DEPENDENCE OF THE POTENTIAL OF THE HYDROGEN ELECTRODE UPON THE pH AND COMPOSITION OF THE SOLUTION UNDER ISOELECTRIC CONDITIONS

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The thermodynamic functions permitting the change in the potential of the platinum hydrogen electrode with changing pH and composition of the solution under isoelectric conditions to be related to the dependence of the absorption of cations and anions upon the electrode potential are considered. A physical interpretation of the quantities entering into the thermodynamic functions is proposed on the basis of a definite model of the double layer at the hydrogen electrode/solution interface. It is shown to what changes in the functions derived a consideration of the presence of dissolved hydrogen leads.

While the application of Gibbs thermodynamics of surface phenomena to the mercury and other electrodes of liquid metals has been confirmed experimentally, and is now generally recognized, the question of the possibility of an analogous treatment of electrocapillary phenomena at the surface of a platinum electrode has been little treated in the literature. The first attempts along this line were made by Frumkin and Shlygin [1]; however, the function that he obtained was presented in a form inconvenient for experimental verification, and the latter can be performed only semiquantitatively. A series of thermodynamic functions were considered by Frumkin, Balashova, and Kazarinov [2]. Frumkin [3] derived an equation for the dependence of the hydrogen potential upon the pH of the solution under isoelectric conditions. In this work we should like to turn once again to some of these functions, paying special attention to the physical interpretation of the quantities that enter into the thermodynamic functions.

We assume that the platinum hydrogen electrode may be considered as reversible with respect to the reaction of ionization of absorbed hydrogen and discharging of hydrogen ions, and we shall limit ourselves to the case of a solution of a binary electrolyte. The assumption of reversibility is fulfilled in practice for the platinized platinum electrode if the solution contains no ions exhibiting pronounced specific adsorption [2] (I^-, Tl^+) within the interval of potentials bonded 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 volume of the solution and in the metal can be neglected in comparison with the amount of hydrogen on the surface of the electrode and that the concentration of hydrogen ions in the solution is small in comparison with the concentration of other cations, so that the chemical potential of the other cations and the C^+ and A^- ions remains practically constant when the hydrogen ion concentration is varied.

The state of the system under consideration can be determined by the chemical potentials of atomic hydrogen μ_H, the hydrogen ion μ_{H^+} and ions of the electrolyte μ_S. As the components from which we shall construct the boundary layer, let us select H atoms, H^+, C^+, and A^- ions, and water molecules H_2O.* Let us denote as Γ_H, Γ_{H^+}, Γ_{C^+}, Γ_{A^-} the surface densities of the components of the system in the Gibbs sense, i.e., the amount of the substance that must be added to the system in order for the composition of the volume phase to remain constant when the surface is increased by a unit. The position of the surface of separation will be defined by the conditions $\Gamma_{H_2O} = 0$. We shall express the quantities Γ and μ in electrical units. It is important that the value of Γ_H includes both the amount of hydrogen that is adsorbed in the form of atoms on the surface of platinum and the amount that is consumed as a result of ionization in the formation of a unit surface. This is precisely the amount that we would find in experiments, if we directly determined the adsorption of hydrogen on an electrode immersed in the solution experimentally at set μ_H and μ_{H^+}.

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*The system could also be constructed from H^+ ions and electrons (instead of H^+ ions and H atoms). The same results are ultimately obtained in this case.

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The quantity $-\Gamma_H$ reflects the reserve of electricity per unit surface of the electrode (the minus sign is due to the fact that the ionization of the H atom leads to the appearance of a negative charge). Similarly, the total amount of negative electricity, stored on the negative electrode of a lead accumulator, is determined by the amount of lead deposited, corrected for the negative charge of the metallic lining of the double layer. In this sense the quantity $-\Gamma_H$ can be called the total charge of a unit surface of the electrode. Γ_H remains constant when the circuit is opened if there is no delivery of electrochemically active substance to the electrode. Then let us denote as σ the surface density of the free energy, as φ_r the electrode potential, measured with respect to the hydrogen electrode in the same solution, existing in equilibrium with H_2 at atmospheric pressure, as φ the electrode potential, measured with respect to the normal hydrogen electrode, and as Q the amount of electricity that must be communicated to the electrode in order to shift its potential at constant μ_{H^+} and μ_S from some initial value φ_r to the set value. A number of relationships exist among the quantities cited, namely:

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

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

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

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

$$d\sigma = -\Gamma_H d\mu_H - \Gamma_{H^+} d\mu_{H^+} - (\Gamma_{C^+} + \Gamma_A)\, d\mu_s. \tag{5}$$

Equations (1) and (2) express the condition of equilibrium between the electrode and solution, while equation (3) expresses the condition of conservation of electrical neutrality of the solution during the process of adsorption. Equation (5) is the Gibbs expression for the total differential of the surface free energy as applied to the case under consideration. Equation (4) follows from what was said above and the value of the quantity Γ_H.*

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

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

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*The correctness of function (4) can also be shown with the aid of the following hypothetical circular process. Let the electrode move along the charging curve at constant composition of the solution from state I to state II, to which the values $(\mu_H)_I$ and $(\mu_H)_{II}$ correspond. In this case an amount of electricity $(Q_{II}-Q_I)S = \Delta QS$ is consumed (S is the electrode surface). The back transition from state II to state I will be performed in a different way, namely, the surface of the electrode in state II is reduced to an infinitesimally small quantity in comparison with S. In this case, by definition, an amount of hydrogen equivalent to $(\Gamma_H)_{II}S$ is liberated. Let the electrode with reduced surface pass into state I along the charging curve. The expenditure of electricity in this case can be neglected. Let us close the cycle by bringing the surface of the electrode up to S. In this case an amount of hydrogen equivalent to $(\Gamma_H)_I S$ is consumed. Thus,

$$(\Gamma_H)_I S - (\Gamma_H)_{II} S = \Delta Q$$

or

$$\Delta\Gamma_H = -\Delta Q.$$

A derivation of Eq. (6) has already been given in [3].* From Eqs. (5) and (1) it follows that

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

Furthermore,

$$\left(\frac{\partial\varphi_r}{\partial\mu_s}\right)_{\Gamma_{\mathrm{H}};\mu_{\mathrm{H}^+}} = -\left(\frac{\partial\Gamma_{\mathrm{H}}}{\partial\mu_s}\right)_{\mu_{\mathrm{H}^+},\varphi_r} \Bigg/ \left(\frac{\partial\Gamma_{\mathrm{H}}}{\partial\varphi_r}\right)_{\mu_{\mathrm{H}^+},\mu_s}. \tag{8}$$

From (7) and (8) we obtain

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

or, according to (2),

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

Equation (9) is analogous to the equation

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

(where ε is the charge of the metallic lining of the double layer), known from the thermodynamic theory of electrocapillarity [4, 5]. However, while the change in φ with μ_s at constant ε is considered in (10), in (9a) the quantity Γ_H should be assumed to be constant. In the thermodynamic theory of electrocapillarity, in the case of a platinum hydrogen electrode, the latter thus plays the same role as the quantity ε in the theory of electrocapillarity of an ideally polarized mercury electrode.† In particular, the maximum of the σ versus φ curve in the case of a platinum hydrogen electrode corresponds not to $\varepsilon = 0$, but to $\Gamma_H = 0$ [2].‡ The quantities $\partial\Gamma_H/\partial\varphi_r$ and $\partial\Gamma_{H^+}/\partial\varphi_r$, contained in Eq. (6), can be found experimentally, the first quantity from the equilibrium charging curves, the second from the dependence of the change in the pH of the solution, observed when it is in contact with the electrode, upon the potential [1, 4]. The state of the system for which $\Gamma_H = 0$ or $\Gamma_{H^+} = 0$ can also be fixed, and consequently, the absolute values of Γ_H and Γ_{H^+} can be found for any φ [1].

The correctness of the thermodynamic functions derived above does not depend upon the interpretation of the physical meaning of these quantities. However, if we wish to relate these quantities to model representations of the structure of the interface, we should inevitably go beyond the framework of purely thermodynamic concepts.

