BRIEF COMMUNICATIONS

QUANTUM THEORY OF THE HYDROGEN OVERVOLTAGE

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A number of papers published over the past few years have developed the theory of electrode oxidizing-reducing reactions involving transport of the electron to the surface of the metal [1-3] or semiconductor [4] electrodes. So far there have only been considered reactions that take place without breaking of the chemical bond. The results of the theory accord well with experiments [3-6].

In this paper the theory is generalized to cover the case of reactions involving destruction of the chemical bond. As an example we have selected the case of hydrogen ion discharge on metals with a high overvoltage (for example, on mercury).

The chief qualitative result of the theory of oxidizing-reducing reactions is the fact that in the elementary act of the electrode process the principal role is played by thermal motion in a polar solvent and by the structure of the electronic spectrum in the electrode material. However, in papers on the theory of hydrogen overvoltage these factors have not been taken into account at all [7], or else inconsistently and incompletely [8]. In attempts to calculate the probability of hydrogen ion discharge, it is assumed in most papers that the proton moves in a classical sense, and that it can be studied by means of the activated complex method [7-9]. As can be seen from what follows, in actual fact the transition of the proton, just as transition of the electron, is essentially of a quantum nature.

Under normal conditions, the frequency ω_i of internal oscillations in the H_3O^+ ion satisfies the inequality $\omega_i \gg kT/\hbar$, so that the oscillations are not excited. Calculations show that the condition of applicability of the quasiclassical theory of the transition complex is the reverse inequality $\omega_i \ll kT/\hbar$. The same result is given by consideration of similar effects (nonradiation transitions) in polar media [10].

In this paper we calculate the current on the metal/solution interface for the following physical model: the slow stage of the process is transition of the proton from the hydroxane ion to the state of a neutral hydrogen atom adsorbed on the metal surface

$$H_3O^+ + e^- \rightleftarrows H_a + H_2O. \tag{1}$$

The next stage is electrochemical desorption

$$H_a + H_3O^+ + e^- \rightleftarrows H_2 + H_2O$$
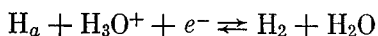
and is considered rapid. The electron participating in reaction (1) may be found at any energy level ε_f in the metal. It is assumed that interaction between the H_3O^+ ion and solvent is strong. A polar solvent is considered as an approximate dielectric continuum with the characteristic frequency of optic oscillations ω_0.

The current flowing through the solution/metal interface can be written down in the form

$$i = 2ec_s \int n(\varepsilon_f)\rho_f W_{ia}(\varepsilon_f)\,d\varepsilon_f, \tag{2}$$

where c_s is the surface concentration of H_3O^+ ions (for the sake of brevity in notation the diffusion of the double layer is not taken into account); $n(\varepsilon_f)$ and ρ_f is the distribution function and density of electron states in the metal; W_{ia} is the probability of electron-proton transition from the initial to the final state (referred to a unit of time).

Probability of the electron-proton transition was calculated in two ways. First, the calculation was made for a model in which it was assumed that the proton in the H_3O^+ ion and adsorbed atom H_a produced harmonic vibrations with different frequencies $\omega_i \approx \omega_a$. Calculation of the probability of electron-proton transition as a harmonic
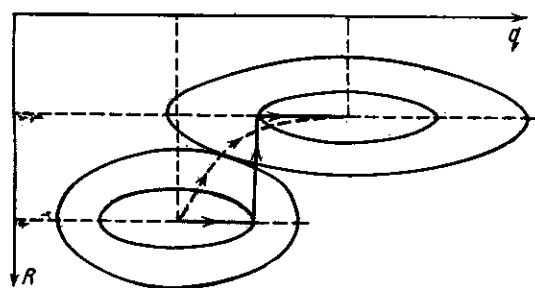
Fig. 1

approximation shows that the transition occurs in the following way: the polar solvent effects a thermal fluctuation of a scale such that the zero proton energies in the initial and final states are equalized. At this moment it becomes possible from the point of view of energy to have a "tunnel" transition of the proton/electron system. This transition is made at fixed values of the generalized coordinates q of the solvent. In Fig. 1 the solid line shows the path of the transition on plane (R, q), where R is the proton's coordinate. The ellipses represent a section of the surface of the electron energy levels in the system U(R, q) = const. The dotted line shows the path of the transition that would have been the case if the transition complex method had been used. An identical result was obtained by another method based on use of the adiabatic theory of disturbances for a virtually arbitrary form of the energy levels.

Taking an electron to be the most rapid subsystem (first adiabatic approximation) and the proton to be a rapid subsystem with respect to heavy nuclei (second adiabatic approximation), we can find the probability of transition W_{ia}. It was found by both methods that the probability of the electron-proton transition took the form:

$$W_{ia} = \varkappa \frac{\omega_0}{2\pi} \exp(-\Delta E/kT); \quad \Delta E = (J_a - J_{if} + E_s)^2/4E_s, \tag{3}$$

where

$$\varkappa = \frac{2\pi}{\omega}(\pi/\hbar^2 kTE_s)^{1/2} \cdot |V_{ai}|^2. \tag{4}$$

Here, E_s is the energy of reorganization of the solvent during transition of the proton into the adsorbed atomic state, J_a and J_{if} are the energies of the final and initial states of the entire system

$$J_{if} = J_{iF}^0 + e\eta + (\varepsilon_f - \varepsilon_F), \tag{5}$$

J_{iF}^0 is the energy of the initial state at potential φ equal to the equilibrium potential φ^0; $\eta = \varphi^0 - \varphi$ is the over-voltage, and ε_F is the Fermi level; V_{ai} is the exchange integral for the electron-proton subsystem.

