

Rearrangement Energy for Electron Transfer at Semiconductor/Electrolyte Interface

Kenkichiro Kobayashi, Masasuke Takata, and Shoichi Okamoto

Faculty of Engineering, Technological University of Nagaoka, Nagaoka, Niigata, 949-54 Japan

Mitsunori Sukigara

Institute of Industrial Science, University of Tokyo, Roppongi, Minato-ku, Tokyo 106 Japan

ABSTRACT

General formulas of the rearrangement energy for the electron transfer at a semiconductor/electrolyte interface are derived by using the dielectric continuum theory. The rearrangement energy of orientational and intramolecular vibrations of solvent and lattice vibration of the semiconductor depends not only on the distance between the electrode surface and redox ions, but also on dielectric constant of the semiconductor. Theoretical values of the rearrangement energy are compared with experimental values.

Nonradiative electron transfer in a polar solvent occurs accompanying the thermal excitation and emission of many phonons and is called a multiphonon process (1). The electron transfer rate in the multiphonon process is governed by the electronic matrix element coupling the initial and the final states of the electron transfer, and by phonon-state density, which is the Franck-Condon factor statistically averaged over the initial state of phonons. The phonon-state density is responsible for the temperature dependence of the electron transfer rate, and it increases with the decrease in the rearrangement energy of various vibrations participating in the electron transfer. The rearrangement energy of orientational vibration of a solvent, $E_s(o_s)$, is one of the important factors determining the phonon-state density for the electron transfer in a polar solvent. The $E_s(o_s)$ values have been estimated from the electron transfer rate constants by assuming the transmission coefficient to be unity (2). This assumption is plausible for an adiabatic electron transfer in which the electronic matrix element is very large. On the contrary, nonadiabatic electron transfer was experimentally found in the electrochemical reductions of Fe^{3+} at the organic crystal electrode (3) and in homogeneous electron transfer reactions including europium ions (4). In the case of the nonadiabatic electron transfer, information about the transmission coefficient or the electronic matrix element is necessary to determine the accurate $E_s(o_s)$ value from the electron transfer rate. The formal application of the adiabatic electron transfer may lead to the overestimation of the $E_s(o_s)$ value by a term of the transmission coefficient. On the other hand, it was reported (5-8) that the $E_s(o_s)$ values can be determined directly from current-voltage characteristics at a semiconductor/electrolyte interface. The advantage of the above method is that, since the phonon-state density can be obtained separately from the electronic matrix element, the estimated $E_s(o_s)$ values do not involve the uncertainty of the transmission coefficient. Such experimentally obtained $E_s(o_s)$ values have been compared with the theoretical $E_s(o_s)$ values for the electron transfer at a metal electrode. The $E_s(o_s)$ values in electrochemical reactions, however, depend on the mirror image force between an electrode and an electron transferred into the oxidant ion (9). This mirror image force is related to the difference in the dielectric constants of the electrode and the solvent. Since the dielectric constant of a metal is infinite, the electric field is everywhere zero in a metal electrode, while there is a nonzero electric field inside a semiconductor. Thus, an $E_s(o_s)$ value obtained at a semiconductor electrode with a small dielectric constant may deviate from that at a metal electrode. The semiconductor is polarized by the electron transferred into the oxidant ion, and thus the

Key words: rearrangement energy, electron transfer, semiconductor electrode.

rearrangement energy of lattice vibrations of the semiconductor electrode should be taken into account. In the present paper, we derived formulas for the rearrangement energy of several vibrations governing the electron transfer rate at the semiconductor/electrolyte interface.

Theory

Model of electron transfer at semiconductor/electrolyte interface.—We are concerned with one-electron transfer from the occupied conduction band of a semiconductor to an oxidant ion, or from a reductant ion to the empty conduction band: $\text{Ox} + e \rightleftharpoons \text{Re}$, where Ox denotes an oxidant ion with the charge $m+$, Re denotes a reductant ion with the charge $(m - 1)+$, and e is an electron in the conduction band. The spatial arrangement at the interface of the semiconductor and electrolyte is schematically shown in Fig. 1. The shape of the oxidant and reductant ions is approximated as a sphere, and the center of the reductant and oxidant ions is located apart from the semiconductor surface by $R/2$. No solvent penetrates inside of the ion sphere r_b . The ion possesses intramolecular vibration of frequency $\omega \approx 10^{13} \text{ s}^{-1}$. A polar solvent such as water possesses not only orientational vibration of a permanent dipole moment but also stretching or deformation vibrations (10). The energy of the orientational vibration of the solvent is about 10^{-4} eV ($\omega \approx 10^{11} \text{ s}^{-1}$), while the energy of the deformation or stretching vibration of the solvent ranges from 0.01 to 0.1 eV ($\omega \approx 10^{13} \sim 10^{14} \text{ s}^{-1}$). For simplicity, we assume that one mode among the intramolecular vibrations of the solvent contributes to electron transfer. Self-trapping of an electron observed in ionic semiconductors is the result of the strong interaction of an electron with the lattice vibration. The electron in the reductant ion located near the ionic semiconductor surface can also interact with the lattice vibration. Since for covalent semiconductors the electron-phonon interaction is weak in comparison with that in ionic semiconductors (11), hereafter we consider only ionic semiconductors. Accordingly, the vibrations taking part in the electron transfer at the semiconductor/electrolyte interface consist of the orientational vibration of the solvent, the intramolecular vibrations of the oxidant ion and of the solvent, and the optical phonons of the lattice vibration in the ionic semiconductor. In the cathodic process, at the final state an electron has been transferred into the oxidant ion and interacts strongly with the orientational vibration of the solvent, the intramolecular vibrations of the ion and of the solvent, and the optical phonons in the ionic semiconductor. At the initial state, an electron in the conduction band is delocalized over the semiconductor, so that its interaction with the said vibrations is negligible. The difference in this electron-phonon interaction results in the shift of the equilibrium coordinate of the interaction

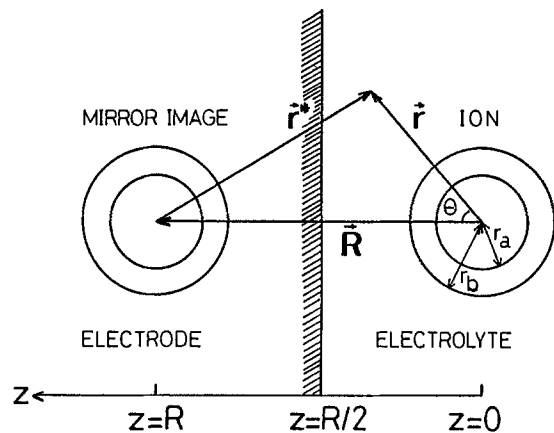


Fig. 1. Geometry in determining the dielectric displacement by an electron transferred into the oxidant ion and the mirror image charge in a semiconductor electrode.

modes of various vibrations, *e. g.*, the ion radius is varied from r_a (oxidant) to r_b (reductant) after electron transfer from the semiconductor to the oxidant ion. The orientational vibration of the solvent with the slow relaxation time cannot respond to the fast change of the ionic radius after the electron transfer and cannot follow the thermal fluctuation of the ionic radius. However, the intramolecular vibration of the solvent can follow the thermal fluctuation of the ionic radius. This indicates that the interaction energy of the electron with the intramolecular vibration of the solvent depends on the coordinate of the intramolecular vibration of the ion (12). For simplicity, in the calculation of the rearrangement energy due to the intramolecular vibration of the solvent, the ionic radius is assumed to be frozen at r_b of the reductant ion.

