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Abstract

Full Text

Physical Chemistry

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Adiabatic Theory of Electronic Processes in Solutions

The present work is devoted to the further development of the theory of electronic processes in polar solvents ⁽¹⁾.

To describe the solvent we shall use the concept of the specific polarization $\mathbf{P}(\mathbf{r})$. Strictly speaking, the macroscopic concept of polarization acquires meaning outside the first solvation shell of the ion. In describing the latter, its discrete structure should be taken into account, especially significant when there is a chemical bond between the ion and the solvent molecules. However, in the present state of the theory of solutions, accounting for the discreteness of the solvation shell does not appear possible. In the present work we shall describe the medium by means of a continuous polarization $\mathbf{P}(\mathbf{r})$, which corresponds to the Born model of the solvent.

In the processes that interest us, the nonstationarity of $\mathbf{P}(\mathbf{r})$ plays an important role and is due to two factors. On the one hand, the molecules of the liquid (solvent) make jumps from one temporary equilibrium position to another. On the basis of diffusion data it is easy to estimate ⁽²⁾ the time between jumps, which proves to be of the order of 10^{-9} sec. This time is very large in comparison with the times of electronic transitions. Therefore the diffusional displacements of solvent molecules may be neglected. For the theory developed below, another type of atomic motion plays an essential role—their oscillations about positions of temporary equilibrium. Strictly speaking, the oscillations of atoms in a liquid do not have a harmonic character. However, only in the harmonic approximation does the problem of electronic processes acquire a fully quantitative character and can be solved quantum-mechanically.

Let us represent the Hamiltonian of the system—ion, electron, and solvent—in the form

$$H(\mathbf{r}, q) = H_e(\mathbf{r}) + H_s(q) + V_{es}(\mathbf{r}, q). \quad (1)$$

In the part of the Hamiltonian H_e are included the kinetic energy of the electron, the energy of interaction of the electron with the ions, and a term taking into account the action on the electron of the static polarization \mathbf{P}_0 created in the solvent by the ions. In H_s are contained the kinetic and potential energy of

the solvent, associated with the polarization \mathbf{P} created by the electron. In what follows, by \mathbf{P} we shall understand only the inertial part of the total polarization (3). Finally, V_{es} is the potential energy of the electron associated with the polarization of the solvent \mathbf{P} induced by it. The Hamiltonian does not include time-independent terms representing the energy of interaction of the ions with one another, the energy associated with the constant part of the polarization \mathbf{P}_0 , and the proper energy of the noninertial part of the polarization created by the electron, \mathbf{P}_e (3).

The main task of the present work is the investigation of electron-exchange reactions between like-charged ions; therefore

we shall carry out all concrete calculations precisely for this case. As will be seen from what follows, the theory developed can easily be extended to the case of other electronic processes in solutions. For the case of interest to us,

$$H'_e(r) = -\frac{\hbar^2}{2m} \nabla_r^2 + U_1(r, R) + U_2(r, R) \equiv H_{e1} + U_2 \equiv H_{e2} + U_1, \quad (2)$$

where R is the distance between the reacting ions, U_1 is the energy of interaction of the electron with the first ion and with the solvent statically polarized by it (U_2 has an analogous meaning). We shall seek the eigenfunctions of operator (1) in the adiabatic approximation:

$$\Psi_n(r, q) = \sum_r \Phi_{rn}(q) v_r(r, q), \quad (3)$$

where v_r are the eigenfunctions of the operators $H_{e1} + V_{es}$ (for $r = \alpha$) and $H_{e2} + V_{es}$ (for $r = \beta$). Substituting (3) into the exact wave equation, multiplying it from the left by $v^*(r, q)$, and carrying out the integration over r , as a result of simple transformations we obtain

$$\begin{aligned} & \{H_s(q) + \varepsilon_r(q) - E_n\} \Phi_{rn}(q) = \\ & = \sum_{r'} \{L_{rr'}(q) - \Delta_{rr'}(q) [H_s(q) + \varepsilon_{r'}(q) - E_n]\} \Phi_{r'n}(q), \end{aligned} \quad (4)$$

where the following notation has been introduced:

$$\begin{aligned} L_{rr'} &= - \int v_r^* [H_s(q), v_{r'}] dr - \int v_r^* U_r v_{r'} dr \equiv L_{rr'}^{(1)} + L_{rr'}^{(2)}; \\ U_r &= \begin{cases} U_1, & r = \alpha; \\ U_2, & r = \beta; \end{cases} \end{aligned} \quad (5)$$

$$\Delta_{rr'} = \begin{cases} 0, & r \text{ and } r' = \alpha \text{ and } \alpha' \text{ or } \beta \text{ and } \beta'; \\ \int v_r^* v_{r'} dr, & r \text{ and } r' = \alpha \text{ and } \beta. \end{cases} \quad (6)$$

$\varepsilon_r(q)$ are the eigenvalues corresponding to the eigenfunctions $v_r(r, q)$. In the approximation of adiabatic perturbation theory the operator $L^{(1)}$, usually called the nonadiabaticity operator, is small. $L^{(2)}$ is an exchange integral, which at large R is also small. For the same reason the second term on the right-hand side of (4) is small. Therefore the usual methods of perturbation theory may be applied to (4), treating the right-hand side as a small quantity. As is not difficult to verify, the second term on the right-hand side of (4) in the first approximation of perturbation theory will not lead to transitions between different electronic states. The probability of an electronic transition under the action of the perturbation $L^{(1)}$ was calculated earlier ⁽¹⁾. In the same work the case was considered in which electronic transitions could be caused by the second term in the expansion of V_{es} in powers of q , i.e. by a term proportional to q^2 , which in a certain sense is equivalent to taking account of the anharmonicity of the vibrations. In the present work the transition probability under the action of $L^{(2)}$ will be determined. In view of the fact that the exchange integral increases as R decreases, it is clear that, for not too large R , the principal role in electronic transitions may be played by $L^{(2)}$.

The probability per unit time for the transition of an electron from one ion to the other is expressed as

$$w_{12} = \frac{2\pi}{\hbar} A v_n \sum_{n'} |\langle \Phi_{\beta n'}^0 | L_{\beta\alpha}^{(2)} | \Phi_{\alpha n}^0 \rangle|^2 \delta(E_{\beta n'}^0 - E_{\alpha n}^0). \quad (7)$$

The indices α and β correspond to the states of the electron at one and at the other ion, respectively; $A v_n$ denotes statistical averaging over

initial phonon state. In addition, summation is carried out over all final states n' , taking account of the law of conservation of energy, which is achieved by introducing a δ -function. Unfortunately, w_{12} cannot in general be calculated. An exact quantitative expression for the transition probability can be obtained only for the case in which there is no frequency dispersion. However, as Kubo showed ⁽⁴⁾, an expression of type (7) can be evaluated approximately for $kT \gg \hbar\omega_D$. Without going into the details of the calculations, we give the expression for w_{12} in the high-temperature approximation:

$$w_{12} = \left(\frac{8\pi^2}{\hbar^2 k T c \int (\mathbf{D}_\alpha^0 - \mathbf{D}_\beta^0)^2 dr} \right)^{1/2} |L_{\beta\alpha}^{(2)}|^2 \exp \left\{ - \frac{\left[I_\alpha - I_\beta + \frac{c}{8\pi} \int (\mathbf{D}_\alpha^0 - \mathbf{D}_\beta^0)^2 dr \right]^2}{\frac{c}{2\pi} \int (\mathbf{D}_\alpha^0 - \mathbf{D}_\beta^0)^2 dr} \frac{1}{kT} \right\};$$

$$kT \gg \hbar\omega. \quad (8)$$

The quantity c is the principal parameter of the theory and is related to the static dielectric constant ε_s and to the refractive index of light $n = \sqrt{\varepsilon_0}$ by the relation

$$c = \frac{1}{\varepsilon_0} - \frac{1}{\varepsilon_s}, \quad (9)$$

where ε_0 is the optical dielectric constant. The quantity I_r entering into (8) is determined from the equality

$$I_r = \varepsilon_r(q_r^0) + \frac{c}{8\pi} \int \mathbf{D}_r^0 dr, \quad (10)$$

where

$$\mathbf{D}_r^0 = \frac{4\pi}{c} \mathbf{P}_r^0 = e \int |v_r(\mathbf{r}', q_r^0)|^2 \frac{\mathbf{r} - \mathbf{r}'}{|\mathbf{r} - \mathbf{r}'|^3} d\mathbf{r}'$$

must be interpreted as the induction of the electrostatic field created by a charge cloud with density $e|v_r|^2$ (q_r^0 determine the equilibrium configuration of the solvent corresponding to the electron state r). According to (8), at high temperatures w_{12} is proportional to $e^{-\Delta E^*/kT}$. On the basis of the theory of absolute reaction rates, the quantity ΔE^* may be regarded as the activation energy for the process under consideration.

