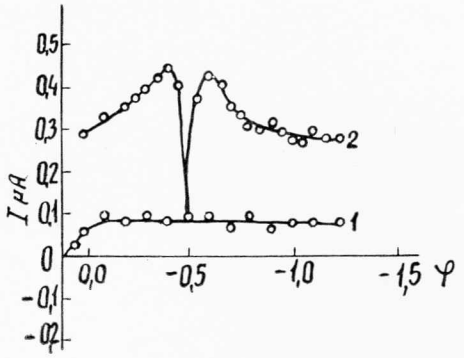

Fig. 6. C.v. curves in 0.28×10^{-4} N $Hg_2(ClO_4)_2$ + 0.002N $KClO_4$ corrected for charging current (NCE). 1, In the absence of an external field, 2, with the external field applied, E = 0.47 v/cm.

charge (21). A more detailed analysis permits us to conclude that in a viscous medium an uncharged drop must fall one and a half times faster than a charged one. The relationship between the velocity of the fall and the charge observed experimentally is compared in Fig. 5 with the theoretical dependence; the velocities of the fall are referred to that of a strongly charged drop, which is in accordance with Stokes law. The slight shift of the experimental curve with respect to the theoretical one can be accounted for quantitatively, if the depolarizing effect of the oxygen traces is taken into consideration.

The electrocapillary motion of droplets with metallic conductivity may arise in any electrolyte. A method was proposed recently to make use of this motion in extracting sulfide inclusions from molten slags (22).

Electrocapillary movements underlie the so-called polarographic maxima. The tangential movement of the drop surface calls forth an extra supply of the depolarizer which, according to Levich (23), is proportional to the square root of the tangential velocity. This fact makes it possible for currents in excess of the normal limiting diffusion current, which can be computed with the help of Ilkovic's equation, to pass through the cell. However, under the usual working conditions of a dropping electrode, the electric field causing the movement of the drop surface depends on complex geometrical conditions at the capillary tip; it is also influenced by the effect of convective diffusion of the depolarizer on the concentration polarization. Moreover the polarization curves are distorted by ohmic potential drops in the solution. Therefore the development of a quantitative theory of polarographic maxima presents great difficulties, which account for the chaotic state of this problem in modern polarographic literature. I shall not dwell here on the attempt made in this direction by myself and Levich, although, as it seems to me, we succeeded in explaining the basic features of the phenomena observed (24). I prefer to confine myself to the consideration of a case, when the polarographic maxima of the first kind may, so to say, be observed in an idealized form. To achieve this in the place of the mechanism of self-generation of motion, which is operative in the case of polarographic maxima of the first kind, we must provide a possibility to generate motion by means of an electric field which would be independent of the current on the drop. For this purpose a dropping mercury electrode was placed in an electrolyte solution and an electric field was applied to the latter by means of two subsidiary electrodes, the ratio of the supporting electrolyte and of the depolarizer concentrations being chosen in such a way that no polarographic maximum of the first kind should occur under normal conditions (25). The results obtained with $0.28N$ $Hg_2(ClO_4)_2 + 0.002N$ $KClO_4$ are given in Fig. 6. Current-voltage curve 1 was obtained without the application of an external electric field, curve 2 with the application of a field having a gradient of 0.47 v/cm. This curve, which is of an unusual shape, is in close agreement with Eq. [2]. Its left-hand branch, corresponding to positive values of ϵ, greatly resembles the positive polarographic maxima of the first kind, as they are observed when the concentration of the supporting electrolyte is not too low. Polarograms obtained under normal conditions, however, show no second maximum at negative values of ϵ. I cannot discuss here the causes of this discrepancy, which, however, may be explained on the basis of the theory mentioned above (24).

The theoretical interpretation of the so-called maxima of the second kind, which depend on the flow of mercury out of the capillary, is much simpler than the interpretation of the maxima of the first kind. In this case, it is of fundamental importance to take into consideration the same inhibition of the surface motion by the double layer charges, which results in the decrease of the velocity of a falling charged drop. The maxima of the second kind play an important role in the theory of the rotating mercury drop electrode of Kolthoff and Okinaka (26).

