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THE THEORY OF THE ELEMENTARY ACT OF THE PROTON TRANSFER IN POLAR MEDIA

By

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The hydrogen evolution reactions at metals were studied during many years. At present there are two different approaches to the calculation of the probability of the elementary act of proton transfer from the molecule AH^z in solution to the adsorbed state at the electrode. One of them treats the proton transfer as the process of gradual stretching of the chemical bond H–A due to the transitions of the proton to the excited vibrational states in the molecule AH^z [1], or as the process of movement of the system on two-dimensional potential energy surface[2]. Possible quantum effects are taken into account by introducing tunnel corrections, describing Gamov tunneling near the top of the potential barrier. This approach ignores entirely the rearrangement of the solvent molecules in the course of the reaction.

The second approach takes into account both the motion of the proton and the reorganization of other intramolecular degrees of freedom of the reactants and the solvent molecules[3,4]. The transition probability of the system from the initial state to the final one is calculated by the quantum-mechanical methods without any *a priori* assumptions concerning the transition path on the potential energy surfaces. The latters are essentially multi-dimensional.

The first approach originates from the work of HORIUCHI and POLANYI[5], who were the first to suggest the microscopic model for the description of the elementary act of the proton transfer process. This work stimulated development of quantum-mechanical calculations for both the heterogeneous and homogeneous proton transfer reactions.

The second approach is largely based on the physical ideas of GURNEY[6] and LIBBY[7] concerning the dynamical role of polar solvent in the charge transfer reactions. This approach differs from the first one in two main

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points: 1) it takes into account all the degrees of freedom of the system, 2) the consistent quantum-mechanical theory is used for the calculation of the transition probability. The general principles of this theory are presented below.

The starting formula for the calculation of the electric current in the case of nonadiabatic reaction is as follows

$$\vec{i} = nec(\delta)\,\delta V \int f(\varepsilon)\, W(\varepsilon)\, \rho(\varepsilon)\, d\varepsilon\,, \qquad (1)$$

where $c(\delta)$ is the reactant concentration near the electrode surface, δV is the reaction volum, $f(\varepsilon)$ is the occupation probability of the energy level ε by the electron in the electrode, $\rho(\varepsilon)$ is the density of states in the electrode, $W(\varepsilon)$ is the probability of an elementary act of the reaction with participation of the electron from the energy level ε in the electrode. This formula is generalization of the phenomenological theory of FRUMKIN[8]. It takes into account the possibility for the electrons occupying various energy levels in the electrode to take part in the reaction. The formula (1) reduces the problem of the calculation of the electric current to the problem of the calculation of the probability of an elementary act of proton transfer between two localized states at fixed electronic energy. This problem is quite similar to the problem of calculation of the probability of the elementary act for the homogeneous proton transfer reaction of the type

$$AH^{z_1} + B^{z_2} \rightarrow A^{z_1-1} + BH^{z_2+1} \qquad (2)$$

Therefore all the results cited below are equally valid for both the electrochemical and homogeneous reactions.

In order to a reaction can proceed the reactants have to be at rather small distances and to be properly oriented. For the sake of simplicity we consider the case where the degrees of freedom of the system describing the movement of the reactants as a whole and their orientation may be treated as a classical (the criteria of the classical and quantum motion will be given below). It can be shown that in this case the transition probability may be calculated at fixed distances and orientations followed by averaging over all configurations possible.

The following model is used for the quantum-mechanical calculations of $W(\varepsilon)$. The solvent outside the coordination sphere of the reactants is treated as a dielectric characterized by the complex dielectric function $\varepsilon(k, \omega)$. The latter takes into account both the frequency dependence of the dielectric constant and the influence of the spatial structure of liquid on the interaction of the solvent with the electric field. The molecules of the solvent inside

the coordination layer are included in the concept "reactant". The harmonic approximation is used for the description of the intramolecular vibrations and the fluctuations of the solvent polarization. The state of the chemical bond A–H which should be broken in the course of the reaction (or B–H for the reverse reaction)*) is described by the Morse-like potentials

$$U(r) = D[1-e^{-\gamma(r-r_0)}]^2 - D, \qquad \gamma^2 = (m\omega^2)/2D \tag{3}$$

where D is the dissociation energy, m is the mass of the proton, ω is the frequency of valence vibrations.

