THE DEPENDENCE OF THE DOUBLE-LAYER CHARGE ON THE PLATINUM HYDROGEN ELECTRODE SURFACE UPON THE POTENTIAL

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(Received July 20th, 1966)

Dedicated to Professor M. von Stackelberg on his 70th birthday

Whereas the application of Gibbs thermodynamics of the surface phenomena to mercury and other liquid metal electrodes has been experimentally substantiated and is at present in common use, the possibility of a similar approach to the electrocapillary phenomena on the surface of the platinum hydrogen electrode has been insufficiently considered in the literature. The first attempt in this direction was made by FRUMKIN AND ŠLYGIN[1] but the formula derived by them was in such a form that it could only be verified semi-quantitatively. Some thermodynamic relations were considered by FRUMKIN, BALASHOVA AND KAZARINOV[2]. In the present study we want to discuss once more some of these relations and to report the results of an experimental verification of one of them, the derivation of which has already been given in more detail by one of the authors[3].

We shall assume that the platinum hydrogen electrode can be considered as being reversible with respect to the ionization reaction of adsorbed hydrogen and the hydrogen ion discharge and will confine ourselves to the case of a binary electrolyte (CA) solution, containing a certain concentration of H^+ or OH^- ions. The assumption of reversibility is practically valid in the case of the platinized-platinum electrode if the solution contains no ions displaying a strongly pronounced specific adsorption[2] (I^-, Tl^+) within the potential range limited on the positive side by the appearance of adsorbed oxygen on the surface. Let us also assume, at first, that the amount of hydrogen dissolved in the bulk of the solution and in the metal can be neglected compared to that present on the electrode surface, and that the concentration of the H^+ ions in the solution is small compared to that of other cations, so that the chemical potential of the cations and anions, C^+ and A^-, remains practically constant with varying hydrogen ion concentration. The state of the system under consideration can be determined by the chemical potentials of atomic hydrogen μ_H, hydrogen ion μ_{H^+}, and the electrolyte ions μ_S. We shall choose the hydrogen atoms H and the ions H^+, C^+ and A^- as the components from which to build the interfacial layer.* Let us

* The system could be also envisaged as composed of H^+ ions and electrons (instead of H^+ ions and H atoms). The final results are the same.

designate by Γ_H, Γ_{H^+}, Γ_{C^+} and Γ_{A^-} the surface densities of these components of the system in the sense of Gibbs, *i.e.*, the amounts of substance that are to be added to the system for the composition of the bulk phase to remain constant with the surface area increased by unity. Let us define the position of the interface by assuming $\Gamma_{H_2O} = 0$. The quantities μ and Γ will be expressed in electrical units. It is essential that the quantity Γ_H includes both the amount of hydrogen adsorbed as H atoms on the platinum surface and the amount expended due to ionization in the formation of a unit surface. This is the quantity that we should find by experiment if we could carry out a direct determination of the hydrogen adsorption on a platinum hydrogen electrode at given μ_{H^-} and μ_{H^+}-values: $-\Gamma_H$ is the electricity stored/unit electrode surface (the minus sign is due to the appearance of a negative charge as the result of ionization of the H atom). In this sense, the quantity $-\Gamma_H$ represents the total charge of unit electrode surface. Γ_H remains constant on open circuit if the supply of electrochemically-active substances to the electrode is hindered. If σ is the surface density of the free energy, φ_r the electrode potential measured against a hydrogen electrode in the same solution, which is in equilibrium with H_2 at atmospheric pressure, φ the electrode potential measured against the normal hydrogen electrode and Q the quantity of electricity to be supplied to the electrode in order to shift its potential at constant μ_{H^+} and μ_S from some initial value, φ_r, to the given one, then these quantities are related by the following formulae:

$$(\mathrm{d}\varphi_r)_{\mu_{H^+},\mu_S} = -(\mathrm{d}\mu_H)_{\mu_{H^+},\mu_S} \tag{1}$$

$$(\mathrm{d}\varphi)_{\mu_S} = (\mathrm{d}\mu_{H^+})_{\mu_S} - (\mathrm{d}\mu_H)_{\mu_S} = (\mathrm{d}\mu_{H^+})_{\mu_S} + (\mathrm{d}\varphi_r)_{\mu_S} \tag{2}$$

$$\Gamma_{H^+} = \Gamma_{A^-} - \Gamma_{C^+} \tag{3}$$

$$\left(\frac{\partial\Gamma_H}{\partial\varphi_r}\right)_{\mu_{H^+},\mu_S} = -\left(\frac{\partial Q}{\partial\varphi_r}\right)_{\mu_{H^+},\mu_S} \tag{4}$$

$$\mathrm{d}\sigma = -\Gamma_H\,\mathrm{d}\mu_H - \Gamma_{H^+}\mathrm{d}\mu_{H^+} - (\Gamma_{C^+} + \Gamma_{A^-})\,\mathrm{d}\mu_S \tag{5}$$

Equations (1) and (2) give the condition of equilibrium between the electrode and the solution, eqn. (3)—the condition of the solution maintaining electroneutrality in the process of adsorption, eqn. (5)—the Gibbs expression for the total differential of the surface free energy for the case under consideration. Equation (4) follows from what has been stated above regarding the value of Γ_H*.

