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The Platinum Electrode

Part III*. Adsorbed Atoms and Ions on the Surface of a Platinum Electrode

By *A. Frumkin* and *A. Slygin*

Introduction

According to classical electrochemistry the potential difference between the electrode and the solution, φ, is determined by a double layer of free charges on the metal surface and ions in the solution. Bowden and Rideal[1] suggested that this potential difference might be caused by adsorbed atoms of hydrogen or oxygen, if a definite dipole moment is ascribed to the bond between these atoms and the metal. This view was criticized by Erdey Gruz and Volmer[2]. Frumkin[3] showed that in the case of a metal which adsorbs gases like platinum, the conditions of equilibrium between the metal and the solution can be satisfied only on the assumption that both the atoms of the adsorbed gas and the ions of the double layer take part in the formation of the potential difference between the metal and the solution.

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* A. Šlygin a. A. Frumkin, Part I. Acta Physicochimica URSS, **3**, 791 (1935); Part II. Acta Physicochimica URSS, **4**, 911 (1936).

[1] Bowden a. Rideal, Proc. Roy. Soc., **120 A**, 59 (1928). Bowden, ibid. **125 A**, 446 (1929).

[2] Erdey Gruz a. Volmer, Z. physik. Chem., **150 A**, 203 (1930).

[3] A. Frumkin, Sow. Phys., **4**, 260 (1933).

In parts I[4] and II[5] a large amount of experimental data was presented concerning the charging process and the adsorption properties of a platinized platinum electrode which enables us to draw some conclusions as to the mechanism of the formation of the potential difference. In the present communication we shall limit ourselves to a theoretical treatment of a part of the material obtained, referring the readers to parts I and II for all the experimental details. The latter contain data which make it possible to establish the degree of precision with which our assumptions concerning the behaviour of the electrode are realized in practice.

Experimental

Three experimental methods have been used to investigate the state of the electrode surface, namely:

1. Following Bowden and Rideal as well as Butler and his co-workers[6], determinations have been made of the amount of electricity per cm², Q, which is necessary to shift the potential of the electrode from a certain initial value in the neighbourhood of the reversible hydrogen potential (in most cases by 0,02 V more anodic than the latter), towards the oxygen potential in a solution with a definite concentration of hydrogen ions. We have found that if the charging process is carried out in a liquid saturated with nitrogen, using platinized electrodes with a very large surface, and if the current density is held within certain limits, the electrode may be considered with a certain approximation to be „completely polarizable" within a definite polarization range; that is, it may be assumed that for a given composition of the solution its state is determined only by the value of Q. The exactness of this approximation decreases with increasing anodic polarization of the electrode; it ceases to be correct when the electrode is covered

[4] Šlygin a. Frumkin, Acta Physicochimica URSS, **3**, 791 (1935); preliminary report C. R. Ac. Sci. URSS, **2**, 176 (1934); Sow. Phys., loc. cit., p. 246.

[5] Šlygin, Frumkin a. Medwedowsky, Acta Physicochimica, URSS, **4**, 911 (1936).

[6] Butler a. Armstrong, Proc. Roy. Soc., **137 A**, 604 (1932); Armstrong, Himsworth a. Butler, ibid. **143 A**, 89 (1933).

with a film of oxide. In acid solutions it holds much better than in alkaline ones. We shall call the curves expressing φ as a function of Q the „charging curves". Let us denote by A the amount of hydrogen adsorbed per cm² of the apparent surface of the metal, by E the free charge per cm², by Γ_H the surface density of hydrogen in the sense of Gibbs' thermodynamics, i. e. the amount of hydrogen which disappears when 1 cm² of the surface layer metal-solution is formed; then, expressing A, Γ_H and E in coulombs per cm² of apparent surface, we have

$$\Gamma_H = A - E. \tag{1}$$

A positive value of E corresponds to a negative value of Γ_H since during the formation of positive charges in the double layer, which occurs through a discharge of hydrogen ions, hydrogen atoms are liberated. Further, denoting by A_0, E_0 and $(\Gamma_H)_0$ the values of these variables, corresponding to $Q = 0$, we obtain:

$$Q = (\Gamma_H)_0 - \Gamma_H = (A_0 - A) + (E - E_0). \tag{2}$$

Thus the charging curve of the electrode gives the relation between Γ_H and φ. The metal-solution interface is assumed to be located in such a way as to make $\Gamma_{H_2O} = 0$. A may also have a negative value which means that there is adsorbed oxygen on the surface of the metal.

The relation between Γ_H and φ is also one between Γ_H and μ_H denoting by μ_H the thermodynamic potential of atomic hydrogen. In fact, expressing the thermodynamic potentials in electrical units we obtain:

$$\varphi = \mu_{H^+} - \mu_H + \text{const}, \tag{3}$$

where μ_{H^+} is the thermodynamic potential of hydrogen ions. Assuming $\mu_H = 0$ for atmospheric pressure of hydrogen and denoting $\varphi - \varphi_0$ by φ_r, where φ_0 is the reversible hydrogen potential in the given solution, we obtain from (3):

$$\mu_H = -\varphi_r. \tag{3a}$$

2. The second method gives the relation between the value of Γ_H and the composition of the solution, e. g. the value of μ_H. The following example makes it clear. The electrode is polarized in a

solution of norm. NaCl + 0,01 norm. HCl until a certain value of φ_r is reached, for which a certain amount of electricity Q is necessary. After this the polarization is stopped, the stability of the potential checked, and in an atmosphere of nitrogen a certain amount of alkali is added to the solution, bringing its composition to, say, norm. NaCl + 0,05 norm. NaOH; the electrode potential is then measured, as well as the amount of electricity required to bring the electrode back to a definite initial value of φ_r from which the measurement of $\varphi_r - Q$ curves is started. In changing the composition of the solution under the conditions described the value of Γ_H is kept constant; thus, on two $\varphi_r - Q$ curves, we find points corresponding to equal values of Γ_H, and hence $(\Delta\Gamma_H)_Q$, the difference between the values of Γ_H corresponding to equal Q's in the two solutions. $(\Delta\Gamma_H)_Q$ should remain constant, irrespective of the choice of Q; as will be seen below, experiment confirms this conlusion with a certain approximation, so long as the value of φ_r does not exceed 0,2 — 0,3 V; at higher anodic polarizations the electrode potential is less stable after the polarizing current is interrupted. Until now this method has been used only on a limited scale, and the data obtained are here published for the first time.