Electric potential inside semiconductor, solvent, and reductant ion.—A solvent and a semiconductor are treated as dielectrics, which are uniform, isotropic, and unsaturated. The electrostatic potential at any point (r, ϑ, φ) inside the sphere r_b is given by (13)

$$V_1(r, \vartheta, \varphi) = \int_{r'=0}^{\infty} \frac{e |\Psi(r', \vartheta', \varphi')|^2}{\epsilon_1 |\mathbf{r} - \mathbf{r}'|} d v' + \sum_{n=0}^{\infty} \sum_{m=-n}^n B_{nm} r^n P_n^m(\cos \vartheta) e^{im\varphi} \quad [1]$$

where e is the charge of an electron, $\Psi(r', \vartheta', \varphi')$ is the electronic wavefunction in the reductant ion at point $(r', \vartheta', \varphi')$, the $P_n^m(\cos \vartheta)$ are the associated Legendre functions, and ϵ_1 is the dielectric constant inside the sphere r_b . The second term in Eq. [1] is the result of the charge distribution outside the sphere r_b . For simplicity, we assume that $|\Psi|^2$ has the spherical symmetry and no probability outside sphere r_b . Under this condition, Eq. [1] reduces to

$$V_1(r, \vartheta, \varphi) = \frac{e}{\epsilon_1 r} \int_{r'=0}^{r=r} |\Psi(r', \vartheta', \varphi')|^2 4\pi r'^2 dr' + \sum_{n=0}^{\infty} \sum_{m=-n}^n B_{nm} r^n P_n^m(\cos \vartheta) e^{im\varphi} \quad [2]$$

The electrostatic potential inside the semiconductor having the dielectric constant ϵ_3 satisfies Laplace's equation and is taken to be zero at $r \rightarrow \infty$. Thus, we have

$$V_3 = \sum_{n=0}^{\infty} \sum_{m=-n}^n \frac{D_{nm}}{r^{n+1}} P_n^m(\cos \vartheta) e^{im\varphi} \quad [3]$$

The electrostatic potential inside the solvent having the dielectric constant ϵ_2 is written as

$$V_2 = \sum_{n=0}^{\infty} \sum_{m=-n}^n \frac{G_{nm}}{r^{n+1}} P_n^m(\cos \varphi) e^{im\varphi} + \sum_{n=0}^{\infty} \sum_{m=-n}^n \frac{C_{nm}}{(r^*)^{n+1}} P_n^m(\cos \vartheta^*) e^{im\varphi^*} \quad [4]$$

where the coordinate $(r^*, \vartheta^*, \varphi^*)$ is related to the coordinate (r, ϑ, φ) as follows

$$r^* = (x^2 + y^2 + (z - R)^2)^{1/2} = (r^2 + R^2 - 2rR \cos \vartheta)^{1/2} \\ \cos \vartheta^* = (R - r \cos \vartheta) / (r^2 + R^2 - 2rR \cos \vartheta)^{1/2} \\ \varphi^* = \varphi \quad [5]$$

At the interface of semiconductor/electrolyte ($z = R/2$), V_2 and V_3 , and the normal component of the dielectric displacement, $-\epsilon_2 dV_2/dz$ and $-\epsilon_3 dV_3/dz$, shall be equal to each other. Thus, for the component of $n = m = 0$, one gets

$$\frac{G_{00}}{[x^2 + y^2 + (R/2)^2]^{1/2}} + \frac{C_{00}}{[x^2 + y^2 + (R/2 - R)^2]^{1/2}} = \frac{D_{00}}{[x^2 + y^2 + (R/2)^2]^{1/2}} \quad [6]$$

and

$$-\epsilon_2 \left\{ \frac{R/2 G_{00}}{[x^2 + y^2 + (R/2)^2]^{3/2}} + \frac{(R/2 - R) C_{00}}{[x^2 + y^2 + (R/2 - R)^2]^{3/2}} \right\} = \frac{-\epsilon_3 R/2 D_{00}}{[x^2 + y^2 + (R/2)^2]^{3/2}} \quad [7]$$

Then, it follows that

$$G_{00} = \frac{\epsilon_2 + \epsilon_3}{2\epsilon_2} D_{00}, \text{ and } C_{00} = \frac{\epsilon_2 - \epsilon_3}{2\epsilon_2} D_{00} \quad [8]$$

In order to get the boundary condition on the surface of sphere r_b , we expand V_2 in powers of $\cos \vartheta$ in the following form

$$V_2 = \sum_{n=0}^{\infty} \sum_{m=-n}^n \frac{G_{nm}}{r^{n+1}} P_n^m(\cos \vartheta) e^{im\varphi} + \sum_{n=0}^{\infty} \sum_{m=-n}^n \frac{C_{nm} P_n^m(\cos \vartheta^*)}{(r^2 + R^2)^{(n+1)/2}} e^{im\varphi} \left[1 + \sum_{k=1}^{\infty} (-1)^k \frac{(n+1)(n+3) \cdots (n+2k-1)}{2^k} \frac{1}{k!} \left(\frac{2Rr \cos \vartheta}{r^2 + R^2} \right)^k \right] \quad [9]$$

where

$$\cos \vartheta^* = (R - r \cos \vartheta) (r^2 + R^2)^{-1/2} \left\{ 1 + \sum_j (-1)^j \frac{1}{2} \frac{3}{2} \cdots \frac{(2j-1)}{2} \frac{1}{j!} \left(\frac{2Rr \cos \vartheta}{r^2 + R^2} \right)^j \right\}$$

