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Abstract

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A SEMICLASSICAL TREATMENT OF THE PROBLEM OF ELECTRON EXCHANGE IN SOLUTIONS

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In papers ([1]-[4]) a rigorous quantum-mechanical theory was developed for oxidation–reduction reactions between like-charged ions in solutions. As an example, the reaction of electron exchange between divalent and trivalent iron ions in water was considered. It should be emphasized that in these papers only the electron mechanism of oxidation–reduction reactions was studied; therefore the formulas obtained there for the activation energy, the activation free energy, and the specific rate constant of the reaction are not applicable to reactions proceeding by other mechanisms (for example, to reactions with proton transfer).

Of particular interest are the formulas obtained in papers ([1]-[4]) in the high-temperature approximation $kT \gg \hbar\omega$ (the physical meaning of the frequency ω is discussed in detail, for example, in the review article ([4])). In this approximation the formula obtained for the specific rate constant of the reaction k_{12} proved, in its external form, to be identical with the well-known formula of the theory of absolute reaction rates

$$k_{12} = \frac{kT}{h} \varkappa \exp\left(-\frac{\Delta F^{\neq}}{kT}\right). \tag{1}$$

Instead of expanding the exact quantum-mechanical formula for the probability of an electron transition in a series in the parameter $\hbar\omega/kT$, as was done in papers ([1]-[4]), in the present work we shall from the outset use a semiclassical approximation, in which the electron is described quantum-mechanically and the solvent classically. The advantage of the semiclassical treatment, in addition to its simplicity and clarity, is that it makes it possible to calculate k_{12} both in the case of nonadiabatic and in the case of adiabatic electron transfer.

For the solvent we shall use the classical Hamiltonian

$$H_s = \frac{\hbar\omega}{2} \sum_k \left(\frac{p_k^2}{\omega^2} + q_k^2\right), \tag{2}$$

where q_k are normal coordinates, and p_k are the corresponding velocities. The Hamiltonian H_s is represented by a $2N$-dimensional parabola in phase space (N is the number of degrees of freedom of the solvent). In view of this, the mathematical calculations connected with calculating the transition probability become very cumbersome. However, it is possible to replace the N-dimensional parabola for the potential energy of Hamiltonian (2) by a one-dimensional parabola. To see this, let us consider two Hamiltonians (see, for example, formula (33) of paper ([4])):

$$H_\alpha = \frac{\hbar\omega}{2}\sum_k \left[(q_k - q^0_{k\alpha})^2 - \frac{\partial^2}{\partial q_k^2}\right] + I_\alpha; \tag{3}$$

$$H_\beta = \frac{\hbar\omega}{2}\sum_k \left[(q_k - q^0_{k\beta})^2 - \frac{\partial^2}{\partial q_k^2}\right] + I_\beta, \tag{4}$$

representing the unperturbed Hamiltonians of the complete system, averaged, respectively, over the initial and final electron wave function. In (3) and (4) we shall make a change of coordinates corresponding to such a translational displacement that the point $q^0_{k\alpha}$ is at the origin, and to such a rotation that the point $q^0_{k\beta}$ is on one of the new axes. In the new variables, (3) and (4) will be written in the form

$$H_\alpha = \frac{\hbar\omega}{2}\left(\eta^2 - \frac{\partial^2}{\partial\eta^2}\right) + I_\alpha + H_0; \tag{5}$$

$$H_\beta = \frac{\hbar\omega}{2}\left[(\eta-\eta_0)^2 - \frac{\partial^2}{\partial\eta^2}\right] + I_\beta + H_0; \qquad \eta_0^2 = \sum_k (q^0_{k\alpha} - q^0_{k\beta})^2. \tag{6}$$

From (5) and (6) it is seen that, when the electron passes from one ion to another, the equilibrium coordinate is displaced for only one oscillator; therefore it may be assumed that the electron interacts with only one oscillator. For simplicity, below we shall consider the "resonance" case, when $I_\alpha = I_\beta = I_0$ ($Fe^{+2} - Fe^{+3}$).

