PHYSICAL CHEMISTRY

R. R. DOGONADZE and Yu. A. CHIZMADZHEV

1962

SovietRxiv

Abstract

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

(Presented by Academician A. N. Frumkin on 31 I 1962)

Most theoretical works devoted to the kinetics of electrode processes are based on the application of formulas from the theory of absolute reaction rates (1). The applicability of the latter to electron-transfer reactions requires justification. Our aim was to calculate, by a quantum-mechanical method, the probability of electron transfer between an electrode and an ion, so that subsequently the current in an oxidation-reduction system could be calculated without the aid of the theory of absolute reaction rates. We shall confine ourselves to considering electron-transfer reactions not complicated by adsorption.

Let us consider a system consisting of an electrode, a polar solvent, an ion A^{3+}, and an electron, which may belong either to the ion or to the electrode. We shall regard the solvent as a continuous dielectric medium characterized by a single frequency of optical vibrations ω (2). Such a description of the solvent is justified when the structure of the first solvation shell of the ion does not change substantially during the electron transfer. The Hamiltonian of the complete system will be written in the form:

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

where the first term represents the kinetic energy of the electron; the second, third, and fourth terms correspond to the potential energy of interaction of the electron with the ion A^{3+}, with the crystal lattice of the electrode, and with the solvent molecules, respectively; V_{is} is the energy of interaction of the ion A^{3+} with the solvent, and H_s is the Hamiltonian of the solvent. By $\varphi(\mathbf{r})$ is denoted the electrostatic potential created by all the ions (except the given ion A^{3+}) and by the electrode. In the case where the electrode is a metal, $\varphi(\mathbf{r})$ will be equal to $\varphi_M = \text{const}$ everywhere inside the metal. However, for semiconductor electrodes $\varphi(\mathbf{r})$ will fall off both in the electrolyte solution and in the electrode.

Fig. 1

Figure 1: Fig. 1

The approximate course of $\varphi(\mathbf{r})$ for these two cases is shown in Fig. 1, where a corresponds to a metallic electrode and b to a semiconductor electrode.

Fig. 1

Treating the solvent as a dielectric medium, we shall characterize it by its total polarization $\mathbf{P}$, consisting of the electronic component $\mathbf{P}_e$ and the polarization $\mathbf{P}_u$ caused by displacements of the solvent particles. The component $\mathbf{P}_e$ is associated with the inertia-free polarization of the electron shells of the solvent molecules. The component $\mathbf{P}_u$, caused by

with displacements of the heavy particles, is inertial. Therefore the instantaneous value of the total polarization $\mathbf{P}$ will no longer be determined by the induction $\mathbf{D}$. However, for the equilibrium polarization $\mathbf{P}_0$ one may still use the formula

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

Taking into account, moreover, that

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

we obtain the equilibrium value of the inertial part $\mathbf{P}_{u0}$:

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

where ε_s denotes the static dielectric constant, and ε_0 the optical one.

We shall 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 associated with the inertial polarization $\mathbf{P}_u$, and W_0 is the static (equilibrium) energy of the solvent in the absence of charges. To find U_p, we introduce a fictitious field induction $\mathbf{D}'$, which is related to the given polarization $\mathbf{P}_u$ by the equilibrium relation

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

The potential energy of the solvent U_p is equal to the work required for the slow formation of the induction $\mathbf{D}'$ and the subsequent rapid switching off of the field from $\mathbf{D}'$ to $\mathbf{D}_0$:

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

In the equilibrium case $\mathbf{P}_u = \mathbf{P}_{u0}$, and

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

By $\mathbf{D}_0$ one should understand the induction of the field of the ion A^{2+} if the electron is located at the ion A^{3+}, or the induction of the field of A^{3+} if the electron belongs to the electrode. We shall denote the corresponding inductions by $\mathbf{D}_{02}$ and $\mathbf{D}_{03}$.

Omitting the term $W_0 = \text{const}$, which does not change in the process of 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 phonon Hamiltonian H_f, which after quantization (2) takes the form:

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

where q_k are the normal coordinates of the solvent.

