KINETICS OF CHEMICAL REACTIONS
IN POLAR LIQUIDS

I: Theory
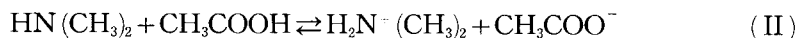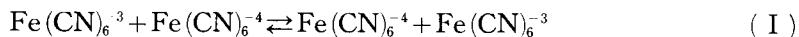
By

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Abstract

The basic results of quantum theory of chemical reaction kinetics in polar medium are reported. The general features of activation energy dependence on energetic characteristic of initial and final states of the system (generalized Brönsted rule) is discussed. General method of calculating activation energy of reaction in polar liquid is formulated.

The reaction carried out in polar solvents are of great importance for chemistry. A peculiar feature of most of these reaction is a strong effect of the solvent on the process rate. This effect is due to two reasons. First, in some cases reagents can form with the nearest molecules of the medium a strong solvation shell, which is often called the near coordination sphere. Second, the interaction energy of the charge with the solvent outside the near coordination sphere can amount to several kilocalories per mole. Thus, the charge redistribution during the reaction will lead to a change in the polarization of the medium, *i.e.*, in the mean dipole moment of unit volume. Therefore, the reaction heat will contain the difference of electrostatic energies of solvation of initial and final states. Then, since in many cases correlations between the reaction heat and the activation energy are observed[1], the interaction of reagents with solvent should make a considerable contribution to the activation energy. The following reactions can serve as examples of reactions involving a considerable change in the solvent polarization :

$$Fe(CN)_6^{-3} + Fe(CN)_6^{-4} \rightleftarrows Fe(CN)_6^{-4} + Fe(CN)_6^{-3} \qquad (I)$$

$$HN(CH_3)_2 + CH_3COOH \rightleftarrows H_2N^-(CH_3)_2 + CH_3COO^- \qquad (II)$$

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$$CH_3-\overset{\text{-}}{C}H-CH_3 \rightleftarrows CH_2-CH_2-CH_3 \tag{III}$$
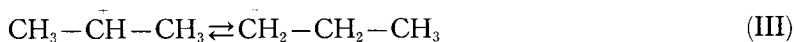
It should be emphasized that even if the charge state of reagents in reaction (III) does not change, a significant redistribution of the electron density takes place in reacting molecules.

The simplest purely electron transfer reactions involving no change in chemical bonds were considered in terms of the absolute reaction rates theory by R. A. MARCUS.[2,3] However, the method developed in these papers cannot be directly used in calculating the rate constants of reactions involving a change of the internal structure of reagents. Much more effective proved to be the quantum theory of purely electron transfer reactions, developed in previous papers[4-7], which was later extended to the case of more complex reactions.[8-14] Below are set forth the main physical assumptions and conclusions of this theory.

First we shall consider a solvent model.[12] In the theory being presented the solvent is described by polarization fluctuating with time, which can be expressed as a set of harmonic oscillators with frequencies ω_i and normal coordinates q_i. Though the potential energy surface is multidimensional, we shall interpret the results on schematic one-dimentional potential curves, considering q as being a certain generalized coordinate describing the solvent state (see Fig. 1). When reacting particles are introduced into the solvent, the interaction of their charges with polarization leads to a shift of the equilibrium coordinate $q=0$ to a new position $q_i=q_{i0}$ and to a change of the equilibrium energy in the total system (medium + reagents). The shift
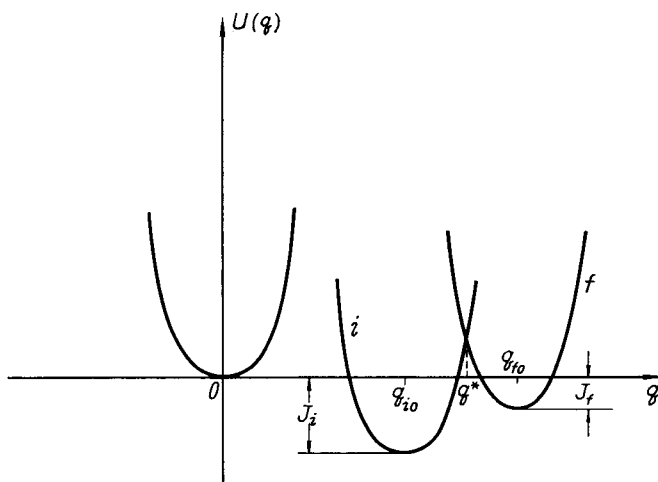

Fig. 1.