* Let us prove eqn. (4) using the following imaginary cycle. Let us transfer the electrode following the charging curve from state I to state II, the values $(\mu_H)_I$ and $(\mu_H)_{II}$ corresponding to these states, respectively. The quantity of electricity expended in this case will be $(Q_{II} - Q_I)S = \Delta QS$ (S is the electrode surface). Let us now reduce the electrode surface in state II to a value which will be infinitesimal compared to S. By definition, a quantity of hydrogen equivalent to $(\Gamma_H)_{II}S$ will be liberated. Let us transfer the electrode with the reduced surface to state I, following the charging curve in the opposite direction. The expenditure of electricity in this case can be neglected. Let us close the cycle, bringing the electrode surface back to S. The quantity of hydrogen expended in this case will be equivalent to $(\Gamma_H)_I S$. Thus $(\Gamma_H)_I S - (\Gamma_H)_{II} S = \Delta QS$ or $\Delta\Gamma_H = -\Delta Q$.

Using the properties of the total differential, we obtain from eqns. (5), (1) and (3) by elementary transformations

$$\left(\frac{\partial\varphi_r}{\partial\mu_{H^+}}\right)_{\Gamma_H,\mu_S} = \left(\frac{\partial\Gamma_{H^+}}{\partial\varphi_r}\right)_{\mu_{H^+},\mu_S} : \left(\frac{\partial\Gamma_H}{\partial\varphi_r}\right)_{\mu_{H^+},\mu_S} = \left(\frac{\partial\Gamma_{H^+}}{\partial\Gamma_H}\right)_{\mu_{H^+},\mu_S} =$$

$$= \left(\frac{\partial\Gamma_{A^-}}{\partial\Gamma_H}\right)_{\mu_{H^+},\mu_S} - \left(\frac{\partial\Gamma_{C^+}}{\partial\Gamma_H}\right)_{\mu_{H^+},\mu_S} \tag{6}$$

The derivation of eqn. (6) has already been given in ref. 3*. It follows from eqns. (5) and (1) that

$$\left(\frac{\partial\Gamma_H}{\partial\mu_S}\right)_{\mu_{H^+},\mu_H} = -\left(\frac{\partial\Gamma_{C^+}}{\partial\varphi_r}\right)_{\mu_{H^+},\mu_S} - \left(\frac{\partial\Gamma_{A^-}}{\partial\varphi_r}\right)_{\mu_{H^+},\mu_S} \tag{7}$$

Then

$$\left(\frac{\partial\varphi_r}{\partial\mu_S}\right)_{\Gamma_H,\mu_{H^+}} = -\left(\frac{\partial\Gamma_H}{\partial\mu_S}\right)_{\mu_{H^+},\varphi_r} : \left(\frac{\partial\Gamma_H}{\partial\varphi_r}\right)_{\mu_{H^+},\mu_S} \tag{8}$$

From (7) and (8) we obtain

$$\left(\frac{\partial\varphi_r}{\partial\mu_S}\right)_{\Gamma_H,\mu_{H^+}} = \left(\frac{\partial\Gamma_{C^+}}{\partial\Gamma_H}\right)_{\mu_{H^+},\mu_S} + \left(\frac{\partial\Gamma_{A^-}}{\partial\Gamma_H}\right)_{\mu_{H^+},\mu_S} \tag{9}$$

or accounting to (2)

$$\left(\frac{\partial\varphi}{\partial\mu_S}\right)_{\Gamma_H,\mu_{H^+}} = \left(\frac{\partial\Gamma_{C^+}}{\partial\Gamma_H}\right)_{\mu_S,\mu_{H^+}} + \left(\frac{\partial\Gamma_{A^-}}{\partial\Gamma_H}\right)_{\mu_S,\mu_{H^+}} \tag{9a}$$

Equation (9) is similar to the equation

$$\left(\frac{\partial\varphi}{\partial\mu_S}\right)_{\varepsilon} = -\left(\frac{\partial\Gamma_{C^+}}{\partial\varepsilon}\right)_{\mu_S} - \left(\frac{\partial\Gamma_{A^-}}{\partial\varepsilon}\right)_{\mu_S} \tag{10}$$

where ε is the charge of the metal side of the double layer, known from the thermodynamic theory of electrocapillarity[4,5]. However, whereas in (10) the change in φ with μ_S is considered at constant ε, in (9a) the quantity Γ_H should be assumed to be constant. Thus in the thermodynamic theory of electrocapillarity in the case of the platinum hydrogen electrode, Γ_H plays the same part as the quantity ε in the theory of