3. The third method consists in measuring the change of the amount of hydrogen ions in a solution, caused by the formation of a double layer at a definite potential. A detailed description of it is given in part II. This method directly yields the value of Γ_{H^+} — the surface density of hydrogen ions. If the measurements are carried out in a solution in which the hydrogen ion concentration is low compared with that of other cations, practically all of the hydrogen ions which might be present in the double layer will be replaced by these cations and appear in the bulk of the solution. In this case the number of hydrogen ions appearing in the solution when the metal surface acquires negative charges, is equal to the number of these charges, that is

$$\Gamma_{H^+} = E \qquad (4)$$

if Γ_{H^+} is expressed in coulombs per cm². The same reasoning holds of course also for a positively charged surface. From (4) and (1) it follows that

$$A = \Gamma_H + \Gamma_{H^+} \qquad (4a)$$

It should be noted that if the hydrogen ions were also held in the surface layer by forces other than electrostatic, and were unable to exchange with other cations of the solution, these ions could not be detected in measuring Γ_{H^+}, and the corresponding part of the surface charge would not be included in E. Hydrogen thus combined would be accounted for not as ionic, but as atomic. It is also evident that in the case of a negatively charged surface immersed in a solution containing no excess of other cations, eq. (4) is no longer justified since in this case as a first approximation $\Gamma_{H^+} = 0$, regardless of the value of E.

We shall call the curve showing the relation between Γ_{H^+} or E and φ_r the adsorption curve of the solution; a combination of this curve with the charging curve enables us to find the values of A according to (1), and hence, by the second method, the dependence of these values on the composition of the solution.

Surface conditions of the platinum electrode in acidulated and alkalized solutions of sodium chloride and sodium bromide

We shall now give the results of the application of these methods to NaCl and NaBr solutions; other electrolytes investigated by the present writers (Na_2SO_4, H_2SO_4, HCl and HBr) either have not been studied so thoroughly, or present some additional difficulties that still need to be elucidated, for which reason we shall not dwell upon them here. Fig. 1 shows the charging curves for acidulated (norm. NaCl + 0,01 norm. HCl, continuous curve Q_I) and alkalized (norm. NaCl + 0,05 norm. NaOH, continuous curve Q_{II}) sodium chloride; Fig. 2 represents similar curves for NaBr. The potentials have been measured against a reversible hydrogen electrode in the same solution.

Further, these figures give the curves showing the relation between φ_r and E (the symbols I and II referring again to the acid and alkaline solutions), and the values of A (dotted curves) obtained by subtracting E from Q for which the abscissa corresponding to $A = 0$ remains as yet undetermined. Let us examine the dotted curves A_I in acid solutions. These curves follow a vertical direction within a rather considerable potential range; within this range the

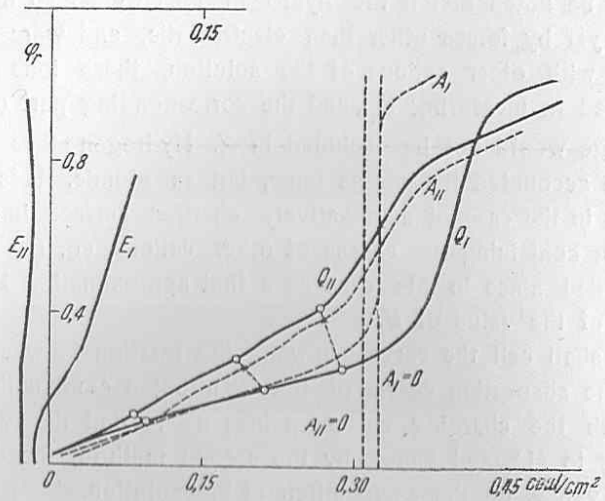

Fig. 1.
Charging curves and adsorption curves in acidulated (I) and alkalized (II) sodium chloride.

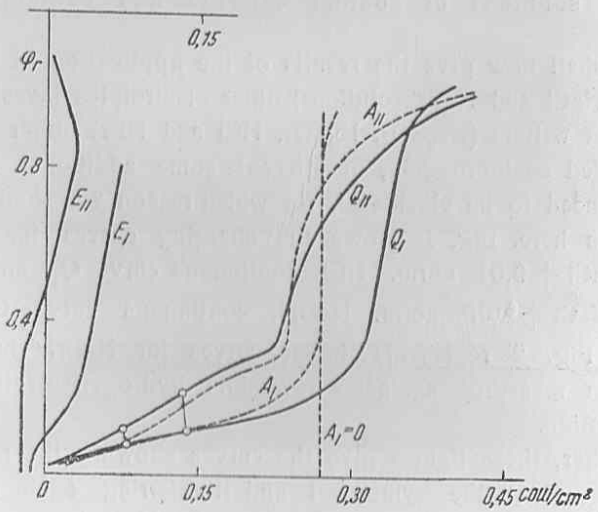

Fig. 2.
Charging curves and adsorption curves in acidulated (I) and alkalized (II) sodium bromide

value of A is independent of φ_r, the total amount of Q being consumed according to equation (2) for an increase of E, i. e. charging

the double layer. The fact that in this interval A is independent of φ_r may be naturally explained on the assumption that $A = 0$, i. e. that within this range the surface of the metal is free from adsorbed gases. At lower values of φ_r, A is positive, and hydrogen is adsorbed on platinum, whilst at higher values A is negative, which corresponds to the oxidation of the electrode. With no experimental values of E available it is still possible to obtain a first approximation of the $\varphi_r - A$ curve in an acid solution by drawing a tangent to the $\varphi_r - Q$ curve in its rectilinear part, and assuming the value of A for each φ_r to be equal to the horizontal distance between this tangent and the $\varphi_r - Q$ curve. This method of computation is based on the assumption that the capacity of the double layer remains constant irrespective of φ_r, which is incorrect; the error, however, but slightly affects the values of A, since the correction for E throughout the greater part of the curve is small when compared to A, whilst in the part where it is large, its value is correctly taken into account.

