QUANTUM THEORY OF KINETICS IN ELECTROCHEMICAL PROCESSES

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The mechanism of electrochemical electron-transfer reactions, hydrogen-ion discharge reactions, and more complex processes accompanied by change in the internal structure of the reagents are discussed. It is shown that the activation factor in the probability of the elementary event in the reaction is determined by reorganization of classical degrees of freedom in the system. The change in the state of the quantum parts of the system determines the magnitude of the preexponential factor. For a certain type of reaction the possibility of existence of a minimum activation energy differing from zero was discovered.

The purpose of the present work was to investigate the general relationships governing electrochemical processes which take place in the absence of diffusion limitations. The most consistent phenomenological theory of retarded discharge has been developed in the papers by Frumkin [1]. In this theory the ratio between the activation energy and the heat of reaction, established experimentally by Bronsted for homogeneous reactions in solution, was applied to the examination of electrode processes for the first time. Attempts were subsequently made by various authors to formulate a microscopic theory of electrode reactions (electron-exchange processes, hydrogen-ion discharge) which were based on the theory of absolute reaction rates and certain quantum-mechanical considerations [2, 3]. A shortcoming of the early theoretical examinations of the elementary event in the electrochemical process was the lack of systematic allowance for the substantial effect which a polar solvent has on the discharge rate and for the role of the continuous energy spectrum of the electrons in the electrode.

In recent years a quantum-mechanical theory has been developed for electron-transfer reactions [4-7] and has subsequently been extended to the case of hydrogen-ion discharge [7, 8] and more complex processes accompanied by change in the internal structure of the reagents [9-11]. Through this it was possible to achieve considerable progress in understanding the physical mechanism of the elementary event and in obtaining quantitative results during calculation of the current and other kinetic parameters. The present paper will set out the fundamental physical premises and conclusions of this theory.

Subsequently we will consider the charges of the individual atoms throughout to be uncorrelated with each other. Consequently, the total discharge current can be represented as the sum of the currents arising from discharge of the individual ions. In addition, for simplicity we will assume that the ψ_1 effect is absent, i.e., that the whole potential drop in the electrolyte is concentrated in the Helmholtz layer. A model of the system, within the scope of which it has been possible to make a quantum-mechanical calculation, will be examined below. (As shown in [12-14], rigid phenomenological examination confirms the principal conclusions of quantum theory based on the model given below.)

Solvent. One of the important parts of the reacting system is the polar solvent. In the theory being expounded a continuous model is adopted where the medium is described by a specific dipole moment (polarization) $\mathcal{P}(\mathbf{r}, t)$ which varies in space and time. Within the scope of the model under examination [15] all

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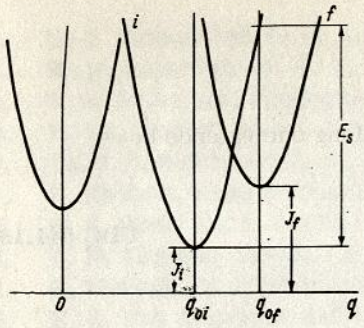

Fig. 1

the characteristics of the polar solvent can be expressed in terms of the complex dielectric constant $\varepsilon(k, \omega)$, which determines the character of the propagation of polarization waves with wavelength $\lambda = 2\pi/k$ (**k** is the wave vector) and frequency ω in the medium. Polarization $\mathcal{P}$ which varies with time can be represented in the form of a set of harmonically vibrating oscillators, characterized by frequencies ω_i and normal coordinates q_i. The frequencies of the oscillators ω_i coincide with those longitudinal electromagnetic field frequencies which are strongly absorbed in the given polar medium, i.e., are determined by an imaginary part of the dielectric constant Im $\varepsilon(k, \omega)$. In the general case the electrochemical charge on the electrode is calculated by taking account of the whole range of frequencies, but for simplicity below we will use a single effective frequency ω_0. In order of magnitude the frequency ω_0 is close to the reciporocal Debye relaxation time τ, which for water amounts to about 10^{-11} sec.