of the equilibrium coordinate q_{i0} and the equilibrium energy J_i depend on the charge distribution in the reacting particles and differ in initial and final states. (Curves i and f in Fig. 1, respectivly). For the model under consideration all the properties of the polar solvent can be expressed in terms of the complex dielectric permeability $\varepsilon(\vec{k}, \omega)$, determining the nature of propagation in the medium of polarization waves with the length $\lambda = \dfrac{2\pi}{|\vec{k}|}$ ($\vec{k}$—the wave vector) and the frequency ω. In particular, the oscillator frequencies ω_i can be determined from the imaginary part of the dielectric permeability $Im \; \varepsilon(\vec{k}, \omega)$. Though the calculation was carried out for the whole frequency spectrum, for simplicity, below we shall make use of only one effective frequency ω_0. In the order of magnitude it coincides with the reciprocal Debye relaxation time τ, which for water is about 10^{-11} sec $\left(\omega_0 \sim \dfrac{1}{\tau} \sim 10^{+11} \; \text{sec}^{-1}\right)$. Moreover, if $\varepsilon(\vec{k}, \omega)$ and the charge distribution in reagents and products are known, it is possible to estimate the basic parameter of the theory -the energy of reorganization of solvent polarization E_s[12]. Unfortunately, at present there are experimental data available only for $\varepsilon(o, \omega)$, *i.e.*, in the range $k \approx 0$. However, for reactions involving significant solvent reorganization at small distances, *e.g.* for small radius ions, the dependence of ε on k is of essential importance. In another limiting case, when reorganization of the medium at small distances is not important, as *e.g.* for large ions, E_s can be written as[12]:

$$E_s = \frac{c}{8\pi} \int [\vec{D}_i - \vec{D}_f]^2 \, dv, \qquad (1)$$

$$c = \frac{1}{\varepsilon_0} - \frac{1}{\varepsilon_s}$$

where ε_0 and ε_s are optical and static dielectric constants, $\vec{D}_i$ and $\vec{D}_f$-inductions set up in the medium by reagents and products. Though in the general case it is impossible to obtain accurate values of E_s by means of formula (1), it can be used for rough calculations. It should be stressed that an accurate expression for E_s obtained in previous paper[12], as well as the approximate formula (1), takes account of the essential dependence of the reorganization energy on the charge redistribution in the course of the reaction. Owing to this circumstance, it is possible in comparing various reactions to draw quantitative conclusions regarding the value of E_s. Thus, for example, it can be said that for a number of reactions involving the same charge redistribution E_s will have the same value. Therefore, for a given series of reactions E_s should be treated as a single empirical pa-

rameter and determined experimentally.

Let us pass now to the discussion of the main kinetic laws for chemical reactions in polar liquids.[12] In the general case, the system consist of a solvent and reacting particles. In the course of reaction the polarization state of the solvent can change as well as the electron states of reacting particles and their molecular structure (including the deformation of valence bonds, their breaking or formation).

The conventional method of calculating the rate constant in the theory of absolute reaction rate is known to involve the calculation of the surface of the system total potential energy, *i.e.*, of the electronic term u_e. In the case of reactions in a polar medium, the term u_e represents the total energy of the system at fixed values of the coordinates $\{q\}$, describing the polarization state of the solvent and the coordinates $\{R\}$-the atoms participating in the reaction. In the absolute reaction rate theory it is assumed that the motion of the system in the course of reaction along the surface $u^e(R, q)$ is classical. Actually, this description corresponds to the subdivision the system into two subsystems: the quantum (electrons) and the classical (all the other particles). It should be stressed that the assumption that all the intramolecular degrees of freedom can be treated as classical which is made whithin the framework of the absolute reaction rates theory, is quite unfounded and at variance, *e.g.* with the well-known experimental data on the temperature dependence of the heat capacity of some molecules.[15]

A quantum calculation performed under rather general assumtion about the nature of chemical reactions in polar liquids has shown that the classical or quantum behavior of any degree of freedom is essentially determined by the exitation energy value ΔE, *i.e.*, by the frequencies of the intramolecular vibrations $(\Delta E = \hbar\omega_m)$ and characteristic frequencies of solvent polarization fluctuations $(\Delta E_0 = \hbar\omega_0)$. It follows from the theory that a vibrational degree of freedom can be considered to be classical if the excitation energy corresponding to it is small compared to kT

$$\Delta E_{\mathrm{clas}} = \hbar\omega_{\mathrm{clas}} < kT \qquad (2)$$

The degrees of freedom for which is valid the inverse inequality

$$\Delta E_{\mathrm{quant}} = \hbar\omega_{\mathrm{quant}} > kT \qquad (3)$$

should be considered as being quantum. Thus, *e.g.* in most chemical reactions proton acts as a quantum particle, since the frequencies of proton vibrations in chemical compounds satisfy the inequality (3) $\omega \sim 10^{14} \ \mathrm{sec}^{-1} > \dfrac{kT}{\hbar}$.

