CALCULATION OF THE PROBABILITY OF THE ELEMENTARY ACT OF SOME HETEROGENEOUS OXIDATION-REDUCTION REACTIONS

R. R. Dogonadze and Yu. A. Chizmadzhev

Institute of Electrochemistry, Academy of Sciences USSR
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Most theoretical work on the kinetics of electrode processes is based on formulas from the theory of absolute reaction rates [1]. The applicability of the latter to electron-exhange reactions requires substantiation. We undertook to calculate the probability of an electron transfer between an electrode and an ion by the quantum mechanical method in order to calculate subsequently the current in an oxidation-reduction system without using the theory of absolute reaction rates. We will limit ourselves to an examination of electron-exchange reactions which are not complicated by adsorption.

Let us examine a system consisting of an electrode, a polar solvent, an ion A^{3+}, and an electron, which may belong to either the ion or the electrode. The solvent will be regarded as a continuous dielectric medium, which is characterized by one frequency of optical vibrations ω [2]. This description of the solvent is justified in the case where the structure of the first solvate envelope of the ion does not change substantially during the electron transfer. We will write the Hamiltonian of the complete system in the form:

$$H = \frac{p_e^2}{2m} + V_{el} - U_0 + V_{es} - e\varphi(\mathbf{r}) + V_{is} + H_s, \tag{1}$$

where the first term represents the kinetic energy of the electron; the second, third, and fourth terms correspond to the potential energy of the interaction of the electron with the ion A^{3+}, the crystal lattice of the electrode, and the solvent molecules, respectively; V_{is} is the energy of interaction of the ion A^{3+} with the solvent; H_s is the Hamiltonian of the solvent. The electrostatic potential created by all the ions (apart from the given ion A^{3+}) and the electrode is represented by $\varphi(r)$. If the electrode is a metal, $\varphi(r)$ will equal φ_m = const everywhere within the metal. However, for semiconductor electrodes, $\varphi(r)$ will fall both in the electrolyte solution and in the electrode. The approximate change in $\varphi(r)$ for these two cases is given in Fig. 1, where a corresponds to a metal and b corresponds to a semiconductor electrode.

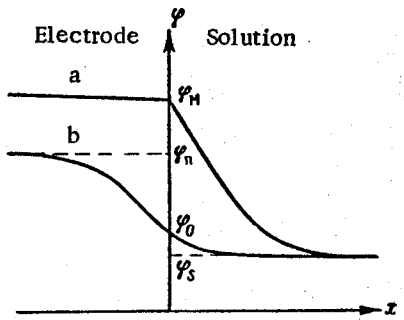

Fig. 1.

In regarding the solvent as a dielectric medium, we will represent its total polarization P as consisting of an electronic component P_e and the polarization P_u caused by the movements of the solvent particles. The component P_e is connected with the inertia-free polarization of the electron shells of the solvent molecules. The component P_u, which is produced by the movements of heavy particles, is inertial. Therefore, the instantaneous value of the total polarization P will no longer be determined by the induction D. However, for the equilibrium polarization P_0, as before it is possible to use the formula

$$\mathbf{P}_0 = \frac{\varepsilon_s - 1}{4\pi\varepsilon_s}\mathbf{D}_0. \tag{2}$$

Moreover, considering the fact that

$$\mathbf{P}_e = \frac{\varepsilon_0 - 1}{4\pi\varepsilon_0}\mathbf{D}_0, \tag{3}$$

we obtained the equilibrium value of the inertial part P_{u0}:

$$\mathbf{P}_{u0} = \frac{1}{4\pi}\left(\frac{1}{\varepsilon_0} - \frac{1}{\varepsilon_s}\right) \equiv \frac{c}{4\pi}\mathbf{D}_0, \tag{4}$$

where ε_s represents the static dielectric constant and ε_0 the optical dielectric constant.

We will write the Hamiltonian of the solvent H_s in the form

$$H_s = T_u + U_p + W_0,$$

where T_u is the kinetic energy of the solvent particles, U_p is the potential energy of the solvent connected with the polarization P_u, and W_0 is the statistical (equilibrium) energy of the solvent in the absence of charges. To find U_p, we introduce an imaginary field induction D', which is related to the given polarization P_u by the equilibrium relation

$$\mathbf{P}_u = \frac{c}{4\pi}\mathbf{D}'.$$

The potential energy of the solvent U_p equals the work necessary for the slow formation of the induction D' and subsequent rapid reduction of the field from D' to D_0:

$$U_p = \int dv \int_0^{D'} \mathbf{D}\, d\mathbf{P}_0 + \int dv \int_{D'}^{D_0} \mathbf{D}\, d\mathbf{P}_e = \frac{2\pi}{c}\int \mathbf{P}_u^2\, dv + \frac{\varepsilon_0 - 1}{8\pi\varepsilon_0}\int \mathbf{D}_0^2\, dv.$$

In the equilibrium case, $P_u = P_{u0}$ and

$$U_{p0} = \frac{\varepsilon_s - 1}{8\pi\varepsilon_s}\int \mathbf{D}_0^2\, dv. \tag{5}$$

The term D_0 represents the induction of the field of the ion A^{2+} if the electron is at the ion A^{3+} or the induction of the field of A^{3+} if the electron belongs to the electrode. We will denote the corresponding inductions by D_{02} and D_{03}.