Of special interest is the question about the relationship between the double layer structure and the nature of the metal. The latter may have an effect on the capacity of the Helmholtz layer as well as on the potential of zero charge. At the present time we are in possession of sufficient experimental data only on the second point. Let us consider first liquid metals. The information which we can obtain on this subject from measurements in

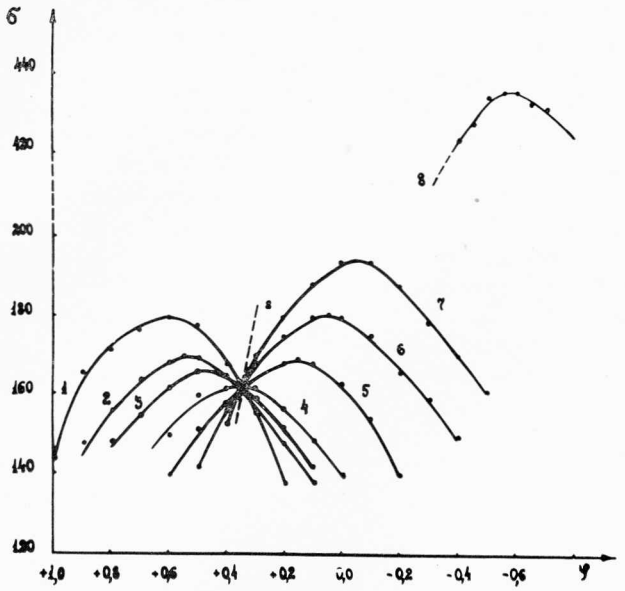

Fig. 7. Electrocapillary curves of Te-Tl alloys in LiCl + KCl. 1, Te; 2, 3.83 at. % Tl; 3, 10.9%; 4, 22.1%; 5, 42.3%; 6, 53.7%; 7, 65.2%; 8, Tl. Reference electrode Pb, LiCl + KCl, 0.1% $PbCl_2$.

aqueous solutions is naturally limited; we get more data with molten electrolytes. Electrocapillary phenomena in melts have been particularly investigated at the Sverdlovsk University (27). Electrocapillary curves for the Te-Tl system, plotted from measurements made by Kusnezov, *et al.*, are shown in Fig. 7. This system is characterized by an exceptionally great difference in the positions of the electrocapillary maxima, i.e., of the points of zero charge, which is as large as 1.25 v. The double layers at the metal-electrolyte interface at the point of zero charge being eliminated, the value given is similar in many respects to the Volta potential between the respective metals measured in vacuum (28). If the orientation of molecules of the solvent and the specific adsorption of ions are not taken into consideration, this value can be regarded as a kind of Volta potential in a material medium. I have already dealt with this problem in a paper which I presented at the 7th Annual Symposium on Colloid Chemistry at Baltimore about 30 years ago. At the present time a similar point of view is held by many electrochemists, e.g., Temkin (29), Rüetschi and Delahay (30). In my opinion, the determination of zero charge potentials gives the most direct answer to the question about the relationship between the difference of potentials between the poles of a galvanic cell with electrodes from different metals and the corresponding Volta potential, which has greatly attracted the attention of electrochemists since the beginning of the 19th century.

However, the similarity between the differences of zero charge potentials and Volta potentials does not necessarily result in a complete coincidence of these values, as the zero charge potentials may be influenced in a varying degree on the two electrodes by the preferential adsorption of one of the ions of the melt or by the orientation of the molecules of the solvent; the presence of a material medium may also have some effect on the distribution of the electronic cloud in the surface layer of the metal.

As a result of these complications the potential difference between water and mercury at the zero charge point of mercury is not equal to the sum of the galvani-potentials at the water-gas and vacuum-mercury interfaces, but exceeds it by an amount which was found by me to be equal to 0.30 v (31). Using more recent values of the Volta-potential between mercury and aqueous solutions (32), and of the zero charge potential of mercury (6) we get the value 0.26 v for this quantity. The assumption that the difference between the potentials of zero charge of two metals coincides with the Volta-potential between them is equivalent to the assumption that there exists a relationship between the zero charge potential and the electronic work function w, which can be expressed by the equation (33)

$$\phi_N - w = \text{constant} \qquad [4]$$

In accordance with the foregoing this relationship can only be approximate; it is not likely that one can make it more exact by introducing a certain coefficient before w, as has sometimes been suggested (34). The problem of the relationship between ϕ_N and w was recently discussed also in American literature (30, 35, 36). In the author's opinion, in order to verify these relationships at the present time, first it is necessary to be in possession of more exact experimental data both on the electronic work function and especially on the zero charge potentials.