The specific feature of reaction in polar media is that at least one clas-

sical subsystem participates in these processes, this being the polar solvent, and therefore the dependence of the reaction rate constant on the temperature is of an activation nature. As is shown by a quantum-mechanical calculation[12,14], the expression for the reaction rate constant can be written as

$$k = \sum_{m,m'} A_{m,m'} \exp\left(-\frac{E_a^{m,m'}}{kT}\right) \tag{4}$$

where m and m' are the numbers of excited levels of the quantum sybsystem in the initial and final states, respectivly, $E_a^{m,m'}$-the partial activation energy, which is practically independent of temperature (see Fig. 4) and the values of $A_{m,m'}$ depend on temperature according to the power law. The preexponential factor will be considered in more detail below. An important conclusion of the theory is that the reaction rate constant depends on the difference $\Delta J = J_f - J_i$, where J_i and J_f are the minimal energies on the potential surfaces of initial and final states, corresponding to the unexcited levels of the quantum subsystem (see *e.g.* Fig. 1). As will be shown, the quantity $(-\Delta J)$ actually coincides with the reaction heat. Therefore, the dependence of k on ΔJ can be treated as a certain generalization of the Brönsted rule. It follows from calculation that formula (4), valid for any value of ΔJ, can be written as

$$k = A \exp\left(-\frac{E_a}{kT}\right) \tag{5}$$

where E_a is the effective activation energy, depending on ΔJ and the reorganization energy of the classical degrees of freedom.

Another important conclusion of the theory refers to the general nature of the dependence of E_a on ΔJ. Calculation shows that at low enough values of ΔJ the effective activation energy E_a remains constant and equal to its minimal value $E_a = E_{\min}$ (Fig. 3). At very large values of ΔJ the dependence of E_a on ΔJ is linear : $E_a = \text{const} + \Delta J$. In the intermediate range the E_a *versus* ΔJ dependence differs for various processes and will be considered in more detail below for some particular cases.

The method of finding the activation energy in this range is as follows. It is necessary to plot the potential energy surfaces for initial and final states as a functions of the coordinates of the classical subsystem only, *i.e.*, the coordinates corresponding to low frequency vibrations (2)*). These are the

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*) Unlike the absolute reaction rates theory, in the general case these surfaces do not represent electronic terms. For some reactions, however, *e.g.* for simplest electron exchange reactions, these potential energy surfaces can coincide with the electronic terms of the system.

coordinates q_i describing the solvent polarization state and some normal coordinates corresponding to intramolecular vibrations with frequences less than $\left(\dfrac{kT}{\hbar}\right)$, which are known from spectroscopic data. On such surfaces the activation energy can be found as the distance from the minimum on the initial surface to the minimum ("saddle") point at the intersection of initial and final surfaces.

As the first example let us take the reaction of type (II), assuming only proton transfer to occur during the reaction, the other parts of molecules remaining essentially unchanged. In this case only the solvent is a classical subsystem. Therefore, the initial and final potential energy surfaces are of the same form as in Fig. 1, and for E_a we can write the expression

$$E_a = \frac{(E_s + \varDelta J)^2}{4E_s}, \quad |\varDelta J| \leqslant E_s \qquad (6)$$

where E_s is the solvent reorganization energy, which can be estimated by means of formula (1). The value of $\varDelta J$ is equal to the difference of energies of the system final and initial states $\varDelta J = J_f - J_i$, J_f and J_i containing the energies of proton zero vibrations in final and initial states, respectively. It should be noted that there is a formal similarity between (6) and the corresponding expression for the activation energy in the purely electron transfer reaction.[5-7] This similarity is due to the fact that both in purely electron trasfer and in purely proton transfer reactions the activation factor is determined by the reorganization of the solvent alone. However, reactions involving not only repolarization of the solvent, but also the rearrangement of other classical degrees of freedom are also possible. In these cases in addition to E_s, the total reorganization energy E^{tot} contains the reorganization energy of all the other classical degrees of freedom E_r, *i.e.*,

$$E^{\mathrm{tot}} = E_s + E_r \qquad (7)$$

Then the expression for the activation energy can be obtained from (6) by substituting formally E_s for E^{tot}. To calculate E_r it is necessary to make use of the spectroscopic data on the frequencies of classical vibrations and the structure of molecules.

The reactions considered above are relatively simple. In a more general case in the course of reaction part of the degrees of freedom can change from classical to quantum, and vice versa. A reaction of the type $AB + C \rightarrow AC + B$ can be taken as an example of this process. In the initial state particle B performs high frequency vibrations in molecule AB (*i. e.*, here we have a quantum degree of freedom), where as particle C is in a solvated

state in solution, *i.e.*, it behaves on the whole in the classical manner. In the course of reaction particle B is substituted by particle C and in the final state particle C behaves in a quantum manner, and particle B in a classical manner.

