

THE DEPENDENCE OF THE DOUBLE LAYER STRUCTURE ON THE NATURE OF THE METAL SURFACE^{*)}

By

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The double layer theory is one of the fundamentals of electrochemical kinetics. At the present time there can be hardly any doubt that it is impossible to understand the mechanism of the electrode processes without knowing the structure of the electric double layer. Our information on the electric double layer structure at the metal-solution interface is based, in the first place, on the data obtained in the investigation of the mercury electrode. In extending the results of these investigations to other metals, it is necessary to know what changes in the double layer structure are involved therein. My paper is devoted to this problem. I intend to confirm myself only to the simplest cases and will not consider the structure of the electric double layer in the presence of surface-active substances. The specific adsorption of inorganic ions will be discussed only in part. The solution of the problem in question depends to a great extent on the possibility to overcome the technical difficulties involved in the investigation of the surface properties of solid, and in part, liquid metals other than mercury. The investigations of the double layer structure at the mercury-solution interface were successful because it was possible to measure the interfacial tension and because in a number of solutions and over a wide potential range the mercury electrode behaves as an ideally polarizable one, this being due to the high value of the hydrogen overvoltage and a relatively poor affinity for oxygen. As will be evident from what follows, of essential importance is also a low adsorption energy of hydrogen and a relatively low value of the adsorption energy of water. The change in the electric double layer structure when passing from mercury to other metals, which has first attracted the attention of the investigators, was the change in the potential of the point of zero charge $\varphi_{e=0}$. At present we have a number of methods at our disposal for the determination of the point of zero charge of solid and liquid metals in aqueous solutions, which on the whole, if chosen critically,

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give fair coincidence. The position of the point of zero charge is of essential importance for electrochemical kinetics. However, as this is not the first time that I have to consider this problem¹⁾ I shall not dwell on it here, but will discuss somewhat later only some particular cases on which the attention has been focussed in recent years.

Let us suppose the position of the point of zero charge to be known. Is it possible then to assume that the same potentials referred to corresponding points of zero charge, *i.e.* the same rational potentials according to GRAHAME²⁾, or the same potentials on the φ -scale according to ANTROPOV³⁾ correspond to comparable electrode states? To answer this question we need quantitative data on the electric double layer structure. However, whereas, as I have already said there are a number of methods at our disposal for the determination of $\varphi_{\epsilon=0}$, until recently there have been available only two sufficiently reliable methods for the determination of the double layer structure at other potentials in the case of solid metals: first, the differential capacity C measurements or an equivalent determination of the dependence of the charge ϵ upon the potential, and second, the direct measurements of the adsorption of cations and anions involved in the formation of the double layer. It seems to me that we have succeeded in finding a third method, about which I shall speak later. The differential capacity measurements are particularly suitable for an experimental verification of the relation which forms the basis of the double layer theory. According to this relation, the double layer can be considered as two capacitors connected in series: the dense or Helmholtz layer and the diffuse or Gouy layer. If we designate by C_H the capacity of the Helmholtz layer and by C_g that of the Gouy layer, we shall have from this conception (first suggested by STERN⁴⁾) that

$$\frac{1}{C} = \frac{1}{C_H} + \frac{1}{C_g} \quad (1)$$

According to the theory of the diffuse double layer, C_g passes through a minimum at the potential of zero charge. This minimum is the more pronounced, the lower is the electrolyte concentration. Therefore, in sufficiently dilute solutions the minimum is observed on the C, φ curve as well, this minimum growing deeper with the dilution of the solution. The existence of these minima was first experimentally proved by VORSINA and FRUMKIN⁵⁾. GRAHAME⁶⁾ found that in the case of NaF, that is of an electrolyte, whose ions are not specifically adsorbed at the potential of zero charge, C can be quantitatively calculated from eq (1), assuming that C_H at a given charge density is independent of the electrolyte concentration and that C_g obeys the diffuse layer

theory of GOUY⁷⁾. The first step in the comparative investigation of the double layer structure on mercury and on other metals was to be the comparison of the corresponding C, φ curves, especially of their dependence upon the composition and concentration of the solution. Indeed when our work on the differential capacity measurements, interrupted during the war, was resumed, BORISOVA, ERSHLER and FRUMKIN⁸⁾ succeeded in showing that minima appear on the C, φ curves of lead, cadmium and thallium in dilute solutions, which disappear with rising concentration of the solutions. This indicates that these minima are associated with the diffuse structure of the double layer near the point of zero charge. The shape of these curves, however, was significantly different from that of similar curves in the case of mercury. Better results were later obtained for lead and silver by LEIKIS at the Institute of Electrochemistry in Moscow⁹⁾ and for lead and tin by RANGLES in Birmingham¹⁰⁾. In the present paper I want first of all to present the data on lead, thallium and silver obtained recently by Mrs. LEIKIS and collaborators at the Institute of Electrochemistry¹¹⁾.

Due to the use of a highly sensitive bridge for a.c. measurements¹²⁾, a thorough pre-treatment of the electrode surface, the purification of the solution as well as to the maximal elimination of the effect of the solution creeping between the electrode and the holder, it was possible to obtain C, φ curves which are quite comparable with those on mercury.

Fig. 1 shows the C, φ curves of lead (99, 9998% purity) in 0,1N NaF, NaBr and NaJ measured at the frequency 1000 cps. The lead surface had been treated with concentrated sulfuric acid, etched in nitric acid and subjected to anodic polarization followed by cathodic reduction. It is clear from the

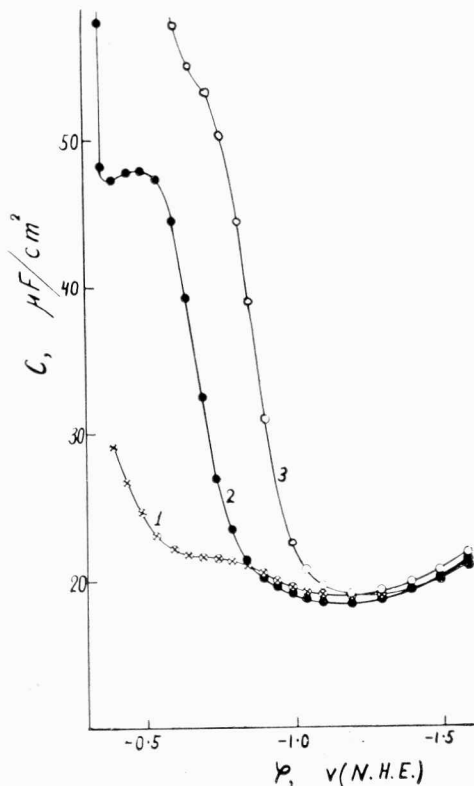


Fig. 1. C, φ curves for Pb. 1—0,1N NaF, 2—0,1N NaBr, 3—0,1N NaJ. Frequency 1000 cps. Potentials referred to N.H.E. (LEIKIS and RYBALKO).

figure that the dependence of the shape of the curves upon the anion nature is quite similar to that observed on mercury. The curves obtained in 0,1N NaBr show a hump just as on the C, φ curves obtained on Hg. This hump is poorly defined in 0,1N NaF and disappears, as in the case of Hg, when passing to the iodide solution. In Fig. 2 are given the C, φ curves of the

