SEMI-CLASSICAL TREATMENT OF ELECTRON EXCHANGE IN SOLUTION

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In a series of papers [1-4] Levich and Dogonadze developed a rigorous quantum mechanical theory for the oxidation–reduction reactions involving like-charged ions in solution. A specific case of electron exchange between ferrous and ferric ions in water was examined. It should be pointed out that only the mechanism of oxidation–reduction reactions involving electron transfer was investigated in those papers so that the equations derived there for the activation energy, free energy of activation, and the rate constant are not applicable to reactions proceeding by a different mechanism (such as proton transfer reactions).

Particularly interesting are the equations derived in [1-4] for the high-temperature approximation, $kT > \hbar\omega$ (the physical meaning of the frequency ω is discussed in detail in the review article [4]). This approximation yields an equation for the specific rate constant k_{12} which outwardly resembles the well known equation in the theory of the 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 equation for the electron transfer probability in a power series of $\hbar\omega/kT$, as was done in [1-4], we will use right from the start a semi-classical approximation in which the electron is treated quantum mechanically and the solvent classically. In addition to its simplicity and clarity the semi-classical treatment has the advantage (and this is perhaps the main reason for doing this work) that it can be used to calculate k_{12} in an adiabatic as well as a non-adiabatic electron transition.

For the solvent we will 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 can be represented as a 2N-dimensional parabola in phase space (N is the number of degrees of freedom of the solvent). Consequently the mathematics involved in computing the transition probability become very tedious. However, it is possible to replace an N-dimensional parabola representing the potential energy in the Hamiltonian (2) by a one-dimensional parabola. To show that this can indeed be done we will examine the two Hamiltonians (see Eq. (33) in [4])

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

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

which are the unperturbed Hamiltonians for the entire system averaged over the initial and final wave functions of the electron respectively. We will translate and rotate respectively the coordinate system in Eq. (3) and (4) in such

a way as to have point $q^0_{k\alpha}$ at the origin and point $q^0_{k\beta}$ on one of the new axes. The transformation will convert Eq. (3) and (4) to

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

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

Equations (5) and (6) show that the transfer of an electron from one ion to another shifts the normal coordinate of only one oscillator and hence one can assume that each electron interacts with only one oscillator. Choosing the simplest case we will examine the "resonance" exchange where $I_\alpha = I_\beta = I_0\,(Fe^{++} - Fe^{+++})$.

To determine the electron transfer probability by the semi-classical treatment we have to solve the wave equation

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

where (for notation see [4]):

$$H = H_e(\mathbf{r}) + V_{es}(\mathbf{r}, \eta) = H_{e1}(\mathbf{r}) + U_2(\mathbf{r}, R) + V_{es}(\mathbf{r}, \eta) = \\ = H_{e2}(\mathbf{r}) + U_1(\mathbf{r}, R) + V_{es}(\mathbf{r}, \eta). \tag{8}$$

The electron wave functions in the initial and final states can be determined from the equation

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

Using $H_{\alpha,\beta}$ in the form given in Eq. (5) and (6) we get

$$\varepsilon_\alpha = I_0; \quad \varepsilon_\beta = I_0 + {}^1/_2\hbar\omega\eta_0^2 - \hbar\omega\eta_0\eta, \tag{10}$$

while the corresponding electronic energy functions are:

$$U_\alpha = I_0 + {}^1/_2\hbar\omega\eta^2; \quad U_\beta = I_0 + {}^1/_2\hbar\omega\,(\eta - \eta_0)^2. \tag{11}$$

We want a solution of the wave equation (7) in the form

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

Substituting this expression in Eq. (7) and multiplying first by ψ^*_α then by ψ^*_β and integrating we get two equations for the functions a_α (t) and a_β (t):

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

where $L^{(2)}_{\alpha\beta} = \int\psi^*_\alpha U_1\psi_\beta d\mathbf{r}$ — is the exchange integral and $p = d\eta/dt$ is the classical velocity along the oscillator coordinate η. The system of equations (13) can be combined into a single second order equation

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

where η is replaced by a new variable $x = \eta - \eta_0/2 = \eta - \eta^*$ and F stands for $\hbar\omega\eta_0$. It can be readily shown that η^* is the point at which the two energy functions intersect, $U_\alpha(\eta^*) = U_\beta(\eta^*)$. If we solve Eq. (14) with the boundary condition $a_\alpha = 1$ when $x \to -\infty$ the electron transfer probability in a single crossing of the system through the intersection point $x = 0$ can be determined from the equation $w_e = 1 - |a_\alpha(+\infty)|^2$. We will not bother to give all the steps involved in solving Eq. (14) but will present only the end result [5]:

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

The total transfer probability is obtained by multiplying w_e by the probability that the system will cross the intersection point η^* in a unit interval if it moves at a rate between p and p + dp and then integrating over all possible rates:

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

To determine w_s we have to remember that the system will cross η^* in the time interval dt only if the oscillator coordinate lies between η^* and η^* + pdt. Hence

$$w_s dp = A \exp\left\{-\frac{{}^1/_2\hbar\omega\,(\eta^{*2} + p^2/\omega^2)}{kT}\right\} p\, dp. \tag{17}$$

Normalization requirements yield $A = \hbar/2\pi kT$. It can be easily shown that ${}^1/_2\,\hbar\omega\eta^{*2}$ gives the activation energy ΔE^* (see Eq. (48) in [4]) and thus Eq. (17) can be rewritten in the form

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

The equations derived before [1-4] were based on the perturbation theory. Whether the perturbation theory is applicable or not will depend on how small w_e is, or more specifically with reference to Eq. (15) on the condition that

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

The approximation being made is that

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

If Eq. (20) and (18) are now substituted in Eq. (16) we get an expression identical to that previously derived for w_{12} (see, for instance, Eq. (45) in [4]).

Of particular interest is the limiting case reverse to that represented by the inequality (19)

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

The new approximation is that $w_e = 1$, so that

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

The results make the following remarks imperative. The equations reported previously [1-4] were derived on the assumption that the perturbation $L_{\alpha\beta}^{(2)}$ is small (see Eq. (19)]. In such cases the electronic energy functions can be presumed to intersect. Consequently the electronic transition should be regarded as a non-adiabatic jump of the system from one electronic state to another. But if the operator $L_{\alpha\beta}^{(2)}$ is large enough to satisfy condition (21) the functions can not intersect and must diverge (as shown in figure). The electronic transition would in this case have to be treated as an adiabatic transition of the system from one potential well into another with the system always resting at the lowest level. A critical parameter which defines the applicability ranges of various approximations is

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

If the exchange integral $|\,L_{\alpha\beta}^{(2)}\,| \gg L_{cr}$. Eq. (22) holds, in the reverse case the equations derived before [1-4] hold. Since the value of the exchange integral depends on the distance between the reacting ions R, the parameter L_{cr} defined above determines the critical interionic distance R_{cr}.

As we have shown before (see Eq. (75) in [4]) K_{12} and w_{12} are connected through the equation

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

Substituting Eq. (22) in (24) and using the theorem of integral averages we get

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

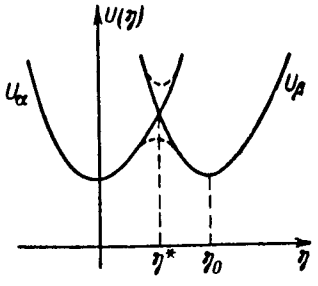

Fig.

The free energy of activation $\Delta F^{\neq}$ can be evaluated by using a rigid conducting sphere as a model. According to Marcus [6] R = 6.8 A. For such a R one would reasonably expect that $\varepsilon_s = 60$. If we therefore use the formula given for $\Delta E^{\neq}$ in [4], $\Delta E^{\neq}_{\text{theor.}} = \frac{c}{32\pi}\int[D^0_\alpha - D^0_\beta]^2\, dv + \frac{6e^2}{\varepsilon_s \overline{R}}$, we get the value of 11.5 kcal/mole for the activation energy. To determine the entropy of activation we have to know ω. If we use for ω the twisting vibrations of a water molecule we get a $\omega \simeq 10^{11}\ \text{sec}^{-1}$. This yields a $\Delta F^{\neq}_{\text{theor.}} = 15.1$ kcal/mole. Combining the calculated results we get a $k_{12}^{\text{theor}} = 49$ liters/mole · sec. The known $k_{12}^{\text{exp.}}$ for this reaction has a magnitude of several liters/mole · sec. The overly large theoretical rate constant may be due to the fact that condition (21) does not rigorously hold. However, considering how crude were the approximations made in our derivations the resulting value of $k_{12}^{\text{theor.}} = 49$ liters/mole · sec seems very good.

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