As a second example let us consider a reaction in which due to the formation of one chemical bond, a quantum degree of freedom appears and a classical degree of freedom disappears. The potential energy surfaces being functions of the coordinates only of the classical subsystem, in the process under consideration the surfaces of initial and final states have a different number of dimentions. These surfaces are shown schematically in Fig. 2, where R is the coordinate of a particle which was initially present
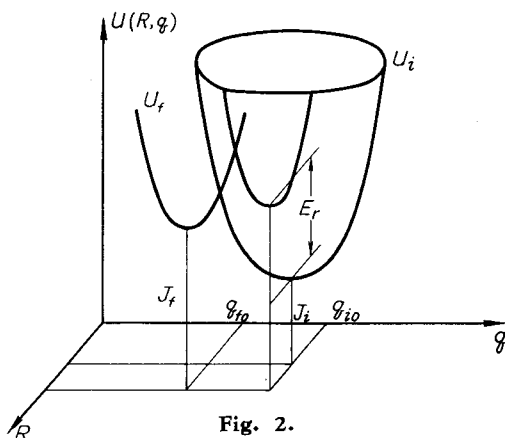

Fig. 2.

in the solution and in the course of reaction forms a chemical bond, q-is one of the generalized coordinates describing the solvent state. In this case, as shown by calculation[22], the activation energy is of the form

$$E_a = \frac{(E_s + \Delta J - E_r)^2}{4E_s} + E_r, \quad |\Delta J - E_r| \leqslant E_s \qquad (8)$$

where E_r is the reorganization energy, corresponding to the disappearing classical degree of freedom.

An interesting feature of formula (8) is the existence of the minimum activation energy of the process $E_a^{\min} = E_r$.

In the foregoing we always considered the cases where the condition $|\Delta J - E_a^{\min}| \leqslant E_s$ or $|\Delta J| \leqslant E_s$, if $E_a^{\min} = 0$, was imposed upon the parameter ΔJ. In what follows the range of ΔJ values satisfying this condition will be called *the normal* region. One of the main conclusions of the theory is that in the normal region the excited states of the quantum subsystem, such

as proton, do not participate in the process, and the proton performs the transition from unexcited initial to the unexcited final state (Fig. 4a). In the case when $\Delta J > E_s$ (this region will be called *"barrierless"*) a contribution to the rate constant is made by the transitions involving the participation of several excited quantum levels of final state (see formula (4)). Similarly, at $\Delta J < -E_s$ (this region will be called *"activationless"*) transition occur from several excited quantum levels of initial state to the ground final state. Calculation shows that the dependence of the activation energy on ΔJ in the general case is of the form shown in Fig. 3. It should be stressed that
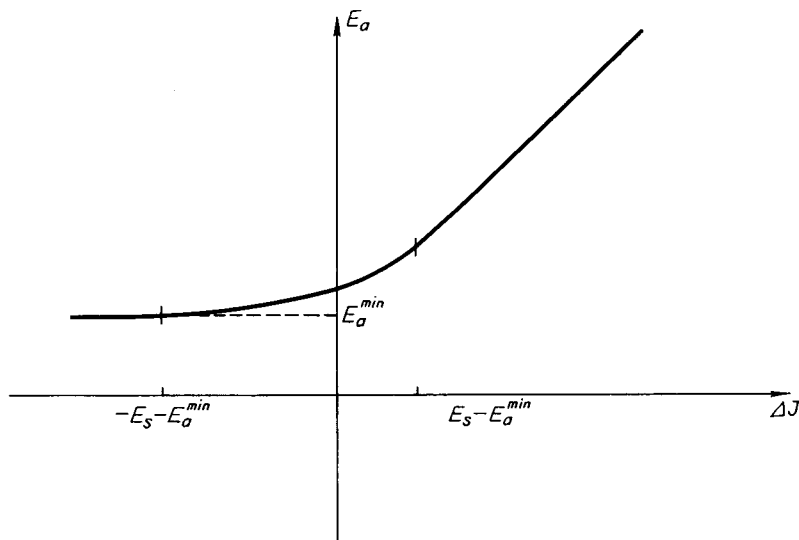

Fig. 3.

the dependence of E_a on ΔJ in the barrierless and activationless regions is of a universal nature, *viz.*, at $\Delta J - E_a^{\min} < -E_s$, E_a attains the minimum value $E_a^{\min}$ and remains constant, whereas at $\Delta J - E_a^{\min} > E_s$ the activation energy rises linearly, with ΔJ: $E_a = E_{a,\text{reverse}}^{\min} + \Delta J$, where $E_{a,\text{reverse}}^{\min}$ is the minimum activation energy for the reverse reaction. In the normal region the dependence of the activation energy on ΔJ is expressed in terms of the classical subsystem parameters. In particular, in purely electron transfer and in simplest proton transfer reactions it is determined by formula (6).