Two points on the charging curve are of particular interest, namely: the intersection of the charging curve with the straight line $A = 0$, which corresponds to $\Gamma_н = 0$, and the point at which $E = 0$, i. e. the point of zero charge of the double layer. The position of this point depends very much on the adsorbability of the anion. This was discussed in detail in part II.

In the case of alkalized solutions the $\varphi_r - A$ curves, obtained by substracting from Q the values of E found experimentally, have no vertical part, and it is therefore impossible to find in this way the value of Q which corresponds to $A = 0$.

The problem can be solved by using the second of the above-described methods. In Fig. 1 and 2 the points coresponding to equal values of $\Gamma_н$ on curves Q_I and Q_{II} are connected by arrows. For $(\Delta\Gamma_н)_Q$, the difference between the values of $\Gamma_н$ corresponding to equal Q's in the acid and alkaline solutions, an average of $1{,}6 \cdot 10^{-2}$ coul/cm² is obtained in NaCl, and of $0{,}2 \cdot 10^{-2}$ coul/cm² in NaBr. If a straight line $A_{II} = 0$ is drawn parallel to $A_I = 0$ at a distance $(\Delta\Gamma_н)_Q$ from it (Fig. 1) the point of intersection of this line with the curve Q_{II} gives the value of φ_r at which $\Gamma_н = 0$ in the alkalized solution, whilst the intersection with the dotted curve A_{II}

gives the value of φ_r which corresponds to a zero value of A in the same solution. Since the alkalized solutions, unlike the acidulated ones, have no polarization range within which A would be equal to zero, the hydrogen zone is not separated in these solutions from the oxygen zone but merges directly into it [7]; in other words, in alkaline solutions the surface of the electrode retains adsorbed gases at all polarizations, and the deposition of oxygen begins before all of the hydrogen has been removed from the surface.

Adsorption of hydrogen on platinum

The values of A thus obtained determine the „characteristic curve" of hydrogen adsorption on platinum, i. e. the relation between the thermodynamic potential $\mu_H = -\varphi_r$ and the amount of adsorbed hydrogen A, which is well known from Polanyi's adsorption theory [8].

In order to obtain this curve in the usual form it is only necessary to rotate the $\varphi_r - A$ curve 180° about the $A = 0$ axis and convert volts and coulombs into calories and mols. We have preferred, however, to retain electrical units throughout. Fig. 3 shows the characteristic curves of hydrogen adsorption on platinum, in acid (I) and alkaline (II) solutions of NaCl. These curves are on the whole similar to those usually obtained in the case of adsorption on porous adsorbents. The great length of the rectilinear part, especially well pronounced on curve I, is of interest. A linear relation between the amount adsorbed and the chemical potential, or the logarithm of hydrogen pressure, may be explained on the assumption either of repulsive forces existing between the adsorbed hydrogen atoms, or of adsorption heat decreasing according to a linear law

[7] In the case of NaBr the inflexion on the dotted curve A_{II} may possibly indicate some separation, although not quite clearly pronounced, between the hydrogen and the oxygen zones. Its position, however, somewhat deviates from what could be expected from experiments conducted by the second method. Curve A_{II} in NaCl does not show this peculiarity.

[8] In one of his early papers Polanyi [Z. physik. Chem., 88, 628 (1914)] has already suggested the possibility of finding the characteristic curve of a metallic deposit from electrode potential measurements.

as the surface is filled up with adsorbed hydrogen (M. Temkin) [4]. If the shape of the characteristic curve is determined by the non-uniformity of the platinum surface, it should change considerably when the deposit is sintered, since the relative number of points having a higher value of adsorption potential, should diminish with a decrease in dispersity. But if a decisive part is played by the forces of interaction between adsorbed atoms, the characteristic curves of deposits with various degrees of dispersity might be expect-

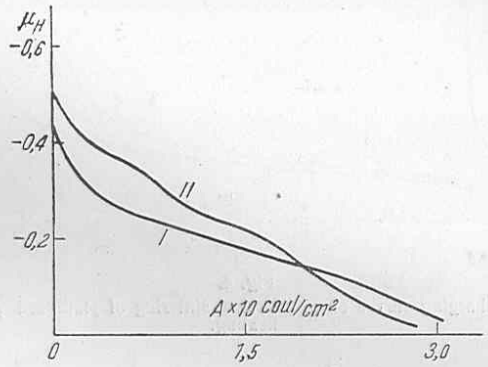

Fig. 3.
Characteristic curves of hydrogen adsorption on platinum in acidulated (I) and alkalized (II) sodium chloride.

ed to differ, as a first approximation, only in the scale of the abscissae axis. As shown by Figs. 4 and 5, experiment decides in favour of the first assumption [9]. Fig. 4 gives the $\varphi_r - Q$ curves of a usual platinized electrode and of the deposits obtained by its sintering during two hours in an atmosphere of hydrogen at 40, 60, 80, 200 and 300° C respectively. After sintering at 300° the electrode surface diminished 30 times.

It should be noted that as the deactivation of the electrode proceeds, the velocity of the ionization of the adsorbed hydrogen is very much reduced. In order to attain a closer approximation to the equilibrium conditions the current densities in the measurements with sintered electrodes were reduced so as to increase

[9] These data are taken from a thesis presented to the chemical faculty of the University of Moscow by A. Chachaew, stud. chem.

the duration of the removal of adsorbed hydrogen to six hours instead of two as in the case of an experiment with the initial electrode. In spite of this, the curves obtained with sintered electrodes give a poorer approximation to equilibrium conditions than normal $\varphi_r - Q$ curves. More detailed data will be published elsewhere.