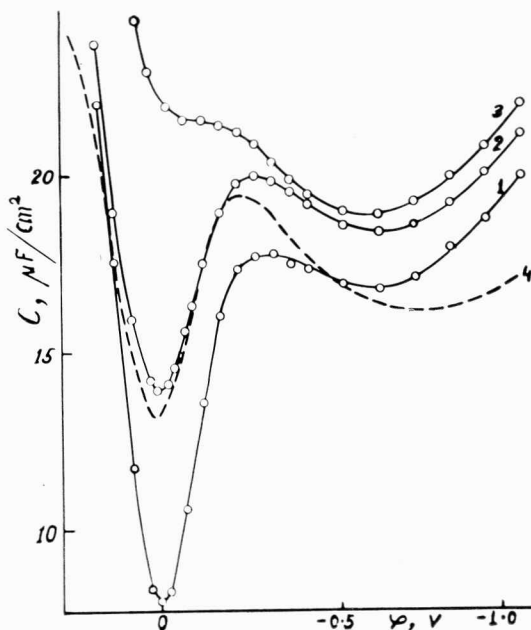


Fig. 2. C, φ curves for Pb and Hg in NaF. 1—Pb in 0,001 N NaF, 2—Pb in 0,01 N NaF, 3—Pb in 0,1 N NaF, dashed curve—Hg in 0,01 N NaF. Potentials referred to $\varphi_{i=0}$ (LEIKIS and RYBALKO)

lead electrode in NaF solutions of varying concentrations and for comparison the C, φ curve of Hg in 0,01N NaF. To make the comparison of the shape of the curves easier, the points of zero charge of Pb and Hg in this figure are made to coincide and the potentials are referred to this common point of zero charge. In actual fact, the point of zero charge of Pb in this solution lies at $-0,56$ v N.H.E., *i.e.* by $0,37$ v more negative than that of Hg. As is clear from the figure, if the points of zero charge are superposed, the C, φ curves of Hg and Pb in 0,01 N NaF nearly coincide over a considerable potential range. At more negative potentials, however, the capacity of the Pb electrode is somewhat higher than that of Hg. On this account, the absolute values of the charge of the lead electrode at the same rational potentials are

somewhat higher than for Hg (Fig. 3). In other words, at the same potentials against N.H.E., the difference in the charges of both electrodes in the region of cathodic polarizations is somewhat less than would be expected from the position of the points of zero charge. This phenomenon, observed in the case of some other electrodes as well, is of importance when comparing the adsorption processes and kinetics of electrochemical reactions on different electrodes. It is possible to suggest some reasons for this phenomenon, but I shall not dwell on them here as they are only hypothetical as yet. Moreover, these reasons may be different for different electrodes.

In Fig. 4 are given the C, φ curves of the lead electrode in 0,01N NaF and 0,001N NaF calculated from the C, φ curve in 0,1N NaF by means of eq (1). Following GRAHAME, C_H was determined from the experimental value of C and the theoretical value of C_g for a 0,1N solution and from this value of C_H and the theoretical values of C_g for 0,01 and 0,001 N solutions the corresponding C values were found. Fig. 4 shows that in the case of 0,01N NaF there is satisfactory agreement between the calculated and experimental values of C , some discrepancies being observed, however, in the case of the 0,001N solution. It is of particular significance that here the observed value of minimal capacity is higher than the theoretical. This discrepancy could be explained by assuming that there are some areas on the electrode surface with a different value of the potential of zero charge, on which the double layer capacity does not pass through a minimum at the point of zero charge of the main surface. In order to verify this hypothesis it is necessary to measure the C, φ curves on separate monocrystal faces, but these measurements are as yet in the initial stage of development. The effect of the homogeneity of the surface upon the C, φ

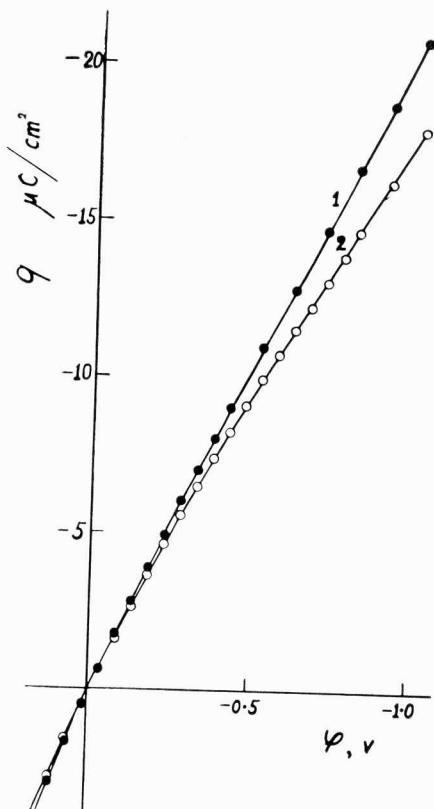


Fig. 3. q, φ curves for Pb and Hg in 0,1N NaF. 1—Pb, 2—Hg. Potentials referred to $\varphi_{\pm=0}$ (LEIKIS and RYBALKO).

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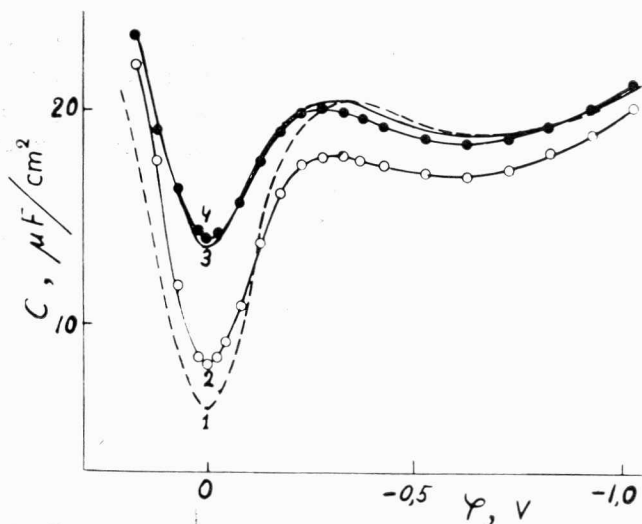


Fig. 4. Experimental C, φ curves for Pb in 0,01 N NaF (4) and 0,001 N NaF (2) and curves calculated according to GRAHAME from the C, φ curve in 0,1 N NaF. Solid curve (3)—0,01 N NaF, dashed curve (1)—0,001 N NaF. Potentials referred to $\varphi_{\epsilon=0}$ (LEIKIS and RYBALKO).

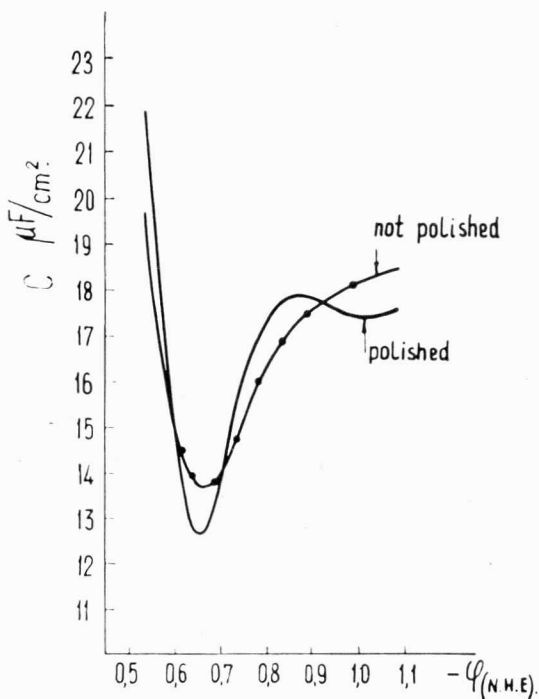


Fig. 5. C, φ curves for 99,9998% Pb in 0,01 N H_2SO_4 before and after electropolishing.

curves is to some extent evident from Fig. 5. If the roughness is eliminated by electropolishing, the minimum becomes narrower and the shape of the curve at the negative potentials approaches that to be expected for a homogeneous surface.

