THE DEPENDENCE OF THE HYDROGEN ELECTRODE POTENTIAL ON THE pH OF THE SOLUTION UNDER ISOELECTRIC CONDITIONS

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We designate as a hydrogen electrode that in which the change in charge density ε of the surface takes place by means of ionization of absorbed hydrogen or discharge of hydrogen ions. We shall in what follows assume that the quantity of molecular hydrogen in the bulk of the solution in which the electrode is placed in equilibrium may be neglected in comparison with the quantity absorbed on the electrode surface. We shall also assume that it is not necessary to take into account the solubility of hydrogen in the bulk metal or the effect of dissolution of hydrogen on the electrode process. The quantity of hydrogen absorbed per square centimeter of surface when expressed in electrical units we shall designate by A_H. Then, in the absence of any external source of electricity, the value of Γ_H, given by

$$\Gamma_H = A_H - \varepsilon \tag{1}$$

will remain constant. The quantity $-\Gamma_H$ expresses the supply of electricity available per unit area of the electrode surface, since the ionization of hydrogen atoms leads to the appearance of a negative charge on the surface. Conditions under which the constancy of H is maintained will be designated isoelectric [1]. We shall use the following notation: σ = surface energy per square centimeter; φ_r = electropotential in relation to reversible hydrogen electrode in the same solution; φ = potential in relation to the normal hydrogen electrode; μ_H and μ_{H+} are the chemical potentials of atomic hydrogen and hydrogen ions; $(\mu_{H+})_0$ is the value of μ_{H+} when $[H^+] = 1$; Γ_{H+} is the absorbed quantity of hydrogen ions per square centimeter in the sense of the Gibbs thermodynamic principles, taking $\Gamma_{H_2O} = 0$. The values of Γ_{H+}; μ_H and μ_{H+} are expressed in electrical units. Since the value of Γ_H determines the total quantity of hydrogen expended in increasing the surface of the electrode by 1 square centimeter, partially in creating an adsorbed layer of hydrogen atoms, partly in charging the surface by ionization, then Γ_H expresses the Gibbs adsorption of the hydrogen. We shall assume that the concentration of hydrogen ions is so small compared with the concentration of other ions in the solution that change in this causes no change in the chemical potentials of other components of the solution, which we shall regard as constant. On the other hand, we shall take into account that change in the value of $[H^+]$ caused by change in A_H is small compared with $[H^+]$ itself. Under these conditions the state of the system is determined by the independent variables μ_H and μ_{H^+} and consequently [2, 3]*

$$d\sigma = -\Gamma_H d\mu_H - \Gamma_{H^+} d\mu_{H^+} \tag{2}$$

Moreover

$$\varphi_r = \text{const} - \mu_H \tag{3}$$

It follows from (2) that

$$\left(\frac{\partial \Gamma_H}{\partial \mu_{H^+}}\right)_{\mu_H} = \left(\frac{\partial \Gamma_{H^+}}{\partial \mu_H}\right)_{\mu_{H^+}} \tag{4}$$

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*When the conditions enumerated have been fulfilled, the state of the system with a given initial solution composition is completely determined by the quantity of electricity Q communicated to the electrode, beginning from some initial moment of time. In this sense, the behavior of the electrode is no different from that of an ideal or completely polarized electrode [2], although the conditions that there must be no exchange of charge between the electrode and the solution, which is usually regarded as a criterion for ideal polarizability [4], is not fulfilled.

From (1), (3) and (4), it follows that

$$\left(\frac{\partial\varphi_r}{\partial\mu_{H^+}}\right)_{\Gamma_H} = -\left(\frac{\partial\Gamma_H}{\partial\mu_{H^+}}\right)_{\mu_H} : \left(\frac{\partial\Gamma_H}{\partial\varphi_r}\right)_{\mu_{H^+}} = \left(\frac{\partial\Gamma_{H^+}}{\partial\varphi_r}\right)_{\mu_{H^+}} : \left(\frac{\partial\Gamma_H}{\partial\varphi_r}\right)_{\mu_{H^+}}$$
$$= 1 : \left(\frac{\partial\Gamma_H}{\partial\Gamma_{H^+}}\right)_{\mu_{H^+}} = 1 : \left[\left(\frac{\partial A_H}{\partial\Gamma_{H^+}}\right)_{\mu_{H^+}} - 1\right]. \tag{5}$$

Since

$$\varphi = \varphi_r + \mu_{H^+} - (\mu_{H^+})_0, \tag{6}$$

then

$$\left(\frac{\partial\varphi}{\partial\mu_{H^+}}\right)_{\Gamma_H} = \left(\frac{\partial\varphi_r}{\partial\mu_{H^+}}\right)_{\Gamma_H} + 1 = \left(\frac{\partial A_H}{\partial\Gamma_{H^+}}\right)_{\mu_{H^+}} : \left[\left(\frac{\partial A_H}{\partial\Gamma_{H^+}}\right)_{\mu_{H^+}} - 1\right], \tag{7}$$

Since $(\partial A_H / \partial\Gamma_{H^+})_{\mu_{H^+}} \leqslant 0$, then according to (7) $1 \geqslant (\partial\varphi / \partial\mu_{H^+})_{\Gamma_H} \geqslant 0$. If A_H is a constant, that is, if A_H is independent of Γ_{H^+}, and therefore of φ_r or μ_H (and in particular if $A_H = 0$) then $(\partial\varphi / \partial\mu_{H^+})_{\Gamma_H} = 0$, that is, the electrode does not function as a hydrogen electrode. If $|(\partial A_H / \partial\Gamma_{H^+})_{\mu_{H^+}}| \gg 1$, then $(\partial\varphi/\partial\mu_{H^+})_{\Gamma_H} \approx 1$, that is, the potential of the electrode depends upon the pH in the same way as the potential of the ordinary reversible electrode. For changes in μ_{H^+} and constant value of Γ_H the value of φ_r in the limited case remains constant. In particular, this should occur in alkalized solutions for not too high values of φ_r, since in this case the value of $(\partial\Gamma_{H^+} / \partial\varphi_r)_{\mu_{H^+}}$ is close to zero.

Equation (7) may also be written by replacing $d\mu_{H^+}$ by (2.3RT/F)dpH, in the form

$$\left(\frac{\partial\varphi}{\partial\,\mathrm{pH}}\right)_{\Gamma_H} = \frac{2{,}3RT}{F}\left(\frac{\partial A_H}{\partial\Gamma_{H^+}}\right)_{\mathrm{pH}} : \left[\left(\frac{\partial A_H}{\partial\Gamma_{H^+}}\right)_{\mathrm{pH}} - 1\right] \tag{8}$$

Equations (7) and (8) are suitable for experimental tests, since the values of $(\partial\varphi / \partial\mathrm{pH})_{\Gamma_H}$ and $(\partial A_H / \partial\Gamma_{H^+})_{\mathrm{pH}}$ may be measured if electrodes with sufficiently developed surfaces are used.

Measurements of the values of the potential shift of the hydrogen electrode when the pH is changed were carried out using a platinum electrode [2], and also a carbon electrode [3]. The results obtained cannot, however, be used for testing Eq. (8), since change of pH was conducted over a very wide intervals, embracing more than 9 pH units. Determination of the values of Γ_{H^+} in [1] were also only of a qualitative kind. It is hoped to make good this deficiency in the near future.

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