The problem of investigating the double layer structure becomes more complicated when dealing with solid metals, although in the place of interfacial tension measurements, which cannot be carried out in this case, there appears an opportunity to study the effect of the double layer on such properties of metals as hardness (37-39), friction (40, 41), electrokinetic potential (42), stability of suspensions or sols. Unfortunately, the interpretation of results obtained from such measurements is not always as unambiguous as it is in the case of electrocapillary measurements. Very much was expected from capacity measurements on solid electrodes, in particular from the determination of zero charge potentials by means of the location of the capacity minimum in dilute solutions of electrolytes (43). However, the investigations carried out hitherto have only partly justified these expectations, as it is not always possible to obtain with solid metals capacity-potential (C,ϕ) curves comparable with those for mercury. Such a curve for the surface of a Zn monocrystal in 0.1N KCl (44), together with curves for Hg and liquid Ga (45) in the same electrolyte, is shown in Fig. 8. The capacity of the Zn monocrystalline surface within the frequency range of 1-10 kilocycles changes but little with frequency (by 5-8%) in contrast to what is observed in the case of polycrystalline zinc. This makes us suppose that the dispersion of the capacity, which interferes with capacity measurements on solid metals, is at least partially accounted for by the unevenness of the surface and the presence of micro-

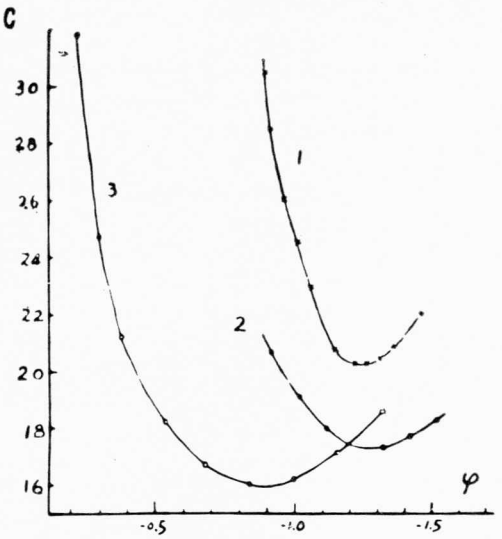

Fig. 8. Relationship between the differential capacity C and the potential ϕ in 0.1N KCl (NHE). 1, Zn monocrystal; 2, liquid Ga (according to Grahame); 3, Hg.

scopic cracks, although other explanations have been given to this phenomenon as well (46).

A curious inference can be made from determinations of zero charge potentials by means of the capacity minimum in dilute solutions (as well as from the hardness maximum) in the case of Pb and PbO_2 electrodes (47). The zero charge potential ϕ_N of PbO_2 is located at 1.8 v vs. NHE, the zero charge potential of Pb at —0.7; the difference between these two values is 2.5 v, which is even greater than the difference of potential between the poles of a lead storage cell.

With the help of capacity measurements Leikis has studied in detail the behavior of a silver electrode. As shown in Fig. 9, a pronounced minimum is observed in a dilute solution of Na_2SO_4 on the C,ϕ curve of silver; the silver wire had been subjected to cleaning with moist glass powder and boiling in an alkaline solution. This minimum disappears with an increase in solution concentration. The zero charge potential found in this way is equal to —0.7 v vs. NHE which coincides approximately with the results of electrocapillary measurments on molten silver

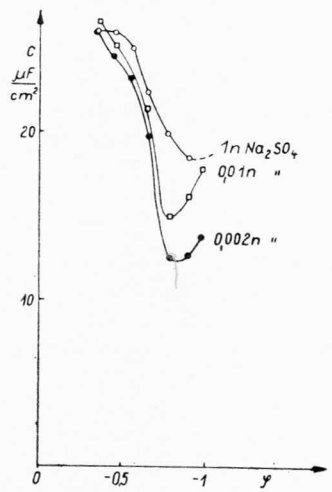

Fig. 9. Differential capacity of an Ag electrode in Na_2SO_4 solutions (NHE).

($\phi_N = -0.6$), but not with other data in the literature. The investigation of the effect of the solution concentration and of the presence of surface active anions and organic substances confirms the correctness of this ϕ_N value.