The nature of the dependence of E_a on ΔJ in the barrierless and activationless regions has a simple physical sense, which can be explained taking as an illustration a purely proton transfer reaction. First of all, it should be noted that both for initial and final system states there exists a set of potential energy surfaces, each of which corresponds to a definite state of
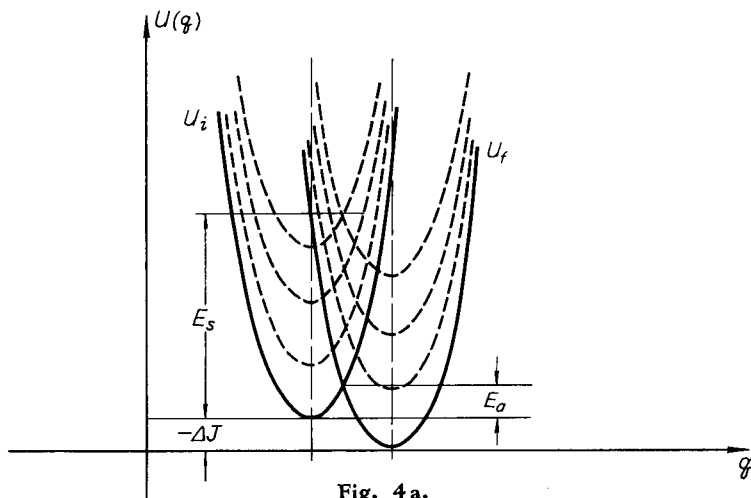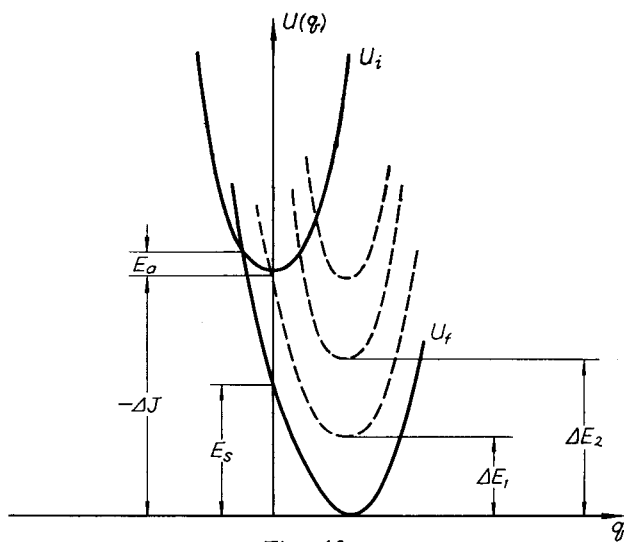
Fig. 4 a.

Fig. 4 b.

the quantum subsystem; ground state, the first excited (m_1 and m_1'), the second excited (m_2 and m_2'), etc. (Fig. 4a). Let us consider the case when $\Delta J < -E_s$. The arrangement of the potential surfaces of initial (i) and final (f) states is schematically shown in Fig. 4b, in which by solid lines are shown the surfaces corresponding to the ground initial and final states of quantum subsystem, and by dashed lines the surfaces corresponding to the first and m-th excited final states of quantum subsystem. As is clear from

this figure, at $\Delta J < -E_s$ the system transition from the ground initial to the ground final state corresponds to the activation energy E_a, whereas the transition from the ground initial to the first excited final state (ΔE_1) does not require any activation energy at all and thus is more advantageous in the given situation Therefore, the reaction rate constant will be mainly determined precisely by this transition. The transitions to more highly excited states (ΔE_m) are not advantageous since they require activation. With decreasing ΔJ, however, the main contribution to the rate constant will be made by the excited level of final state for which activation energy is zero.

The scheme presented above is physically obvious, but somewhat simplified. Actually, as shown by calculation, an essential contribution to the reaction rate constant in the "activationless" region is made by several excited levels of final state, so that the transition from the normal reaction region to the activationless one is described by smooth curve (Fig. 4b). Mathematically, this can be accounted for by the fact that although the distance between the quantum subsystem levels (ΔE) is greater then kT (for proton it is several kilocalories per mole), ΔE is much less than E_s, which is usually equal to some tens of kilocalories per mole. From what has been said above it is clear why in the normal region the transition occurs from the ground initial to the ground final state : the trasitions to the excited final states prove to be less advantageous than the transition to the ground state owing to a large activation energy. The excited initial states do not participate in the process since the probability of pre-excitation is proportional to $\exp\left(-\dfrac{\Delta E_n'}{kT}\right)$ (Gibbs factor), whereas the gain in the activation energy does not compensate this factor. However, when passing to the barrierless region, when the value of ΔJ becomes similar to that of E_s, both these factors compensate each other and the transitions from the excited initial states start to make a contribution to the reaction rate constant[*].

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[*] In his recently published papers R. A. Marcus, being apparently unfamiliar with the studies[8-14], made an attempt to apply the formulae derived by him for purely electron transfer reactions to the description of some arbitrary chemical reactions in liquids and gas phases. For the free activation energy he used formula (6) with some additional conditions $E_a = 0$ at $\Delta J \leqslant -E_s$ and $E_a = \Delta J$ at $\Delta J \geqslant E_s$. As emphasized by the author himself, this is a purely empirical approach, which does not reveal the physical significance of the parameters appearing in the theory. It follows from the results of present study that the physical mechanism of the process involving the breaking or deformation of chemical bonds is of a much more complex nature than in the case of electron transfer reactions. The activation energy can not be presented by means of a universal formula for arbitray reactions (see, *e.g.* (6), (7) and (8)). In the normal