In the other limiting case, namely at low temperatures, w_{12} takes the form:

$$w_{12} = \frac{2\pi |L_{\beta\alpha}^{(2)}|^2}{\hbar^2 \omega_0 \left(\frac{I_\beta - I_\alpha}{\hbar\omega_0} \right)!} \exp \left[-\frac{c}{8\pi\hbar\omega_0} \int (\mathbf{D}_\alpha^0 - \mathbf{D}_\beta^0)^2 dr \right] \times \\ \times \left[\frac{c}{8\pi\hbar\omega_0} \int (\mathbf{D}_\alpha^0 - \mathbf{D}_\beta^0)^2 dr \right]^{(I_\beta - I_\alpha)/\hbar\omega_0} \exp \left[-\frac{I_\beta - I_\alpha}{kT} \right]; \quad kT \ll \hbar\omega_0. \quad (11)$$

Thus, the transition probability also assumes an activation form at low temperatures, the role of the activation energy now being played by the quantity $(I_\beta - I_\alpha)$.

In addition to the activation energy ΔE^* , it is necessary to know other thermodynamic quantities, such as the free energy of activation ΔF^* and the entropy

of activation ΔS^* . According to a well-known formula of statistical physics, we have

$$\Delta F^* = F^* - F_\alpha = -kT \ln \frac{z^*}{z_\alpha}, \quad (12)$$

where z^* and z_α are the statistical sums for the activated and initial states. As noted above, activation quantities can be used only at high temperatures; therefore the statistical

sums should be calculated in the quasiclassical approximation. As the calculation has shown, the free energy of activation has the form

$$\Delta F^* = \Delta E^* - kT \ln \left[\frac{\sum_k \hbar^2 \omega_k^3 (q_{k\alpha}^0 - q_{k\beta}^0)^2}{(kT)^2 \sum_k \omega_k (q_{k\alpha}^0 - q_{k\beta}^0)^2} \right]^{1/2} = \Delta E^* - T\Delta S^*. \quad (13)$$

The expression for ΔS^* , which should be interpreted as the entropy of activation, takes an especially simple form in the absence of frequency dispersion,

$$\Delta S^* = -k \ln \frac{kT}{\hbar\omega_0} < 0. \quad (14)$$

At present there are a number of works devoted to calculating the rate constant of electron-transfer reactions in solutions. On the basis of the theory of absolute reaction rates, the authors of these works represent the transition probability w_{12} in the form of the product

$$w_{12} = w_s w_e, \quad (15)$$

where w_s is the probability of formation of the activated complex, and w_e is the probability of an electronic transition in the activated state. In some works⁽⁵⁾ the quantity w_e is calculated, while w_s is treated as an empirical quantity; in others⁽⁶⁾, on the contrary, they restrict themselves to calculating the probability w_s . The work of R. A. Marcus, who calculated the free energy of activation by a purely thermodynamic method, appears to us the most interesting and closest to the theory developed here. In order to indicate a quantitative criterion for the applicability of Marcus' formulas, let us carry out the following considerations. Denote by $\tau^* \simeq 2\pi/\omega_0$ the lifetime of the activated complex, and by $\nu_e(R)$ the frequency of electron exchange between ions located at a distance R from one another. If R is such that $\nu_e(R)\tau^* \gg 1$, i.e. $2\pi\nu_e(R) \gg \omega_0$, then one may assume that $w_e \simeq 1$.

In conclusion it should be noted that the electronic mechanism of oxidation-reduction reactions adopted in the present work is not the only possible one. Other mechanisms, such as, for example, reactions with proton transfer, await theoretical consideration.

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