From the boundary condition of $V_1 = V_2$ and $-\epsilon_1 dV_1/dr = -\epsilon_2 dV_2/dr$ at $r = r_b$, we have

$$\frac{e}{\epsilon_1 r_b} + B_{00} = \frac{C_{00}}{(r_b^2 + R^2)^{1/2}} + \frac{G_{00}}{r_b} + \frac{C_{10} R}{(r_b^2 + R^2)^{3/2}} + O(h) \quad [10]$$

and

$$e^2/r_b^2 = \frac{r_b \epsilon_2^2 C_{00}}{(r_b^2 + R^2)^{3/2}} + \frac{\epsilon_2 G_{00}}{r_b^2} + \frac{3 \epsilon_2 C_{10} R r_b}{(r_b^2 + R^2)^{5/2}} + Q(h) \quad [11]$$

where $O(h)$ and $Q(h)$ are the high order terms arising from C_{n0} ($n \geq 2$). We neglect the multipole potential arising from the terms of $n \geq 1$ in V_1 , V_2 and V_3 . Under this approximation, the work for charging the sphere r_b is given by

$$\frac{eB_{00}}{2} = -\frac{e^2}{2\epsilon_1 r_b} + \frac{eC_{00}}{2(r_b^2 + R^2)^{1/2}} + \frac{eG_{00}}{2r_b} \quad [12]$$

From Eq. [10] and [11], we have

$$D_{00} = e \left\{ \frac{\epsilon_2 + \epsilon_3}{2} + \frac{\epsilon_2 - \epsilon_3}{2} \frac{r_b^3}{(r_b^2 + R^2)^{3/2}} \right\}^{-1} \quad [13]$$

We take into account only the term of $n = m = 0$, so that the subscript, 00, in G , C , D , are omitted hereafter for simplifying the description. As seen in Eq. [2], the multipole potential is not the result of the charge distribution inside the sphere r_b , but of the mirror image effect (14): the electron in the reductant ion induces the charge at the semiconductor/electrolyte interface if there is the difference in the dielectric constants between the semiconductor and the solvent. The charge induced at the semiconductor/electrolyte interface polarizes the sphere, and, in consequence, the induced dipole moment appears at the surface of the sphere r_b . The multipole potential is generated in the same manner.

Interaction of an electron with dielectrics.—The polarization of the solvent \mathbf{P}_2 consists of the electronic polarization \mathbf{P}_{2e} , the ionic polarization due to the intramolecular vibration \mathbf{P}_{2i} , and the orientational polarization of the permanent dipole moment of the solvent \mathbf{P}_{2d} . When the distribution of the electron is changed slowly, the polarization induced inside the solvent is written as

$$\mathbf{P}_2 = \mathbf{P}_{2e} + \mathbf{P}_{2i} + \mathbf{P}_{2d} = \chi_{2s} \mathbf{E}_{2s} = \frac{\epsilon_{2s} - 1}{4\pi} \mathbf{E}_{2s} \quad [14]$$

where χ_{2s} is the dielectric susceptibility of the solvent and \mathbf{E}_{2s} is the static electric field inside the solvent. Similarly, for the slow fluctuation of the electron distribution, the polarization induced inside the semiconductor is written as

$$\mathbf{P}_3 = \mathbf{P}_{3e} + \mathbf{P}_{3i} = \chi_{3s} \mathbf{E}_{3s} = \frac{\epsilon_{3s} - 1}{4\pi} \mathbf{E}_{3s} \quad [15]$$

where χ_{3s} is the dielectric susceptibility of the semiconductor and \mathbf{E}_{3s} is the electric field inside the semiconductor. The static electric field inside the solvent \mathbf{E}_{2s} is given by

$$\mathbf{E}_{2s} = G_s \frac{\mathbf{r}}{|\mathbf{r}|^3} + C_s \frac{\mathbf{r}^*}{|\mathbf{r}^*|^3} \quad [16]$$

Similarly, the static electric field inside the semiconductor is

$$\mathbf{E}_{3s} = D_s \frac{\mathbf{r}}{|\mathbf{r}|^3} \quad [17]$$

where the coefficients, G_s , C_s , and D_s , are obtained by substituting the static dielectric constant of the solvent ϵ_{2s} and that of the semiconductor ϵ_{3s} into Eq. [8] and [13], instead of ϵ_2 and ϵ_3 , respectively. When the change in the distribution of the electron is so fast that the orientational vibration of the solvent cannot follow but both the lattice vibration of the semiconductor and the intramolecular vibration of the solvent can follow, the polarization induced inside the solvent is

$$\mathbf{P}_2 = \mathbf{P}_{2i} + \mathbf{P}_{2e} = \chi_{2r} \mathbf{E}_{2r} = \frac{\epsilon_{2r} - 1}{4\pi} \mathbf{E}_{2r} \quad [18]$$

and that inside the semiconductor is

$$\mathbf{P}_3 = \mathbf{P}_{3i} + \mathbf{P}_{3e} = \chi_{3r} \mathbf{E}_{3r} = \frac{\epsilon_{3r} - 1}{4\pi} \mathbf{E}_{3r} \quad [19]$$

where ϵ_{2r} and ϵ_{3r} are the dielectric constants of the solvent and the semiconductor in the infrared region, respectively. The electric field \mathbf{E}_{2r} or \mathbf{E}_{3r} is given by replacing G_s , C_s , and D_s by G_r , C_r , and D_r , in which the dielectric constants in the infrared region are used instead of the static dielectric constants. For the very fast change in the distribution of the electron, the electronic polarization of the solvent

$$\mathbf{P}_{2e} = \chi_{20} \mathbf{E}_{20} = \frac{\epsilon_{20} - 1}{4\pi} \mathbf{E}_{20} \quad [20]$$

and the electronic polarization of the semiconductor

$$\mathbf{P}_{3e} = \chi_{30} \mathbf{E}_{30} = \frac{\epsilon_{30} - 1}{4\pi} \mathbf{E}_{30} \quad [21]$$

can follow the change. In Eq. [20] and [21], ϵ_{20} and ϵ_{30} denote the optical dielectric constants of the solvent and the semiconductor, and in the expression of \mathbf{E}_{20} and \mathbf{E}_{30} the coefficient, G_o , C_o , and D_o , are written with the optical dielectric constants.