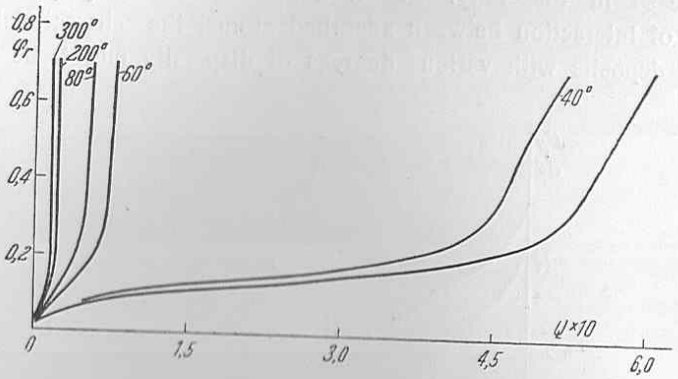

Fig. 4.
Change of charging curves on progressive sintering of platinized platinum by heating.

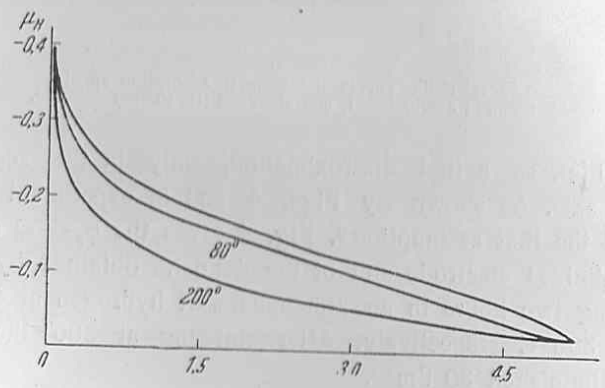

Fig. 5.
Change of the characteristic curves of hydrogen adsorption on heating platinized platinum. Abscissae: A × 10; 80° A × 110; 200° A × 230.

From these curves, using the approximate method as described above, characteristic curves have been calculated. Fig. 5 gives the $\mu_H - A$ curves for the initial deposit and the deposites sintered at 80° and 200°. By an appropriate choice of the abscissae scale the points of the curves corresponding to $\mu_H = -0{,}02$ V, have been

brought to coincidence. It follows from Fig. 5 that the sintering of the deposit not only produces a decreas of its total surface, but also a change in the shape of the characteristic curves just in the direction which might be expected for a non-uniform surface.

The sintering of the deposit is very much influenced by the nature of the gas in which it is heated. In air after a two-hours heating to 100° the surface decreases only by 8 per cent, and after a heating to 300° only by 50 per cent; it is evident that in this

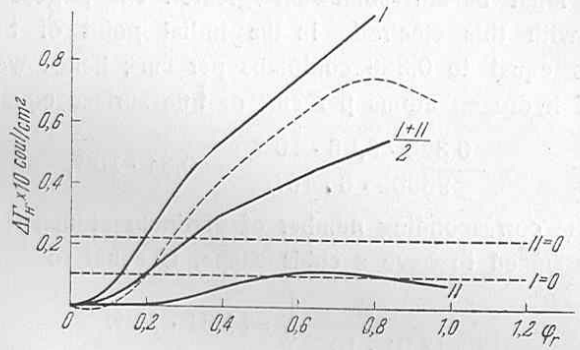

Fig. 6.
Calculated---- and observed—— adsorption curves in sodium chloride.

case the layer of chemically bound oxygen stabilizes the platinum crystallites.

A comparison of the $\mu_H - A$ curves obtained in acid and alkaline solutions (Fig. 3) shows that the adsorption potential of hydrogen depends strongly on μ_H, and that with low values of A the adsorption potential is much higher in an alkaline solution, whilst with larger values of A, the sign of this effect is reversed. Some consequences of this peculiar relation between the two $\mu_H - A$ curves will be considered in the following discussion.

A considerable interest is attached also to the question of the maximum amount of hydrogen taken up by the electrode per unit surface. To solve it, it is necessary, however, to know the true value of the surface of the platinum electrode. The most reliable data may be obtained by comparing the capacity of the platinized electrode with that of a smooth one within the interval of potentials in which on the surface of both of them there is only

an electric double layer. Measurements carried out at the Karpov Institute by B. Ershler gave within this range of potentials a value of $17 \cdot 10^{-6}$ farads/cm² for the double layer capacity of a smooth platinum electrode in norm. HCl, which may be compared with the value of 0,101 farads/cm² obtained with a platinized electrode in acidulated KCl. If we consider the true surface of a smooth electrode to be equal to the apparent one, the true surface of this particular platinized electrode exceeded its apparent surface $6 \cdot 10^3$ times. Actually this ratio must be still somewhat greater. The largest value of A, observed with this electrode in the initial point of the charging curve, was equal to 0,326 coulombs per cm²; hence we obtain the number of hydrogen atoms per cm² of true surface equal to

$$\frac{0{,}326 \cdot 6{,}06 \cdot 10^{23}}{96500 \cdot 6 \cdot 10^3} = 0{,}34 \cdot 10^{15},$$

whereas the corresponding number of platinum atoms, if the crystallites are assumed to have a cubic shape, is equal to

$$\frac{2}{(3{,}91 \cdot 10^{-8})^2} = 1{,}31 \cdot 10^{15}.$$

Thus, the ratio of hydrogen to platinum atoms is about one to four [10].

The platinum electrode as a two-component adsorption system

The $E - \varphi_r$ curves for acidulated (I) and alkalized (II) solutions of NaCl and NaBr are given in Figs. 6 and 7 [11]. If the capacity of the double layer remained constant with a change in φ_r, and the metal-hydrogen bond had no dipole moment, the $E - \varphi_r$ curve should become a straight line. Actually these curves have a rectilinear course only in the interval of values which corresponds to $A = 0$, considerably deviating from it with other values of φ_r,

[10] In part I a considerably higher value was given for the surface concentration of hydrogen. This was based on the assumption of the equality of the capacity of the double layer on platinum and mercury, which turned out to be wrong.

