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Abstract

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THE RATE OF ELECTRON-EXCHANGE REACTIONS IN SOLUTIONS

(Presented by Academician A. N. Frumkin on 1 IV 1960)

On the basis of the adiabatic perturbation theory, in papers ([1,2]) the probability of an electronic transition per unit time, $w_{12}(R)$, was calculated between like-charged ions situated at a distance R from one another. To relate w_{12} to the specific rate constant of the reaction, it is necessary to derive the kinetic equation of the reaction. For simplicity, let us consider the reaction

$$\mathrm{Fe}^{2+} + \mathrm{Fe}^{*3+} \to \mathrm{Fe}^{3+} + \mathrm{Fe}^{*2+}. \tag{1}$$

However, as will be seen from the calculation, analogous results can also be obtained for any electron-exchange reactions.

Let us denote the concentrations of Fe^{2+}, Fe^{*2+}, Fe^{3+}, Fe^{*3+}, respectively, by c_2, c_2^*, c_3, c_3^*. The number of Fe^{*2+} ions formed in unit volume during the time dt can be written in the form

$$dc_2^* = (c_2\rho + c_2^*\rho^*)dt, \tag{2}$$

where ρ is the probability that a given Fe^{2+} ion will pass into Fe^{3+} per unit time, and ρ^* has an analogous meaning. Since the number of Fe^{*3+} ions in a volume element dv, situated at a distance R from Fe^{2+}, is equal to $c_3^* e^{-\psi(R)/kT} dv$, and the probability of electron transfer per unit time is w_{12}, ρ can be represented in the form

$$\rho = \int w_{21}(R) c_3^* e^{-\psi(R)/kT}\, dv \equiv k_{12} c_3^*, \tag{3}$$

where $\psi(R)$ is the interaction energy of the Fe^{2+} and Fe^{*3+} ions located at the distance R. Similarly, for ρ^* we have

$$\rho^* = \int w_{21}(R) c_3 e^{-\psi(R)/kT}\, dv \equiv k_{21} c_3 = k_{12} c_3. \tag{4}$$

After substituting (3) and (4) into (2), we obtain the desired equation

$$dc_2^*/dt = k_{12}(c_2 c_3^* - c_2^* c_3). \tag{5}$$

Let us write the solution of this equation under the initial condition

$$c_2 = c_{20}, \qquad c_3^* = c_{30}^*, \qquad c_2^* = c_3 = 0 \quad \text{at } t = 0. \tag{6}$$

It is easy to see that at any moment of time the relations

$$c_2^* = c_3, \qquad c_2 + c_2^* = c_{20}, \qquad c_3 + c_3^* = c_{30}^* \tag{7}$$

hold. Consequently, (5) can be rewritten as

$$dc_2^*/dt = k_{12}\left[(c_{20} - c_2^*)(c_{30}^* - c_2^*) - (c_2^*)^2\right] = k_{12}\left[c_{20} c_{30}^* - (c_{20} + c_{30}^*) c_2^*\right]. \tag{8}$$

The solution of equation (8) with the initial condition (6) has the form

$$\ln\left(1 - \frac{c_{20} + c_{30}^*}{c_{20} c_{30}^*}\, c_2^*\right) = -k_{12}(c_{20} + c_{30}^*) t. \tag{9}$$

As $t \to \infty$, as is seen from (9),

$$c_2^* \to \frac{c_{20} c_{30}^*}{c_{20} + c_{30}^*} = c_{2\infty}^*, \tag{10}$$

therefore (9) can be rewritten in the form

$$\ln(1 - c_2^*/c_{2\infty}^*) = -k_{12}(c_{20} + c_{30}^*) t. \tag{11}$$

Formula (11), as is known, was first obtained by McKay (^{3}).

The quantity k_{12}, which was determined in (^{3}), is the specific rate constant of the reaction, determined experimentally. At low concentrations, the Debye potential can be used as $\psi(R)$

$$\psi(R) = 3.2\, e^2 e^{-\varkappa R}/\varepsilon_s R, \tag{12}$$

where $\varkappa$ is the inverse Debye length, ε_s is the static dielectric constant. From physical considerations it is clear that $1/\varkappa$ is much greater than the distance over which $w_{12}(R)$ decreases; therefore the exponential in (12) can be replaced by unity, i.e., one may assume that $\psi(R)$ is expressed by the formula

$$\psi(R) = 6e^2/\varepsilon_s R. \tag{13}$$

Thus,

$$k_{12} = 4\pi \int_0^\infty w_{12}(R) e^{-6e^2/\varepsilon_s RkT} R^2\, dR, \tag{14}$$

or, substituting the expression w_{12} found in (2):

$$k_{12} = \frac{kT}{h} \int_0^\infty \left(\frac{512\pi^6}{\hbar^2 \omega_0^2 kTc \int (\mathbf{D}_1 - \mathbf{D}_2)^2\, dr} \right)^{1/2} |L_{21}^{(2)}|^2 e^{-\frac{\Delta F^* + 6e^2/\varepsilon_s R}{kT}} R^2\, dR. \tag{15}$$