The total Hamiltonian for the electron and the polarization of dielectrics is written as (15)

$$\mathbf{H} = \mathbf{H}_e + \mathbf{H}_p \quad [22]$$

The Hamiltonian for the electron, \mathbf{H}_e , is the sum of the interaction of the electron with the polarization, \mathbf{H}_{ep} , and another term independent of the polarization \mathbf{H}_e'

$$\mathbf{H} = \mathbf{H}_{ep} + \mathbf{H}_e' \quad [23]$$

The Hamiltonian for the polarization inside the dielectrics, \mathbf{H}_p , is written as (15)

$$\mathbf{H}_p = \sum_{n=2}^3 \int \frac{\gamma_{ni}}{2} \dot{\mathbf{P}}_{ni}^2(\mathbf{r}') d^3\mathbf{r}' + \sum_{n=2}^3 \int \frac{\gamma_{ni}}{2} \omega_{ni}^2 \mathbf{P}_{ni}^2(\mathbf{r}') d^3\mathbf{r}' + \int \frac{\gamma_{2d}}{2} \dot{\mathbf{P}}_{2d}^2(\mathbf{r}') d^3\mathbf{r}' + \int \frac{\gamma_{2d}}{2} \omega_{2d}^2 \mathbf{P}_{2d}^2(\mathbf{r}') d^3\mathbf{r}' \quad [24]$$

where the coefficient γ has been determined from Lagrange's equation of the polarization (12). In Eq. [24], the first and second terms denoted by the subscript, $n = 2$ and $n = 3$, are the kinetic and potential energy of the ionic polarization of the solvent, and those of the semiconductor, respectively. The third and fourth terms in Eq. [24] are the kinetic and potential energy of the orientational vibration of the solvent. The interaction of an electron with the polarization is given by

$$\mathbf{H}_{ep} = \int \int \Psi(\mathbf{r}^*) \Psi(\mathbf{r}) \frac{e(\mathbf{r} - \mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|^3} \cdot \mathbf{P}(\mathbf{r}') d^3\mathbf{r}' \quad [25]$$

In the previous section, we assumed that the distribution of an electron has the spherical symmetry with respect to the center of the reductant ion, and that the probability of the electron outside the sphere r_b is zero. Under these conditions, Eq. [25] reduces to

$$\begin{aligned} \mathbf{H}_{ep} &= - \int \frac{e \mathbf{r}'}{|\mathbf{r}'|^3} \cdot \mathbf{P}(\mathbf{r}') d^3\mathbf{r}' \\ &= - \int \mathbf{E}_v(\mathbf{r}') \cdot \mathbf{P}(\mathbf{r}') d^3\mathbf{r}' \quad [26] \end{aligned}$$

where \mathbf{E}_v is the electric field originating from the electron in the reductant ion in the vacuum.

The electric field at \mathbf{r} induces the polarization $\mathbf{P}(\mathbf{r})$ inside the dielectrics, and thus the dielectric is attracted by the force

$$\mathbf{F} = (\mathbf{P} \cdot \nabla) \mathbf{E}_v \quad [27]$$

The work done against this electrical force in carrying the dielectrics from $|\mathbf{r}| = \infty$ to $|\mathbf{r}'|$ is $-\int_{r=\infty}^{r'} \mathbf{F}(\mathbf{r}) \cdot d\mathbf{r}$. Thus, the total energy provided from external system is (13)

$$W = - \int d^3\mathbf{r}' \int_{r=\infty}^{r'} \mathbf{F}(\mathbf{r}) \cdot d\mathbf{r} = - \int d^3\mathbf{r}' \int \mathbf{P} \cdot d\mathbf{E}_v \quad [28]$$

This energy W is also obtained by calculating the difference between the field energy inside the dielectrics and

that in the vacuum (16)

$$W = \frac{1}{4\pi} \int d^3\mathbf{r}' \int \mathbf{E} \cdot d\mathbf{E}_v - \frac{1}{8\pi} \int \mathbf{E}_v^2 d^3\mathbf{r}' \quad [29]$$

The field energy is the work for charging the sphere r_b . Consequently, the subtraction of $eB/2$ in the vacuum from $eB/2$ in the dielectrics

$$eG/2r_b + \frac{eC}{2(r_b^2 + R^2)^{1/2}} - e^2/2r_b \quad [30]$$

must accord with W in Eq. [29]. But in the zero order approximation, $n = m = 0$, there is a small deviation between the work W in Eq. [29] and W in Eq. [30], because the electric field in Eq. [16] includes the high order terms of $\cos \vartheta$, while those terms are neglected in $eB/2$ in Eq. [12]. The work given by Eq. [28] or [29] is converted to both the interaction energy of the electron with the dielectrics, H_{ep} , and the work to polarize the dielectrics, W_p . From Eq. [26] and [28], W_p is written as

$$W_p = - \int d^3\mathbf{r}' \int \mathbf{P} \cdot d\mathbf{E}_v + \int \mathbf{P} \cdot \mathbf{E}_v d^3\mathbf{r}' = \int d^3\mathbf{r}' \int \mathbf{E}_v \cdot d\mathbf{P} \quad [31]$$

Substituting \mathbf{E}_v and \mathbf{P} into Eq. [31], we have

$$W_p = -W = -\frac{1}{2} H_{ep} \quad [32]$$

The relation of $W_p = -W$ leads to

$$W_p = e^2/2r_b - \frac{1}{8\pi} \int \mathbf{E}_{2s} \cdot \mathbf{E}_v dv_2 - \frac{1}{8\pi} \int \mathbf{E}_{3s} \cdot \mathbf{E}_v dv_3 \quad [33]$$

and the relation of $W_p = -1/2 H_{ep}$ yields to

$$W_p = \frac{1}{2} \int \mathbf{P}_{2s} \cdot \mathbf{E}_v dv_2 + \frac{1}{2} \int \mathbf{P}_{3s} \cdot \mathbf{E}_v dv_3 \quad [34]$$

where the volume elements dv_2 and dv_3 indicate that the volume integral must be taken over the space where the solvent is present, and over the space where the semiconductor is present, respectively. Substituting the relations of Eq. [16] and [17] into Eq. [33] or [34], we have

$$W_p = e^2/2r_b - \frac{1}{8\pi} \int (G_s \frac{\mathbf{r}}{|\mathbf{r}|^3} + C_s \frac{\mathbf{r}^*}{|\mathbf{r}^*|^3}) \cdot \frac{e\mathbf{r}}{|\mathbf{r}|^3} dv_2 - \frac{1}{8\pi} \int D_s \frac{\mathbf{r}}{|\mathbf{r}|^3} \cdot \frac{e\mathbf{r}}{|\mathbf{r}|^3} dv_3 \quad [35]$$

$$W_p = \frac{\epsilon_{2s} - 1}{8\pi} \int (G_s \frac{\mathbf{r}}{|\mathbf{r}|^3} + C_s \frac{\mathbf{r}^*}{|\mathbf{r}^*|^3}) \cdot \frac{e\mathbf{r}}{|\mathbf{r}|^3} dv_2 + \frac{\epsilon_{3s} - 1}{8\pi} \int D_s \frac{\mathbf{r}}{|\mathbf{r}|^3} \cdot \frac{e\mathbf{r}}{|\mathbf{r}|^3} dv_3 \quad [36]$$