[11] The ordinates are plotted from the value of $E = \Gamma'_H$ which corresponds to $\varphi_r = 0$. The true position of the zero values of E is given by the dotted straight lines $I = 0$ and $II = 0$.

which shows that adsorbed hydrogen and oxygen have both a marked influence upon the course of the $E - \varphi_r$ curve. In this paper we shall limit ourselves to the study of the hydrogen region.

The anomalies observed in the hydrogen zone ($A > 0$), which have already been discussed in part II, may be interpreted, at least qualitatively, by making the assumption that the introduction of hydrogen atoms into the surface layer increases the value of φ, if E is kept constant, at the same time diminishing the capacity of the double layer. The first of these conclusions appears rather unexpected,

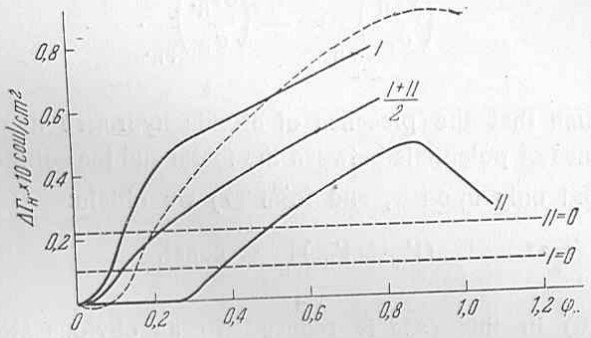

Fig. 7.
Calculated- - - -and observed——adsorption curves in sodium bromide.

but as will be shown presently, it may be confirmed by an independent method.

The state of the surface of the platinum electrode in an acidulated or alkalized NaCl solution is determined by the surface densities Γ_H, $\Gamma_{H'}$, $\Gamma_{Cl'}$ and $\Gamma_{Na'}$; according to Gibbs we have the following relation:

$$d\sigma = -\Gamma_H \, d\mu_H - \Gamma_{H'} \, d\mu_{H'} - \Gamma_{Cl'} \, d\mu_{Cl'} - \Gamma_{Na'} \, d\mu_{Na'}, \qquad (5)$$

where σ is the interfacial tension at the metal-solution interface.

Since $\mu_{Cl'}$ and $\mu_{Na'}$ under the conditions of our experiment may be considered as practically constant, equation (5) is reduced to

$$d\sigma = -\Gamma_H \, d\mu_H - \Gamma_{H'} \, d\mu_{H'} \qquad (5a)$$

From equation (5a) it follows that

$$\left(\frac{\partial \Gamma_H}{\partial \mu_{H'}}\right)_{\mu_H} = \left(\frac{\partial \Gamma_{H'}}{\partial \mu_H}\right)_{\mu_{H'}} \qquad (6)$$

or

$$\left(\frac{\partial \Gamma_H}{\partial \mu_{H\cdot}}\right)_{\varphi_r} = -\left(\frac{\partial \Gamma_{H\cdot}}{\partial \varphi_r}\right)_{\mu_{H\cdot}}. \qquad (6a)$$

Relations similar to equation (6) have proved to be very useful in the study of electrocapillary phenomena [12].

A particular case of equation (6) has already been applied by one of us to the hydrogen electrode. From (6) and (3) it follows:

$$\left(\frac{\partial \Gamma_H}{\partial \varphi}\right)_{\mu_H} = -\left(\frac{\partial \Gamma_{H\cdot}}{\partial \varphi}\right)_{\mu_{H\cdot}}. \qquad (7)$$

If we assume that the presence of atomic hydrogen does not affect the difference of potentials between the metal and the solution, $\Gamma_{H\cdot} = E$ must depend only upon φ, and from (7) we obtain:

$$(\Gamma_H + \Gamma_{H\cdot})_{\mu_H} = \text{const.} \qquad (8)$$

Equation (6) in this case is reduced to an obvious stoichiometric relation between the hydrogen disappearing from the gaseous phase and the hydrogen ions appearing in the solution. Equation (8) was confirmed within a certain range by measuring the amount of hydrogen, which disappears when alkali is adsorbed on platinized charcoal in a hydrogen atmosphere [13], but is not applicable to a platinum electrode.

In order to check the more general thermodynamic relation (6) it is necessary to know two $\varphi_r - Q$ curves, corresponding to slightly different values of $\mu_{H\cdot}$ and to determine for some value of φ_r the change of Γ_H with $\mu_{H\cdot}$ by the second method. Equation (6a) allows one then to find the $\Gamma_{H\cdot} - \varphi_r$ curve if its initial point is known and to compare it with the experimental curve. Unfortunately the experimental material available does not allow us yet to carry out the calculations in this way. When measuring the $\varphi_r - Q$ curve it is difficult to maintain the hydrogen ion concentration strictly constant;

[12] Frumkin, Z. Physik, **35**, 792 (1926); Frumkin a. Gorodetzkaja, Z. physik. Chem., **136**, 451 (1928).

[13] Bruns a. Frumkin, Z. physik. Chem., **147 A**, 125 (1930).

moreover, the calculation of $\frac{\partial \Gamma_H}{\partial \mu_{H\cdot}}$ would lead to excessively great errors if the difference between the Γ_H values used is very small. Therefore we have contented ourselves with a more approximate verification, that is, from the $\varphi_r - Q$ curves of an acidulated and an alkalized solution and from the values of $(\Delta\Gamma_H)_Q$ as determined by the second method, the values of the ratio $\left(\frac{\Delta\Gamma_H}{\Delta\mu_{H\cdot}}\right)_{\varphi_r}$ for different φ_r's have been determined, $\Delta\mu_{H\cdot}$ being equal in our case to 0,62 V. From these values the $\Delta\Gamma_{H\cdot} - \varphi_r$ curve was calculated according to equation

$$\Delta\Gamma_{H\cdot} = \Gamma_{H\cdot} - (\Gamma_{H\cdot})_{\varphi_0} = -\int_0^{\varphi_r} \left(\frac{\Delta\Gamma_H}{\Delta\mu_{H\cdot}}\right)_{\varphi_r} d\varphi,$$

where $(\Gamma_{H\cdot})_{\varphi_0}$ is the value of $\Gamma_{H\cdot}$ for $\varphi = \varphi_0$.