Leikis's experiments produced a noteworthy result. In electrochemical measurements wide use is made of a technique for cleaning electrode surfaces by means of vigorous cathodic polarization. But if a silver electrode is subjected to cathodic polarization in N Na_2SO_4 up to $\phi = -1.25$ v vs. NHE, the conditions of the surface, as it can be inferred from capacity measurements, change markedly, and at $\phi = -1.35$ v this change becomes irreversible. C,ϕ curves obtained with such an electrode differ widely from normal curves.

There exists still another reason why care must be exercised in interpreting the results of the measurements of C,ϕ curves when solid electrodes are used. In the presence of adsorbed hydrogen or oxygen on the electrode surface along with the double layer capacity a pseudocapacity is measured, the value of which depends on the exchange current between the adsorbed layer and the solution (48). In these cases the minima observed on C,ϕ curves may represent pseudocapacity minima and therefore tell us nothing about the zero charge potential. Apparently, such is the case with active platinum electrodes (49), and this accounts for the relationship observed between the location of the minimum on C,ϕ curves of Pt and the pH of the solution (50). While making measurements in dilute solutions at high frequencies Kabanov and Birinzeva could find no capacity minimum on platinum which could be interpreted as corresponding to the most diffuse state of the double layer at the point of zero charge (51). This is possibly due to a marked heterogeneity of the surface of an activated platinum electrode.

It is evident that in the case of an extremely heterogeneous surface the measurable potential of zero charge represents a certain mean value at which occurs the transition from a preferential anion adsorption to a preferential cation adsorption. Such a potential of zero charge does not necessarily correspond to the most diffuse structure of the double layer.

In the case of solid electrodes with a large surface, the formation of the double layer causes marked changes in the composition of the solution, which are known to produce errors in pH measurements with the help of platinized platinum electrodes if the system is insufficiently buffered. The determination of these changes in the composition can serve as a method for the investigation of the double layer structure. This method was applied successfully to such substances as platinum and activated carbon. Two results obtained recently may be mentioned in this connection. As the zero charge potential for platinum is more positive than the normal hydrogen potential, this metal is negatively charged when placed in a hydrogen atmosphere in acid solutions. The formation of the double layer, for instance in an acidified N Na_2SO_4 solution, is accompanied therefore by a transfer of hydrogen ions to the solution and by an increase in solution acidity, which can be

measured if platinized electrodes are used. However, in the presence of surface active halogen anions, the mechanism of the establishment of the equilibrium potential difference is changed; with the increase of the anion adsorbability the double layer formed by negative charges on the metal surface and cations attracted by them is replaced by a double layer with a negative sheet formed by adsorbed anions. In the case of a N NaI-solution acidified up to $p\mathrm{H} \sim 3$, as has been found by Balashova and Kasarinov (52), the potential difference due to the adsorption of anions becomes so great that at the equilibrium hydrogen potential the sign of the charge of the platinum is reversed. Under these conditions the formation of the double layer is accompanied by a decrease in the solution acidity, and not by an increase in the latter.

A hydrogen electrode with a still better developed surface can be made by depositing some platinum on the surface of activated carbon. Such platinized carbon in a hydrogen atmosphere adsorbs from neutral solutions of salts considerable amounts of cations, which are replaced by hydrogen ions. The magnitude of the adsorption effect depends on the final pH of the solution just as would be expected from the theory outlined, if one assumes that ϕ_N for "hydrogen" carbon is equal to 0.03 v (53).

The idea according to which the electrolyte adsorption on activated carbon is a process connected with the establishment of the equilibrium potential difference was met with opposition. A number of scientists preferred to interpret these phenomena on the same lines, as is done in the case of adsorption on ion exchange resins, i.e., without taking into account the electronic conductivity of carbon. However, the "electrochemical" theory of electrolyte adsorption on carbon received recently a conclusive corroboration in the investigations carried out by Strazhesko at the Ukrainian Academy of Sciences in Kiev (54). Strazhesko found that the acidification caused by cation adsorption from solution increases markedly (2-3 times), when solutions in nonaqueous solvents, e.g., acetone, are used instead of aqueous ones. Such a phenomenon, quite inexplicable on the basis of the "chemical" theory of electrolyte adsorption on carbon, can be interpreted, if one assumes that the zero charge potential of carbon, as well as that of mercury, is shifted toward more positive values when molecules of acetone are substituted for those of water. In this case at the reversible hydrogen potential the carbon surface must really carry a more negative charge in a nonaqueous solvent.