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* In the case of an electrode in a solution of an acid, HA, without additions of other cations, we obtain by similar reasoning

$$\left(\frac{\partial\varphi_r}{\partial\mu_\pm}\right)_{\Gamma H} = 2\left(\frac{\partial\Gamma_{H^+}}{\partial\Gamma_H}\right)_{\mu_\pm} \tag{6a}$$

where $\mu_\pm$ is the mean value of the chemical potentials of H^+ and A^- ions.

an ideal polarizable mercury electrode*. In particular, the maximum of the σ,φ curve in the case of the platinum hydrogen electrode corresponds to $\Gamma_H = 0$, and not to $\varepsilon = 0$ **[2]. The quantities $\partial\Gamma_H/\partial\varphi_r$ and $\partial\Gamma_{H^+}/\partial\varphi_r$ in eqn. (6) can be determined experimentally, the former from the equilibrium charging curves and the latter from the dependence of the change in pH of the solution, observed when the solution comes into contact with the electrode, upon the potential[1,7]. We can also determine the system states for which $\Gamma_H = 0$ or $\Gamma_{H^+} = 0$, and hence find the absolute values of Γ_H and Γ_{H^+} for[1] any φ.

The validity of the thermodynamic relations derived above is independent of the interpretation of the physical significance of these quantities. If we wish,however, to relate the quantities in question with some model representation of the interface, we are obliged to go beyond the purely thermodynamic treatment.

Let us consider first the quantity $\Gamma_{H^+} = \Gamma_{A^-} - \Gamma_{C^+}$. The changes in the concentration of the H^+ ions upon contact of the solution with the electrode can be due both to the transition of the H^+ ion of the solution into the state of an adsorbed H atom with a positive charge appearing on the surface, and to the transition of the H^+ ion from the bulk of the solution to the ionic side of the double layer (and to the corresponding reverse processes)***. Moreover, in the latter case, the adsorbed H^+ ions can be attracted by the negative surface charges or can be *specifically* adsorbed, retaining their ionic nature. The latter is unlikely, as in the case of mercury the H^+ ion behaves as the Li^+ ion, showing no signs of *specific* adsorptivity[9]. Whatever may be the case, we shall not make an allowance for the possibility of intermediate formations between H_{ads} and electrostatically-attracted H^+ ions appearing in the electric double layer. If, however, specifically adsorbed H^+ ions are present in the surface layer, we shall treat them as adsorbed atoms and add their charge to that of the metal surface. Further, we shall assume the relative concentrations of the H^+ ions and other cations in the bulk of the solution to be chosen in such a way that it would be possible to ignore the electrostatic adsorption of the H^+ ions along with Γ_{C^+}. We shall also assume that, being adsorbed, all the remaining ions of the solution retain their charges. In other words, we shall not add to the charge of the metal surface that part of the charge of these ions which on adsorption passes to the metal. In this respect our method of calculation is conditional and, undoubtedly does not represent the real physical picture of the process, as the bond between platinum and the ions with strong

* The hydrogen platinum electrode is not ideally polarizable in the usual sense of this term in modern electrochemical terminology, since it is possible for an electrochemical reaction to occur on its surface. But it is *perfectly* polarizable (vollkommen polarisierbar) in PLANCK's sense[6], *viz.*, its state is completely determined by the quantity of electricity, Q, supplied to it, beginning with some initial state. Nothing will be changed if the presence of some hydrogen dissolved in the electrolyte and in the metal is taken into consideration, provided the solution volume is limited and equilibrium is maintained between dissolved hydrogen and that adsorbed on the surface during all changes in the state of the system.

** The method of determination of the potential corresponding to $\Gamma_H = 0$ is given in ref. 1.

*** We are faced here with the same difficulty as in the consideration of the double layer at the interface between zinc amalgam and a solution containing Zn^{2+} ions[8].