The potential energy of the solvent, due to deviation of the polarization from the equilibrium value (equal to zero in the absence of external charges), depends on the polarization value, i.e., on the normal coordinates q. Since the number of normal coordinates describing the polarization of unit volume of solvent is macroscopically large, the potential energy surface as a function of q is substantially multivariate. However, for simplicity, we will interpret the results of the theory on schematic one-dimensional potential curves for U(q) (Fig. 1). When the reacting particles are introduced into the solvent interaction of their charges with the medium leads to displacement of the equilibrium coordinate $q = 0$ to a new position $q = q_0$ and to change (related to solvation of the ion) in the equilibrium energy in the medium – ion system. The displacement of the equilibrium coordinate q_0 and the equilibrium energy J depend on the characteristics of the solvent and the charge distribution in the ions and differs for the initial and final states (curves i and f).

As will be seen from what follows, an important parameter of the theory is the energy of repolarization of the solvent E_s, which represents the work required (at one of the potential surfaces) to change the polarization of the medium from the equilibrium value corresponding to the initial reagent to the equilibrium value corresponding to the final products (Fig. 1). From this it follows that E_s is determined both by the characteristics of the solvent and by the redistribution of charge during the reaction. Accurate calculation of the E_s value requires a knowledge of the dependence of the dielectric constant on the wave vector **k**; which so far has been little investigated, and it is therefore reasonable to regard E_s as an empirical parameter which can be determined from experimental data. The value of E_s can be determined by means of the following equation [4-6]:

$$E_s = \frac{1}{8\pi}\left(\frac{1}{\varepsilon_0} - \frac{1}{\varepsilon_s}\right)\int (\mathbf{D}_i - \mathbf{D}_f)^2\, dv, \qquad (1)$$

where ε_0 and ε_s are the optical and static dielectric constants, and $\mathbf{D}_i$ and $\mathbf{D}_f$ are the inductions in the initial and final states, created by the reagents and products.

Electrode. The characteristics of the electrode on which the electrochemical reaction takes place are introduced into the theory mainly in terms of the electron distribution function among the energies $n(\varepsilon)$ and the density of the electronic states $\rho(\varepsilon)$. In describing the energy distribution of electrons in a metal it is usual to employ a one-electron approximation, which corresponds to a distribution function of a Fermi type [16]:

$$n(\varepsilon) = \{1 + \exp[(\varepsilon - \varepsilon_F)/kT]\}^{-1}. \qquad (2)$$

Reagents. To describe the inner state of the molecules and ions participating in the electrochemical discharge processes, use is made of the widely known (in molecular theory) adiabatic approximation (the Born – Oppenheimer approximation) [12]. Within the scope of the adiabatic approximation the motion of heavy particles (nuclei) is described by the concept of electronic terms which represent the effective potential energies of the nuclei averaged over the electronic state. In the general case, for quantitative calculation of the electrochemical discharge rate in complex ions, it is necessary to know the geometrical configuration of the ions participating in the process, all the characteristic frequencies of the molecular

vibrations in the initial and final states, and also the energies of the chemical bonds. The calculation simplifies substantially in some simple cases where it is known that the majority of the molecular degrees of freedom do not change during the process. For example, for hydrogen-ion discharge satisfactory results are obtained in some cases by considering the vibrations of the proton only along one valence bond.

The intramolecular vibrations in the reagents can usually be considered to be harmonic. In other cases, when this approximation proves inadequate, other more accurate potential curves (e.g., the Morse potential) can be used for the potential energy of the intramolecular vibrations. It should be noted that if the reacting ion forms a stable chemical bond with the nearest solvent molecules (i.e., a complex) then the reagent should be taken to mean the whole complex, including the ion and the solvent molecules coordinated around it.