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*For a hydrogen electrode immersed in a solution of acid HA without addition of extraneous cations, we can obtain analogously

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

where $\mu_\pm$ is the average chemical potential of the ions of the acid.

†The hydrogen electrode is not ideally polarized in the sense in which this term is usually taken in the modern electrochemical literature, since an electrochemical reaction may occur on its surface. However, it is completely polarizable (Vollkommen polarisierbar) in the sense that Planck invests in this term [6], namely, its state is entirely determined by the amount of electricity communicated beginning with some initial state. Nothing is changed in this if we also consider the presence of some amount of hydrogen, dissolved in the electrolyte and in the metal, under the condition that the volume of the solution is limited, and that equilibrium is maintained between the dissolved hydrogen and the hydrogen adsorbed on the surface in the presence of all changes of state of the system.

‡The method of determining the potential corresponding to $\Gamma_H = 0$ is indicated in [1].

Let us consider first the quantity $\Gamma_{H^+} = \Gamma_{A^-} - \Gamma_{C^+}$. Changes in the concentration of H^+ ions when the solution is in contact with the electrode may arise both as a result of transition of the H^+ ion of the solution to the state of an adsorbed atom, with the appearance of a positive charge in the surface, and as a result of transition of a H^+ ion to the ionic lining of the double layer (and the corresponding reverse processes).* Furthermore, the adsorbed H^+ ions may be attracted by the negative charges of the surface or may be adsorbed "specifically," retaining their ionic character. The latter is rather improbable, since in the case of mercury, the H^+ ion behaves like a Li^+ ion, i.e., does not exhibit any signs of "specific" adsorbability [9]. Nevertheless, we shall not consider the possibility of the appearance of formations intermediate between H_{ads} and electrostatically attracted H^+ ions in the electrical double layer, and if there are still specifically adsorbed H^+ ions in the surface layer, we shall consider them as adsorbed atoms, and add their charge to the charge of the metal surface.

Furthermore, we assume that the relative concentrations of H^+ ions and other cations in the volume of the solution were selected in such a way as to be able to neglect electrostatic adsorption of H^+ ions, together with the quantity Γ_{C^+}. We shall also assume that all the remaining ions of the solution, being adsorbed, retain their charges; in other words, we shall not add that portion of the charge of these ions that is transferred to the metal during adsorption to the charge of the metal surface. In this respect, our method of calculation is arbitrary, and undoubtedly does not correspond to the real physical picture of the process, since the bond between Pt and ions with pronounced specific adsorbability, such as I^- or Tl^+, approaches the covalent.† However, judging by the measurements of Lorenz [12], a partial transfer of charge also occurs in the specific adsorption of ions on mercury; and yet, the charge transferred in this case also is not included in the charge of the metal surface in a consideration of the structure of the electrical double layer. If we make the enumerated assumptions, then the quantity Γ_{H^+} becomes identical with ε —the charge of the lining of the double layer turned toward the metal, at the electrode/solution interphase:

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

In contrast to Γ_H, the quantity Γ_{H^+} should have been called the free charge of the surface. Under these assumptions, the quantity Γ_H can be broken down into two components; one component is determined by the adsorption of hydrogen in the form of H atoms, while the other is determined by the transfer of hydrogen in the form of H^+ ions to the volume of the solution:

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

where A_H denotes the amount of atomic hydrogen adsorbed per cm^2 of surface, expressed in electrical units. The increase in Γ_{H^+} evidently corresponds to a decrease in Γ_H.‡