Omitting the term W_0 = const, which does not change during the electron transfer, we write the Hamiltonian H_s in the form:

$$H_s^{\alpha} = \frac{2\pi}{c}\int\left(\mathbf{P}_u^2 + \frac{1}{\omega^2}\dot{\mathbf{P}}_u^2\right) dv + \frac{\varepsilon_0 - 1}{8\pi\varepsilon_0}\int \mathbf{D}_{0\alpha}^2\, dv, \quad \alpha = 2,3. \tag{6}$$

The first term in this expression corresponds to the Hamiltonian of the H_f, which, after quantization [2], assumes the form:

$$H_f(q) = \frac{\hbar\omega}{2}\sum_k\left(q_k^2 - \frac{\partial^2}{\partial q_k^2}\right),$$

where q_k represents the normal coordinates of the solvent.

Finally, we find V_{es} and V_{is}:

$$V_{es} + V_{is} = -\int\left[\mathbf{D}_{03}(\mathbf{r}' - \mathbf{R}) + \mathbf{D}_{0e}(\mathbf{r}' - \mathbf{r})\right]\mathbf{P}_u(\mathbf{r}')\, dv' - \int \mathbf{D}_{0\alpha}\mathbf{P}_e\, dv,$$

or, after quantization,

$$V_{es} + V_{is} = \sum_k [v_k(\mathbf{r}) + u_k(\mathbf{R})]\, q_k - \frac{\varepsilon_0 - 1}{8\pi\varepsilon_0}\int \mathbf{D}_{0\alpha}^2\, dv, \tag{7}$$

where R is the coordinate of the ion A^{3+} and r is the coordinate of the electron. We will not write out here the explicit form of the functions $v_k(\mathbf{r})$ and $u_k(\mathbf{R})$; we should only note that $v_k(\mathbf{r}) = 0$ when $x < 0$ (the half-space $x < 0$ corresponds to the electrode and $x > 0$ solution). Physically this requirement means that an electron belonging to the electrode should not produce a change in the polarization about the ion A^{3+}. This condition will be well fulfilled if it is assumed that the ion A^{3+} is sufficiently far from the electrode. Finally the full Hamiltonian H is rewritten in the form:

$$H = \frac{\mathbf{p}_e^2}{2m} + V_{el} - U_0 - e\varphi(\mathbf{r}) + \sum_k (v_k + u_k) q_k + H_f - \frac{\varepsilon_0 - 1}{8\pi\varepsilon_0} \int \mathbf{D}_{0\alpha}^2 \, dv. \tag{8}$$

In accordance with the adiabatic pertubation theory, we will look for wave functions of the electron with constant q_k:

$$\left[\frac{\mathbf{p}_e^2}{2m} - U_0 - e\varphi(\mathbf{r})\right] \psi_f = \varepsilon_f' \psi_f; \tag{9}$$

$$\left[\frac{\mathbf{p}_e^2}{2m} + V_{el} - e\varphi(\mathbf{r}) + \sum_k v_k q_k\right] \psi_2 = \varepsilon_2(q)\, \psi_2, \tag{10}$$

where ψ_2 is the wave function of an electron at the ion A^{3+} and ψ_f is the wave function of an electron at the electrode in the state f. As $\varphi(\mathbf{r})$ changes weakly at atomic distances, into $\varepsilon_2(q)$ we introduce an additive term $-e\varphi(\mathbf{r})$. In addition, taking only the first term in the expansion of $\varepsilon_2(q)$ with respect to powers of q, as is usual, we obtain:

$$\varepsilon_2(q) = \varepsilon_2 + \sum_k v_{k2} q_k - e\varphi(\mathbf{R}); \quad v_{k2} = \int |\psi_2|^2 v_k(\mathbf{r})\, dv, \tag{11}$$

where the energy of the electron in A^{2+} in the gas phase is denoted by ε_2. As was mentioned above, in the case of a metal electrode $\varphi(\mathbf{r}) = \varphi_m$ when $x < 0$; therefore

$$\varepsilon_f' = \varepsilon_f - e\varphi_M - U_0. \tag{12}$$

In the case of a semiconductor electrode, in accordance with the band theory, at the surface there will be a bend in the bands:

$$\varepsilon_f' = \varepsilon_f - e\varphi(x) - U_0. \tag{13}$$

The energy diagrams for these two cases in the band approximation are given in Fig. 2. In view of the approximation we adopted, according to which R is large, we will consider that the electron transfer occurs at the