In Fig. 6 are compared the C, φ curves for silver and mercury the potentials being referred to the potential of zero charge. As has been shown by LEIKIS and collaborators, the point of zero charge of the silver electrode in solutions of surface nonactive electrolytes lies at $-0,70$ v vs. N.H.E., this value being independent of pH of the solution, which could be varied within 3,4—12. But in order to compare the curves in this case the superposition of the points of zero charge did not suffice as, unlike the lead electrode, the

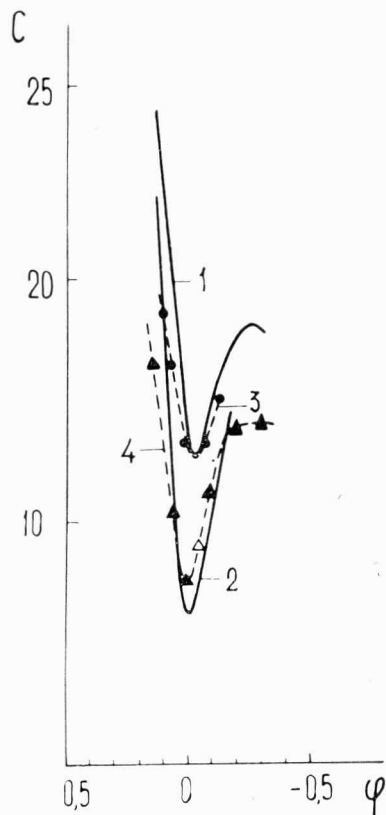


Fig. 6. C, φ curves for Ag and Hg in Na_2SO_4 . 1,2-Hg; 3,4-Ag; 1,3-0,01 N Na_2SO_4 ; 2,4-0,001 N Na_2SO_4 . Potentials referred to $\varphi_{\epsilon=0}$ (DAGA-EVA, LEIKIS and SEVASTYANOV).

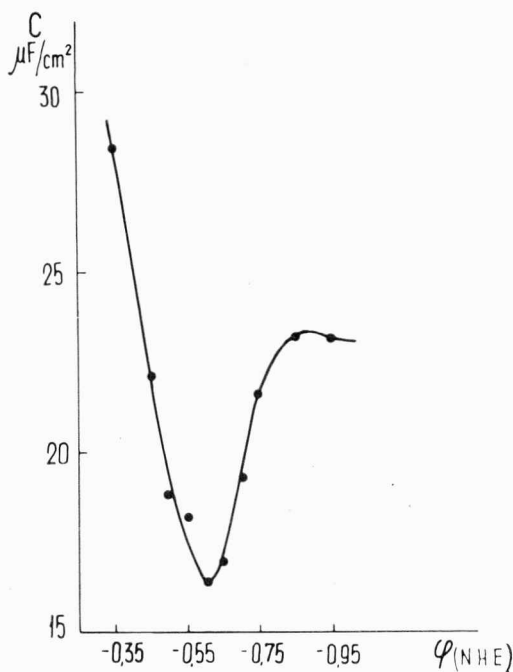


Fig. 7. C, φ curve for the face (III) of silver in 0,01 N Na_2SO_4 . Potentials referred to N.H.E. (SEVASTYANOV and VITANOV).

silver electrode cannot be prepared with a completely smooth surface. Therefore, the scale of the ordinate axis was chosen in such a way that the minimal capacities of both electrodes in 0,01N H_2SO_4 should coincide. The observed capacity values for the Ag electrode were to be halved, the roughness factor of the silver electrode being, apparently, close to 2. It is clear from the figure that under these conditions, the C, φ curves for Ag and Hg nearly coincide over a rather wide potential range both in 0,01N and 0,001N solutions. Fig. 7 shows the C, φ curve of the (111) face of a silver monocrystal measured by SEVASTYANOV and VITANOV at Prof. KAISHEV'S laboratory in Sophia, Bulgaria¹³. The point of zero charge lies at $-0,061$ (N.H.E.) *i.e.* somewhat more positive than that of polycrystalline silver. We expect in the nearest future in collaboration with the Bulgarian Academy of Sciences to go on with our investigation of the C, φ curves on separate monocrystal faces.

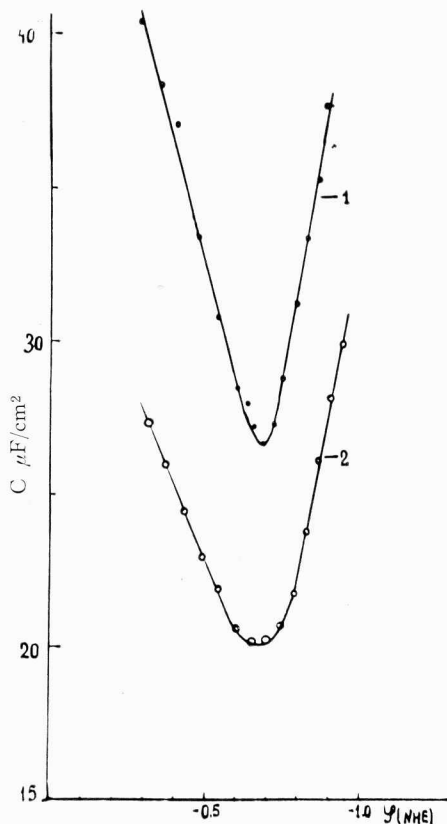


Fig. 8. C, φ curves for nonamalgamated (1) and amalgamated (2) Ag in 0,01N Na_2SO_4 . Potentials referred to N. H. E. (DAGAEVA and LEIKIS).

The result obtained in the deposition of some mercury on the silver electrode surface was rather surprising¹¹⁾. The C, φ curve of such amalgamated silver electrodes could be expected to be similar to those of silver and mercury with an intermediate position of the point of zero charge. However, actually, as is evident from Fig. 8, in this case the minimum on the C, φ curve is much wider. With increasing amount of mercury deposited, the minimum continues to widen. Such C, φ curves can appear if there are on the electrode surface areas with different values of the potential of zero charge, whose linear dimensions are comparable or greater than the thickness of the diffuse layer. This shows that it is possible to obtain the C, φ curves with the shape that would be consistent with the diffuse double layer theory only in the case of the surfaces with a definite degree of chemical and crystallographic homogeneity. The differences in the electric double layer structure on different parts of the surface of the amalgamated silver electrode appear to be to a considerable extent eliminated by cathodic polarization. In fact, if the C, φ curves are measured in the presence of a surface-active substance—hexyl alcohol, the

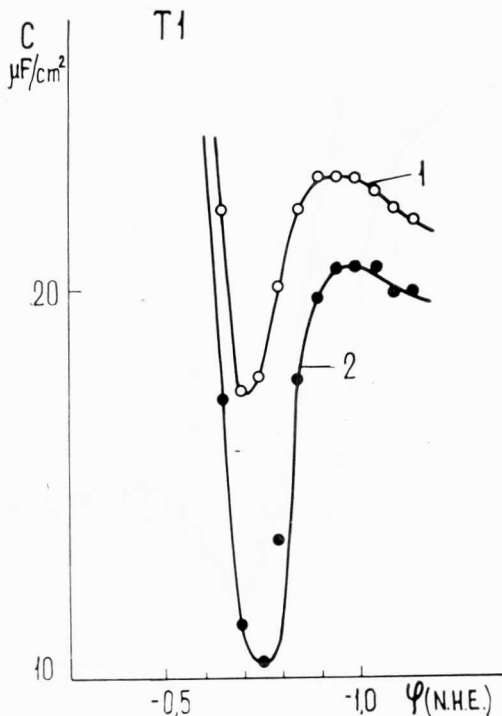


Fig. 9. C, φ curves for Tl. 1—0.01 N NaF, 2—0.001 N NaF. Potentials referred to N. H. E. (DAGAeva and LEIKIS).

curve of the amalgamated silver electrode—show a typical cathodic desorption peak of the adsorbed organic substance, which although being wider and lower than that of the non-amalgamated silver electrode, is sufficiently well pronounced. The peak of the amalgamated electrode is somewhat shifted in the direction of less negative potentials, as it would be expected from the position of the points of zero charge of Hg and Ag.