An original method for the determination of the zero charge point of platinum was proposed recently (42, 55). The presence of the diffuse double layer causes two metallic surfaces in an electrolyte solution to repel and prevents them from drawing together. Voropaeva, Derjaguin, and Kabanov measured the force necessary for establishing at different potentials a conducting contact between two crossed platinum wires immersed in a dilute KCl solution. As seen in Fig. 10, there is a pronounced minimum on the curve showing the relationship

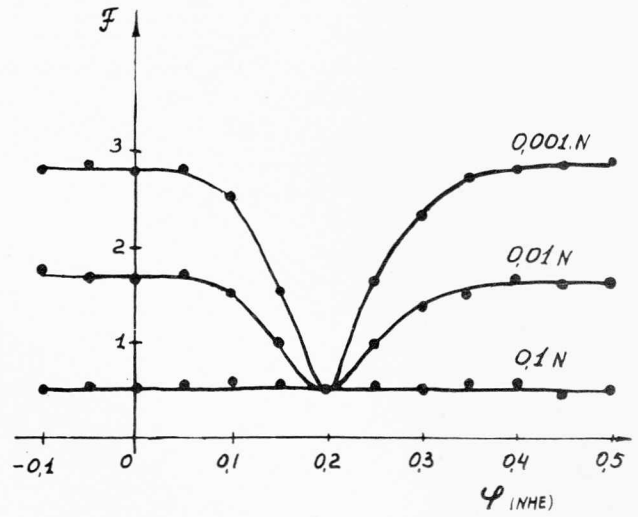

Fig. 10. Relationship between the potential and the force F, which must be applied in order to establish a contact between two platinum wires in KCl solutions.

between the force and the potential, at the zero charge potential. The value of ϕ_N found in this way is in good agreement with the results of adsorption measurements. It is not quite clear why in this case we do not meet with the difficulties, which were encountered during the attempts to determine the location of the zero charge potential of platinum from the capacity minimum in dilute solutions.

When dealing with the problem of points of zero charge, the supposed existence of an essential difference between the case of a reversible electrode and that of an ideal polarized one has been sometimes mentioned in the literature (30, 56). It seems to me however that there are no theoretical grounds for such a differentiation (39). Although the mechanism of the formation of the double layer in these two cases is, generally speaking, different, its structure and, consequently, the physical meaning of the zero charge potential must be similar. In accordance with this it was possible to show that the change in the double layer capacity with electrolyte concentration at the zero charge potential of thallium amalgams in dilute solutions of electrolytes proceeds in conformity with the same laws as those for mercury, although the equilibrium concentration of Tl^+ ions in the solution at the zero charge potential reaches in this case a measurable value (57).

The concept about the existence of the electric double layer was not made use of in the first investigations of the kinetics of electrochemical processes. This could not have been expected, since at the time the net velocity of electrochemical processes was associated with purely chemical or diffusion steps. Only after the idea of the finite velocity of electrochemical steps proper and of their dependence on the interfacial potential difference had been introduced in the theory of electrode processes (Audubert, Butler, Erdey-Gruz, and Volmer), did it become possible to combine the double layer theory and the principles of electrochemical kinetics. The first attempt in this direction was seemingly made by the author (58); it was supposed

that the reacting particles follow the Boltzmann distribution law and that only a part of the potential difference is effective in determining the rate of the process. The original conclusions referred to the case of the hydrogen ion discharge. If we generalize the expression obtained for the case when an electron is transferred to a particle carrying n charges, where n can be either positive or negative, the result assumes the following form (59)

$$i = \mathrm{K} \exp\left[-\alpha(\phi-\phi_1) - n\phi_1\right] F/RT \qquad [5]$$