specific adsorptivity, such as I^- or Tl^+, is nearly covalent*. LORENZ's results[10], however, indicate that a partial charge transfer occurs also in the specific adsorption of a number of ions on mercury. But in this case as well, in considering the structure of the electric double layer, the transferred charge is not added to that of the metal surface. Under the above assumptions, Γ_{H^+} is identical to ε, the charge of the metallic side of the double layer at the electrode–solution interface:

$$\Gamma_{H^+} = \Gamma_{A^-} - \Gamma_{C^+} = \varepsilon \tag{11}$$

In contradistinction to Γ_H, Γ_{H^+} should be termed the free surface charge. Under the same assumptions, the quantity Γ_H can be represented as the sum of two terms, one of which is determined by hydrogen adsorption in the form of H atoms and the second —by hydrogen ionization, the H^+ ions formed entering into the bulk of the solution:

$$\Gamma_H = A_H - \Gamma_{H^+} = A_H - \varepsilon \tag{12}$$

where A_H is the amount of atomic hydrogen adsorbed/cm^2 of the surface, expressed in electrical units. An increase of Γ_{H^+} corresponds evidently to a decrease of Γ_H.**

In the case of adsorption from alkaline solutions, we shall assume likewise that the OH^- ions being displaced by other anions do not form part of the ionic side of the double layer and that the change in the concentration of the OH^- ions is determined by that in the surface charge and hence, by the process of ionization of adsorbed hydrogen***.

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* Another treatment of such systems is possible. Thus, the platinum electrode in a solution containing for example, Na^+, Cd^{2+} and SO_4^{2-} ions, can be considered as a platinum–cadmium one. In this case we should add the charges of the adsorbed Cd^{2+} ions to those of the metal surface (as we have done in the case of the H^+ ions) and assume the ionic side of the double layer to be formed only by the Na^+ and SO_4^{2-} ions. In the case of such treatment, the wording will be qualitatively different from that in the text. Thus, whereas according to the concepts used in our paper the adsorption of the Cd^{2+} ions shifts the point of zero charge of platinum in the positive direction[1], assuming cadmium to be adsorbed as atoms, we must conclude that the point of zero charge is shifted in the negative direction. A similar statement has already appeared in the treatment of the adsorption of iodine ions on iron and its effect upon adsorption of organic cations[11]. Following the same reasoning, we state that the adsorption of Tl^+ ions from the solution on mercury shifts the point of zero charge towards more positive φ-values, whereas the adsorption of Tl atoms from Tl amalgam causes an opposite effect[12]. In the latter case we can, however, establish the desired chemical potential of the atomic form regardless of the electrode potential, which is impossible in the case of the Pt–Tl surface alloy formation *via* adsorption of the ions from the solution.

** The relation

$$\Gamma_H = A_H - \varepsilon$$

can also be directly derived from the cycle given in the footnote to p. 505.

*** The picture in the case of alkaline solutions is more complicated than in the case of acid solutions, since over a certain potential range, adsorbed hydrogen and oxygen can co-exist, as is evident from the shape of the charging curves[1,13], and the change in the OH^- ion concentration can be equally well be connected with the appearance of O_{ads} or of OH_{ads} on the surface. This, however, does not affect the formal aspect of the calculation, since the simultaneous presence of H_{ads} and O_{ads} (or OH_{ads}) means the chemisorption of water and, consequently, if the condition $\Gamma_{H_2O} = 0$ is satisfied, the increase in Γ_O is formally equivalent to a decrease in Γ_H.

It follows from eqns. (6) and (12) that[4]

$$\left(\frac{\partial \varphi_r}{\partial \mu_{H^+}}\right)_{\Gamma_H,\mu_S} = \frac{1}{\left(\frac{\partial A_H}{\partial \Gamma_{H^+}}\right)_{\mu_{H^+},\mu_S} - 1} \tag{13}$$

$$\left(\frac{\partial \varphi}{\partial \mu_{H^+}}\right)_{\Gamma_H,\mu_S} = \frac{\left(\frac{\partial A_H}{\partial \Gamma_{H^+}}\right)_{\mu_{H^+},\mu_S}}{\left(\frac{\partial A_H}{\partial \Gamma_{H^+}}\right)_{\mu_{H^+},\mu_S} - 1} \tag{14}$$

Equation (6) and its equivalent eqns. (13) and (14) can be verified, since all the quantities in these equations can be determined by direct experiment*. In this sense, the platinized-platinum electrode has an advantage over the mercury electrode, because for the latter, eqn. (10), which is of the same type as eqn. (6), can be verified only using data calculated from the interfacial tension or differential-capacitance measurements. For comparison with experiment, it is most convenient to write eqn. (6) in the form

$$\left(\frac{\partial \varphi_r}{\partial \mu_{H^+}}\right)_{\Gamma_H,\mu_S} = -\left(\frac{\partial \Gamma_{H^+}}{\partial \varphi_r}\right)_{\mu_{H^+},\mu_S} : \left(\frac{\partial Q}{\partial \varphi_r}\right)_{\mu_{H^+},\mu_S} \tag{15}$$