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

†Another treatment of systems of this kind is also possible. Thus, the platinum electrode in a solution containing, for example, Na^+, Cd^{+2}, and SO_4^{-2} ions, may be considered as a platinum-cadmium electrode, adding the charges of the adsorbed Cd^{+2} ions to the charges of the metal surface (as we did in the case of H^+ ions), and considering that the ionic lining of the double layer is formed only by Na^+ and SO_4^{-2} ions. Such a treatment leads to formulas differing qualitatively from those used in the text. While according to the latter, the adsorption of Cd^{+2} ions shifts the point of zero charge of Pt in the positive direction [1], assuming that cadmium is adsorbed in the form of atoms, we should arrive at the conclusion that the zero charge is shifted in the negative direction as a result of the formation of a Pt-Cd surface alloy. An analogous formulation of the question has already arisen in a consideration of the adsorption of iodine on iron and its influence upon the adsorption of organic cations [10]. Also to some degree analogous is a comparison of the adsorption of Tl ions from a solution on mercury, shifting the zero point to more positive φ, and the adsorption of Tl atoms from Tl amalgam, causing the opposite effect [11]. In the latter case, however, we can set the chemical potential of the atomic form independent of the electrode potential, which cannot be done in the case of the formation of a surface alloy through the adsorption of ions from solution.

‡The function $\Gamma_H = A_H - \varepsilon$ can also be obtained directly from the cycle considered in the note to function (4).

In the case of adsorption from alkalinized solutions, we assume similarly that OH^- ions are not contained in the ionic lining of the double layer, being displaced by other anions, and that the change in the OH^- ion concentration is determined by the change in the charge of the surface, and consequently, by the process of ionization of adsorbed hydrogen.*

From Eqs. (6) and (12) it follows that [4]

$$\left(\frac{\partial\varphi_r}{\partial\mu_{H+}}\right)_{\Gamma_H, \mu_s} = 1\Big/\left[\left(\frac{\partial A_H}{\partial\Gamma_{H+}}\right)_{\mu_{H+}\ \mu_s} - 1\right], \tag{13}$$

$$\left(\frac{\partial\varphi}{\partial\mu_{H+}}\right)_{\Gamma_H, \mu_s} = \left(\frac{\partial A_H}{\partial\Gamma_{H+}}\right)_{\mu_{H+}, \mu_s}\Big/\left[\left(\frac{\partial A_H}{\partial\Gamma_{H+}}\right)_{\mu_{H+}, \mu_s} - 1\right]. \tag{14}$$

Equation (6) and Eqs. (13) and (14), equivalent to it, are accessible to experimental verification, since all the quantities that enter into these equations can be determined experimentally.† In this sense, a platinized platinum electrode is favorably distinguished from a mercury electrode, in the case of which a verification of Eq. (10), monotypically with Eq. (6), can be performed only using data calculated for measurements of the interfacial tension of differential capacitance. For a comparison with the experimental data, Eq. (6) is more conveniently represented in the form

$$\left(\frac{\partial\varphi_r}{\partial\mu_{H+}}\right)_{\Gamma_H; \mu_s} = -\left(\frac{\partial\Gamma_{H+}}{\partial\varphi_r}\right)_{\mu_{H+}, \mu_s}\Big/\left(\frac{\partial Q}{\partial\varphi_r}\right)_{\mu_{H+}, \mu_s} \tag{15}$$

An experimental verification of Eq. (15) for a platinized platinum electrode was conducted in [14]. In the case of a solution of 1 N KCl+ 0.01 N KCl found according to Eq. (15), using the experimental value of Γ_{H^+} at $\varphi_r = 0$, the dependence of Γ_H^+ upon φ_r proved to agree with the experimental value, which shows the applicability of the Gibbs thermodynamics to a platinum-hydrogen electrode. The calculations and measurements performed simultaneously in [14] gave a new method for determining the point of zero charge.

The functions derived in this work and the experimental determination of the quantities $(\partial\varphi_1/\partial\mu_H^+)\Gamma_H, \mu_s$ and $(\partial\varphi_r/\partial\mu_s)\Gamma_H, \mu_s$ permit us to obtain supplementary information on the structure of the interface between the platinum electrode and the solution. Thus, the use of Eq. (15) evidently permits a determination of $\partial\Gamma_{H^+}/\partial\varphi_r$ with an accuracy exceeding the accuracy permissible in direct measurements. In conjunction with measurements of Γ_{H^+} at $\varphi_r = 0$, this makes it possible to increase the accuracy of the determination of Γ_H^+ at φ_r, which would be extremely desirable for finding the quantity $(\partial\Gamma_H^+/\partial\mu_H^+)\mu_H$. The latter is essential for a calculation of the quantities $X = (\partial\varphi/\partial A_H)\Gamma_H^+$ and $Y = (\partial\varphi/\partial\Gamma_H^+)A_H$, which are of interest since they determine to what degree the potential at the interface of the platinum hydrogen electrode/solution depends upon the adsorbed atoms and to what degree it depends upon the electrical double layer. Frumkin and Shlygin [1] gave expressions for the quantities X and Y [Eqs. (10) and (10a) of the cited work], which after some transformation, can be represented in the form