In Fig. 9 are given the C, φ curves of thallium in NaF solutions which are similar in their shape to those of lead⁽¹¹⁾. Of all the metals which have been so far studied by the method of the C, φ curves measurements in dilute solutions, thallium and cadmium have the most negative values of $\varphi_{z=0}$ (in the case of thallium $-0,75$ v vs. N. H. E.).

Judging by the C, φ curves obtained by LEIKIS and collaborators, the structure of the double layer in the case of lead, silver and thallium is similar to that at the mercury-solution interface notwithstanding some differences mentioned above. On the basis of RANDES's data⁽¹⁰⁾, tin can be added to the list of these "mercury-like" metals, as well as bismuth, which was recently investigated by PALM and PAST at the Tartu University⁽¹⁴⁾. In Fig. 10 are

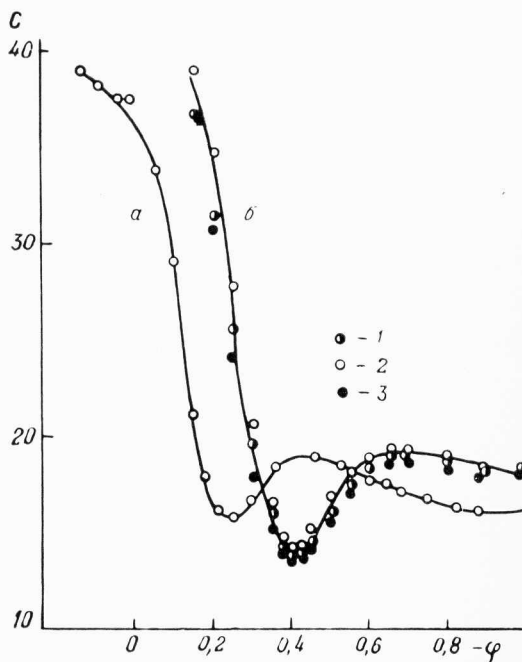


Fig. 10. C, φ curves for Hg and Bi in 0.01N KCl. a—Hg, b—Bi. Potentials referred to N. H. E. (PALM, PAST and FULLERITS), 1—200 cps, 2—1000 cps, 3—3000 cps.

given the C, φ curves of mercury (a) and bismuth (b) in 0,01 N KCl. A smooth bismuth electrode was prepared by solidifying a liquid Bi drop in a hydrogen atmosphere. The C, φ curve of Bi was measured at the frequencies: 200, 1000 and 3000 cps. As is clear from the figure, in the case of a solid electrode with a smooth surface the capacity does not depend on frequency. The shape of the C, φ curves of Hg and Bi is quite similar. A somewhat lower capacity value at the point of zero charge in the case of Bi is due to lesser adsorptivity of the Cl^- ion on the Bi surface as compared to mercury. This result was confirmed by the measurements with bromide and iodide solutions. In dilute solutions of chlorides and sulfates the point of zero charge of Bi lies at $-0,4$ v (N.H.E.).

More significant differences compared to the mercury electrode were observed in the investigation of the electrocapillary and capacity behaviour of gallium, carried out by BAGOTSKAYA, POLIANOVSKAYA, GRIGORYEV and the author¹⁵⁾. A considerable part of the results on gallium were reported at the 15th CITCE Meeting and I shall consider here only the more recent data.

The C, φ curve of gallium sharply rises when passing to less negative potential values, beginning with those which are by 0,3 v more negative than the point of zero charge, lying at $-0,068$ vs. N.H.E. (Fig. 11, curve 5). As it follows from the dependence of the C, φ curve upon the composition of the solution, which was considered in the report mentioned, this rise, unlike that of the C, φ curves of mercury, cannot be explained by the adsorption of anions, but is determined by the re-orientation of the water molecules adsorbed on the gallium surface, which turn with their oxygen side towards the metal with the potential shifting in the direction of less negative values^{*}). The concept of such re-orientation of the water molecules was resorted to also in the case of mercury to explain the appearance of the "hump" on the differential capacity curves¹⁶⁾. As I have already mentioned, such a hump is observed on the C, φ curves of Pb¹¹⁾. In any case, this phenomenon is much more pronounced on

*) MÜLLER²⁹⁾ attempted recently to give another explanation of this rise based on the assumption of an "intensified contact adsorption" of anions which should occur more easily in the case of a positively charged Ga surface than in the case of positively charged mercury. According to MÜLLER, this effect should be observed on Ga with Cl^- and Br^- but be absent for ClO_4^- . However, as it is shown by curve 5 of Fig. 11, the rise of the differential capacity of Ga is pronounced in ClO_4^- solutions as well, which shows that the explanation proposed by MÜLLER is inadequate. Moreover, in the main part of the potential region for which this capacity rise is characteristic the charge of the Ga surface is negative or zero and the anion adsorption is somewhat smaller than on Hg. At the anodic end of the capacity curve the differential capacity of Ga is smaller in J^- than in Cl^- or SO_4^{2-} solutions. The experimental results are therefore in complete disagreement with MÜLLER's theory.

gallium. This is, probably, due to stronger adsorption of water by gallium compared to mercury, which is evident from the comparison of the free energies of wetting with water of the uncharged mercury and gallium surfaces.

When passing to more dilute solutions on the ascending branch of the C, φ curve of gallium appears a minimum, which can be seen already in 0,01N perchlorate solutions (Fig. 11) and grows deeper with further dilution¹⁵⁾.

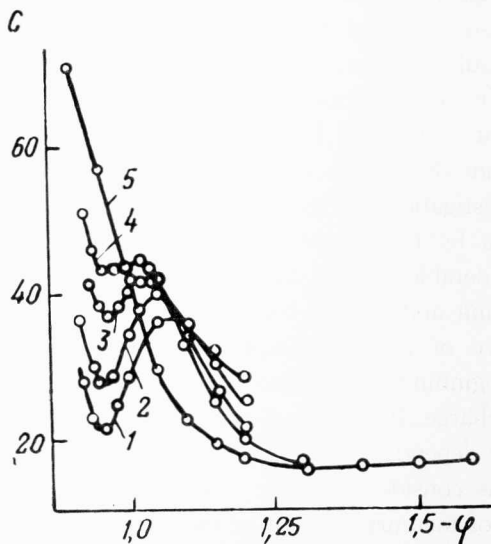


Fig. 11. C, φ curves for Ga in $x \text{ HClO}_4 + y \text{ NaClO}_4$. 1— $x=0,01 \text{ N}$, $y=0$; 2— $x=0,008 \text{ N}$, $y=0,012$; 3— $x=0,008 \text{ N}$, $y=0,042 \text{ N}$; 4— $x=0,008 \text{ N}$, $y=0,092 \text{ N}$; 5— $x=0,01 \text{ N}$, $y=1 \text{ N}$. Potentials referred to N.C.E. (FRUMKIN, GRIGORYEV and BAGOTSKAYA).