Equation (15) was verified for a solution of composition, N KCl + 0.01 N HCl. Figure 1 shows the dependence of $\left(\frac{\partial \varphi}{\partial \mu_{H^+}}\right)_{\Gamma_H,\mu_S}$ upon φ, found experimentally. In accordance with (2)

$$\left(\frac{\partial \varphi}{\partial \mu_{H^+}}\right)_{\Gamma_H,\mu_S} = \left(\frac{\partial \varphi_r}{\partial \mu_{H^+}}\right)_{\Gamma_H,\mu_S} + 1 \tag{2a}$$

In Fig. 2, the calculated Γ_{H^+},φ_r curve is compared with the experimental one. The value of $\partial\varphi_r/\partial\mu_{H^+}$ was determined directly from measurements of the potential change with changing pH of a platinum hydrogen electrode, which had been previously polarized to a definite φ_r in a solution saturated with helium. The change of pH was carried out under isoelectric conditions, *i.e.*, preserving[2,14] the constancy of Γ_H. The value of $\left(\frac{\partial \varphi}{\partial \mu_{H^+}}\right)_{\Gamma_H,\mu_S}$ was found from $\left(\frac{\partial \varphi_r}{\partial \mu_{H^+}}\right)_{\Gamma_H,\mu_S}$ using eqn. (2a). The value of $\partial Q/\partial\varphi_r$ was found from the charging curve and the value of Γ_{H^+} from the change in the acidity of the solution upon contact with the electrode. When integrating the values of $\partial\Gamma_{H^+}/\partial\varphi_r$ calculated by means of eqn. (15), in order to obtain the theoret-

* Using similar arguments, we obtain from eqn. (6a) for the case of a platinum hydrogen electrode in a solution of an acid that does not contain foreign cations:

$$\left(\frac{\partial \varphi}{\partial \mu_\pm}\right)_{\Gamma_H} = \left[\left(\frac{\partial A_H}{\partial \Gamma_{H^+}}\right)_{\mu\pm} + \left(\frac{\partial \Gamma_{H^+}{}^i}{\partial \Gamma_{H^+}}\right)_{\mu_\pm} + 1\right] : \left[\left(\frac{\partial A_H}{\partial \Gamma_{H^+}}\right)_{\mu\pm} + \left(\frac{\partial \Gamma_{H^+}{}^i}{\partial \Gamma_{H^+}}\right)_{\mu_\pm} - 1\right] \tag{14a}$$

The quantity Γ_{H^+} in this case cannot be equated with ε, as the H^+ ions, in the absence of foreign cations, can participate in the formation of the ionic part of the double layer, $\Gamma_{H^+}{}^i = \Gamma_{H^+} - \varepsilon$.

ical Γ_{H^+},φ_r curve, use was made of the value of Γ_{H^+} corresponding to $\varphi_r = 0$, determined by direct adsorption measurements. The values of Γ_{H^+} in Fig. 2 are given per unit of the true electrode surface, the latter having been determined from the length of the hydrogen section of the charging curve under the assumption that at $\varphi_r = 0$, A_H is 210 μC/cm^2*. The above method of verification has been chosen for the reason that of the three derivatives appearing in eqn. (15), $\partial\Gamma_{H^+}/\partial\varphi_r$ can be determined with least accuracy. The technique used will be described in detail elsewhere[16].

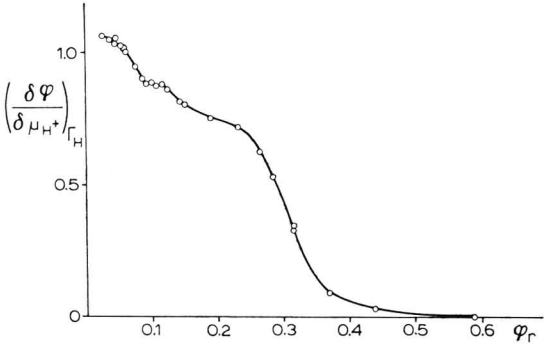

Fig. 1. Dependence of $\left(\frac{\partial\varphi}{\partial\mu_{H^+}}\right)_{\gamma_H}$ on φ_r.

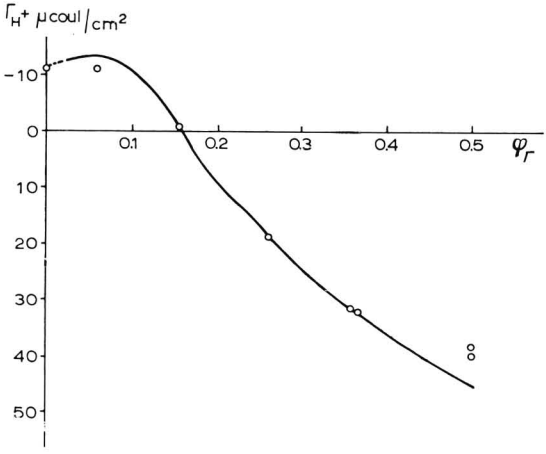

Fig. 2. Dependence of Γ_{H^+} on φ_r. The curve was calculated according to eqn. (15). The circles are experimental values.