Now let us examine the structure of the preexponential factor A in formula (5). As shown by calculation, the preexponential A is to a considerable extent determined by the exchange integral value

$$L = \int \phi_f^* \, V \phi_i \, \mathrm{d}v \tag{9}$$

where ϕ_f and ϕ_i are the wave functions of final and initial states of subsystem, which remains quantum during the reaction (*e.g.*, of electrons or protons), V the potential inducing the reaction, *e.g.* for a purely electron transfer reaction V is the interaction energy of electron with the oxidant ion. In the case of a purely proton transfer reaction V can be considered as being the potential of interaction between proton and a molecule-acceptor (in this case it is possible to use the Morse potential as V). Apart from the exchange integral, the preexponential factor contains some parameters characterizing the remaining degrees of freedom : both classical and those which in the course of the reaction undergo mutual transformations from quantum to classical. Below for simplicity, we shall consider in more detail the preexponential factor for the case when solvent is the only classical subsystem, and electrons and proton-the quantum subsystem. Here the quantity A can be written as

$$A = \frac{\omega_0}{2\pi} \, \text{æ} \tag{10}$$

where ω_0 is the characteristic frequency of the solvent and æ-the transmisson coefficient, which can be written as

$$\text{æ} = \begin{cases} \dfrac{|\int \phi_f^* \, V \phi_i \mathrm{d}v|^2}{\hbar \omega_0 \sqrt{\dfrac{E_s kT}{4\pi^3}}} = \dfrac{L^2}{L_{cr.}^2}, & \text{at } L^2 < L_{cr}^2 \\ \\ 1 & , \text{at } L^2 \geqslant L_{cr}^2 \end{cases} \tag{11}$$

The transmission coefficient æ has a quite definite significance in the theory. The activation factor determines the probability of the system attaining the intersection "point" of the potential curves of initial and final states (the point q_i^* in Fig. 1). But in this case the system can either remain on the

region the specific form of the expressions for the activation energy dependes essentially on the type of the reaction. Although the *Ea* versus *ΔJ* dependence in activationless and in the barrierless regions is a universal one, in intermediate regions between the normal region and the activatiolness and barrierless ones the *Ea* versus *ΔJ* dependence is rather complex and is not described by the simple analytical formulae such as (6)–(8).[18]

initial term, or pass to the term of the final state. The value of α determines the transition probability from the initial to the final potential curve when the system passes this "point". The reactions for which the transmission coefficient $\alpha < 1$ are generally called nonadiabatic and those with $\alpha = 1$-adiabatic. In the case of an adiabatic process the probability of a transition from the initial to the final potential curve is equal to unity after the system reaches the intersection point of the terms. As it follows from formula (11), for the process to be adiabatic it is necessary that either the exchange integral L should be large, or that the velocity of the system passing the intersection point of the terms should be small, *i.e.* that the factor ω_0 in the denominator should be small (11). It should be noted that, unlike the Gamow factor used in some studies[19] to calculate the transmission coeffitient α, the result obtained by us is of a different physical nature. This follows directly from the fact that even at small values of the exchange integral the reaction can occur as an adiabatic process if the velocity of the motion of the classical subsystem is small enough. (It should be recalled that ω_0 for water has a very small value).

The comparison of formula (10) with the corresponding factor obtained in the absolute reaction rates theory shows that the quantity $\Delta S^\# = k \ln \dfrac{\hbar \omega_0}{kT}$ can be considered as the activation entropy. It should be stressed, however, that here the notion of the activation entropy is only formally used, since it is well-known that no equilibrium formation can correspond to the transition state[20] and thus it cannot be characterized by conventional thermodynamic quantities. On the other hand, "thermodynamic characteristic of the activated state" are not measured experimentally. It is possible to measure experimentally without making use of any model theoretical considerations, only the reaction rate constant and its temperature dependence and, besides, various thermodynamic functions of initial and final states. Therefore, all the correlations observed experimentally should represent the relationships between those quantities. In fact, in many experiments correlations were established between the logarithms of the reaction rate and equilibrium constants (*e.g.* the Brönsted relation for proton transfer reactions).

In order to substantiate these dependences in terms of the theory presented above it is necessary first of all to establish the relation between the basic parameters ΔJ and E_s and the thermodynamic characteristics of the system, taking into consideration that not all degrees of freedom of the system were treated in the theory in a similar manner. Thus, a dynamic description having been used for intramolecular degrees of freedom, it is

possible to find for them the thermodynamic characteristics from the energy spectrum by a conventional method. If the classical subsystem consists of a set of harmonic oscillators with the frequencies $\hbar\omega_k < kT$, the free energy is equal to

$$F_{\mathrm{dyn}} = F_{\mathrm{dyn}}^{\mathrm{quant}} + F_{\mathrm{dyn}}^{\mathrm{clas.}} = F_{\mathrm{nyn}}^{\mathrm{quant}}$$
$$+ kT \sum_{k=1}^{N} \ln\left(1 - e^{-\frac{\hbar\omega_k}{kT}}\right) + \sum_{k=1}^{N} \frac{\hbar\omega_k}{2} + u_0 \tag{12}$$

where the last term u_0 is equal to the minimum potential energy of the classical subsystem. Taking into consideration that the excitation energies of the quantum system $\varepsilon_n - \varepsilon_0$ are large and $\hbar\omega_k < kT$, formulla (12) can be written in the approximate form

$$F_{\mathrm{dyn}} = \varepsilon_0 + u_0 + kT \sum_{k=1}^{N} \ln\frac{\hbar\omega_k}{kT} + \sum_{k=1}^{N} \frac{\hbar\omega_k}{2} \tag{13}$$

In this approximation the entropy can be written as

$$S_{\mathrm{dyn}} = -k \sum_{k=1}^{N} \ln\frac{\hbar\omega_k}{kT} + kN \tag{14}$$

where N is the number of classical degrees of freedom.