$$X = -\left[\left(\frac{\partial\Gamma_{H+}}{\partial\mu_H}\right)_{\mu_{H+}} + \left(\frac{\partial\Gamma_{H+}}{\partial\mu_{H+}}\right)_{\mu_H}\right]\Big/ Z, \tag{16}$$

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*The situation in the case of alkaline solutions is more complex than in the case of acid solutions, since within a definite range of potentials in alkaline solutions, adsorbed hydrogen and oxygen can coexist, which is clear from the shape of the charging curves [13,1], and the change in the concentration of OH^- ions can with equal justification be related to the appearance of O_{ads} or OH_{ads} on the surface. This, however, has no effect upon the formal aspect of the calculation, since the simultaneous presence of H_{ads} and O_{ads} (or OH_{ads}) denoted chemisorption of water, and, consequently, when the condition $\Gamma_{H_2O} = 0$ is fulfilled, an increase in Γ_O is formally equivalent to a decrease in Γ_H.

†For a hydrogen electrode in acid solution without the addition of extraneous cations, the quantity Γ_H^+ can no longer be set equal to ε, since the H^+ ions may be contained in the ionic lining of the double layer. The functions pertaining to this case will be considered in another communication.

$$X+Y=\left[\left(\frac{\partial\Gamma_{H}}{\partial\mu_{H}}\right)_{\mu_{H+}}+\left(\frac{\partial\Gamma_{H+}}{\partial\mu_{H}}\right)_{\mu_{H+}}\right]\Big/ Z, \tag{17}$$

$$Z=\left(\frac{\partial\Gamma_{H}}{\partial\mu_{H}}\right)_{\mu_{H+}}\left(\frac{\partial\Gamma_{H+}}{\partial\mu_{H+}}\right)_{\mu_{H}}-\left(\frac{\partial\Gamma_{H+}}{\partial\mu_{H}}\right)^{2}_{\mu_{H+}} \tag{18}$$

Finding the remaining quantities that enter into Eqs. (16)-(18), in addition to $(\partial\Gamma_{H^+}/\partial\mu_{H^+})\mu_H$, presents no difficulties.

Equation (9) has not yet been subjected to experimental verification; it is extremely probable that it can be used in practice only in the case of not too strong specific adsorption of ions of the neutral electrolyte. A comparison of the results of measurement of the quantities $(\partial\varphi_r/\partial\mu_{H^+})\Gamma_H$, μ_s and $(\partial\varphi_r/\partial\mu_s)\Gamma_{H,\mu_{H^+}}$ considering Eqs. (6) and (9), would permit a determination of the dependence of the quantities Γ_{C^+} and Γ_{A^-} upon Γ_H, and consequently, upon φ_r as well, and a comparison of the results obtained with the results of a measurement of the adsorption of C^+ and A^- by the method of labeled atoms [15].

An expression analogous to Eq. (6) also is not difficult to derive for the oxygen portion of the charging curve of the platinum electrode. It may be that at not too positive potentials, ionization of the adsorbed oxygen proceeds sufficiently reversibly for these functions to be able to be used at least in the form of a first approximation. In this respect, certain other metals of the platinum group, such as, for example, iridium, may have advantages over platinum.