The volume integrals in Eq. [35] and [36] are carried out by the variable change as follows (see Fig. 2 and 3)

$$\int \frac{\mathbf{r}}{|\mathbf{r}|^3} \cdot \frac{\mathbf{r}}{|\mathbf{r}|^3} dv_2 = \int_{r>r_b} \frac{4\pi r^2}{r^4} dr - \int_{z=R/2}^{\infty} \int_{y=0}^{\infty} \frac{2\pi y dy dz}{(z^2 + y^2)^2} = 4\pi/r_b - 2\pi/R \quad [37]$$

$$\int \frac{\mathbf{r}}{|\mathbf{r}|^3} \cdot \frac{\mathbf{r}^*}{|\mathbf{r}^*|^3} dv_2 = \int_{r=r_b}^{\infty} \int_{\vartheta=0}^{\pi} \frac{(r^2 - Rr \cos \vartheta) 2\pi r^2 \sin \vartheta d\vartheta dr}{2r^3 (r^2 + R^2 - 2Rr \cos \vartheta)^{3/2}} - \int_{r=r_b}^{\infty} \int_{\vartheta=0}^{\pi} \frac{(r^2 - Rr \cos \vartheta) 2\pi r^2 \sin \vartheta d\vartheta dr}{2r^3 (r^2 + R^2 - 2Rr \cos \vartheta)^{3/2}} = 2\pi/R \quad [38]$$

$$\int \frac{\mathbf{r}}{|\mathbf{r}|^3} \cdot \frac{\mathbf{r}}{|\mathbf{r}|^3} dv_3 = \int_{z=R/2}^{\infty} \int_{y=0}^{\infty} \frac{2\pi y dy dz}{(z^2 + y^2)^2} = 2\pi/R \quad [39]$$

Accordingly, the work W_p is written as

$$W_p = e^2/2r_b - eG_s/2r_b - eC_s/2R \quad [40]$$

or

$$W_p = e \epsilon_{2s} G_s/2r_b - eG_s/2r_b - eC_s/2R \quad [41]$$

But W_p in Eq. [41] deviates from W_p in Eq. [40] by the small term of $2^{-1}e^2b^2 (b^2 + R^2)^{-3/2} (\epsilon_{2s} - \epsilon_{3s}) (\epsilon_{2s} + \epsilon_{3s})^{-1}$, which disappears when the distance R is larger than r_b . This deviation is ascribed to the inaccuracy of the zero order approximation of the coefficient G , C , and D . The rearrangement energy for one vibrational mode is defined as the energy required to attain the new equilibrium of the interaction mode after electron transfer. Except for the electronic polarization, the ionic and orientational polarization can be related to the characteristic vibrations. The rearrangement energy due to one vibrational mode can be defined as the work required to induce the polarization arising from such vibrational mode. The polarization of the solvent, \mathbf{P}_{2e} , \mathbf{P}_{2i} , and \mathbf{P}_{2d} is independently determined by using the response time to the fluctuation of the electron distribution. The energy W_p in Eq. [40] is the total work to induce the electronic, ionic, and orientational polarization inside the dielectrics. Since the semiconductor has no low energy vibration such as the orientational vibration of the solvent, the rearrangement energy due to the orientational vibration of the solvent

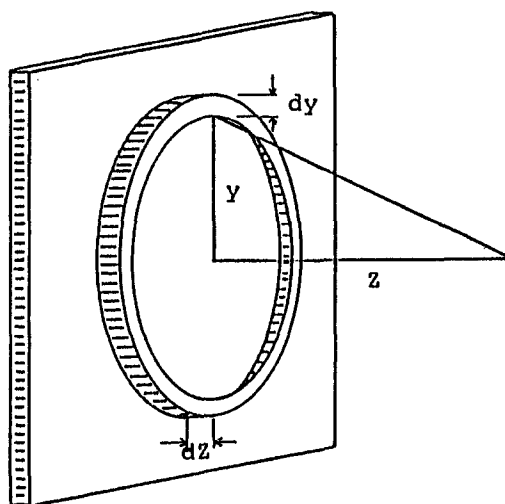


Fig. 2. Volume element considered for determining the volume integral in Eq. [37].

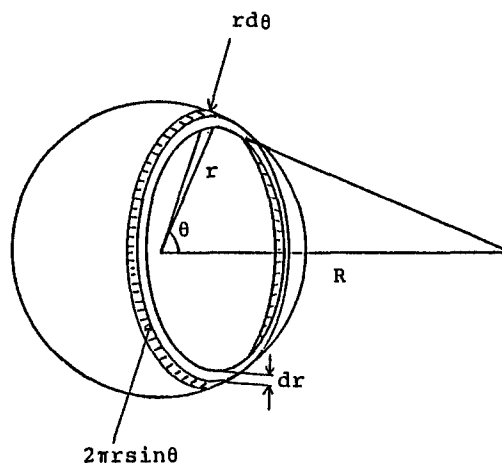


Fig. 3. Volume element considered for determining the volume integral in Eq. [38].

can be obtained by subtracting the work required to induce the polarization in the infrared region, $W_p(\text{IR})$ from the total work W_p

$$E_s(\text{os}) = \frac{e}{2r_b} (G_r - G_s) + \frac{e}{2R} (C_r - C_s) \quad [42]$$

The rearrangement energy for the high energy vibration $E_s(\text{IR})$ is

$$E_s(\text{IR}) = \frac{e}{2r_b} (G_o - G_r) + \frac{e}{2R} (C_o - C_r) \quad [43]$$

The response time of the lattice vibration is similar to that of the intramolecular vibration of the solvent, so that the rearrangement energy due to the lattice vibration cannot be separated from that for the intramolecular vibrations of the solvent. The residual term due to the electronic polarization modifying the electronic energy has been usually included in H_e' (15).

For comparison, we show the formulas of $E_s(\text{os})$ and $E_s(\text{IR})$ for the electron transfer at the metal/electrolyte interface. Dielectric constant of a metal is infinite, because the electric field inside a metal is screened by free electrons. By introducing the relation of $\epsilon_{3s} = \epsilon_{3r} = \epsilon_{3o} = \infty$ into Eq. [42] and [43], we have

$$E_s(\text{os}) = e^2 (1/\epsilon_{2r} - 1/\epsilon_{2s}) (1/2 r_b - 1/2 R) (1 - r_b^3 (r_b^2 + R^2)^{-3/2})^{-1} \quad [44]$$

$$E_s(\text{IR}) = e^2 (1/\epsilon_{3o} - 1/\epsilon_{2r}) (1/2 r_b - 1/2 R) (1 - r_b^3 (r_b^2 + R^2)^{-3/2})^{-1} \quad [45]$$

When the distance R is large enough compared with r_b , Eq. [44] and [45] coincide with Marcus formulas for $E_s(\text{os})$ and $E_s(\text{IR})$ at a metal electrode. That is, Marcus formulas for $E_s(\text{os})$ for heterogeneous electron transfer reactions are valid for the limiting case of $R \geq r_b$ (17). In the practical case that the distance R is at least larger than $2r_b$, the correction due to the term $1/[1 - b^3 (b^2 + R^2)^{-3/2}]^{-1}$ is less than 8%.