The $\Delta\Gamma_{H\cdot} - \varphi_r$ curves for NaCl and NaBr, thus calculated, are given in Figs. 6 and 7 (dotted curves), together with the experimental $\Delta\Gamma_{H\cdot} - \varphi_r$ curves for norm. NaCl + 0,01 norm. HCl and norm. NaBr + 0,01 norm. HBr (I), and similar curves for norm. NaCl + 0,05 norm. NaOH and norm. NaBr + 0,05 norm. NaOH (II). Curves representing the arithmetic mean of the experimental values observed in acid and alkaline solutions are also drawn in these figures. From Figs. 6 and 7 it will be seen that the calculated $\Delta\Gamma_{H\cdot} - \varphi_r$ curve possesses all the characteristic peculiarities of the observed ones: at the beginning the curve is almost horizontal, then rises sharply, passes into a nearly rectilinear part and finally reaches a maximum.

Although there is no strict quantitative coincidence between the calculated $\Delta\Gamma_{H\cdot} - \varphi_r$ curves and the curves which give mean values $^1/_2$ (I + II) from experimental data, their resemblance is most striking. This fact confirms the correctness of our interpretation of the $\Gamma_H - \varphi_r$ curves and of those conclusions concerning the properties of adsorbed hydrogen, which we drew from their examination. We hope that a refinement of the experimental procedure will enable

us to eliminate the discrepancies between the observed and calculated $\Delta\Gamma_{H^\cdot} - \varphi_r$ curves.

The influence of the atomic and ionic coating on the magnitude of the potential difference is determined by the values of

$$X = \left(\frac{\partial\varphi}{\partial A}\right)_{\Gamma_{H^\cdot}} \text{ and } Y = \left(\frac{\partial\varphi}{\partial\Gamma_{H^\cdot}}\right)_{A}.$$

These quantities may be determined if the charging curves and the adsorption curves for different $\mu_{H^\cdot}$ are known. From the relation $d\varphi = XdA + Yd\Gamma_{H^\cdot}$ we obtain by introducing independent variables μ_H and $\mu_{H^\cdot}$ and substituting according to (3)

$$d\mu_{H^\cdot} - d\varphi \text{ for } d\mu_H:$$

$$X\left(\frac{\partial A}{\partial\mu_H}\right)_{\mu_{H^\cdot}} + Y\left(\frac{\partial\Gamma_{H^\cdot}}{\partial\mu_H}\right)_{\mu_{H^\cdot}} = -1 \qquad (9)$$

$$X\left[\left(\frac{\partial A}{\partial\mu_H}\right)_{\mu_{H^\cdot}} + \left(\frac{\partial A}{\partial\mu_{H^\cdot}}\right)_{\mu_H}\right] + Y\left[\left(\frac{\partial\Gamma_{H^\cdot}}{\partial\mu_H}\right)_{\mu_{H^\cdot}} + \left(\frac{\partial\Gamma_{H^\cdot}}{\partial\mu_{H^\cdot}}\right)_{\mu_H}\right] = 0.$$

From equations (9), (6) and (4a) it follows:

$$X = -\left(\frac{\partial A}{\partial\mu_{H^\cdot}}\right)_{\mu_H} : Z \qquad (10)$$

and

$$Y = \left[\left(\frac{\partial A}{\partial\mu_{H^\cdot}}\right)_{\mu_H} + \left(\frac{\partial A}{\partial\mu_H}\right)_{\mu_{H^\cdot}}\right] : Z, \qquad (10a)$$

where

$$Z = \left(\frac{\partial\Gamma_{H^\cdot}}{\partial\mu_{H^\cdot}}\right)_{\mu_H}\left(\frac{\partial A}{\partial\mu_H}\right)_{\mu_{H^\cdot}} - \left(\frac{\partial\Gamma_{H^\cdot}}{\partial\mu_H}\right)_{\mu_{H^\cdot}}\left(\frac{\partial A}{\partial\mu_{H^\cdot}}\right)_{\mu_H} =$$

$$= \left(\frac{\partial\Gamma_H}{\partial\mu_H}\right)_{\mu_{H^\cdot}}\left(\frac{\partial\Gamma_{H^\cdot}}{\partial\mu_{H^\cdot}}\right)_{\mu_H} - \left(\frac{\partial\Gamma_H}{\partial\mu_{H^\cdot}}\right)^2_{\mu_H}.$$

Finally, from (10) and (10 *a*) we obtain

$$\left(\frac{\partial\Gamma_{H^\cdot}}{\partial A}\right)_\varphi = -\frac{X}{Y} = \frac{\left(\frac{\partial A}{\partial\mu_{H^\cdot}}\right)_{\mu_H}}{\left(\frac{\partial A}{\partial\mu_H}\right)_{\mu_{H^\cdot}} + \left(\frac{\partial A}{\partial\mu_{H^\cdot}}\right)_{\mu_H}}. \qquad (11)$$

It seems natural to assume that under all conditions the introduction of a hydrogen atom into the surface layer exercises a smaller influence upon the potential difference than the introduction of an ion and a corresponding opposite charge; the absolute value of $\left(\frac{\partial\Gamma_{H^\cdot}}{\partial A}\right)_\varphi$ must therefore be less than unity. Since $\left(\frac{\partial A}{\partial\mu_H}\right)_{\mu_{H^\cdot}} > 0$ the sum $\left(\frac{\partial A}{\partial\mu_H}\right)_{\mu_{H^\cdot}} + \left(\frac{\partial A}{\partial\mu_{H^\cdot}}\right)_{\mu_H}$ must therefore be positive too.