It follows from Fig. 1 that $\left(\frac{\partial\varphi}{\partial\mu_{H^+}}\right)_{\Gamma_H,\mu_S}$ is close to unity at small values of φ_r. In other words, the dependence of the potential upon pH is similar to that observed in the case of an electrode that is in equilibrium with hydrogen gas at constant

* This coefficient was recently verified by electrode surface measurements using the BET method[15].

pressure. It follows from eqn. (14), however, that this is due not to the character of the dependence of A_H upon φ_r, (*e.g.*, to a considerable surface coverage with H_{ads} at small φ_r) but to the fact that at small φ_r, Γ_{H^+} changes only slightly with φ_r. With increasing φ_r, the value of $\left(\frac{\partial\varphi}{\partial\mu_{H^+}}\right)_{\Gamma_H,\mu_S}$ diminishes and at $\varphi_r \sim 0.5$ V becomes equal to zero. In other words, the electrode no longer operates as a hydrogen electrode, which is a natural result of A_H vanishing. Taking into consideration eqn. (14) and the complex nature of the A_H *vs.* φ_r dependence one should not be surprised at the complexity of the shape of the $\left(\frac{\partial\varphi}{\partial\mu_{H^+}}\right)_{\Gamma_H,\mu_S}$, φ_r curve .

It is evident from Fig. 2 that at values of φ_r not greater than 0.4 V, the calculated values of Γ_{H^+} coincide with the experimental values within the accuracy of measurements of Γ_{H^+} and, which is of particular importance, the calculated curve intersects the abcissa at the same value of φ_r as the experimental value. This corroborates the validity of the treatment of the surface of the platinized-platinum electrode as an equilibrium system the state of which at constant μ_S is determined by the independent variables μ_H and μ_{H^+}, and the correctness of the experimental determination of the point of zero charge. In the case of the system investigated, the latter lies at $\varphi_r = 0.16$, whence, in accordance with the earlier determinations[1,2] $\varphi_{\varepsilon=0} = 0.04$, whereas the total charge of the electrode surface, $-\Gamma_H$, determined as described in ref. 1, vanishes at $\varphi_r = 0.25$, *i.e.*, $\varphi = 0.14$.

It is interesting to note that at $\varphi_r < 0.06$, the value of $\left(\frac{\partial\varphi}{\partial\mu_{H^+}}\right)_{\Gamma_H,\mu_S}$ exceeds unity, *i.e.*, $\left(\frac{\partial\varphi_r}{\partial\mu_{H^+}}\right)_{\Gamma_H,\mu_S}$ is positive . According to (15) this is possible only if $\left(\frac{\partial\Gamma_{\mu^+}}{\partial\varphi_r}\right)_{\mu_{H^+},\mu_S}$ is negative. In other words, there should be a minimum on the curve of the Γ_{H^+} *vs.* φ_r dependence. Such a possibility was not envisaged in refs. 1 and 3. The accuracy of the experimental determination of Γ_{H^+} achieved in the present investigation is not sufficient to solve the problem of the actual existence of this minimum*. At $\varphi_r = 0.5$, there is some discrepancy between the experimental and the calculated values of Γ_{H^+}. It is possible that at this potential, the assumption of the reversibility is not completely valid, but this problem requires further investigation.

The possible effect of hydrogen dissolved in the metal and in the solution layers near the electrode, on the results of these measurements merits separate consideration. Although under the conditions of our experiments the amount of

* Dr. N. BALASHOVA communicated to us that in a number of experiments on the determination of the dependence of the adsorption of alkali-metal cations on platinum upon the potential by the tracer method, a weakly-expressed maximum of Γ_{C^+} was observed in the hydrogen region, which corresponds to a minimum of Γ_{H^+}. But as this effect was just within the accuracy of the measurements, it was not taken into consideration when plotting the curves of the dependence of adsorption upon the potential.