The quantity $L_{21}^{(2)}$ is the exchange integral; $\mathbf{D}_{1,2}$ is the induction of the electrostatic field created by the electron in the initial (or final) state, and c is expressed by the formula

$$c = 1/\varepsilon_0 - 1/\varepsilon_s, \tag{16}$$

where ε_0 is the optical dielectric constant. In the same work (2) it was shown that

$$\Delta F^* = \frac{c}{32\pi} \int (\mathbf{D}_1 - \mathbf{D}_2)^2\, dr + kT \ln \frac{kT}{\hbar\omega_0} \equiv \Delta E^* - T\Delta S^*. \tag{17}$$

In order to compare the expression obtained for k_{12} with the known formula of the theory of absolute reaction rates,

$$k_{12} = \frac{kT}{h} \varkappa e^{-\Delta F^\ddagger/kT}, \tag{18}$$

we shall use the mean-value theorem for integrals. The factor $R^2 e^{-6e^2/\varepsilon_s RkT}$ decreases sharply with decreasing R and grows as R^2 with increasing R, while the remaining part of the integrand falls sharply with decreasing R. The integrand reaches a maximum at some $R = \overline{R}$ and has a rather small width δR. Therefore the expression under the integral sign in (15) can be taken outside the integral sign at the point $\overline{R}$ and multiplied by δR, as a result of which we obtain a formula that coincides exactly with (18), with

$$\Delta F^{\ddagger} = \Delta F^{*}(\overline{R}) + 6e^2/\varepsilon_s\overline{R}, \tag{19}$$

and the transmission coefficient is expressed by the formula

$$\varkappa = \left(\frac{512\pi^6}{\hbar^2\omega_0^2 kTc\int|\mathbf{D}_1(\overline{R}) - \mathbf{D}_2(\overline{R})|^2\,dr}\right)^{1/2} |L_{21}^{(2)}|^2\overline{R}^2\delta R. \tag{20}$$

For comparison with experiment, one should use expression (19) for the free energy of activation and expression (21) for the activation energy

$$\Delta E^{\neq} = \Delta E^{*}(\overline{R}) + \frac{6e^2}{\varepsilon_s\overline{R}} = \frac{c}{32\pi}\int[\mathbf{D}_1 - \mathbf{D}_2]^2\,dr + \frac{6e^2}{\varepsilon_s\overline{R}}. \tag{21}$$

Knowing the wave function of the $3d$-electron of the Fe^{2+} ion in water, one could calculate the integral entering into (21), and thereby determine $\Delta E^{\neq}$ as a function of $\overline{R}$. However, to estimate the magnitude of $\Delta E^{\neq}$ we can use the model of rigid conducting spheres proposed by Marcus (^{4}):

$$\mathbf{D}_1 = \begin{cases} 0, & r < a; \\ e\mathbf{r}/r^3, & r > a; \end{cases} \qquad \mathbf{D}_2 = \begin{cases} 0, & |\mathbf{r} - \overline{\mathbf{R}}| < a; \\ \dfrac{e(\mathbf{r} - \overline{\mathbf{R}})}{|\mathbf{r} - \overline{\mathbf{R}}|^3}, & |\mathbf{r} - \overline{\mathbf{R}}| > a, \end{cases} \tag{22}$$

where a is the radius of the sphere. In this case

$$\Delta E^{\neq} = \frac{6e^2}{\varepsilon_s R} + \frac{ce^2}{4}\left(\frac{1}{a} - \frac{1}{R}\right). \tag{23}$$

To determine $\overline{R}$ without using experimental data, it is necessary to investigate the integral (15) in more detail. At the same time we shall indicate a way in which the value of k_{12} can be estimated if Slater functions are taken as the electron wave functions. Considering reaction (1) as an example, we write the electron wave function in the form

$$\psi_1(\mathbf{r}) = \psi_2(\mathbf{r} + \mathbf{R}) = \psi_{3d_{z^2}} = \frac{1}{3}\alpha^3\sqrt{\frac{2\alpha}{\pi}}\,r^2 e^{-\alpha r}\cos^2\theta. \tag{24}$$

The parameter α, according to Slater' s method, is equal for the $3d$-electron of Fe^{2+} to

$$\alpha = z_{\text{eff}}/n_{\text{eff}}a_0\varepsilon_s = 6.25/3a_0\varepsilon_s. \tag{25}$$

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Following the method adopted in semiconductor theory, instead of the Bohr radius a_0 we have introduced a quantity ε_s times larger, in order to take the solvent into account. The choice of the angular part of the wave function (24) is due to the fact that it is precisely the $\psi_{3d_{z^2}}$-functions that give the greatest overlap. To simplify the calculations, we shall use the functions (24) only in determining the exchange integral $L_{21}^{(2)}$; for the other quantities we shall assume that approximation (22) is valid.