The rearrangement energy due to the interaction between an electron and the intramolecular vibration in an ion, $E_s(\text{intra})$, is written as (2, 9)

$$E_s(\text{intra}) = \sum_j \frac{f_j \times f_j^*}{f_j + f_j^*} (\Delta q_j)^2 \quad [46]$$

where f_j and f_j^* are the force constants of the j th interaction mode in the oxidant and reductant ions, respectively, and Δq_j is the change in the equilibrium coordinate of the interaction mode before and after electron transfer.

Results and Discussion

The experimental $E_s(\text{os})$ values have been estimated from the electron transfer rate constants by using Marcus formula (9), or from the I-V characteristics (5-8). In order to compare theoretical $E_s(\text{os})$ and $E_s(\text{IR})$ values with experimental values, we consider the role of the rearrangement energy on the electron transfer rate. When the non-adiabatic electron transfer occurs from the occupied conduction band to the oxidant ion, the cathodic current density is given by (19)

$$i = \frac{4 \pi e}{\hbar} \int C_o(x) dx \int | \langle \Psi_i(E) | U(x, E) | \Psi_f(x, E) \rangle |^2 \rho_D(x, E) \rho_{sc}(E) dE \quad [47]$$

where C_o is the concentration of the oxidant ion, Ψ_i is the wavefunction of the electron in the conduction band, Ψ_f is the wavefunction of the electron in the reductant ion, ρ_D represents the state density of phonons, ρ_{sc} represents the state density of the conduction band, U is the perturbation causing the electron transfer, x is the distance between the semiconductor surface and the center of the reductant ion, and E is the energy of the transferring electron. The phonon-state density depends on the dis-

tance between the electrode surface and the center of the ion, because the phonon-state density is dependent on the rearrangement energy, which is a function of the distance x . Since the square of the matrix element in Eq. [47] decreases quickly with the increase in the distance, Eq. [47] can be approximated as follows (20)

$$i = \frac{4 \pi e}{\hbar} C_o d \int | \langle \Psi_i(E) | U(d, E) | \Psi_f(d, E) \rangle |^2 \rho_D(d, E) \rho_{sc}(E) dE \quad [48]$$

where d is nearly the sum of the ion radius r_b and the thickness of the Helmholtz layer d_H . The current density, which is observed experimentally at a metal or a semiconductor/electrolyte interface, may provide information about $E_s(\text{os})$ and $E_s(\text{IR})$ values at $R/2 = r_b + d_H$. For the comparison of theoretical $E_s(\text{os})$ and $E_s(\text{IR})$ values with experimental values we calculated the theoretical $E_s(\text{os})$ and $E_s(\text{IR})$ values at $R/2 = b + d_H$. The calculated $E_s(\text{os})$ and $E_s(\text{IR})$ values for some redox species are listed in Table I.

As is seen in Table I, the theoretical $E_s(\text{os})$ values at two semiconductor electrodes are larger than that at metal electrodes. The variation of the theoretical $E_s(\text{os})$ values among electrodes arises from the difference in the magnitude of the induced mirror image charge. Besides theoretical $E_s(\text{os})$ values, the large theoretical $E_s(\text{IR})$ values due to the intramolecular vibration of the solvent and the lattice vibrations in ionic semiconductors were evaluated for $\text{Fe}^{2+/3+}$, $\text{Ce}^{3+/4+}$, and $\text{Fe}(\text{bpy})_3^{2+/3+}$ at the SnO_2 and TiO_2 electrodes. Further, the appreciable $E_s(\text{intra})$ values due to the symmetric breathing mode of metal-ligand stretching vibration in the first coordinational sphere (M-L vibration) have been obtained experimentally for $\text{Fe}^{2+/3+}$ and $\text{Ce}^{3+/4+}$. This result implies that the electron transfer at an ionic semiconductor/electrolyte interface occurs with accompanying the excitation and emission of multiphonons in these high energy vibrations. The role of M-L vibration on the electron transfer in polar solvents was first considered classically by Hush and Marcus (2, 21). Subsequently, quantum treatment of M-L vibration was carried out by Kestner *et al.* (18), who gave the phonon-state density as

$$\rho_D(d, E) = \left(\frac{1}{4 \pi K T E_s(\text{os})} \right)^{1/2} \sum_{m=-\infty}^{\infty} \exp [- (E - E^\circ - E_s(\text{os}) - m \hbar \omega_c)^2 / 4 K T E_s(\text{os})] \times \exp [- Z_c \cosh(\hbar \omega_c / 2 K T) + m \hbar \omega_c / 2 K T] I_m(Z_c) \quad [49]$$

where $Z_c = E_s(\text{intra})/\hbar \omega_c \times \text{cosech}(\hbar \omega_c / 2 K T)$, and $I_m(Z_c) =$

$(Z_c/2)^m \sum_{k=0}^{\infty} (Z_c/2)^{2k} / [k!(m+k)!]$. In Eq. [49], E° is the electronic

energy corresponding to the standard redox potential, $\hbar \omega_c$ is the energy of the M-L vibration. High energy vibrations in the initial state are not sufficiently excited at room temperature. For endothermic or small exothermic reactions, the phonon state density arising from these high energy vibrations accords approximately with the Franck-Condon factor between the ground vibrational state at the initial state and that at the final state, and is independent of the free energy difference. In such case, only $E_s(\text{os})$ values can be determined from the free energy relationship of the electron transfer rate (17). For large exothermic reactions, since electron transfer can occur via excited vibrational states in the final state and the phonon-state density is influenced by high energy vibrations, the electron transfer rate is prompted. In order to evaluate quantitatively the effect of the high energy vibrations on the phonon-state density, we quote experimental values of the rearrangement energy estimated from the electrochemical rate constants at the zero overvoltage, or values from the isotropic exchange rate. If the exponential term of the phonon-state density at zero-free energy difference, $\Delta E = E - E^\circ = 0$, is formally written as $\exp(-E_s/4kT)$, the total rearrangement energy E_s at room temperature is approximately given by (18, 19, 22)

Table I. Theoretical and experimental rearrangement energy for several redox species