Equation (3) corresponds to classical transition across the top of the barrier during motion along the solvent's coordinate and to quantum transition relative to the coordinates of the electron and proton. By substitution of (3) into (2) we get a subintegral function with a maximum for energy $\varepsilon_f = \varepsilon *$ satisfying the equation

$$dn/d\varepsilon_f - \frac{n(\varepsilon_f)}{kT} \cdot \alpha(\varepsilon_f) \cdot d(J_a - J_{if})/d\varepsilon_f = 0 \tag{6}$$

or

$$n(\varepsilon_f) = \frac{1}{2} + \frac{J_{iF}^0 - J_a}{2E_s} + \frac{e\eta}{2E_s} + \frac{\varepsilon_f - \varepsilon_F}{2E_s}, \tag{7}$$

where

$$\alpha(\varepsilon_f) = d\Delta E/d(J_a - J_{if}), \tag{8}$$

$\varepsilon *$ has the sense of the level that contributes most to the current. Equation (8) reminds us in appearance of the Bronsted relationship [11]. In the case of body reactions ΔJ coincides with the heat of the reaction. The specific nature of the electrochemical reactions is that $J_a - J_{if}$ is a nonthermodynamic quantity, and the given relationship therefore cannot be regarded as a Bronsted relationship. However, we may introduce the quantity $\alpha* = \alpha(\varepsilon*)$, which is an analogue of the Bronsted coefficient in electrochemical reactions. It can be demonstrated from Eq. (7) that

$$\alpha^* = 1 - n(\varepsilon^*). \tag{9}$$

Analytical expressions for the current take different forms in different overvoltage regions. In the region of small overvoltages,

$$(kT < e\eta \lesssim J_a - J_{iF}{}^0 - E_s) \quad n(\varepsilon^*) \ll 1, \quad \alpha^* \approx 1$$

and

$$i = 2e\rho^* c_s \omega_0 (kTE_s/\pi)^{1/2} \cdot \exp[(e\eta + J_{iF}{}^0 - J_a)/kT] \quad . \tag{10}$$

Expression (10) takes the form of the Tafel equation with a transport coefficient $\alpha^* \approx 1$. The activation energy of the process in this region is $\Delta E = E_s$. It can be shown that this activation energy corresponds to barrier-free transitions, recently derived experimentally by Krishtalik [12]. Since $n(\varepsilon^*) \ll 1$, the chief contribution to the current is made by electrons from the levels $\varepsilon^* > \varepsilon_F$, i.e., electrons moving from the upper, poorly filled levels.

When the cathodic overvoltage is increased, in the region $|e\eta - (J_a - J_{iF}{}^0)| < E_s$,

$$i = \varkappa c_s \rho^* e \omega_0 kT \exp\left\{ -\frac{E_s}{4kT} + \frac{(e\eta - J_a + J_{iF}{}^0)}{2kT} \cdot \left[1 + \frac{J_a - J_{iF}{}^0 - e\eta}{E_s} \right] \right\} \quad . \tag{11}$$

Over the overvoltage region $|e\eta - (J_a - J_{iF}{}^0)| \ll E_s$ Eq. (11) changes into the Tafel equation with $\alpha^* \approx \frac{1}{2}$. In this region the main contribution to the current is made by electrons coming from the Fermi level $\varepsilon^* \approx \varepsilon_F[n(\varepsilon^*) \simeq \frac{1}{2}]$. If it is assumed that $E_s \sim 2\text{-}4$ eV, then $\alpha^* = \frac{1}{2}(1 \pm 0.1)$ over the interval $\eta \sim 0.4\text{-}0.8$ V.

Finally, at very high overvoltages

$$i = 2e c_s \rho^* \omega_0 (kTE_s/\pi)^{1/2} = \text{const.} \tag{12}$$

Here $\alpha^* = 0$, $n(\varepsilon^*) = 1$, i.e., the principal contribution to the current is provided by transitions from filled levels $\varepsilon^* < \varepsilon_F$. Here ΔE proves equal to 0, so that the transitions are nonactivational in nature.

The theory gives us an opportunity of describing in full the isotropic effect, which is connected both with variation in the quantity $(J_a - J_{iF}{}^0)$, as well as in V_{ai} (for nonadiabatic reactions when $(\varkappa < 1)$ when the proton is replaced by a deuteron or triton. Dependence of the overvoltage on the metal is connected first and foremost with variation in $J_a - J_{iF}{}^0$, as well as with variation in ρ and V_{ai}. Dependence of the process on the nature and state of the solvent is characterized by E_s.

Thus, the theory makes it possible to describe the process in its entirety from a single viewpoint and quantitatively, to boot.

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