Calculating the transition probability it is necessary to take into account the Frank-Condon principle. According to Frank-Condon principle the rearrangement of the electronic state of the reactants, leading to the breaking of any chemical bonds and to the creation of other chemical bonds, takes place only if their energy levels of the initial and final states are equalized. The position of the electronic energy levels depends on the coordinate of the heavy particles which interact with the electrons.

For the proton transfer reactions in polar liquids the energy of electrons in the molecule AH^z depends on the proton coordinate r, the coordinates of the intramolecular degrees of freedom of the reactant Q and the normal coordinates q, describing the polarization state of the solvent.

The values of the heavy particle coordinates corresponding to the Frank-Condon condition determine the transitional configuration of the reacting system. The transitional configuration corresponds to the intersection of the potential energy surfaces of the initial and final states. The rearrangement of the electronic state in the transitional configuration, which depends on the time during which the latter exists, leads to the transition of the syetem from the potential energy surface of the initial state to that of the final state.

Thus for the calculation of the transition probability it is necessary to calculate the probability for the system to reach the transitional configuration and the probability of the rearrangement of the electronic state in this configuration.

It should be noted that for the calculation of the transition probability it is important not only the statistical distribution of the particles over the coordinates but also their dynamical behaviour. This is of importance for the calculation of the probability of the electronic state rearrangement becuase the latter largely depends on the time during which the transi-

*) In the case of a homogeneous reaction B is a molecule, in the case of the electrochemical reaction B is an electrode.

tional configuration exists.

One of the main conclusions of the theory is concerned with the way of attaining the transitional configuration. It may be achieved by the gradual classical change of the normal coordinates or by the quantum tunneling through the potential barrier. The character of the transition for a given degree of freedom is determined by the competition of two factors. The Gibbs' factor, determining the occupation of the energy levels, decreases with the increase of the energy. The probability of tunneling through the potential barrier increases with the increase of the energy.

The mathematical criteria of the classical and quantum transition for a given degree of freedom have a form[3)]

$$\Delta E \ll kT, \qquad \Delta E \gg kT, \tag{4}$$

where ΔE is the chracteristic spacing of the energy levels in the potential well arising due to the reflection in the abscissa of the potential barrier along this degree of freedom.

For the oscillators describing the polarization fluctuations these criteria are approximately reduced to the conditions for the value of the vibrational quantum

$$\hbar\omega \ll kT, \qquad \hbar\omega \gg kT. \tag{5}$$

The degrees of freedom for which the first conditions are met, are referred to as classical. Those for which the reversed conditions are valid, are referred to as quantum.

The probability of stretching of the chemical bond is described by the quantum-statistical formula

$$\Phi(r) = \sum_{n=0} e^{-(E_n - E_0)/kT} \left|\phi_n(r)\right|^2 \Big/ \sum_{n=0} e^{-(E_n - E_0)/kT}, \tag{6}$$

where E_n are the vibrational energy levels, $\phi_n(r)$ are the wave functions, describing the vibrational state of the chemical bond.

The calculation of the probability of stretching of the proton chemical bond in a molecule AH using the Morse-like potential with the parameters: $\omega = 4.10^{14}\,\mathrm{sec}^{-1}$, $D = 172.5$ kcal/mole, $T = 300°\mathrm{K}$, has shown that $\Phi(r)$ coincides practically with the first term of the sum in the formula (6) $\Phi_{\mathrm{quant}} = |\phi_0(r)|^2$, corresponding to the unexcited vibrational state of the proton, up to the distances equal to the $r - r_0 \approx 2.5$ Å. Only if $r - r_0 \gtrsim 4$ Å the probability of bond stretching is described by the classical BOLTZMANN formula. Thus the proton transition may be treated as a classical one only for a transition to a large distance. However the activation energies corresponding to these distances are close to the dissociation energy of the chemical bond A–H.