We should consider separately to what changes in the functions derived a consideration of the hydrogen dissolved in the metal and in the layers of solution adjoining the electrode leads. Let us consider the behavior of the hydrogen electrode under conditions of constancy of the total reserve of electricity, in the form of the electrochemically active substance—hydrogen and the free charges of the surface, discarding the assumption that the amount of dissolved hydrogen is small in comparison with the amount of adsorbed hydrogen, but assuming the presence of equilibrium between dissolved and adsorbed hydrogen. Let us denote the volume concentration of hydrogen dissolved in the metal, expressed in electrical units, of C_H; the volume of the electrode, calculated per unit surface, as v_s (the same consideration is also applicable to hydrogen dissolved in the electrolyte, if v_s denotes the volume of the solution per unit surface of the electrode). We shall consider the concentration of the neutral electrolyte as constant ($\mu_s = \text{const}$). Let us introduce the function

$$\Pi_H = \Gamma_H + v_s c_H. \tag{19}$$

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

$$\left(\frac{\partial\varphi_r}{\partial\mu_{H+}}\right)_{\Pi_H}=-\left(\frac{\partial\Pi_H}{\partial\mu_{H+}}\right)_{\varphi_r}\Big/\left(\frac{\partial\Pi_H}{\partial\varphi_r}\right)_{\mu_{H+}}. \tag{20}$$

But since C_H depends only upon μ_H and not upon μ_{H^+}, from (19), (4), and (1) it follows that

$$\left(\frac{\partial\Pi_H}{\partial\mu_{H+}}\right)_{\varphi}=\left(\frac{\partial\Gamma_H}{\partial\mu_{H+}}\right)_{\varphi_r}=-\left(\frac{\partial\Gamma_{H^+}}{\partial\varphi_r}\right)_{\mu_{H+}}. \tag{21}$$

From (20) and (21) it follows that

$$\left(\frac{\partial\varphi_r}{\partial\mu_{H+}}\right)_{\Pi_H}=\left(\frac{\partial\Gamma_{H+}}{\partial\varphi_r}\right)_{\mu_{H+}}\Big/\left(\frac{\partial\Pi_H}{\partial\varphi_r}\right)_{\mu_{H+}}. \tag{22}$$

Considering Eqs. (19) and (12), Eq. (22) can still be written in the form

$$\left(\frac{\partial\varphi_r}{\partial\mu_{H+}}\right)_{\Pi_H}=1\Big/\left(\frac{\partial\Pi_H}{\partial\Gamma_H}\right)_{\mu_{H+}}=1\Big/\left[\left(\frac{\partial A_H}{\partial\Gamma_{H+}}\right)_{\mu_{H+}}+v_s\left(\frac{\partial c_H}{\partial\Gamma_{H+}}\right)_{\mu_{H+}}-1\right]. \tag{23}$$

Furthermore, evidently

$$\left(\frac{\partial \Pi_H}{\partial \varphi_r}\right)_{\mu_{H+}} = \left(\frac{\partial \Gamma_H}{\partial \varphi_r}\right)_{\mu_{H+}} + v_s \frac{\partial c_H}{\partial \varphi_r} = -\left(\frac{\partial Q}{\partial \varphi_r}\right)_{\mu_{H+}}, \tag{24}$$

where Q, just as in Eq. (4), is the amount of electricity communicated to the electrode to reach the potential φ_r, calculated per unit surface of the electrode. From (22) and (23) it follows that

$$\left(\frac{\partial \varphi_r}{\partial \mu_{H+}}\right)_{\Pi_H} = -\left(\frac{\partial \Gamma_{H+}}{\partial \varphi_r}\right)_{\mu_{H+}} \Bigg/ \left(\frac{\partial Q}{\partial \varphi_r}\right)_{\mu_{H+}}. \tag{25}$$

Equation (25) differs from Eq. (15), derived without considering the presence of dissolved hydrogen, only in the fact that the dependence of φ_r upon μ_{H^+} is considered not at constantΓ_H, but at constant Π_H. Thus, the presence of hydrogen dissolved in the metal or electrolyte should not have any effect upon the results of testing of Eq. (15), if only conservation of equilibrium between the dissolved and adsorbed hydrogen is ensured in the case of all changes in the state of the system. However, it follows from Eq. (23) that with increasing v_s, the quantity $(\partial\varphi_r/\partial\mu_{H^+})_{\Pi_H}$ should approach zero, i.e., the dependence of the electrode potential upon the pH should approach the dependence observed for the usual hydrogen electrode.

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