Finally, since $Y > 0$, it follows from (10a) that $Z > 0$ and hence X has a sign opposite to that of $\left(\frac{\partial A}{\partial\mu_{H^\cdot}}\right)_{\mu_H}$.

From equation (10) and Fig. 3 we see that when the values of A are not too high, $X > 0$; in other words, the introduction of a hydrogen atom into the surface layer increases the difference of potentials between metal and solution. This effect may be due to two causes: 1) the metal-hydrogen bond is of a polar character; 2) the introduction of hydrogen lowers the capacity of the ionic double layer, owing to which with a constant $\Gamma_{H^\cdot}$ the potential difference in the double layer increases in its absolute value. If we consider that in the latter case the value of $\left(\frac{\partial\varphi}{\partial A}\right)_{\Gamma_{H^\cdot}}$ should always have the same sign as $\Gamma_{H^\cdot}$ and become equal to zero together with $\Gamma_{H^\cdot}$, an examination of the curves given in Fig. 1 shows that the second factor cannot explain the positive values of X observed in the range in question. In fact, let us take, for example, the points corresponding to $\mu_H = -0{,}3$ on curves A_I and A_{II} (Fig. 1). The value of $\Gamma_{H^\cdot}$ for an acidulated and an alkalized solutions are in this case

close in magnitude and opposite in sign, the mean value of $\Gamma_{H\cdot}$ within the whole $\mu_{H\cdot}$ range therefore approaching zero. However, just in the neighbourhood of this μ_H value, X attains its maximum. Thus the observed phenomena cannot be explained without ascribing a dipole moment to the metal-hydrogen bond.

If we assume that the centers of the hydrogen atoms lie nearer to the solution than the external layer of the metal lattice, then, in order to account for the effect observed, hydrogen is to be considered as the negative end of the dipole. It may be more probable that the hydrogen atoms lie deeper in the metal than the external layer of the metal lattice and carry a positive charge; however, the data available do not enable us to solve this problem.

With high values of A, $\left(\frac{\partial A}{\partial \mu_{H\cdot}}\right)_{\mu_H}$ becomes positive, and X negative. It may be supposed that the difference of potentials, determined by the dipole moments of the metal-hydrogen bonds, passes through a maximum when the amount of hydrogen is increased and then falls, — as is the case with layers of Cs on W; such an assumption, however, is not necessary. In this region of A values $\Gamma_{H\cdot}$ is negative with all $\mu_{H\cdot}$, and the negative value of X may be accounted for by a decrease in the capacity of the double layer caused by the introduction of hydrogen. That such a decrease in the capacity actually takes place may be proved by measurements of the relation between $\Gamma_{H\cdot}$ and $\mu_{H\cdot}$ for platinized platinum saturated with hydrogen at atmospheric pressure, i. e. for a usual reversible hydrogen electrode [14]. These experiments [15] which will be described in detail elsewhere were carried out by the method of potentiometric titration. 20 c. c. of norm. NaCl + 0,0009 norm. HCl were first titrated with norm. NaCl + 0,024 norm. NaOH using an ordinary small hydrogen electrode, and curve *a* in Fig. 8 was obtained; then, the same titration was carried out with a large platinized electrode, having an apparent surface of 39,6 cm^2, on which 2,1 g of platinum had been deposited [16]. The curve obtained is given in Fig. 8b. From these two curves of potentiometric titration it is easy to calculate the amount of alkali adsorbed by the electrode at different potentials and hence to find the relation between $\Gamma_{H\cdot}=E$ and the potential of the electrode φ, which varies in this case with $\mu_{H\cdot}$ at constant μ_H.

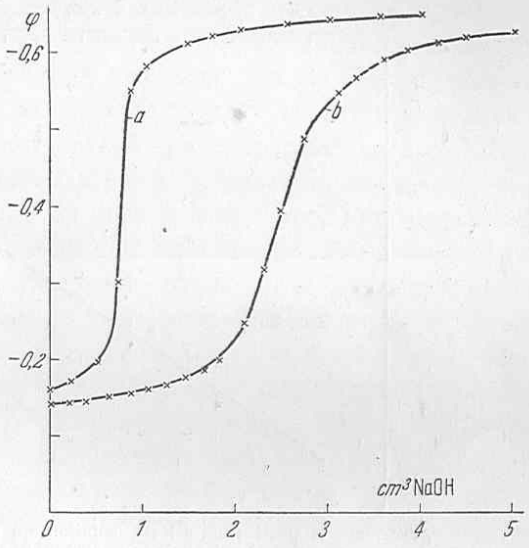

Fig. 8.
Potentiometric titration of NaCl + HCl with a NaCl + + NaOH solution using a small (*a*) and a large (*b*) platinum electrodes.

As is shown by Fig. 9 the $\Gamma_{H\cdot} - \varphi$ curve obtained has a nearly rectilinear character [17] unlike the adsorption curves observed when the electrode potential is changed by polarization at constant $\mu_{H\cdot}$. This is easy to understand since in this case the complications produced in the structure of the double layer by changes of the atomic layer are largely removed. The average capacity of the electrode calculated from the curve of Fig. 9 is, however, 3,7 times smaller than the capacity observed with the same electrode in the rectilinear part of the charging curve of acidulated sodium chloride, in which we deal with a double layer deposited on a bare surface

[14] It would be more correct to conduct the measurements not at constant atmospheric pressure of hydrogen, but with a constant value of A, but as it follows from the curves in Fig. 3, the value of A near the reversible hydrogen potential does not change very much with a change of $\mu_{H\cdot}$ if μ_H is kept constant.

[15] From a thesis presented to the chemical faculty of the Moscow University by A. Platonov, stud. chem.

[16] This electrode had a true surface several times exceeding the surface of the electrodes with which the curves given in Figs. 1 a. 2 were obtained.