(For example, in the framework of the model of the proton transfer, used in[1] the activation energy at equilibrium potential is equal to $E_a=98$kcal/mole. This model leads to the value of the symmetry factor β equal to unity almost at all experimentally attainable potentials).

In real life situations the proton transfer to small distances take place. The calculations using various models[3] have shown that the physical picture of the transition is as follows. At fixed distance between the reactants the gradual change of the coordinates of the classical degrees of freedom of the solvent and intramolecualr degrees of freedom of the reactants takes place, the proton being in the unexcited initial vibrational state. The transitional configuration corresponds to the values of the coordinates of the classical degrees of freedom of the system at which the electron and proton energies of the initial and final states are equalized. In the transitional configuration the rearrangement of the electronic state of the reactants and the change of the proton state occur, the latter going from the initial unexcited vibrational state into the final unexcited vibrational state by quantum tunnel subbarrier transition. Thus the system surmounts the activation barrier E_a by the change of the configuration of the solvent molecules and the molecules of the classical intramolecular degrees of freedom. The change of the proton state as well as that of the electronic state determine the value of the transmission coefficient κ. For the interpretation of the transition on the potential energy surfaces it is convenient to introduce (instead of the electronic terms) the potential energy surfaces, corresponding to the fixed quantum states of the electrons and proton (electron-proton terms). At small values (in absolute value) of the heat of the reaction the potential energy surfaces of unexcited initial and final vibrational proton states are sufficient for the calculation of the transition probability. The activation energy of the transition is equal to the distance from the minimum of the initial potential energy surface to the saddle point at the intersection of these surfaces. The transmission coefficient determines the probability of the transition from the initial potential energy surface to the final one at saddle point.

In the case of the simplest proton transfer reactions, where the state of only one proton is changed by the reaction, and the change of the parameters of other chemical bonds in the reactants may be neglected, the expression for the probability of the elementary act of the reaction has a form[3,9]

$$W=(\omega_{\mathrm{eff}}/2\pi)\,\kappa_{00}\cdot e^{-[E_s+\Delta J]^2/4E_skT}, \tag{7}$$

$$\kappa_{00}=2(\Delta E_{\mathrm{ep}}/2)^2/(\hbar^2\omega_{\mathrm{eff}}^2 kTE_s\pi^{-3})^{1/2}, \tag{8}$$

where E_s is the reorganization energy of the solvent molecules outside the coordiantion sphere of the reactants, $(-\Delta J)$ is the free energy of the reaction, ω_{eff} is the effective frequency of the solvent polarization fluctuations[3,9], κ_{00} is the transmission coefficient, determining the transition probability between the unexcited initial and final states of the proton, ΔE_{ep} is the resonance splitting of the ground initial and final vibrational levels of the proton.

In the case of the hydrogen evolution reaction from the ion H_3O^+ the reaction leads to the change of the state of all three protons, since the leaving of one proton causes the change of the angle between the O–H bonds in the water molecule. However, since all vibrations in the ions H_3O^+ and in the molecule H_2O are quantum, the change of the state of protons affects only the valus of the transmission coefficient. The expression for κ is formally given by eq. (8) but in this case ΔE_{ep} is the resonance splitting of the ground vibrational levels of all proton subsystem.

The change of the state of the vibrational degrees of freedom of the reactants and solvent, characterized by high vibrational frequencies ($\hbar\omega_i = \hbar\omega_f \gg kT$), leads to the temperature independent factor $\exp(-\sigma)$ in the expression for the transition probability where $\sigma = \sum_l E_{rl}/\hbar\omega_l$ is the tunneling factor. Here E_{rl} is the reorganization energy of the l-th quantum degree of freedom.