dissolved hydrogen was small*, this problem is of fundamental importance. Let us consider, therefore, the behaviour of the platinum hydrogen electrode under the condition of constancy of the total quantity of electricity stored as electrochemically-active substance—hydrogen, or present as the free surface charge, giving up the assumption according to which the amount of dissolved hydrogen is small compared to the amount of adsorbed hydrogen. We shall assume however the existence of equilibrium between dissolved and adsorbed hydrogen. Let us denote the bulk concentration of hydrogen dissolved in the metal (expressed in electrical units) by c_H and the electrode volume calculated/unit surface by v_S (the same reasoning holds in the case of hydrogen dissolved in the electrolyte if v_S denotes the solution volume/unit electrode surface). The concentration of the indifferent electrolyte will be considered to be constant ($\mu_S = \text{const.}$). Let us introduce the function

$$\Pi_H = \Gamma_H + v_S c_H \tag{16}$$

The state of the system is determined by two of the three variables $\varphi_r = \text{const.} - \mu_H$, Π_H and μ_{H^+}. Consequently,

$$\left(\frac{\partial \varphi_r}{\partial \mu_{H^+}}\right)_{\Pi_H} = -\left(\frac{\partial \Pi_H}{\partial \mu_{H^+}}\right)_{\varphi_r} : \left(\frac{\partial \Pi_H}{\partial \varphi_r}\right)_{\mu_{H^+}} \tag{17}$$

But as c_H depends only on μ_H and is independent of μ_{H^+}, it follows from (16), (4) and (1) that

$$\left(\frac{\partial \Pi_H}{\partial \mu_{H^+}}\right)_{\varphi_r} = \left(\frac{\partial \Gamma_H}{\partial \mu_{H^+}}\right)_{\varphi_r} = -\left(\frac{\partial \Gamma_{H^+}}{\partial \varphi_r}\right)_{\mu_{H^+}} \tag{18}$$

It follows from (17) and (18) that

$$\left(\frac{\partial \varphi_r}{\partial \mu_{H^+}}\right)_{\Pi_H} = \left(\frac{\partial \Gamma_{H^+}}{\partial \varphi_r}\right)_{\mu_{H^+}} : \left(\frac{\partial \Pi_H}{\partial \varphi_r}\right)_{\mu_{H^+}} \tag{19}$$

When eqns. (16) and (12) are taken into consideration, eqn. (19) can be also written in the form

$$\left(\frac{\partial \varphi_r}{\partial \mu_{H^+}}\right)_{\Pi_H} = 1 : \left(\frac{\partial \Pi_H}{\partial \Gamma_{H^+}}\right)_{\mu_{H^+}} = \frac{1}{\left(\frac{\partial A_H}{\partial \Gamma_{H^+}}\right)_{\mu_{H^+}} + v_S \left(\frac{\partial c_H}{\partial \Gamma_{H^+}}\right)_{\mu_{H^+}} - 1} \tag{20}$$

* According to the measurements of GILEADI, FULLENWIDER AND BOCKRIS, whose results have been kindly communicated to one of us by Dr. GILEADI, hydrogen solubility in platinum under cathodic polarization in the presence of As_2O_3 is only 2.7×10^{-5} g atom/cm^3 (at 70°). Since the volume of platinum black on our electrodes was *ca.* 0.02 cm^3, and the amount of adsorbed hydrogen at $\varphi_r = 0$, *ca.* 4.3×10^{-5} g atom, the amount of hydrogen dissolved in platinum black could be ignored. The true surface of our electrodes was more than one thousand times as large as the visible one. Under these conditions, the effect of hydrogen dissolved in the platinum gauze which underwent platinization[17] can also be neglected. The amount of hydrogen dissolved in the whole volume of the solution at the smallest value of φ_r, at which the measurements were performed ($\varphi_r = 0.03$), did not exceed 10% of that adsorbed, and in the absence of stirring only a small part of it could come into equilibrium with adsorbed hydrogen.

Further, it is evident that

$$\left(\frac{\partial \Pi_H}{\partial \varphi_r}\right)_{\mu_{H^+}} = \left(\frac{\partial \Gamma_H}{\partial \varphi_r}\right)_{\mu_{H^+}} + v_S \frac{\partial c_H}{\partial \varphi_r} = \left(\frac{\partial Q'}{\partial \varphi_r}\right)_{\mu_{H^+}} \tag{21}$$

where Q', as Q in eqn. (4), is the quantity of electricity that must be supplied to the electrode for the latter to attain the potential, φ_r, calculated/unit electrode surface.

It follows from (19) and (21) that

$$\left(\frac{\partial \varphi_r}{\partial \mu_{H^+}}\right)_{\Pi_H} = -\left(\frac{\partial \Gamma_{H^+}}{\partial \varphi_r}\right)_{\mu_{H^+}} : \left(\frac{\partial Q'}{\partial \varphi_r}\right)_{\mu_{H^+}} \tag{22}$$

Equation (22) differs from eqn. (15) (derived without making an allowance for the presence of dissolved hydrogen) in that the φ_r *vs.* μ_{H^+} dependence is considered at constant Π_H rather than at constant Γ_H. Thus, the presence of hydrogen dissolved in metal or electrolyte should have no effect upon the results of the verification of eqn. (15), provided equilibrium between dissolved and adsorbed hydrogen is to be maintained at all changes in the state of the system. It follows from eqn. (20), however, that with increasing v_S, $\left(\frac{\partial \varphi_r}{\partial \mu_{H^+}}\right)_{\Pi_H}$ should approach zero, *i.e.*, the dependence of the potential of the electrode under consideration upon pH should approach that observed in the case of the usual hydrogen electrode.