Unfortunately, in the case of gallium it is impossible to carry out measurements at concentrations below 0,006 N, since it is necessary to maintain the acidity of the solution at a definite level to prevent the gallium surface from being oxidized. The reciprocals of the minimal capacities in perchlorate solutions (the ClO_4^- ions are not specifically adsorbed on the gallium surface) are a linear function of $c^{-1/2}$, as they should be in accordance with the theory of the diffuse double layer, but the slope of this dependence differs from the theoretical. Formally this difference can be explained by ascribing to the dielectric constant of water within the diffuse double layer a larger value than that of water in the bulk, viz. 120. At present it is not yet possible to draw final conclusions from this fact, but the deviation from eq (1) observed in the case of gallium results perhaps from the disturbance of the water structure beyond the dense double layer, *i.e.* they are due to a stronger hydrophilic nature of the gallium electrode

compared to the mercury electrode. It is interesting that in some respects the gallium electrode affords better opportunities to observe the diffusivity of the electric double layer than the mercury electrode. Namely, due to a higher value of C_H and partly to a somewhat lesser adsorptivity of the anions, the minima on the C, φ curves are in the case of gallium retained up to higher concentrations than with mercury. This is evident from Fig. 11 in which the minimum is clearly seen at 0.1 N ClO_4^- concentration, and the more so from Fig. 12, in which are given the C, φ curves of gallium in the presence

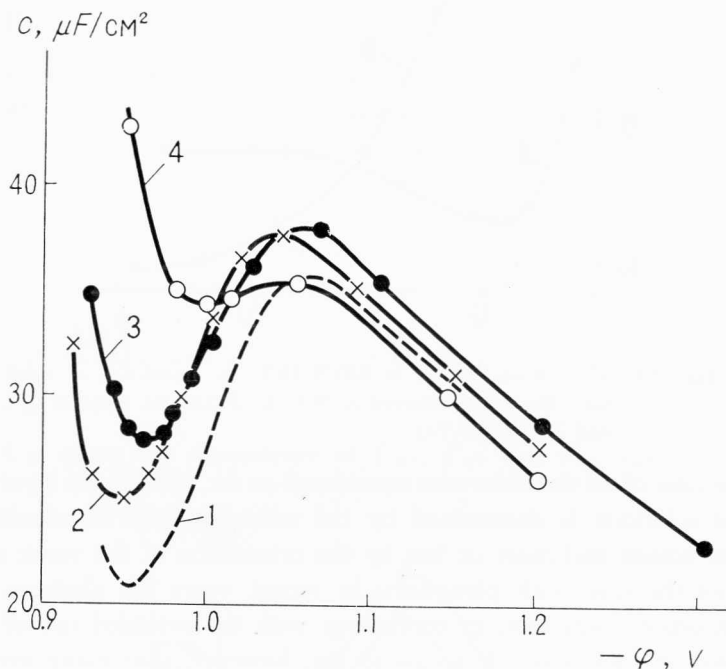


Fig. 12. C, φ curves for Ga in the presence of halide ions. 1—0.008 N HClO_4 , 2—the same +0.001 N KCl , 3—the same +0.001 N KBr , 4—the same +0.001 N KI . Potentials referred to N.C.E. (FRUMKIN, GRIGORYEV and BAGOTSKAYA).

of halogen anions. The minimum is retained at 10^{-3} N J^- concentration, whereas in the case of the mercury electrode it disappears already in the presence of 10^{-4} N KJ . When a liquid gallium drop solidifies in the solution, the minimum on the C, φ curve in 0.01 N HCl disappears (Fig. 13), to appear again when solid gallium melts¹⁷⁾. Apparently, the surface of solid gallium formed under such conditions is crystallographically inhomogeneous and the $\varphi_{i=0}$ are different in different areas.

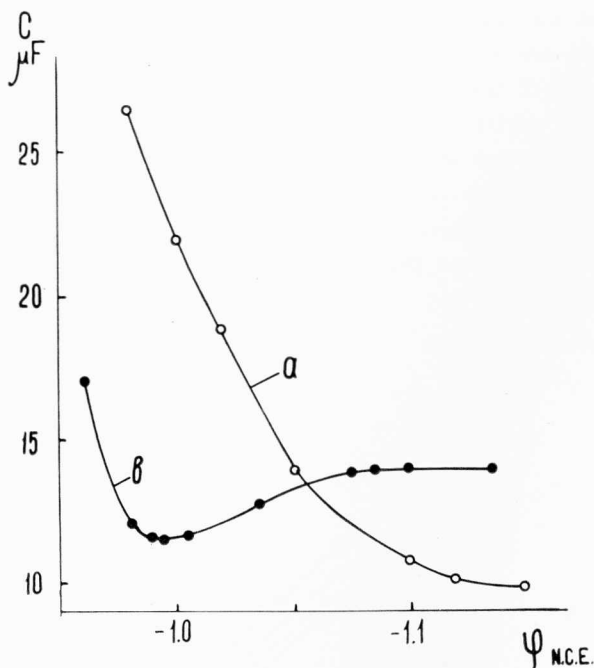


Fig. 13. C, φ curves for Ga in 0,01 N HCl. b—liquid Ga, a—solid Ga. Potentials referred to N. C. E. (FRUMKIN, GRIGORYEV and BAGOTSKAYA).

In the case of all the electrodes considered so far, the double layer structure in aqueous solutions is determined by the adsorption and distribution of the cations and anions and more or less by the orientation of the water molecules. This is not the case with platinum. In recent years the platinum electrode has drawn especial attention in connection with the intended use of platinum as a catalyst in fuel cells. It seems to me, however, that many investigators have not taken due account of the fundamental differences in the conditions of the setting up of the potential in the case of the mercury-like and the platinum-like electrodes. Therefore, in the concluding part of my paper I want to consider this problem at greater length. But first it is necessary to recapitulate briefly some of the results obtained already a long time ago⁽¹⁸⁾.

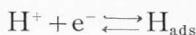
The adsorption of cations and anions from the solution involving the formation of the electric double layer at the platinum-electrolyte interface can be readily measured if the electrodes used are of platinized platinum and their surface is large enough. Let us assume, *e.g.* that we have an acidified KCl solution and let us designate the adsorptions of hydrogen ions, potassium cations and chlorine anions found experimentally, calculated per cm^2 of true surface

and expressed in electric units as Γ_{H^+} , Γ_{C^+} and Γ_{A^-} , respectively. From the electroneutrality condition it follows that

$$\Gamma_{H^+} = \Gamma_{C^+} - \Gamma_{A^-} \quad (2)$$

Γ_{C^+} and Γ_{A^-} can be determined, *e.g.* by the method of radioactive tracers^{19,20} and Γ_{H^+} — directly from the change in the acidity of the solution upon contact with the platinum electrode.

I shall consider here only those cases when the appearance of the charge on the platinum surface is due to the reaction of hydrogen ionization



i.e., when we have a platinum-hydrogen electrode.

The appearance of the negative charge on the platinum surface involves hydrogen ionization, with hydrogen ions entering the solution. When a positive charge arises the process is reversed, the hydrogen ions concentration in the solution decreasing. We shall assume the ratio of the concentrations of hydrogen ions and other cations in the bulk of the solution to have been chosen in such a way that the hydrogen ions content in the side of the double layer facing the solution could be neglected. In this case, Γ_{H^+} is determined entirely by hydrogen ionization and is a measure of the charge density ε :

$$\Gamma_{H^+} = \varepsilon. \quad (3)$$

In Fig. 14 is given the dependence of Γ_{H^+} , Γ_{C^+} and Γ_{A^-} upon the potential

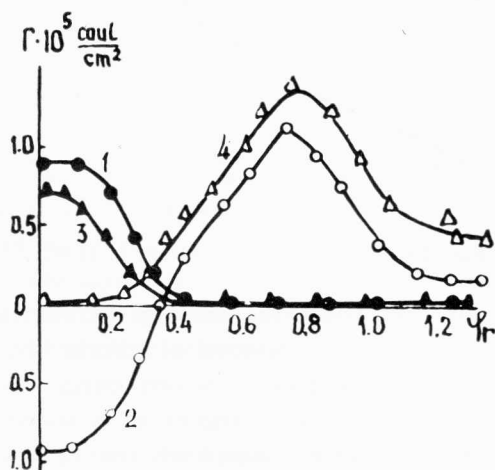


Fig. 14. φ_r -dependence of Γ_{Cs^+} (1), Γ_{H^+} (2) in 0,018 N Cs_2SO_4 + 0,002 N H_2SO_4 and Γ_{Cs^+} (3), $\Gamma_{SO_4^{2-}}$ (4) in 0,01 N Cs_2SO_4 + 0,01 N H_2SO_4 (BALASHOVA and KAZARINOV).