If in addition to the change of the polarization state of the medium outside the coordination sphere of the reactants the reaction causes the change of the state of the harmonic classical intramolecular degrees of freedom ($\hbar\omega_k \ll kT$), the frequencies being unchanged ($\omega_k^i = \omega_k^f$), the eq. (7) for the transition probability is also applicable with the substitution of E_s by $E_s + E_r^c$, where $E_r^c = \sum_k \frac{1}{2}\hbar\omega_k (Q_{k0}^i - Q_{k0}^f)^2$ is the reorganization energy of the classical intramolecular degrees of freedom of the reactants.

If in addition the state of the intramolecular degrees of freedom, characterized by the intermediate frequencies ($\hbar\omega_s \sim kT$), is changed, the expression for the transition probability is of a more complex form[10]. However for small values (modulo) of ΔJ

$$(\hbar\omega_s/kT)|\Delta J| \ll 2(E_s + E_r^c) + 2\sum_s E_{rs}(\hbar\omega_s/2kT)/\left[\text{sh}\,(\hbar\omega_s/2kT)\right], \quad (9)$$

and unchanged vibrational frequencies ($\omega_s^i = \omega_s^f$) the eq. (7) is still valid with the substitution of E_s by

$$E_s + E_r^c + \sum_s E_{rs}(\hbar\omega_s/2kT)/\left[\text{sh}\,(\hbar\omega_s/2kT)\right], \quad (10)$$

and adding the quantity $\{-\sum_s (E_{rs}/\hbar\omega_s)[\mathrm{ch}(\beta\hbar\omega_s)/2-1-(1/2)(\beta\hbar\omega_s/2)^2]/\mathrm{sh}(\beta\hbar\omega_s/2)\}$ to the exponent of eq. (7), where E_{rs} is the reorganization energy of the degrees of freedom, characterized by the intermediate frequencies.

If in the course of the reaction the change of the state of a classical degree of freedom characterized by the nonharmonic vibrations takes place, the expression for the transition probability has a form[11]

$$W = (\omega_{\mathrm{eff}}/2\pi)\,\kappa_0 e^{\left\{\varepsilon_a(\Delta j^*)+\frac{[E_r+\Delta J-\Delta j^*]^2}{4E_r}\right\}/kT}, \tag{11}$$

where $\varepsilon_a(\Delta j^*)$ is the activation barrier surmounted by the system along this degree of freedom at the value of the partial heat of the reaction equal to Δj^*. The value Δj^* is determined by the equation

$$\frac{1}{2}+\frac{\Delta J-\Delta j^*}{2E_r}=\frac{\partial\varepsilon_a(\Delta j^*)}{\partial\Delta j}. \tag{12}$$

The above results are valid in the normal region of the reaction, where $|\Delta J|$ is not large. In this case the main contribution to the reaction is due to the proton transitions from the ground initial state to the ground final state. When $|\Delta J|$ increases the transitions with participation of the excited vibrational levels of the proton becomes of importance.

At $\Delta J > E_r$ the activation energy for the transition from the unexcited initial state to the unexcited final one is higher than that for the transitions from the excited initial proton vibrational states. In this region the main contribution to the reaction is due to the transitions from the excited initial states for which the activation energy is close to ΔJ (barrierless transition).

At $\Delta J < -E_r$ the main contribution to the reaction is due to the transitions from the unexcited initial state to the excited final states for which the activation energy is close to zero (activationless transition).

The said above leads to certain conclusions about the dependence of the probability of the elementary act of the proton transfer on various factors. Sincs the activation energy is largely determined by the reorganization of the medium molecules it depends on the solvent properties and the rearrangement of the charge density in the course of the reaction. The properties of the chemical bonds of the proton with the reactant and the metal do not affect directly the activation energy. They determine the value of the transmission coefficient κ. Since the proton transition is of the subbarrier character the significant isotopic effect has to be observed in the case of nonadiabatic reaction. The isotopic effect depends on the nature of metal and on the electric field acting the reactant. The poorer is the proton localization in the chemical compound and in the adsorbed state

and the closer is the reactant to the electrode, the smaller is the isotopic effect. These conclusions were experimentally confirmed by KRISHTALIK *et al.*[12,13]

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