Transfer Probability and Current Density

The elementary event in an electrochemical process is accompanied by the transfer of one or several electrons from the electrode to the discharging particle or vice versa. Below for the sake of definiteness we will only consider a cathodic process at a metal electrode. Since an electron which participates in a cathodic process can be at any energy level in the metal, the expression for the cathodic current in the case of a one-electron process has the following form [16]:

$$i = ef(c_s) \int W_{if}(\varepsilon) n(\varepsilon) \rho(\varepsilon) d\varepsilon, \tag{3}$$

where $f(c_S)$ is a function expressing the dependence of the electrochemical discharge rate on the concentration of the reagents, and W_{if} is the probability of the elementary event of the reaction in unit time accompanied by transfer of an electron from a certain energy level ε.

As known, the method usually adopted in the theory of absolute reaction rates for calculating the reaction rate constant involves construction of the full potential energy surface of the system, i.e., the electronic term U^e. In the case of a reaction in a polar medium the U^e term represents the full energy of the whole system with fixed values for the q coordinates describing the polarization state of the solvent and for the R coordinates of all the reagents participating in the reaction. In the theory of absolute reaction rates in its standard form it is assumed that motion of the system over the surface $U^e(R, q)$ during the reaction process is classical. Such a description does in fact correspond to breaking down of the full system into two subsystems – a quantum (electron) and a classical (all remaining particles) system. It must be emphasized that the assumption, made in the theory of absolute reaction rates, that the intramolecular degrees of freedom can be regarded as classical is completely unfounded. Such an assumption is not only obvious but in a number of cases, as shown by calculation, is also not justified [8, 9, 11].

Quantum calculation [12] has shown that the classical or quantum behavior of one or the other degree of freedom is largely determined by the magnitude of the excitation energy ΔE, i.e., the frequencies of the intramolecular vibrations ($\Delta E = \hbar\omega_m$) and the characteristic frequencies of the fluctuations in the polarization of the solvent ($\Delta E = \hbar\omega_0$). It follows from the theory that the vibrational degree of freedom can be considered to be classical if the corresponding excitation energy is small in comparison with the thermal energy kT:

$$\Delta E_{cl} = \hbar\omega_{cl} \ll kT. \tag{4}$$

The degree of freedom for which the opposite inequality is fulfilled,

$$\Delta E_q = \hbar\omega_q \gg kT, \tag{5}$$

should be regarded as quantum. Thus, for example, in the majority of chemical reactions the proton acts as a quantum particle, since the frequencies of the vibrations of the proton in chemical compounds satisfy the following inequality:

$$\omega \sim 10^{14}\ \text{sec}^{-1} > kT/\hbar.$$

The main conclusion of the quantum theory can be formulated as follows: The whole system should be divided into two subsystems, i.e., a quantum subsystem (electron and intramolecular degrees of freedom,

having frequencies of $\omega > kT/\hbar$) and a classical subsystem (solvent and molecular degrees of freedom, characterized by excitation energies of $\Delta E < kT$); having fixed the state of the quantum subsystem it is necessary to determine the probability of transition in the classical subsystem. As shown by calculation, the latter has the Arrhenius form

$$W^{mn}(\varepsilon) = A^{mn} e^{-E^{mn}(\varepsilon)/kT}, \tag{6}$$

where m and n are the numbers of fixed vibrational excited levels of the quantum subsystem in the initial and final states. In order to determine the "partial" activation energy E^{mn} it is necessary to construct the potential energy surface for the initial and final states as a function of the coordinates of the classical subsystem alone, by including the energies of the quantum subsystem in the "partial" thermal effect ΔJ^{mn}. On such surfaces the activation energy $E^{mn}(\varepsilon)$ will correspond to the distance from the minimum at the initial surface to the "saddle" point at the intersection of the initial and final surfaces. The meaning of the preexponential factor in Eq. (6) will be discussed a little later. The total probability of an elementary event involving participation of an electron which before discharge of the ion is at a fixed level ε in the electrode can be obtained if $W^{mn}(\varepsilon)$ is summed over all the quantum indices of the final state n and averaged statistically among the initial states m:

$$W_{if}(\varepsilon) = \sum_{m,n} A^{m,n} e^{-E^{mn}(\varepsilon)/kT} \rho_m, \tag{7}$$

where ρ_m is the Gibbs distribution function among the energies of the initial state.