We write the exchange integral $L_{21}^{(2)}$ in the form

$$L_{21}^{(2)} = \int \psi_2^* \frac{3e^2}{\varepsilon_s|\mathbf{r}-\mathbf{R}|}\,\psi_1\,d\mathbf{r}. \tag{26}$$

After simple but lengthy calculations (the integral should be taken in elliptic coordinates), the formula obtained was

$$L_{21}^{(2)} = \frac{\alpha e^2 e^{-\alpha R}}{24\varepsilon_s}\left(48+48\alpha R+20\alpha^2R^2+4\alpha^3R^3+\alpha^4R^4+\frac{11}{15}\alpha^5R^5\right) \equiv P_5(R)e^{-\alpha R}. \tag{27}$$

Since the square root standing under the integral in (15) changes very slowly, it may be taken outside the integration sign and k_{12} written in the form

$$k_{12} = \frac{4\pi}{\hbar e}\sqrt{\frac{\pi a}{ckT}}\,e^{-ce^2/4akT}\int_0^\infty P_{12}(R)\,e^{-2\alpha R-(6/\varepsilon_s-c/4)e^2/kT\,R}\,dR, \tag{28}$$

where the polynomial of the 12th degree $R^2P_5^2(R)$ has been denoted by $P_{12}(R)$.

If it is assumed that ε_s does not depend on R, the integral in (28) can be evaluated exactly. Indeed, denoting $(6/\varepsilon_s - c/4)e^2/kT$ by γ, the desired integral can be represented as the sum $\sum_{n=2}^{12} A_nI_n$, where[5]

$$I_n = \int_0^\infty R^n e^{-2\alpha R-\gamma/R}\,dR = 2(2\alpha)^{n-1}(2\alpha\gamma)^{(n+1)/2}K_{n+1}(\sqrt{8\alpha\gamma}). \tag{29}$$

Thus, integral (28) is expressed in terms of Macdonald functions. As is seen from (29), such a calculation is valid for electron exchange between isotopes with charges z and $z+1$ only under the condition that $\gamma > 0$, since α is always positive. This means that $z(z+1)/\varepsilon_s - c/4 > 0$, or, after simple transformations,

$$\varepsilon_s < \varepsilon_0(2z+1)^2. \tag{30}$$

The calculation presented is sufficiently rigorous if the integrand in (28) reaches its maximum at such an R_M that ε_s can already be regarded as independent of

R. One can estimate R_M by setting equal to zero the derivative of the exponent in (28), assuming ε_s independent of R:

$$-2\alpha + \gamma/{R_M^0}^2 = 0, \qquad R_M^0 = \sqrt{\gamma/2\alpha}. \tag{31}$$

However, because $P_{12}(R)$ is present under the integral, R_M will be somewhat larger than R_M^0.

For reaction (1), condition (30) requires that $\varepsilon_s < 45$. Unfortunately, the dependence of ε_s on R is difficult to investigate theoretically. However, the data of Laidler[6] show that $\varepsilon_s < 45$ for $R < 5$ Å. It follows from this that the most probable distance at which electron transfer occurs in reaction (1) is less than 4 Å. When considering exchange reactions between ions with charges 3 and 4, condition (30) is satisfied automatically, and equation (31) can be written as

$$R_M^{(0)} = 13.9\sqrt{n_{\text{eff}}/z_{\text{eff}}}\ \text{Å}. \tag{32}$$

Therefore, one may expect that R_M is sufficiently large to make it possible to neglect the dependence of ε_s on R. For example, for the electron-exchange reaction in the system $\text{Ce}^{3+} - \text{Ce}^{4+}$, R_M^0 is found to be of the order of 8.2 Å ($n_{\text{eff}} = 4$ and $z_{\text{eff}} = 11.4$); i.e., the scheme developed above for calculating k_{12} can be used with a good degree of accuracy.

It is interesting to note that the expression for the activation energy for an electron-exchange reaction between identical ions differing only in valence state, obtained in the present work (23), coincides with the free energy of activation calculated by Marcus[4]. For reaction (1), Marcus obtained the value $\Delta F^\ddagger = 9.8$ kcal/mol; therefore, according to our theory, $\Delta E^\ddagger = 9.8$ kcal/mol, which agrees very well with the experimental value $\Delta E^\ddagger_{\text{exp}} = 9.9$ kcal/mol.

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

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