On the other hand, the solvent was described by means of a fluctuating polarization. Although this can be represented by a set of oscillators with frequences ω_i, some thermodynamic functions for the solvent can differ from those of ordinary oscillators. If for simplicity we use the Born model[21], the free energy of the solvent in the presence of the charge is of the form

$$F_{\mathrm{solv}} = -\frac{1}{8\pi}\left(1 - \frac{1}{\varepsilon_s}\right)\!\!\int\!\vec{D}^2 \mathrm{d}v + \sum_{i=1}^{N_{\mathrm{solv}}} \frac{\hbar\omega_i}{2} + kT \sum_{i=1}^{N_{\mathrm{solv}}} \ln\frac{\hbar\omega_i}{kT} \tag{15}$$

and the entropy is determined by the formula

$$S_{\mathrm{solv}} = -k \sum_{i=1}^{N_{\mathrm{solv}}} \ln\frac{\hbar\omega_i}{kT} + kN_{\mathrm{solv}} + \frac{1}{8\pi}\frac{1}{\varepsilon_s^2}\frac{\mathrm{d}\varepsilon_s}{\mathrm{d}T}\!\!\int\!\vec{D}^2\mathrm{d}v \tag{16}$$

The difference between formula (16) and (14) can be significant only if ε_s strongly depends on temperature. Below we shall show that the last term in (16) is usually of no importance for the processes under consideration. Using (13) and (15), let us write the free energy of the reaction as

$$\Delta F_0 = \left\{\Delta\varepsilon_0 + \Delta u_0 + \sum_{k=1}^{N_f} \frac{\hbar\omega_k^f}{2} - \sum_{k=1}^{N_i} \frac{\hbar\omega_k^i}{2} - \frac{1}{8\pi}\left(1 - \frac{1}{\varepsilon_s}\right)\!\!\int\![\vec{D}_f^2 - \vec{D}_i^2]\,\mathrm{d}v\right\}$$
$$+ kT \sum_{k=1}^{N_f} \ln\frac{\hbar\omega_k^f}{kT} - kT \sum_{k=1}^{N_i} \ln\frac{\hbar\omega_i^f}{kT} \tag{17}$$

where summation is made over all classical degrees of freedom of the solvent and classical intramolecular degrees of freedom. The relation between ΔF_0 and ΔJ can be found if we take into consideration that the expression in braces in (17) is the difference of minimum energies of initial and final states, *i.e.* it coincides with ΔJ

$$\Delta F_0 = \Delta J + kT \sum_{k=1}^{N_f} \ln \frac{\hbar \omega_k^f}{kT} - kT \sum_{k=1}^{N_i} \ln \frac{k\omega_k^i}{kT} \tag{18}$$

It follows from (18) that ΔJ coincides with ΔF_0 in the case if the number of classical degrees of freedom of the reactants does not change during the reaction. For example, $\Delta J \neq \Delta F_0$ if the number of molecules in the solvation shell of the reagent changes during the reaction. If *e.g.* one molecule leaves the solvation shell, $\Delta J - \Delta F_0 \approx -3kT \ln \frac{\hbar \omega}{kT}$. If we take for evaluation $\omega \sim 10^{12} \text{ sec}^{-1}$, this difference will be $\sim 10 kT = 6.0 \text{ kcal/mol}$. For reactions involving a change in the number of classical degrees of freedom, the entropy ΔS_0 should also change significantly

$$\Delta S_0 = k(N_f - N_i) - k \sum_{k=1}^{N_f} \ln \frac{\hbar \omega_k^f}{kT} - k \sum_{k=1}^{N_i} \ln \frac{\hbar \omega_k^i}{kT}$$
$$+ \frac{1}{8\pi} \frac{1}{\varepsilon_s^2} \frac{d\varepsilon_s}{dT} \int [\vec{D}_f^2 - \vec{D}_i^2] \, dv \tag{19}$$