One of the important conclusions of the theory lies in the fact that each term of the sum in Eq. (7) depends only on the corresponding difference $\Delta J^{mn} = J_f^0 - J_i^0 + \varepsilon_n - \varepsilon_m$, where J_f^0 and J_i^0 are the minimum energies at the potential surfaces of the final and initial states with allowance for the energy of the zero-point vibrations of the quantum subsystem, and ε_n and ε_m are the excitation energies of the quantum subsystem measured from the energies of the ground state. Here it is found that the total probability of the transition W_{if} depends only on the difference ΔJ^0. Since the energy of the initial state contains the energy of the electron in the metal $\varepsilon - e\varphi$, where φ is the electrode potential, the value of ΔJ^0 can be represented in the following form:

$$\Delta J^0 = \Delta J_F^0 + (\varepsilon_F - \varepsilon) - e\eta, \tag{8}$$

where ε_F is the Fermi level of the electron in the metal, η is the overpotential, and ΔJ_F^0 corresponds to the difference in the minimum energies of the final and initial states. When the electron is at the Fermi level the potential of the electrode is equal to the equilibrium value, and the quantum vibrational levels ($\hbar\omega > kT$) in the initial and final states are not excited.

We will assume that the quantum subsystem is in an unexcited level both in the initial and the final states. Here we will consider only one term in Eq. (7), corresponding to $m = n = 0$, and $E_a^{0,0}(\varepsilon, \eta)$ is the activation energy of the transition, corresponding to the energy of the electron ε and the overpotential η. For the sake of specificity the electron-transfer reaction and hydrogen-ion discharge can be regarded as examples, assuming that in the course of these reactions the transition is not accompanied by substantial changes in the other parts of the molecules. In these reactions the classical subsystem which is reorganized in the course of the discharge is only the solvent. Therefore the initial and final potential energy surfaces have the same form as in Fig. 1, and the following expression can be written for $E_a^{0,0}$:

$$E_a^{0,0} = (E_s + \Delta J^0)^2/(4E_s), \tag{9}$$

where E_S is the energy for reorganization of the solvent, which can be evaluated from Eq. (1). The ΔJ^0 value for the hydrogen-ion discharge reaction includes the difference of the zero-point vibration energies of the proton in the final and initial states. If the reactions under consideration involve not only repolarization of the solvent but also rearrangement of the other classical degrees of freedom, in addition to E_S the total energy of reorganization will contain a contribution from the reorganization of these classical degrees of freedom E_r, i.e.,

$$E_{tot} = E_s + E_r. \tag{10}$$

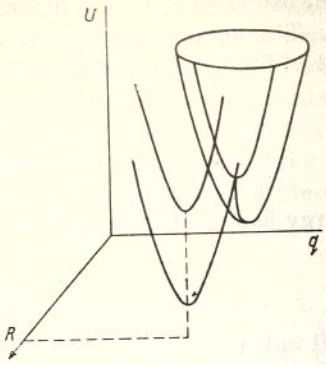

Fig. 2

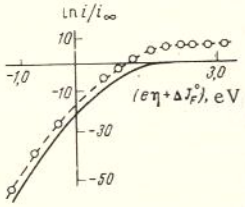

Fig. 3

Here it is possible to obtain an expression for the activation energy [9] from Eq. (9) by formal substitution of E_s by E_{tot}. In order to calculate E_r it is necessary to make use of spectroscopic data on the intramolecular vibrational frequencies and on the structure of the molecules.