φ_r referred to a hydrogen electrode in the same solution for an acidified Cs_2SO_4 solution.²⁰⁾ It is clearly seen that these dependences are anomalous. In fact, Γ_{H^+} , *i.e.* the charge ε , rises with φ_r only within a limited potential range. At less positive potentials ε is practically independent of φ_r , at more positive potentials it even decreases with rising φ_r . The comparison of these data with the results of the electrical measurements shows these deviations to be due to the presence on platinum of adsorbed hydrogen at small φ_r and of oxygen at large φ_r . Several methods of electrical measurements can be used for the platinum electrode, the simplest of them being the charging curves method, *i.e.* the determination under galvanostatic conditions of the dependence of the potential upon the quantity of electricity applied to the electrode. A typical charging curve is shown in Fig. 15. Three distinct regions can be seen on

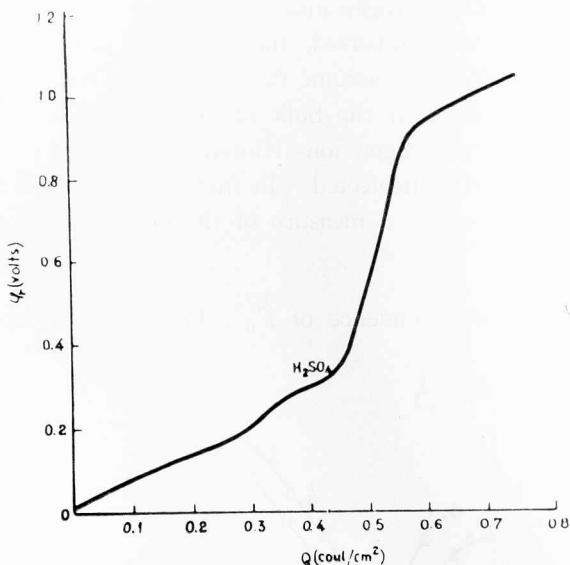


Fig. 15. Charging curves for Pt in H_2SO_4 .

it: the hydrogen region, in which the quantity of electricity applied to the electrode is expended mainly in the removal of adsorbed hydrogen, the double layer region and the oxygen region in which oxygen is adsorbed on the surface. However, in the double layer region, as is shown by more accurate measurements, the platinum surface is completely free of adsorbed gases only in the presence of specifically adsorbed anions, such as Cl^- or Br^- . In sulfate solutions, adsorbed hydrogen or oxygen are present on the surface, although in not very large amounts, even in this region. The comparison of Fig. 14

and 15 shows that an anomalous dependence of the charge upon the potential is observed at those potentials at which considerable amounts of adsorbed hydrogen and oxygen are present on the surface. Hence it is evident that along with the surface charges and the ions of the double layer, adsorbed hydrogen and oxygen are involved in the setting up of the metal-solution potential difference. I cannot dwell on this problem at greater length here, but will only state that in alkaline solutions, in which there is a continuous transition from the hydrogen to the oxygen regions of the charging curve, the anomalous nature of the ε , φ_r curve is even more pronounced, as is clear from Fig. 16.

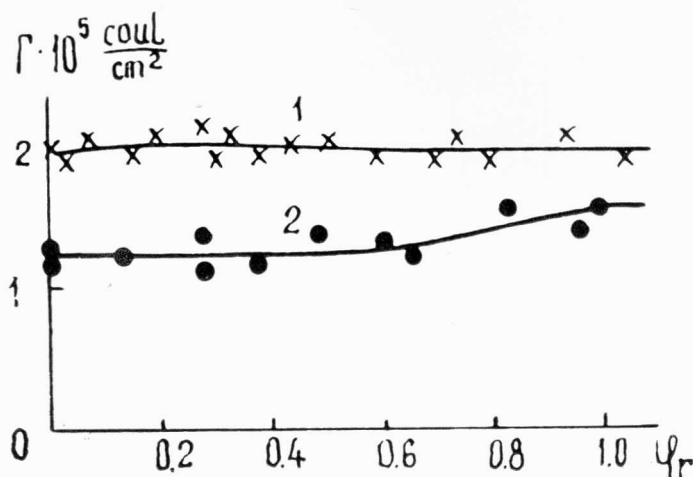


Fig. 16. φ_r -dependence of Γ_{Cs^+} (1) and Γ_{Na^+} (2) in 10^{-2} N CsOH and 10^{-2} N NaOH (BALASHOVA and KAZARINOV).

In this case the adsorption of the cations, which form the ionic side of the double layer, is nearly independent of φ_r , *i.e.* the total potential change is determined by that in the amount of adsorbed H and O atoms.

In what follows we shall confine ourselves to the consideration of the hydrogen and the double layer regions. In this part of the curve, the quantity of electricity applied to the electrode ΔQ is consumed partly in removing adsorbed hydrogen and partly in charging the double layer. Evidently

$$\Delta Q = -\Delta A_{\text{H}} + \Delta \varepsilon \quad (4)$$

where A_{H} is the change in the amount of adsorbed hydrogen in electrical units. The determination of A_{H} from the charging curve in the case of N KCl+0.01 N HCl solution is shown in Fig. 17⁽²¹⁾.

Under the assumption of the absence of the H^+ ions in the ionic side of

the double layer made above, the potential at which $\Gamma_{A^-} = \Gamma_{C^+}$ or $\Gamma_{H^+} = 0$ is the potential of zero charge. It lies at 0,17–0,19 v vs. N.H.E. in acidified 10^{-2} N sulfate solutions with pH=2,4–3,3 and shifts in the negative direction in the solutions of halogen anions. Thus, in acidified N KCl $\varphi_{z=0} = 0,04$ and in acidified N NaBr $\varphi_{z=0} = -0,02$. The results of the determination of the point of zero charge by the adsorption measurements are in agreement with the data obtained by other methods, in particular from the deviation of a platinum wire in an electric field²²⁾. It would be natural to compare these data with

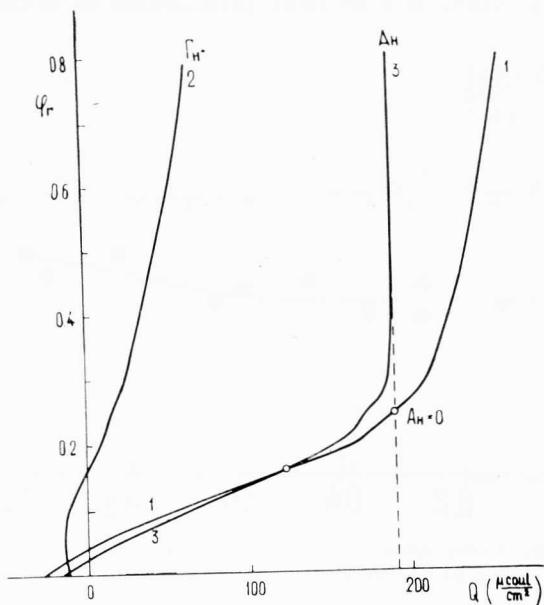


Fig. 17. Charging curve (1), adsorption curve (2) and A_H - Q dependence for Pt in N KCl+0,01 N HCl (PETRY, MARVET and FRUMKIN).

those obtained by the method of the C, φ curves in dilute solutions, which proved helpful in other cases. But the use of this method in the case of the platinum electrode presents some difficulties. When the alternating current is applied to the Pt electrode, it is not only the charging current of the double layer that is measured but also the exchange current of the reaction



The exchange current measured can be reduced by increasing the a. c. frequency, but the measurements using the high frequency alternating currents in dilute solutions involve the well known technical difficulties. These difficulties would

be still greater if the electrodes with a large surface were used. Therefore, it is necessary to use instead of platinized electrodes smooth ones, which are easily poisoned even in thoroughly purified solution. As the result, a number of attempts to determine $\varphi_{i=0}$ of platinum from the C, φ curves in dilute solutions^{23,24)} led to inconsistent results. Lately this problem has again become the focus of attention of investigators.