Electrode	Solvent	Redox species		Helmholtz layer thickness (Å)	$E_s(o_s)$ (eV)	$E_s(IR)$ (eV)	$E_s(intra)$ (eV)	E_s (eV)
SnO ₂ $\epsilon_{30} = 4^a$ $\epsilon_{3r} = 10^b$ $\epsilon_{3s} = 10^a$	H ₂ O $\epsilon_{20} = 1.78$	Fe ^{2+/3+}	(A)	3.0	0.39	0.58	(0.46)	1.00
			(B)	1.0	0.37	0.55	(0.46)	0.97
			(B)	—	(0.5) ^d	—	0.46 ^e	1.20 ^f
	Ce ^{3+/4+}	(A)	3.0	0.36	0.53	(0.10)	0.62	
		(B)	1.0	0.34	0.52	(0.10)	0.60	
		(B)	—	0.65 ^g	—	0.10 ^e	1.75 ^f	
Fe(bpy) ₃ ^{2+/3+}	(A)	3.0	0.20	0.29	(0.0)	0.30		
	(B)	1.0	0.19	0.29	(0.0)	0.29		
	(B)	—	0.15 ^h	—	0.0 ⁱ	—		
TiO ₂ $\epsilon_{30} = 7.6^c$ $\epsilon_{3r} = 89^c$ $\epsilon_{3s} = 89^c$	H ₂ O $\epsilon_{20} = 1.78$	Fe ^{2+/3+}	(A)	3.0	0.33	0.57	(0.46)	0.93
			(B)	1.0	0.29	0.54	(0.46)	0.88
			(B)	—	(0.5) ^d	—	0.46 ^e	—
	Ce ^{3+/4+}	(A)	3.0	0.31	0.53	(0.10)	0.57	
		(B)	1.0	0.27	0.51	(0.10)	0.53	
		(B)	—	—	—	0.10 ^e	—	
Fe(bpy) ₃ ^{2+/3+}	(A)	3.0	0.16	0.29	(0.0)	0.26		
	(B)	1.0	0.14	0.28	(0.0)	0.23		
	(B)	—	—	—	0.0 ⁱ	—		
Metal	H ₂ O $\epsilon_{20} = 1.78$	Fe ^{2+/3+}	(A)	3.0	0.32	0.46	(0.46)	0.89
			(B)	1.0	0.27	0.38	(0.46)	0.81
			(B)	—	—	—	0.46 ^e	1.2 ^j , 1.5 ^k
	Ce ^{3+/4+}	(A)	3.0	0.3	0.42	(0.10)	0.53	
		(B)	1.0	0.25	0.36	(0.10)	0.46	
		(B)	—	—	—	0.10 ^j	1.3 ^j , 2.1 ^m	
Fe(bpy) ₃ ^{2+/3+}	(A)	3.0	0.15	0.21	(0.0)	0.22		
	(B)	1.0	0.13	0.19	(0.0)	0.19		
	(B)	—	—	—	0.0 ⁱ	0.35 ⁿ		

(A): Theoretical values of rearrangement energy.

(B): Experimental values of rearrangement energy.

^a From Ref. (27). ^b From Ref. (28). ^c From Ref. (29). ^d From Ref. (3). ^e From Ref. (30). ^f From Ref. (5). ^g From Ref. (7). ^h From Ref. (23). ⁱ From Ref. (31). ^j From Ref. (32). ^k From Ref. (33). ^l From Ref. (34). ^m From Ref. (35). ⁿ From Ref. (36).

$$E_s = E_s(o_s) + \frac{4KTE_s(IR)}{\hbar\omega_r} [\coth(\hbar\omega_r/2kT) - \operatorname{cosech}(\hbar\omega_r/2kT)] + \frac{4KT E_s(intra)}{\hbar\omega_c} [\coth(\hbar\omega_c/2kT) - \operatorname{cosech}(\hbar\omega_c/2kT)] \quad [50]$$

where $\hbar\omega_c$ is the M-L vibrational energy and $\hbar\omega_r$ is the energy of the lattice vibration or the intramolecular vibration of the solvent. In the calculation of the E_s values in Table I, the vibrational energy $\hbar\omega_r$ was assumed to be about 0.01 eV, which is the intramolecular vibrational energy of H₂O (10). The experimental E_s values at metal electrodes in Table I were estimated not only from the electrochemical reaction rate constants at metal electrodes, but also from the isotropic exchange rate constants, by using Marcus' formulas (9).

For Fe(bpy)₃^{2+/3+}, the theoretical $E_s(o_s)$ value at the SnO₂ electrode is consistent with the experimental value of 0.15 eV (23). Furthermore, theoretical E_s value is also close to the experimental E_s values. The good agreement between theory and experiment for the E_s values is attributable to the validity of the application of the adiabatic electron transfer to Fe(bpy)₃^{2+/3+}. In the reductant ion, Fe(bpy)₃²⁺, appreciable 3d electron density is found in the ligand π^* orbitals by virtue of the back-donation interaction. Similarly, in the oxidant ion, Fe(bpy)₃³⁺, the acceptor d orbital extends to the ligands. Thus, for the isotropic reaction of Fe(bpy)₃²⁺ - Fe(bpy)₃³⁺ and the electrochemical reaction of Fe(bpy)₃^{2+/3+} at a metal electrode, the electronic matrix element coupling the initial and final states of the electron transfer is expected to be large, leading to the adiabatic electron transfer (24).

The rearrangement energy for Fe^{2+/3+} and Ce^{3+/4+} reported by Memming and Möller (5) may be close to E_s

values rather than $E_s(o_s)$ values, because I-V curves at the SnO₂ electrode were measured at the high overvoltage region. Though the experimental $E_s(o_s)$ values for Fe^{2+/3+} were not obtained for two semiconductor electrodes listed in Table I, the $E_s(o_s) = 0.5$ eV was estimated at the organic crystal electrodes (3). The variation of the theoretical $E_s(o_s)$ values at the two semiconductor electrodes in Table I is not so large that the experimental $E_s(o_s)$ value for Fe^{2+/3+} at a semiconductor electrode may not be different significantly from 0.5 eV. The theoretical $E_s(o_s)$ values for Fe^{3+/3+} and Ce^{3+/4+} are smaller than the experimental values. Concerning the E_s values of Fe^{2+/3+} and Ce^{3+/4+}, the agreement between theory and experiment is very poor. This discrepancy was ascribed to the nonadiabaticity of the electron transfer (24). In fact, the transmission coefficient smaller than unity ($\kappa = 0.012$) was obtained for the reduction of Fe³⁺ by Willig *et al.* (3). For cerium ions, the accurate transmission coefficient has not been determined. Balzani *et al.* (4) reported that, from the consideration of the intensity of spectroscopic transition, the transmission coefficient is about 10⁻⁵ for the electron transfer reactions between Eu²⁺ or Eu³⁺ and an adiabatic-type partner, and that $\kappa = 10^{-10}$ for Eu²⁺-Eu³⁺ exchange reaction. Such a nonadiabatic behavior observed for lanthanide ions such as cerium or europium was interpreted in terms of the strong shield of the 4f orbitals by the 5s and 5p orbitals (4, 25). Consequently, a small transmission coefficient may be expected for the electron transfer including Ce³⁺ or Ce⁴⁺.