where i is the current density, c the bulk concentration of the reacting particle, if necessary corrected for concentration polarization, and α a constant satisfying the condition $0<\alpha<1$. The problem of the physical interpretation of the value α is yet open to discussion and in practical use of the equations of electrochemical kinetics α must be considered as an empirical constant. An accurate determination of the meaning of ϕ_1 is of great importance. The value ϕ_1 was regarded primarily as the potential in the center of the charge of the reacting particle at its equilibrium location in the Helmholtz layer, although the possibility to refer it to the location of the charge center in the transition state of the reaction should be considered too.[2] As was shown by the experiments of Bagozky (62) and others, Eq. [5] expresses exactly the relationship between the H_3O^+ ion discharge rate in KCl + HCl solutions and the concentrations of the components, if the value ϕ_1 is considered as the potential in the plane of the closest approach of cations to the electrode surface and this potential is computed on the basis of the classical theory of the diffuse double layer. Thus, neglecting the details of the double layer structure involves no great errors in the case when the reacting particle is an H_3O^+ cation, repelled by K^+ or H_3O^+ cations which form the ionic sheet of the double layer. However, much greater difficulties were encountered, when a different group of reactions was considered, i.e., the electroreduction processes of multivalent anions, during which the reacting particles are attracted by the ions present in the ionic sheet of the double layer. These reactions, which have been studied in detail in Moscow since 1949, are characterized by an anomalous form of c.v. curves (59, 63). Namely, the usual increase in the current, which occurs when the cathodic polarization is increased, is followed by a sharp falling off, taking place at potentials in the vicinity of the zero charge potential or more negative than the latter. When the potentials become still more negative, the current rises again. In many but not in all cases (64) these anomalies disappear with an increase in the concentration of the supporting electrolyte. As an example of these anomalous c.v. curves, a curve for the reduction of the $S_2O_8^{2-}$ ion on an amalgamated rotating disk electrode in the presence of $0.01N$ Na_2SO_4 is shown in Fig. 11.

The pecularities of the electroreduction of multivalent anions are explained by the repulsion between the reacting particle and the negatively

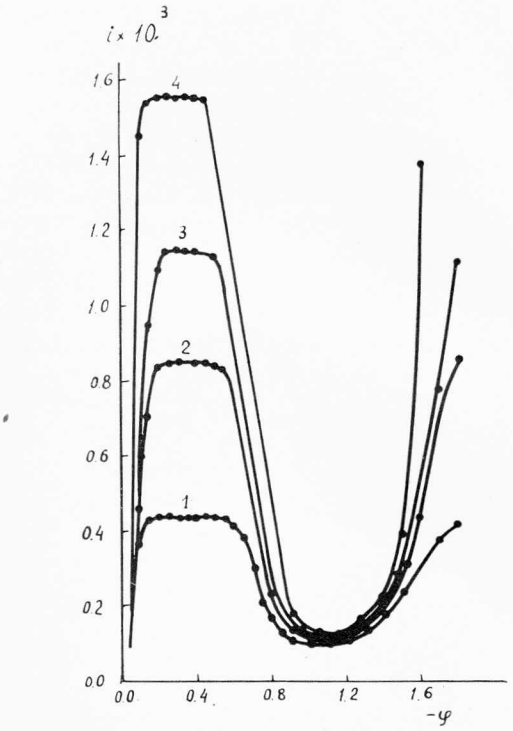

Fig. 11. C.v. curves for the reduction of 10^{-3} N $K_2S_2O_8$ in the presence of 10^{-2} N Na_2SO_4 on a rotating amalgamated disk electrode. Rates of rotation: 1, 650; 2, 2800; 3,5000; 4, 9000 rpm.

charged electrode surface. In Eq. [5] this effect is accounted for by the term containing ϕ_1; in fact, it is easy to show, that at $n = -2$ or $n = -3$ and with a reasonable value assumed for α, Eq. [4] represents a c.v. curve with a minimum in the region of potentials corresponding to negative surface charges. Although in some cases the experimental c.v. curves, corrected for concentration polarization, can be expressed even quantitatively by means of Eq. [5], a more detailed study of this problem shows that the concepts used as a basis in the derivation of this equation in this case are insufficient. As it is beyond the scope of this paper to discuss all the aspects of the problem, which, moreover, have been dealt with lately in a number of reviews (65), I intend to mention only the following point. Equation [5] is derived on the assumption that within the double layer the reacting particles follow the Boltzmann distribution law. As Levich's calculations have shown (66), this distribution cannot be realized at sufficiently high current densities in the case when the sign of the charge of a reacting multivalent particle is opposite to that of the charge of the electrode surface, if the distribution of potentials is in accordance with the classical theory of the double layer. In fact the rate of the penetration of such particles through the double layer and therefore the rate of their transfer from the bulk to the electrode surface under the conditions stated would be insufficient. Moreover the theoretical rate values obtained under these assumptions are several orders of magnitude lower than those observed.