To determine the probability of an electron transition in the semiclassical approximation, one must solve the wave equation

$$i\hbar\frac{\partial\Psi}{\partial t} = H\Psi, \tag{7}$$

where (the notation is the same as in paper ([4])):

$$H = H_e(\mathbf{r}) + V_{es}(\mathbf{r},\eta) = H_{e1}(\mathbf{r}) + U_2(\mathbf{r},\mathbf{R}) + V_{es}(\mathbf{r},\eta) =$$

$$= H_{e2}(\mathbf{r}) + U_1(\mathbf{r}, \mathbf{R}) + V_{es}(\mathbf{r}, \eta). \tag{8}$$

The electron wave functions in the initial and final states are determined from the equations:

$$[H_{e1,2} + V_{es}]\psi_{\alpha,\beta} = \varepsilon_{\alpha,\beta}\psi_{\alpha,\beta}. \tag{9}$$

From the form of $H_{\alpha,\beta}$ (see formulas (5) and (6)) we obtain that

$$\varepsilon_\alpha = I_0; \qquad \varepsilon_\beta = I_0 + \tfrac{1}{2}\hbar\omega\eta_0^2 - \hbar\omega\eta_0\eta, \tag{10}$$

and the corresponding electronic terms have the form

$$U_\alpha = I_0 + \tfrac{1}{2}\hbar\omega\eta^2; \qquad U_\beta = I_0 + \tfrac{1}{2}\hbar\omega(\eta - \eta_0)^2. \tag{11}$$

We seek the solution of the wave equation (7) in the form

$$\Psi = [a_\alpha(t)\psi_\alpha + a_\beta(t)\psi_\beta] \exp\left\{-\frac{it}{\hbar}\left(\varepsilon_\alpha + \int |\psi_\alpha|^2 U_2\, dr\right)\right\}. \tag{12}$$

Substituting this expression into (7), multiplying the latter once by ψ_α^*, and another time by ψ_β^*, and integrating, we obtain two equations for the functions $a_\alpha(t)$ and $a_\beta(t)$:

$$i\hbar p\, da_\alpha/d\eta = L_{\alpha\beta}^{(2)} a_\beta; \qquad i\hbar p\, da_\beta/d\eta = L_{\alpha\beta}^{(2)*} a_\alpha + (\varepsilon_\beta - \varepsilon_\alpha)a_\beta, \tag{13}$$

where $L_{\alpha\beta}^{(2)} = \int \psi_\alpha^* U_1 \psi_\beta\, dr$ is the exchange integral; $p = d\eta/dt$ is the classical velocity corresponding to the oscillator coordinate η. The system of equations (13) can be reduced to a single second-order equation

$$\frac{d^2 a_\alpha}{dx^2} - i\frac{F}{\hbar p} x \frac{da_\alpha}{dx} + \frac{|L_{\alpha\beta}^{(2)}|^2}{\hbar^2 p^2} a_\alpha = 0, \tag{14}$$

where, instead of η, a new variable $x = \eta - \eta_0/2 = \eta - \eta^*$ has been introduced, and F denotes $\hbar\omega\eta_0$. It is easy to verify that η^* corresponds to the point of intersection of the terms: $U_\alpha(\eta^*) = U_\beta(\eta^*)$. If (14) is solved with the boundary condition $a_\alpha = 1$ as $x \to -\infty$, then the probability of an electron transition during a single passage of the system through the intersection point $x = 0$ can be determined with the aid of the relation $w_e = 1 - |a_\alpha(+\infty)|^2$. We shall not dwell here on the exposition of the course of the solution of equation (14), and shall indicate only final result (5):

$$|a_\alpha(+\infty)|^2 = \exp\left\{-\frac{2\pi}{\hbar F}\frac{|L^{(2)}_{\alpha\beta}|^2}{|p|}\right\}. \tag{15}$$

To determine the total transition probability w_e, it must be multiplied by the probability that, per unit time, the system will pass through the point of intersection of the terms η^* with a velocity lying in the interval from p to $p + dp$, and integrated over all possible velocities:

$$w_{12} = \int_{-\infty}^{+\infty} w_e w_s \, dp. \tag{16}$$

To determine w_s, it is necessary to take into account that the system will pass through η^* during the time dt if the oscillator coordinate lies in the interval from η^* to $\eta^* + pdt$. Therefore

$$w_s dp = A \exp\left\{-\frac{1/2\,\hbar\omega\,(\eta^{*2} + p^2/\omega^2)}{kT}\right\} p\, dp. \tag{17}$$

The factor A is determined from the normalization condition and is equal to $\hbar/2\pi kT$. It is not difficult to see that $1/2\,\hbar\omega\eta^{*2}$ is the activation energy ΔE^* (see, for example, formula (48) of work ([4])); therefore (17) can be rewritten in the form

$$w_s = \frac{\hbar|p|}{2\pi kT} e^{-\Delta E^*/kT} e^{-\hbar p^2/2\omega kT}. \tag{18}$$

The formulas obtained in works ([1–4]) are based on perturbation theory. The criterion for the applicability of perturbation theory is the smallness of w_e, i.e., according to (15),

$$2\pi|L^{(2)}_{\alpha\beta}|^2/\hbar F|p| \ll 1. \tag{19}$$

In this approximation

$$w_e = 2\pi|L^{(2)}_{\alpha\beta}|^2/\hbar F|p|. \tag{20}$$

If (20) and (18) are substituted into (16), one obtains a formula exactly coinciding with the expression for w_{12} found earlier (see, for example, formula (45) of work ([4])).