The examples of reactions given above are relatively simple. In the more general case part of the degrees of freedom can change during the reaction from quantum to classical degrees of freedom and vice versa. As an example, we will examine the reaction in which, as a result of the formation of a chemical bond, a quantum degree of freedom appears and a classical degree of freedom disappears. Such a situation, let us say, can arise when a particle which is vibrating in a solution with "classical" frequency of $\omega < kT/\hbar$ passes into the adsorbed state on the electrode and forms with the latter a chemical bond characterized by a "quantum" frequency of $\omega > kT/\hbar$. Since the potential energy surface should be regarded as a function of the coordinates of only the classical subsystem, in the process under examination the surfaces of the initial and final states have different numbers of measurements. Such surfaces are shown diagramatically in Fig. 2, where R is the coordinate of the particle which was initially in the solution and during the reaction forms a chemical bond, and q denotes one of the generalized coordinates describing the state of the solvent. In this case, as shown by calculation [11], the activation energy takes the following form:

$$E_a^{0,0} = (E_s + \Delta J^0 - E_r)^2/(4E_s) + E_r, \tag{11}$$

where E_r is the energy of reorganization corresponding to the "disappearing" classical degree of freedom. It should be noted that the activation energy $E_a^{0,0}$, determined by Eq. (11), does not become equal to zero at any ΔJ^0 value. Thus, in the general case, the minimum activation energy of the process $E_{a\,min}^{0,0}$ differs from zero.

We will now pass on to calculation of the current. By substituting Eq. (7) in Eq. (3), we obtain

$$i = \sum_{mn} i_{mn} = \sum_{mn} ef(c) \int A_{mn} e^{-E^{m,n}(\Delta J^{m,n})/kT} n(\varepsilon)\rho(\varepsilon)\,d\varepsilon. \tag{12}$$

We will examine the expression for the partial current $i^{0,0}$. In calculating the integral in Eq. (12), of considerable importance is competition between the two functions – the exponential function (activation factor) and the Fermi [$n(\varepsilon)$] – since $\rho(\varepsilon)$ is a very smooth function [12]. The activation energy decreases with increase in the energy of the electron, and this leads to an increase in the exponential factor. On the other hand, the population of the highly excited level [$n(\varepsilon)$] is small. This leads to the occurrence of a sharp maximum in the expression under the integral sign in Eq. (12) at a certain ε^* value, and a contribution to the current is made by only a narrow range of electronic levels in the metal. According to Eq. (12), ε^* can be determined from the following condition:

$$kT \cdot \frac{d \ln n(\varepsilon^*)}{d\varepsilon} = \frac{dE_a^{0,0}}{d\varepsilon}\Big|_{\varepsilon=\varepsilon^*} = \frac{dE_a^{0,0}}{d\Delta J_F^0}\Big|_{\varepsilon=\varepsilon^*}. \tag{13}$$

The $\alpha^{0,0}$ value, determined by the relationship

$$\alpha^{0,0}(\varepsilon, \eta) = dE_a^{0,0}/d\varepsilon, \tag{14}$$

can be regarded as a "partial" microscopic transfer coefficient, and Eq. (14) itself can be regarded as a microscopic Bronsted equation for electrode processes. As the calculation shows, the dependence of the macroscopic current $i^{0,0}$ on the overpotential is characterized by the value

$$\alpha^{0,0}(\varepsilon^*) \equiv \alpha^{0,0*} = \frac{dE_a^{0,0}}{d\varepsilon}\Big|_{\varepsilon=\varepsilon^*} = \frac{dE_a^{0,0}}{de\eta}\Big|_{\varepsilon=\varepsilon^*}. \tag{15}$$