The relation derived in the present study as well as the experimental determination of the values of $\left(\frac{\partial \varphi_r}{\partial \mu_{H^+}}\right)_{\Gamma_H,\mu_S}$ and $\left(\frac{\partial \varphi_r}{\partial \mu_S}\right)_{\Gamma_H,\mu_{H^+}}$ provide additional information on the structure of the platinum electrode–solution interface. Thus, the use of eqn. (15) apparently permits the determination of $\partial \Gamma_{H^+}/\partial \varphi_r$ with an accuracy greater than that obtainable in direct measurements. If this equation is used in conjunction with the measurements of Γ_{H^+} at $\varphi_r = 0$, it will be possible to increase the accuracy of the determination of Γ_{H^+} at any φ_r, which would be very helpful in finding the values of $\left(\frac{\partial \Gamma_{H^+}}{\partial \mu_{H^+}}\right)_{\mu_H}$. The latter quantity is necessary for calculating the important quantities $X = \left(\frac{\partial \varphi}{\partial A_H}\right)_{\Gamma_{H^+}}$ and $Y = \left(\frac{\partial \varphi}{\partial \Gamma_{H^+}}\right)_{A_H}$, which determine the degree of the dependence of the potential at the platinum hydrogen electrode–solution interface upon the adsorbed atoms and upon the electric double layer. In ref. 2 the expressions are given for the quantities X and Y (eqns. (15)–(17) of the paper cited), which after some transformation can be written as:

$$X = -\left[\left(\frac{\partial \Gamma_{H^+}}{\partial \mu_H}\right)_{\mu_{H^+}} + \left(\frac{\partial \Gamma_{H^+}}{\partial \mu_{H^+}}\right)_{\mu_H}\right] : Z \tag{23}$$

$$X + Y = \left[\left(\frac{\partial \Gamma_H}{\partial \mu_H}\right)_{\mu_{H^+}} + \left(\frac{\partial \Gamma_{H^+}}{\partial \mu_H}\right)_{\mu_{H^+}}\right] : Z \tag{24}$$

$$Z = \left(\frac{\partial \Gamma_H}{\partial \mu_H}\right)_{\mu_{H^+}} \left(\frac{\partial \Gamma_{H^+}}{\partial \mu_{H^+}}\right)_{\mu_H} - \left(\frac{\partial \Gamma_{H^+}}{\partial \mu_H}\right)^2_{\mu_{H^+}} \quad (25)$$

The determination of all the other quantities appearing in eqns. (23)–(25), except $\left(\frac{\partial \Gamma_{H^+}}{\partial \mu_{H^+}}\right)_{\mu_H}$, presents no difficulties.

So far eqn. (9) has not been verified experimentally. It is quite possible that it can be used in practice only in the case of not too strong specific adsorption of the indifferent electrolyte ions. If the results of the measurements of the quantities $\left(\frac{\partial \varphi_r}{\partial \mu_{H^+}}\right)_{\Gamma_H,\mu_S}$ and $\left(\frac{\partial \varphi_r}{\partial \mu_S}\right)_{\Gamma_H,\mu_{H^+}}$ were compared, taking into consideration eqns. (6) and (9), it would be possible to determine the dependence of Γ_{C^+} and Γ_{A^-} upon Γ_H, and, hence, upon φ_r, and to compare the results obtained with those of the adsorption measurements of C^+ and A^- by the tracer method[18].

An expression similar to eqn. (6) can be readily derived for the oxygen section of the charging curve of the platinum electrode. It is possible that at not too positive potentials, ionization of adsorbed oxygen occurs with sufficient reversibility for these relations to be used, at least to the first approximation. In this respect, some other metals of the platinum group, such as iridium, may have some advantages compared with platinum.

CONCLUSIONS

It has been shown that by determining the dependence of the hydrogen electrode potential upon the pH of the solution at a constant quantity of electricity stored on its surface, it is possible to calculate the dependence of adsorption of the hydrogen ions upon the electrode potential. In the case of N KCl + 0.01 N HCl, the relations obtained are in agreement with experiment, which proves the applicability of Gibbs thermodynamics of the surface phenomena to the platinum hydrogen electrode, and at the same time provides a new method for the determination of the point of zero-charge. A physical interpretation of the quantities contained in the thermodynamic relations, on the basis of a definite model of the double layer at the hydrogen electrode–solution interface, has been suggested. The changes in the relations derived that result if the presence of dissolved hydrogen is taken into consideration have been discussed.

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