Of special interest is the limiting case inverse to (19),

$$2\pi|L_{\alpha\beta}^{(2)}|^2/\hbar F|p| \gg 1. \tag{21}$$

In this approximation $w_e = 1$, and therefore

$$w_{12} = \frac{\hbar}{2\pi kT} e^{-\Delta E^*/kT} \int_0^\infty p e^{-\hbar p^2/2\omega kT} dp = \frac{\omega}{2\pi} e^{-\Delta E^*/kT}. \tag{22}$$

Concerning the results obtained, it is necessary to make the following remark. The formulas obtained in works ([1–4]) were derived under the assumption that the perturbation $L_{\alpha\beta}^{(2)}$ is small (see (19)). In this case one may assume that the electronic terms intersect. Therefore the electronic transition should be regarded as a nonadiabatic jump of the system from one term to another. If, however, the operator $L_{\alpha\beta}^{(2)}$ is so large that condition (21) is fulfilled, then the intersection of the terms will be impossible, and the curves will separate (as shown in Fig. 1). In this case the electronic transition should be regarded as an adiabatic transition of the system from one potential well to another, while the system remains on the lower term the entire time. The critical parameter determining the domains of applicability of the different approximations is the quantity

$$\hbar F|p|/2\pi \simeq \hbar\omega\sqrt{kT\Delta E^*} \equiv L_{\text{cr}}. \tag{23}$$

If the exchange integral $|L_{\alpha\beta}^{(2)}| \gg L_{\text{cr}}$, formula (22) is valid; in the opposite case, the formulas obtained in ([1]-[4]) are valid. Since the magnitude of the exchange integral depends on the distance between the reacting ions R, the introduced parameter L_{cr}, in turn, determines the critical distance R_{cr} between the ions.

As was shown earlier (see, for example, formula (75) of ([4])), k_{12} is related to w_{12} by the formula

$$k_{12} = 4\pi \int_0^\infty w_{12} \exp\left(-\frac{6e^2}{\varepsilon_s RkT}\right) R^2\, dR. \tag{24}$$

Substituting (22) into (24) and making use of the integral mean-value theorem, we obtain

$$k_{12} = \frac{4\pi}{3}\overline{R}^3 \frac{\omega}{2\pi} \exp\left(-\frac{\Delta E^{\neq}}{kT}\right) = \frac{kT}{h} \exp\left(-\frac{\Delta F^{\neq}}{kT}\right) \frac{4\pi}{3}\overline{R}^3. \tag{25}$$

The value of the activation free energy $\Delta F^{\neq}$ can be estimated by using the model of a rigid conducting sphere. According to Marcus ([6]), $\overline{R} = 6.8$ Å. With this choice of $\overline{R}$ it is reasonable to take $\varepsilon_s = 60$. In this case the activation energy $\Delta E^{\neq}$, calculated from formula ([4]):

Fig. 1

Figure 1: Fig. 1

$$\Delta E^{\neq}_{\text{teor}} = \frac{c}{32\pi} \int |D^0_\alpha - D^0_\beta|^2 \, dv + \frac{6e^2}{\varepsilon_s \overline{R}},$$

is equal to 11.5 kcal/mole. To calculate the activation entropy it is necessary to know ω. If the frequency of the torsional vibrations of water molecules is taken as ω, it turns out that $\omega \simeq 10^{11}$ sec^{-1}. This leads to $\Delta F^{\neq}_{\text{teor}} = 15.1$ kcal/mole. Using these data for k_{12}^{teor}, we obtain the value 49 l/mole $\cdot$ sec. For the reaction under consideration, k_{12}^{exp} is several l/mole $\cdot$ sec. The overestimate of k_{12}^{teor} can be explained by insufficiently good fulfillment of condition (21). However, taking into account the crudeness of the approximation, the value $k_{12}^{\text{teor}} = 49$ l/mole $\cdot$ sec can nevertheless be regarded as reasonable.

Fig. 1

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