The estimation of the last term equal to

$$\frac{1}{\varepsilon_s^2} \cdot \frac{1}{(1 - 1/\varepsilon_s)} \cdot \frac{d\varepsilon_s}{dT} \frac{1}{8\pi} \left(1 - \frac{1}{\varepsilon_s}\right) \int [\vec{D}_f^2 - \vec{D}_i^2] \, dv$$
$$\equiv \frac{1}{\varepsilon_s^2 (1 - 1/\varepsilon_s)} \frac{d\varepsilon_s}{dT} \Delta F_0^{\text{el-stat. u.}} \tag{20}$$

shows that usually it does not exeed k and can be dropped. It is evident from (19) that in reactions involving trasformation of the quantum degrees of freedom to classical and vice versa, the main contribution to the entropy change is due to the difference between the second and the third terms. Comparing the structure of formulae (18) and (19), we see that ΔJ is nearly equal to the difference of internal energies of reaction ΔE_0

$$\Delta J = \Delta E_0 - kT(N_f - N_i) \tag{21}$$

For comparison with experiment, it is more convenient to relate ΔJ to the reaction heat $(-\Delta H_0)$

$$\Delta H_0 = \Delta J + p \Delta V + kT(N_f - N_i) \tag{22}$$

Usually the change in volume during the reaction in a solution is not large

(by estimation $p\ \Delta V \sim 10^{-2}$ kcal). Therefore, we can consider ΔJ to coincide practically with the reaction enthalpy, if the number of classical degrees of freedom does not change significantly.

As has been pointed out in the beginning of the present study, the reaction rate constant is a function of ΔJ. In its turn ΔJ is related to the reaction free energy (18) and the reaction heat (22). To find the correlation of the logarithm of the reaction rate constant with the reaction heat for a number of similar reactions, it is necessary that the series of reactions under consideration should satisfy the following conditions. First, it is necessary that the reorganization energy E^{tot} should be constant for the whole series. Second, the preexponential factor should also remain unchanged. If a correlation with the reaction free energy, *i. e.*, with the equilibrium constant is sought for, rather than with the reaction heat, another condition should be added, *viz.* that the reaction entropy should be the same for all the reactions of the series. On the other hand, if correlations of this kind are observed for a number of compounds, this should mean that the reactions being studied satisfy the above conditions.

A more detailed comparison of the theory presented above with the experimental data will be given in the next paper.

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References

1) S. W. BENSON, *The Foundations of Chemical Kinetics*, McGrow-Hill Book Co, Inc. New York, Toronto, London, 1960.

2) R. A. MARCUS, J. Chem. Phys. **24**, 966 (1966).

3) R. A. MARCUS, J. Chem. Phys. **26**, 876 (1957).

4) V. G. LEVICH and R. R. DOGONADZE, Dokl. Akad. Nauk **124**, 123 (1959).

5) V. G. LEVICH and R. R. DOGONADZE, Coll. Czech. Chem. Commun. **26**, 193 (1961).

6) R. R. DOGONADZE, A. M. KUZNETSOV and A. A. CHERNENMO, Uspekhi Khim. **34**, 1779 (1965).

7) V. G. LEVICH, Advances in Electrochemistry and Electrochemical Engineering (ed. Delahay, Tobias) **5**, 1965; Phys. Chem., **9 B**, 986 (1970)

8) R. R. DOGONADZE, A. M. KUZNETSOV and V. G. LEVICH, Electrokhimia **3**, 739 (1967).

9) R. R. DOGONADZE and A. M. KUZNETSOV, Electrokhimia, **3**, 1324 (1967).

10) V. G. LEVICH, Simposium on "Electrochemical Processes and the Energy States of Electros", Schloss Elmau, CITCE 18-th Meeting 1967.

11) R. R. DOGONADZE, A. M. KUZNETSOV and V. G. LEVICH, Simposium on "Electrochemical Processes and the Energy States of Electrons", Schloss Elmau, CITCE 18-th Meeting 1967.

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12) R. R. DOGONADZE, and A. M. KUZNETSOV, Itogi Nauki, Electrokhimia 1967, Moskva, 1969; R. R. Dogonadze, in *Reactions of Molecules at electrodes*, ed. by N. Hush, Wiley, L. 1971.

13) V. G. LEVICH, R. R. DOGONADZE and A. M. KUZNETSOV, Dokl. Akad. Nauk **179**, 137 (1968).

14) R. R. DOGONADZE, A. M. KUZNETSOV and V. G. LEVICH, Electrochimica Acta, **13**, 1025 (1968).

15) E. FERMI, *Molekule und Kristalle*

16) R. A. MARCUS, J. Phys. Chem. **72**, 891 (1968).

17) R. A. MARCUS, J. Phys. Chem. **72**, 4249 (1968).

18) E. D. GERMAN, R. R. DOGONADZE, A. M. KUZNETSOV, V, G. LEVICH and Yu. I. KHARKATS, Electrochim. Acta, **15**, 353 (1970).

19) R. P. BELL, *The Proton in Chemistry*, NY, 1959.

20) M. I. TEMKIN, in the book of N. N. SEMENOF *O nekotorykh problemakh khimicheskoy kinetiky i reakzionnoy sposobnosty*, ed. Acad. of Sci. of USSR, Moscow, 1958.

21) R. A. ROBINSON and R. H. STOKES, *Electrolyte Solution*, London, Butterworths Scientific Publications, 1959.

22) A. M. KUZNETSOV, Electrokhimia, **5**, 479 (1969).