This last equation serves as a generalization of the normal Bronsted equation for electrochemical processes. From Eqs. (13) and (15) it follows that if $n(\varepsilon)$ is the Fermi distribution function, $n(\varepsilon^*) = 1 - \alpha^{0,0*}$. Since n varies between 0 and 1, the corresponding values of $\alpha^{0,0*}$ lie between 0 and 1. The various energy states of the electrons make a contribution to the total current, depending on the value of the overpotential η. With low overpotentials,

$$e\eta < \Delta J_F^0 + E_s - E_{a\,\min}^{0,0}, \tag{16}$$

it is found that $\varepsilon^* > \varepsilon_F$, $n^* \leq 1$, and $\alpha^{0,0*} \simeq 1$. Here the effective activation energy has the following form:

$$E_a^{0,0} = \Delta J_F^0 - e\eta + E_{\min}^{rev}, \tag{17}$$

where E_{min}^{rev} is the minimum activation energy for the reverse process. We will call this region of overpotentials the barrierless region. This name is to some extent arbitrary since, (as seen from Fig. 2) although the transfer coefficient $\alpha^{0,0*}$ in this region is equal to unity, generally speaking nevertheless the system has to overcome an additional activation barrier. In the region of overpotentials where

$$|\Delta J_F^0 - E_{a,\min}^{0,0} - e\eta| < E_s, \tag{18}$$

it is found that $\varepsilon^* \simeq \varepsilon_F$ and $\alpha^{0,0*}$ varies smoothly from 1 to 0. We will call this region of overpotentials the normal region. At high overpotentials where

$$e\eta > \Delta J_F^0 - E_{a,\min}^{0,0} - E_s, \tag{19}$$

$\varepsilon^* < \varepsilon_F$, $n^* \simeq 1$, and $\alpha^{0,0*} \approx 0$, while the activation energy does not depend on the overpotential and coincides with the lowest possible value. The corresponding region of overpotentials can be called arbitrarily the activationless region. The existence of a minimum activation energy differing from zero for reactions during which one or several new quantum degrees of freedom are formed is of fundamental significance, since at $E_{a,\min} = 0$ the activationless current can be greater than the limiting diffusion current, as a result of which the activationless region will not be observed experimentally.

We notice that the dependence of the current on overpotential in the barrierless and activationless regions is universal. In the normal region the dependence of the current on overpotential differs for different processes and depends on the specific form of the relationship between the activation energy and ΔJ^0. As an illustration, Fig. 3 shows the polarization curve for discharge of hydrogen ions, calculated by means of an electronic computer for a wide range of overpotentials without allowance for excited states of the proton.

The contribution from transitions involving excited states of the quantum subsystem to the total current i depends on the magnitude of the activation energies $E^{m,n}$ and the preexponential factors $A^{m,n}$. The activation energy of a process in which a quantum subsystem changes from an excited initial m-th state to an excited final n-th state in practice only differs from the activation energy $E_a^{0,0}$ in the replacement of ΔJ^0 by $\Delta J^{m,n}$.

The preexponential factors $A^{m,n}$ are proportional to the transmission coefficients $\varkappa^{m,n}$, which determine the probability of transition of the system from the initial state when the system passes through the saddle point at the intersection of the potential energy surfaces of the initial and final states. The values of the transmission coefficients depend substantially on the overlapping of the wave functions of the quantum subsystem.

In Fig. 3 the polarization curve calculated with allowance for the excited states of the proton during the hydrogen-ion discharge process is shown by the dotted line. As seen from the figure, the contribution from the excited states is only appreciable in the barrierless and activationless regions. Analysis shows that the role of excited states of the quantum subsystem is usually not very substantial in electrode reactions. On the other hand, in homogeneous reactions with charge transfer, where there is no continuous electronic spectrum, the existence of excited states in the quantum subsystem is very important and substantially determines the behavior of the activation energy in the barrierless and activationless regions.

The ideas set out above for the mechanism of electrode reactions differ substantially from the considerations of electrode processes based on the theory of absolute reaction rates. The reason for this difference has already been indicated above when seeking the activation energy of the reactions. Moreover, unlike the theory of absolute reaction rates where the transmission coefficient $\varkappa$ is a fairly indefinite quantity, in the theory set out in the present work the transmission coefficient has a precise physical meaning and can be calculated if the wave functions of the quantum subsystem are known. This is of great importance for comparison of theory with experiment and for selection of the right mechanism for the process.

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