[17] At present it is difficult to decide, whether the observed deviations from linearity have a real significance.

of the metal, not covered by adsorbed hydrogen. The prolongation of the straight line in Fig. 9 cuts the abscissae axis at $\varphi = 0{,}24$; at this value of φ $\Gamma_{H^+} = 0$. In other experiments somewhat different values were obtained, the average being 0,29. The position of the zero charge point thus determined distinctly differs from that found experimentally from the adsorption curves obtained when the electrode is polarized. This difference is due to the fact that in the

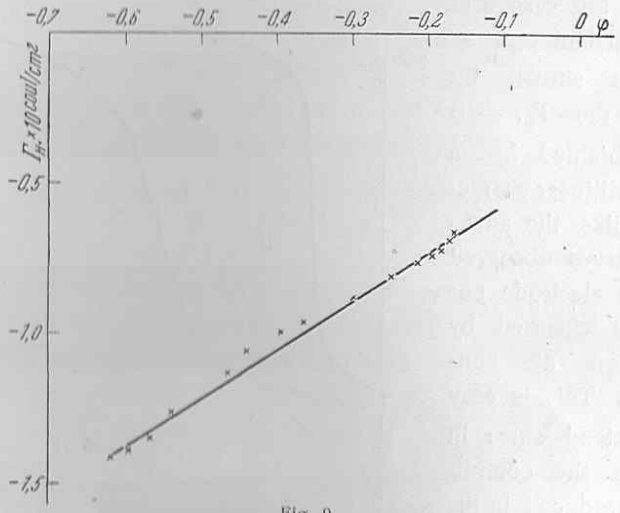

Fig. 9.
Adsorption of alkali from a NaCl solution on a reversible hydrogen electrode at different potentials (The amount of alkali adsorbed is equal to Γ_{H^+}).

former case we have a surface carrying a much greater amount of adsorbed hydrogen than in the latter. Moreover, the points of zero charge, as found experimentally in acid solutions of sodium chloride and sodium bromide, are shifted under the influence of the specific adsorption of the anion. The latter factor probably practically vanishes in acidulated Na_2SO_4 solution (see Part II); in this case the point of zero charge lies at $\varphi = 0{,}11$. The corresponding value of A constitutes about one third of the value observed for an electrode saturated with H_2 at atmospheric pressure. If the potential difference produced by the adsorbed hydrogen is considered to be approximately proportional to the value of A, which is of course a very rough approximation, then on a surface completely free from adsorbed hydrogen, the point of zero charge should lie at $\varphi = 0{,}02$. The presence of adsorbed hydrogen may thus produce a potential difference of about 0,3 V. On account of the assumptions made in computing this quantity it may be however largely in error. Moreover, this quantity has been calculated for the case of an absence of any ionic charge, and may change considerably in the presence of ions in the double layer. From this fact, as well as from the above-stated influence of adsorbed hydrogen upon the capacity of the double layer it follows that the potential difference cannot be represented in the form of a sum of two terms, one of which would be dependent only on the ions, and the other on the atoms. On the basis of equations (10) and (10a) an attempt may be made to build up a theory in which the value of φ would be represented as a more complicated function of A and E. The experimental material available is, however, as yet not exact enough for this purpose and we think it more correct to postpone such an attempt until more complete data are obtained. The theory of the platinum electrode here developed, according to which part of the adsorbed hydrogen is assumed to be present in the form of atoms, while the other is ionised and may exchange with other ions, — has many points in common with the theory of adsorbed layers of alkaline metals, which has been so extensively developed during last years. It should be borne in mind, however, that while in the case of adsorbed atoms of alkaline metals all intermediate states between adatom and adion are possible, and they freely pass one into another, in the presence of an aqueous solution, the formation of ions is connected with a hydration process and is therefore a reaction with a definite activation energy, due to which we should make a strict distinction between the adsorbed atom and the adsorbed ion of hydrogen.

Conclusions

Briefly, the main results may be summarized as follows: we have investigated in the region between the reversible hydrogen and oxygen potentials the change in the potential of the platinized electrode when charging it with direct current (charging curves) and determined the relation between the number of ions adsorbed by the electrode and the potential (adsorption curves) as well as the influence of a change in the composition of the solution on the potential of a previously insulated polarized electrode. The totality of these data enables us to determine the amount of adsorbed gases at the elec-

trode surface and the charge of the double layer. In acid solutions there exists a potential range within which the surface of the electrode is practically free of adsorbed gases and carries only an ionic double layer whose charge in this case fully determines the value of the potential difference; in all other cases it is necessary to consider the influence of adsorbed gases on the potential difference. In the neighbourhood of the reversible hydrogen potential, especially in alkaline solutions, the change of the potential difference during anodic polarization is determined almost solely by the change in the amount of adsorbed hydrogen, the charge of the double layer remaining constant. However, if the potential of the electrode is varied at atmospheric pressure of hydrogen as a function of the acidity of the solution (potentiometric titration with a large platinized electrode), i. e. under conditions when the amount of hydrogen adsorbed changes but slightly, an approximately linear relation between the potential of the electrode and the charge of the double layer is obtained.

The effect of adsorbed hydrogen upon the difference of potential metal-solution may be interpreted on the assumption that the introduction of hydrogen into the surface layer increases the difference of potential metal-solution, at the same time decreasing the capacity of the double layer.

A combined use of the charging and the adsorption curves enables one to find the relation between the thermodynamic potential and the amount of hydrogen adsorbed, that is, to determine the characteristic curve of hydrogen adsorption on platinum. With the help of these curves the changes in the properties of the platinum surface on progressive heating and the influence of the composition of the solution on hydrogen adsorption can be investigated.

Considering the surface of platinum as an adsorption system the state of which is determined by the surface densities of both hydrogen and hydrogen ions, we obtain a relation (6) which enables us to find the adsorption curve from two charging curves measured at different values of p_H. of the solution and from a determination of the change in the potential of an insulated electrode caused by substitution of one solution for another. The results of such a calculation are in semi-quantitative agreement with experiment.

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