GILEADI, RUBIN and BOCKRIS²⁵⁾ have made an attempt to avoid the difficulties due to the presence of adsorbed gases by using a previously degassed platinum electrode. They observed in dilute HClO_4 solutions a minimum on the C, φ curve, which they interpreted as corresponding to the maximal diffusivity of the double layer. They arrived at the conclusion that at $\text{pH}=3$ $\varphi_{i=0}$ of platinum lies at 0,48 N.H.E. and shifts by 58 mv in the negative direction with pH increased by 1. This result is at variance with the data obtained by us and calls in question the validity of the interpretation of the values of Γ determined by us. The method used by GILEADI is open to certain objections, which I shall not discuss here. Having provided for an equilibrium coverage with hydrogen to be established on the Pt electrode, SHEVCHENKO, PSHENICHNIKOV and BURSHTEIN²⁶⁾ obtained in dilute H_2SO_4 solutions the C, φ curves, which are presented in Fig. 18. These curves show a minimum at $\varphi=0,23$, *i.e.* rather close to the point of zero charge determined by the adsorption measurements, which could be considered with equal reason as the minimum found by Gileadi as the potential of zero charge of the Pt electrode. However, systematic experimental investi-

gations will be necessary before we can draw an unambiguous conclusion about the double layer structure on the Pt electrode on the basis of a.c. measurements in dilute solutions. It seems to me that much more certain results can be

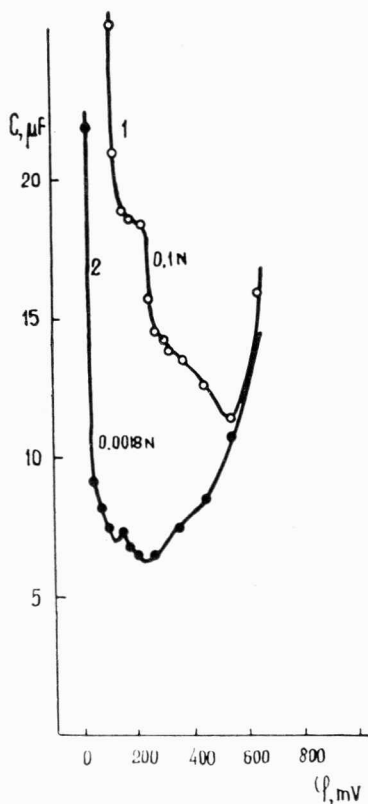


Fig. 18. C, φ curves for activated smooth Pt in H_2SO_4 solutions. 1—0,1 N H_2SO_4 , 10.000 cps; 2—0,0018 N H_2SO_4 , 5.100 cps. Potential referred to N.H.E. (BURSHTEIN, PSHENICHNIKOV and SHEVCHENKO preliminary data).

obtained using another method, also based on electrical measurements, which was recently developed at the Moscow University by FRUMKIN, PETRY and MARVET^{20,27,28}). From the GIBBS thermodynamic theory of electrocapillarity it is possible to derive the equations relating the change in the electrode potential at constant charge and varying concentration of the solution with the cation and anion adsorption. However, in the case of the mercury electrode, the condition of the constancy of the charge with varying concentration of the solution is difficult and perhaps even practically impossible to realize experimentally and these equations cannot be considered as an independent method of the determination of Γ values. This is not the case with the platinized platinum electrode, since its large surface makes it possible without much difficulty to measure the potential changes of an isolated electrode with adsorbed hydrogen present on its surface when the composition of the solution is varied. However, since with changing composition of the solution, the adsorbed hydrogen can be ionized or the hydrogen ions can be discharged changing into atoms, it can be readily seen that it is $A_{\text{H}} - \varepsilon$ (which will be designated by us as Γ_{H}) that will remain constant rather than ε . From the Gibbs thermodynamics of the surface phenomena it is easy to derive the relation

$$\left(\frac{\partial \Gamma_{\text{H}^+}}{\partial \varphi_r} \right)_{\mu_{\text{H}^+}} = - \left(\frac{\partial \varphi_r}{\partial \mu_{\text{H}^+}} \right)_{\Gamma_{\text{H}}} \left(\frac{\partial Q}{\partial \varphi_r} \right)_{\mu_{\text{H}^+}} \quad (5)$$

(μ_{H^+} — the chemical potential of the H^+ ion in electrical units), which permits to calculate the dependence of Γ_{H^+} upon φ_r from the change in the potential with varying acidity of the solution (the chemical potentials of the other ions remaining practically constant in this case) and the slope of the charging curve.

In Fig. 19 are given the changes in the potential of the platinum electrode in N KCl + 0.01 N HCl with varying acidity, but instead of $\left(\frac{\partial \varphi_r}{\partial \mu_{\text{H}^+}} \right)_{\Gamma_{\text{H}}}$, the $\left(\frac{\partial \varphi}{\partial \mu_{\text{H}^+}} \right)_{\Gamma_{\text{H}}}$ values are given referred to a constant reference electrode, which gives a better idea of the nature of this phenomenon. It is evident that at small φ_r , $\left(\frac{\partial \varphi}{\partial \mu_{\text{H}^+}} \right)_{\Gamma_{\text{H}}}$ is close to unity, *i.e.* with constant Γ_{H} the electrode behaves as an ordinary hydrogen electrode. With the removal of hydrogen from the electrode surface, however, $\left(\frac{\partial \varphi}{\partial \mu_{\text{H}^+}} \right)_{\Gamma_{\text{H}}}$ decreases and in the double layer region vanishes. In Fig. 20 are given the Γ_{H^+} , φ_r values calculated by means of eq (5) from the experimental values of $\left(\frac{\partial \varphi_r}{\partial \mu_{\text{H}^+}} \right)_{\Gamma_{\text{H}}}$ and $\left(\frac{\partial Q}{\partial \varphi_r} \right)_{\mu_{\text{H}^+}}$ (the solid curve) and compared with the experimental values of Γ_{H^+} . The

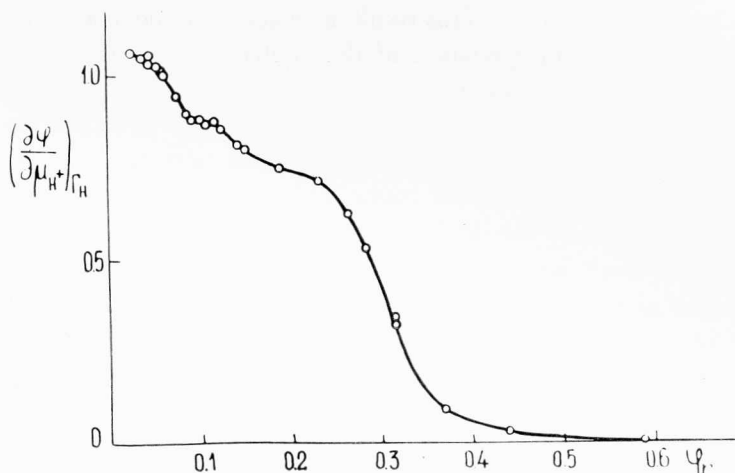


Fig. 19. $\left(\frac{\partial \varphi}{\partial \mu_{H^+}}\right)_{\Gamma_H} - \varphi_r$ dependence for a platinized platinum electrode in N KCl+0,01 N HCl (FRUMKIN, PETRY and MARVET).