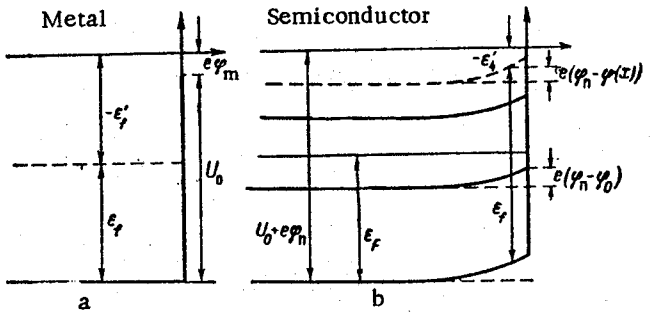

Fig. 2.

semiconductor surface so that

$$\varepsilon_f' = \varepsilon_f - e\varphi(0) - U_0. \tag{14}$$

For the sake of convenience, formulas (12) and (14) will be written in one form:

$$\varepsilon_f' = \varepsilon_f - e\varphi_0 - U_0, \tag{15}$$

where $\varphi_0 = \varphi_m$ in the case of a metal electrode and $\varphi_0 = \varphi(0)$ for a semiconductor electrode; as Fig. 2 shows, $\varepsilon_f \geq 0$.

We will look for the solution of the equation

$$H\Psi = E\Psi \tag{16}$$

in the form

$$\Psi = \chi_2(q)\,\psi_2(\mathbf{r}) + \sum_f \chi_f(q)\,\psi_f(\mathbf{r}). \tag{17}$$

By substituting (17) in (16), multiplying this equation once by ψ_2^* and then by ψ_f^*, and integrating with respect to r, we obtain:

$$[H_2(q) - E]\,\chi_2 = \sum_f L_{2f}\,\chi_f, \qquad [H_0(q) - E]\,\chi_f = L_{f2}\chi_2, \tag{18}$$

where

$$H_2(q) = H_f(q - q_{02}) + I_2; \quad q_{02k} = -\frac{v_{k2} + u_k}{\hbar\omega}; \quad H_0(q) = H_f(q - q_{03}) + I_f;$$
$$q_{03k} = -\frac{u_k}{\hbar\omega}; \quad I_2 = \varepsilon_2 - e\varphi(\mathbf{R}) - \frac{\varepsilon_s - 1}{8\pi\varepsilon_s}\int \mathbf{D}_{02}^2\,dv; \quad I_f = \varepsilon_f - e\varphi_0 - U_0 -$$
$$- \frac{\varepsilon^s - 1}{8\pi\varepsilon_s}\int \mathbf{D}_{03}^2\,dv.$$

At sufficiently large values of R, the exchange integrals in (18)

$$L_{2f} = \int \psi_2^* V_{ei}\,\psi_f\,dv; \quad L_{f2} = \int \psi_f^* U_0 \psi_2\,dv \tag{19}$$

may be regarded as a perturbation and the probability of an electron transfer between the ion and the electrode may be found from the normal perturbation theory. If we observe that equation (18) formally has the same form as the corresponding equations for electron exchanges in homogeneous reactions, we may use formula (46) from [2] for the probability of the transfer. At high temperatures ($kT > \hbar\omega$), in a semiclassical approximation, the probability of the transfer of an electron from the ion to the electrode at the level f is determined by the formula:

$$w_{2f} = \left(\frac{\pi}{\hbar^2 kTE_s}\right)^{1/2} |L_{f2}|^2 \exp\left\{-\frac{(I_f - I_2 + E_s)^2}{4E_s kT}\right\}, \tag{20}$$

where we introduce the symbol

$$E_s = \frac{c}{8\pi}\int (\mathbf{D}_{03} - \mathbf{D}_{02})^2\,dv.$$

To determine the probability of the reverse transfer it is possible to use formula (20) with the indices f and 2 transposed.

From formula (20) it follows that the probability of an electron transfer actually has the exponential form:

$$W = K\exp\left(-\frac{\Delta E^*}{kT}\right), \tag{21}$$

as in the theory of absolute reaction rates. The calculation presented, apart from proving (21), leads to an explicit expression for the activation energy ΔE^* and pre-exponential factor K.

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