It seems to me that the only way to overcome this difficulty is to take into consideration the discrete

[2] An equation similar to Eq. [5] and differing from the latter only in that 1/2 is substituted for α, was recently deduced on a different basis, that of a theory developed by Marcus (60, 61).

structure of the ionic sheet of the double layer and the interaction between the reacting anions and the neighboring cations. Another solution of this problem would be to assume that not those anions which are predominant in the bulk of the solution react on the cathode, but ionic pairs with a smaller charge, as, for instance, the $MeS_2O_8^-$ ions in the case of a $Me_2S_2O_8$ solution (66, 67) and $Me_2Fe(CN)_6^-$ ions in the case of a $Me_3Fe(CN)_6$ solution. But difficulties are encountered if we are to follow this hypothesis consistently, i.e., improbably low values must be ascribed to α. Furthermore the thickness of the reaction layer in the case of reactions of the type

$$Me^+ + S_2O_8^= \rightleftharpoons MeS_2O_8^- \qquad [6]$$

in all probability is so small that the formation of those ionic pairs which react on the electrode must take place within the double layer. Thus, if we accept this assumption, we still must make an allowance for the interaction between oppositely charged ions within the double layer.

It appears that in that range of potentials for which reliable determinations of the c.v. curves can be made, it is possible to account for the phenomena observed during the reduction of multivalent anions by means of the theory of slow discharge, taking into account the formation of cationic bridges in the double layer. But involuntarily one is led to think that at sufficiently negative potentials a different mechanism of the electrode process is possible, consisting of a transfer of electrons from the electrode to particles located at distances comparable with the thickness of the diffuse double layer. As such a transfer would remove the difficulties connected with the repulsion of anions by the electrode surface, it would seem that in the case of anion reduction the most favorable conditions for such a mechanism are realized. Gurney was the first to point out the possible role of such electronic transfers in discharge processes (68), although the example chosen by him–the hydrogen ion discharge–was undoubtedly not suitable, as the high value of the adsorption energy of the product of the reaction–the hydrogen atom–makes the discharge at a distance from the metal surface energetically unfavorable. We must admit however that the feasibility of such transfers even in the case of anion reduction has not hitherto been corroborated by experiment, although we do not have sufficient reasons to deny their reality in the case when the cations of the electrolyte, as for example Li^+ cations, have a relatively low tendency to form ionic pairs. The research work in this direction must be continued, particularly taking into account what is known about the existence of solvated electrons in many solvents. Generally speaking, it may be said that the state of our knowledge about the transfer of electrons over long distances in the case of electrode processes is about the same as in the case of redox reactions occurring in the bulk of the solution.

The idea of the importance of the structure of the double layer for the kinetics of electrode processes has gradually become firmly established in electrochemistry, as for instance is shown by the review of Breiter, Kleinerman, and Delahay (69). However, one must mention the progress made in research in another, at first sight opposite, direction. Investigations carried out after the war, in particular in Czechoslovakia, have shown that the net rate of a great number of electrode processes is determined by chemical reactions resulting in the formation of an electroactive substance from inactive components in the bulk of the solution and therefore, as it would seem, independent of the double layer structure. At present it appears, however, that such a contraposition of these two concepts would be incorrect, as in a number of cases the thickness of the reaction layer becomes comparable with that of the diffuse double layer (70). Under these conditions it is necessary to take into consideration the effect of the electric field of the double layer upon the kinetics of the process, although it is a chemical and not an electrochemical one. Unfortunately we know as yet very little how this is to be done.