Kestner *et al.* (17) derived first the formula of $E_s(o_s)$ for homogeneous electron transfer, in which the ionic radius is changed after electron transfer. In their paper, the electric displacement was expressed by the charge of the oxidant or reductant ions, and the obtained formula of $E_s(o_s)$ gave the same representation of $E_s(o_s)$ as Marcus' formula if no variation of the ionic radius occurs after electron

transfer. If the ionic radius is changed, the formula of E_s (o_s) derived by Kestner *et al.* increases with the increase in the charge of the oxidant ion. In principle, the formula of $E_s(o_s)$, which reflects the interaction of the electron in the reductant ion with the solvent, is independent of the charge of the oxidant ion (26). The conflicting result can be explained as follows: the ionic radius of the reductant ion, r_b , is larger than that of the oxidant ion r_a . Thus, the vacant space with the shell structure is generated by the contraction of the ionic radius after the electron transfer from the reductant ion to the electrode. The generated vacant space is filled with the solvent surrounding the ion. The solvent in the vacant space is not polarized by the transferring electron, but is polarized by the charge of the oxidant ion. According to the description of the electric displacement by Kestner *et al.*, this polarization energy of the solvent by the charge of the oxidant ion was necessarily included in the formula of $E_s(o_s)$. This polarization energy should be taken into the total adiabatic potential energy (the total free energy) rather than the rearrangement energy of the orientational vibration of the solvent, $E_s(o_s)$.

Acknowledgment

The support of this research by Grant-in-Aid for Scientific Research, is gratefully acknowledged.

Manuscript submitted July 5, 1983; revised manuscript received March 5, 1984.

The Technological University of Nagaoka assisted in meeting the publication costs of this article.

REFERENCES

- R. Kubo and Y. Toyozawa, *Prog. Theor. Phys.*, **13**, 160 (1955); K. Freed and J. Jortner, *J. Chem. Phys.*, **52**, 6272 (1970); C. H. Henry and D. V. Lang, *Phys. Rev. B*, **15**, 989 (1977).
- R. A. Marcus, *Electrochim. Acta*, **13**, 995 (1968); K. W. Frese, Jr., *J. Phys. Chem.*, **85**, 3911 (1981).
- F. Willig, G. Scherer, and W. Röthamel, *Ber. Bunsenges. Phys. Chem.*, **77**, 921 (1973).
- V. Balzani, F. Scandola, G. Orlandi, N. Sabbatini, and M. T. Indelli, *J. Am. Chem. Soc.*, **103**, 3370 (1981).
- R. Memming and R. Moller, *Ber. Bunsenges. Phys. Chem.*, **76**, 475 (1972).
- K. E. Heusler and K. S. Yun, *Electrochim. Acta*, **22**, 977 (1977).
- K. Kobayashi, Y. Aikawa, and M. Sukigara, *Bull. Chem. Soc. Jpn.*, **55**, 2820 (1982).
- K. W. Frese, Jr., M. J. Madou, and S. R. Morrison, *This Journal*, **128**, 1527 (1981); S. R. Morrison, M. J. Madou, and K. W. Frese, Jr. in "Photoeffect at Semiconductor-Electrolyte Interfaces," A. J. Nozik, Editor, ACS Symposium Series 146, American Chemical Society (1981).
- R. A. Marcus, *J. Chem. Phys.*, **43**, 679 (1965).
- J. B. Hasted, "Aqueous Dielectrics," Chapman and Hall, London (1973).
- W. A. Harrison, "Solid State Theory," McGraw-Hill, New York (1970).
- H. Fröhlich, *Adv. Phys.*, **3**, 325 (1954).
- K. W. H. Panosky and M. Philips, "Classical Electricity and Magnetism," Addison-Wesley, London (1969).
- J. G. Kirkwood, *J. Chem. Phys.*, **2**, 351 (1934).
- H. Haken, "Quantenfeldtheorie des Festkörpers," B. G. Teubner, Stuttgart, Germany (1973).
- R. A. Marcus, *J. Chem. Phys.*, **24**, 979 (1956).
- R. D. Cannon, *Chem. Phys. Lett.*, **49**, 299 (1977).
- N. R. Kestner, J. Logan, and J. Jortner, *J. Phys. Chem.*, **78**, 2148 (1974).
- K. Kobayashi, Y. Aikawa, and M. Sukigara, *J. Electroanal. Chem.*, **134**, 11 (1982).
- V. G. Levich, in "Physical Chemistry, an Advanced Treaty," Vol. 9B, H. Eyring, D. Henderson, and W. Jost, Editors, p. 985, Academic Press, New York (1970).
- N. S. Hush, *Trans. Faraday Soc.*, **57**, 557 (1961).
- R. R. Dogonadze, A. M. Kuznetsov, and M. A. Vorotyntsev, *Z. Phys. Chem.*, **100**, 1 (1976).
- K. Kobayashi, M. Takata, S. Okamoto, Y. Sekine, Y. Aikawa, and M. Sukigara, *Chem. Phys. Lett.*, **104**, 253 (1984).
- M. Chou, C. Creutz, and N. Sutin, *J. Am. Chem. Soc.*, **99**, 5615 (1977).
- H. Taube, *Adv. Chem. Ser.*, **162**, 127 (1977).
- J. O'M. Bockris and S. U. M. Khan, "Quantum Electrochemistry," Plenum Press, New York (1979).
- R. Summitt, *J. Appl. Phys.*, **39**, 3762 (1968).
- P. Siders and R. A. Marcus, *J. Am. Chem. Soc.*, **103**, 741 (1981); J. B. Hasted, "Aqueous Dielectrics," Chapman and Hall, London (1973).
- F. A. Grant, *Rev. Mod. Phys.*, **31**, 646 (1959); W. D. Kingery, H. K. Bowden, and D. R. Uhlmann, "Introduction to Ceramics," John Wiley and Sons, New York (1976).
- J. M. Hale, in "Reactions of Molecules at Electrodes," N. S. Hush, Editor, John Wiley and Sons, London (1971).
- C. Creutz, M. Chou, T. L. Netzel, M. Okumura, and N. Sutin, *J. Am. Chem. Soc.*, **102**, 1309 (1980).
- J. Silverman and R. W. Dodson, *J. Phys. Chem.*, **56**, 846 (1952); K. W. Frese, Jr., *ibid.*, **85**, 3911 (1981).
- D. Jahn and W. Vielstich, *This Journal*, **109**, 849 (1962).
- B. Siegler and B. Masters, *J. Am. Chem. Soc.*, **79**, 6353 (1957); K. W. Frese, Jr., *J. Phys. Chem.*, **85**, 3911 (1981).
- R. Greef and H. Aulich, *J. Electroanal. Chem.*, **18**, 295 (1968).
- I. Ruff and M. Zimonyi, *Electrochim. Acta*, **18**, 515 (1973).