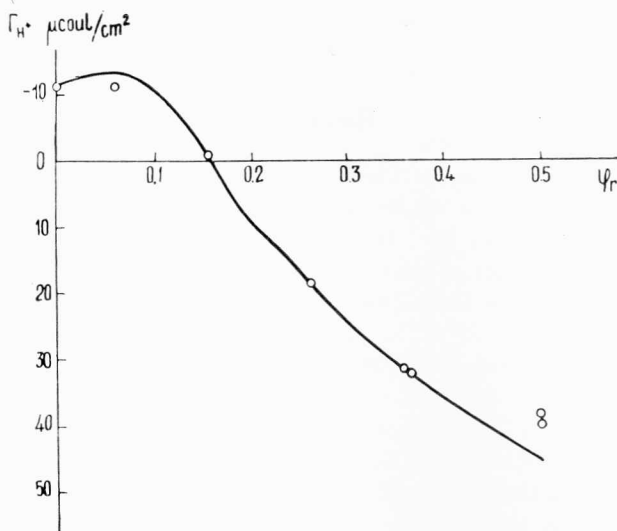


Fig. 20. Theoretical $\Gamma_{H^+} - \varphi_r$ dependence (solid curve) and experimental values of Γ_{H^+} for N KCl+0,01 N HCl (FRUMKIN, PETRY and MARVET).

experimental value of Γ_{H^+} at $\varphi_r=0$ was used to determine the integration constant. Taking into consideration the complex shape of the Γ_{H^+}, φ_r curve, the agreement between theory and experiment is to be regarded as being quite satisfactory. In particular, the value of $\varphi_{\varepsilon=0}$ thus calculated completely coincides

with the experimental one.^{*)} This result, as it seems to me, conclusively proves the correctness of the interpretation of the double layer structure of the Pt-H electrode based on the adsorption measurements. As has been pointed out above, it follows from this interpretation that adsorbed hydrogen and oxygen atoms make contribution to the setting up of the potential difference at the platinum-solution interface of the same order of magnitude as the surface charges and the ions of the double layer¹⁸⁾.

I shall not dwell here on the conclusions to be made in this connection relative to the dipole nature of the Pt-H and Pt-O bonds, as well as on the behaviour of such strongly specifically adsorbed ions as Cd^{2+} or Tl^+ , which, when in adsorbed state on platinum, should be regarded as atoms rather than as ions²⁰⁾. To be sure, the platinum electrode is not an exception. In particular, other metals of the platinum group behave in a similar way. The effect of the adsorbed atoms upon the double layer structure should be taken into consideration in the case of the metals of the iron group as well. No information is as yet available on the double layer structure at the interface with such metals as aluminium or tantalum, whose surface in aqueous solutions is practically always covered with a firmly bound oxide film.

References

- 1) A. FRUMKIN, J. Electroanalyt. Chem., **9**, 173 (1965); Z. Elektrochem., **59**, 807 (1955); Svensk. Kemisk Tidskrift, **77**, 300 (1965).
- 2) D. C. GRAHAME, Chem. Rev., **41**, 441 (1943).
- 3) L. ANTROPOV, Kinetics of electrode processes and null points of metals, Counc. Scient. Ind. Res. New Delhi, 1960; Zhur. Fiz. Khim., **37**, 965 (1963); Ukr. Khim. Zhurn., **29**, 557 (1963).
- 4) O. STERN, Z. Elektrochem., **30**, 508 (1924).
- 5) M. VORSINA and A. FRUMKIN, Compt. Rend. Acad. Sci. URSS, **24**, 918 (1939).
- 6) D. C. GRAHAME, J. Amer. Chem. Soc., **68**, 301 (1946).
- 7) G. GOUY, J. Physique, **9**, 457 (1910).
- 8) T. BORISOVA, B. ERSHLER and A. FRUMKIN, Zhur. Fiz. Khim., **22**, 925 (1948); T. BORISOVA and B. ERSHLER, *ibid.*, **24**, 337 (1950).
- 9) D. LEIKIS, Dokl. Akad. Nauk SSSR, **135**, 1429 (1960); D. LEIKIS and B. KABANOV, Trans. Inst. Phys. Chem. (New Methods of Physicochemical Investigations) Moscow, **6**, 5 (1957).
- 10) J. B. RANGLES, private communication.
- 11) K. RYBALKO and D. LEIKIS, Elektrokimiya, **3**, 383 (1967); *ibid.*, in press; J. DAGA-EVA, D. LEIKIS and E. SEVASTYANOV, *ibid.*, **2**, 820 (1966); *ibid.*, in press.

*) Other cases for which experimental Γ_{H^+} , φ_r curves could be compared with calculated ones are considered in²⁸⁾.

- 12) E. BUDNITZKAYA, D. LEIKIS, E. SEVASTYANOV, A. SHURPACH, *Elektrokhimiya*, **2**, 501 (1966).
- 13) E. SEVASTYANOV and T. VITANOV, *Elektrokhimiya*, **3**, 402 (1967).
- 14) U. PALM, V. PAST and R. PULLERITS, *Elektrokhimiya*, **2**, 604 (1966).
- 15) A. FRUMKIN, N. POLYANOVSKAYA, N. GRIGORYEV and I. BAGOTSKAYA, *Electrochimica Acta*, **10**, 793 (1965); A. FRUMKIN, N. GRIGORYEV and I. BAGOTSKAYA, *Elektrokhimiya*, **2**, 329 (1966).
- 16) R. WATTS-TOBIN, *Phil. Mag.*, **6**, 133 (1961); B. DAMASKIN, *Elektrokhimiya*, **1**, 1258 (1965); **2**, 828 (1966).
- 17) I. BAGOTSKAYA and A. MOROZOV, unpublished results.
- 18) A. FRUMKIN, *Advances in Electrochemistry*, P. Delahay, ed. Vol. 3, Interscience, N. Y. 1963, p. 287; A. Šlygin and A. FRUMKIN, *Acta Physicochim. URSS*, **3**, 791 (1934).
- 19) N. BALASHOVA and V. KAZARINOV, *Usp. Khim.*, **31**, 1721 (1965).
- 20) A. FRUMKIN, N. BALASHOVA and V. KAZARINOV, *J. Electrochem. Soc.*, **113**, 1011 (1966).
- 21) O. PETRY, R. MARVET and A. FRUMKIN, *Elektrokhimiya*, **3**, 116 (1967).
- 22) N. BALASHOVA and A. FRUMKIN, *Dokl. Akad. Nauk SSSR*, **154**, 1432 (1964).
- 23) T. BIRINTSEVA and B. KABANOV, *Dokl. Akad. Nauk SSSR*, **132**, 868 (1960); Zhur. Fiz. Khim., **31**, 1992 (1952).
- 24) V. KHEIFETS and B. KRASIKOV, *Zhur. Fiz. Khim.*, **31**, 1992 (1952).
- 25) J. O'M. BOCKRIS, S. ARGADE and E. GILEADI, *J. Phys. Chem.*, **70**, 2044 (1966); E. GILEADI, B. RUBIN and J. O'M BOCKRIS, *ibid.*, **69**, 3335 (1965); E. GILEADI, *J. Electrochem. Soc.*, **113**, 1020 (1966).
- 26) R. BURSHTEN, A. PSHENICHNIKOV and M. SHEVCHENKO, *J. Electrochem. Soc.*, **113**, 1022 (1966).
- 27) A. FRUMKIN, O. PETRY and R. MARVET, *J. Electroanal. Chem.*, **12**, 504 (1966); O. PETRY, R. MARVET and A. FRUMKIN, *Elektrokhimiya*, **3**, 116 (1967); O. PETRY, A. KOSSAYA and Y. TYURIN, *ibid.*, **3**, N 5 (1967).
- 28) A. FRUMKIN, O. PETRY, A. KOSSAYA, V. ENTINA and V. TOPOLEV, *J. Electroanal. Chem.*, in press.
- 29) K. MÜLLER, *This Journal*, **14**, 224 (1967).