I have dealt hitherto only with the direct effect of the double layer on the reactions on the electrode. But its indirect effects are perhaps of still greater importance. The adsorption of surface active ions and of neutral molecules depends on the electric field of the double layer and these ions and molecules, in their turn, may act as catalyzers or inhibitors in electrochemical processes. It would be beyond the scope of the present paper to dwell on this problem, the study of which has given us many conclusive proofs of the existence of a close connection between the structure of the interface and the kinetics of the electrode processes (71, 65). However, I want to consider at least one particular case, that of the adsorption of anions which do not take a direct part in the electrode process. I have chosen this case because its consideration brings us, in a sense, to the limits within which we may use those very elementary concepts on whose basis Eq. [5] and some other similar relationships were deduced. In accordance with Eq. [5] the specific adsorption of anions must shift the ϕ_1 — potential toward more negative values and consequently increase the velocity of the processes of cation reduction. As might be easily proved, this conclusion holds for anodic processes of cation formation as well. It was first confirmed in the work of Jofa, Kabanov, *et al.*, for the case of the discharge of hydrogen ions on a Hg cathode (72) and later for a number of other reactions, many of which are well known from polarographic literature (73). However, at present, we know that in some cases the adsorption of anions on solid electrodes results not in an acceleration, but in a retardation of reactions of discharge and of formation of cations (74, 75). Thus, the adsorption of the Br^- ion and particularly of the I^- ion greatly retards the ionization of H_2 on a Pt electrode (76, 77), as well as the ionization of the hydrogen on the β phase of the Pd-H system (78). Apparently, the bond between the adsorbed anion and the metal surface becomes so firm in these cases that it is the modification of the properties of the electrode surface by the adsorbed

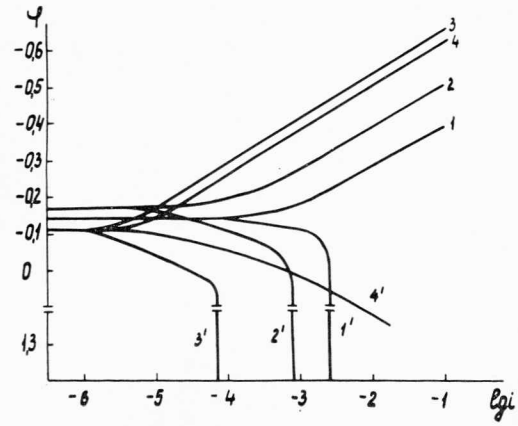

Fig. 12. Cathodic and anodic c.v. curves for stainless steel. 1, 1^1 10N H_2SO_4; 2, 2^1 10N H_2SO_4 + 0.01N KBr; 3, 3^1 10N H_2SO_4 + 0.001N KI; 4, 4^1 10N H_2SO_4 + 0.2N KI. The potentials are referred to a hydrogen electrode in 10N H_2SO_4.

anions, which results in a kind of passivity, that is of principal importance and not the change in the distribution of the potential in the double layer. This passivity probably is caused by the saturation of the free valencies of the electrode surface by chemisorbed anions and is accompanied by a decrease in the double layer capacity (79). The fact that this phenomenon is observed with solid electrodes only suggests that it is connected somehow with the presence on the electrode surface of active centers with high values of adsorption energies which strongly influence the kinetics of the process. An interesting example of this kind of action of anions is seen in the behavior of a stainless steel with 17% Cr and 9% Ni in the presence of I^- ions (80). As shown in Fig. 12, the addition of I^- ions to 10*N* H_2SO_4 increases the hydrogen overvoltage and facilitates the anodic passivation of steel. The inhibition of the cathodic and anodic processes results in a great diminution (4000 times) in the rate of the spontaneous dissolution of this steel in 10*N* H_2SO_4. The dissolution rate passes through a minimum at a I^- ion concentration of about 0.01% and increases again with further increase in the latter, not attaining, however, its original value. As it appears to me, these results show conclusively that metal passivation does not necessarily involve the covering of the surface with a protective layer forming a phase.

The investigation of the effect of anions on the kinetics of electrode processes permits us to draw the conclusion that the development of the theory of the double layer on the basis of purely electrostatic concepts must be considered as only a step in the building up of a surface chemistry of metals on a wider scale.

My address was concerned with the double layer on the metal-solution interface, but in order to understand their electrical properties it is essential to compare phenomena occurring on different kinds of interfaces. In a paper presented at the 7th Symposium on Colloid Chemistry I gave particular consideration to the comparison between the orientation of organic molecules on the metal-solution and solution-gas interfaces. It is very instructive as well to compare the results of electrocapillary measurements in solutions containing aromatic compounds (71, 81) with the results of determinations of the electron work function in the presence of adsorbed layers of molecules of this kind (82). Great attention has been paid lately to the problems of the semiconductor-vacuum and the semiconductor-electrolyte interfaces. The application of ideas developed in the investigation of the metal-electrolyte interface to the study of these interfaces has already given important results and undoubtedly will be still more fruitful in the future.

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