Finally, let us find V_{es} and V_{is}:

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

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 $\mathbf{R}$ is the coordinate of the ion A^{3+} and $\mathbf{r}$ is the coordinate of the electron. We shall not write here the explicit form of the functions $v_k(\mathbf{r})$ and $u_k(\mathbf{R})$; let

Fig. 2

Figure 2: Fig. 2

us only note that $v_k(\mathbf{r}) = 0$ for $x < 0$ (the half-space $x < 0$ corresponds to the electrode, and $x > 0$ to the solution). Physically, this requirement means that an electron belonging to the electrode must not cause a change in the polarization around the ion A^{3+}. This condition will be well satisfied if it is assumed that the ion A^{3+} is located sufficiently far from the electrode.

Fig. 2

Finally, we rewrite the complete Hamiltonian H in the form:

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

According to adiabatic perturbation theory, we shall seek the electron wave functions for fixed q_k:

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

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

where ψ_2 is the wave function of the electron located at the ion A^{3+}, and ψ_f is the wave function of the electron located in the electrode in the state f. Since $\varphi(\mathbf{r})$ varies only weakly over atomic distances, the term $-e\varphi(\mathbf{r})$ will enter $\varepsilon_2(q)$ additively. In addition, restricting ourselves, as usual, to the first term in the expansion of $\varepsilon_2(q)$ in powers of q, we obtain:

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

where ε_2 denotes the energy of the electron in A^{2+} in the gas phase. As noted above, in the case of a metallic electrode $\varphi(\mathbf{r}) = \varphi_M$ for $x < 0$; therefore

$$\varepsilon'_f = \varepsilon_f - e\varphi_M - U_0. \quad (12)$$

In the case of a semiconductor electrode, according to band theory, band bending will occur at the surface:

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

The energy diagrams for these two cases in the band approximation are shown in Fig. 2. In view of the approximation adopted by us, according to which R is large, we shall assume that the electronic transition occurs at the surface of the semiconductor, so that

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

For convenience, we shall write formulas (12) and (14) in a single form:

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

where $\varphi_0 = \varphi_{\mathrm{m}}$ in the case of a metallic electrode and $\varphi_0 = \varphi(0)$ for a semiconductor electrode; as is seen from Fig. 2, $\varepsilon_f \geqslant 0$.

We shall seek the solution of the equation

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

in the form

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

Substituting (17) into (16) and multiplying this equation once by ψ_2^*, and another time by ψ_f^*, and integrating over $\mathbf{r}$, 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

$$H_2(q) = H_f(q - q_{02}) + I_2; \qquad q_{02k} = -\frac{v_{k2} + u_k}{\hbar\omega}; \qquad H_0(q) = H_f(q - q_{03}) + I_f;$$

$$q_{03k} = -\frac{u_k}{\hbar\omega}; \qquad I_2 = \varepsilon_2 - e\varphi(\mathbf{R}) - \frac{\varepsilon_s - 1}{8\pi\varepsilon_s}\int \mathbf{D}_{02}^2\,dv; \qquad I_f = \varepsilon_f - e\varphi_0 - U_0 -$$

$$-\frac{\varepsilon_s - 1}{8\pi\varepsilon_s}\int \mathbf{D}_{03}^2\,dv.$$

The exchange integrals entering into (18),

$$L_{2f} = \int \psi_2^* V_{ei} \psi_f \, dv; \qquad L_{f2} = \int \psi_f^* U_0 \psi_2 \, dv \tag{1.9}$$

for sufficiently large R, may be regarded as a perturbation, and the probability of an electronic transition between the ion and the electrode may be found from the usual perturbation theory. Noting that equations (18) formally have the same form as the corresponding equations for electron-transfer reactions in the case of homogeneous reactions, we may use formula (46) of work (^{2}) for the transition probability. At high temperatures ($kT > \hbar\omega$), in the semiclassical approximation the probability of transition of an electron from the ion into the electrode to level f is determined by the formula:

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

where the notation

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

has been introduced.

To determine the probability of the reverse transition, one may use formula (20), in which the indices f and 2 should then be interchanged.

It follows from formula (20) that the probability of electron transition indeed has an exponential form:

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

as in the theory of absolute reaction rates. The calculation presented, besides substantiating (21), leads to explicit expressions for the activation energy ΔE^* and the pre-exponential factor K.

We express our gratitude to Corresponding Member of the Academy of Sciences of the USSR V. G. Levich for discussion of the results and useful comments.

Institute of Electrochemistry
Academy of Sciences of the USSR

Received
30 I 1962

CITED LITERATURE

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Note: Figure translations are in progress. See original paper for figures.