# Theory of Ion-Transfer Processes at Electrodes and Solution*

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An extensive review is given of the author's theory of ion-transfer processes at electrodes and in solution. The exposition concerns only those features which are independent of any assumptions about the mechanism of the particular process. The theory allows extension to many specific cases by adoption of simple models.

My lecture will concern some general aspects of the theory of ion-transfer processes in solution including various important homogeneous and heterogeneous reactions such as acid-base catalysis, hydrogen evolution and dissolution at electrodes, electrodeposition and dissolution of metals, anodic oxidation of metals *etc.* I like to review briefly some earlier[1-6] and more recent[7-10] results of my work in this field.

An ion-transfer reaction can be written as

$$AX^+ + B = A + X^+B$$
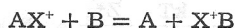
where X^+ is the ion, A and B are atoms or atomic groups, in particular A may be the solvation shell of the ion and B a metal electrode. In this way, taking into account the interactions of the ion with the medium we can express the potential energy $V(x_1, x_2, \ldots x_i \ldots)$ of the entire system as a function of all nuclear coordinates $(x_1, x_2, \ldots x_i \ldots)$ describing the motions of both reacting particles and solvent molecules. A strict adiabatic approximation, *i. e.* a complete separation of motions of nuclei and electrons is not absolutely necessary for this description[7]. In general, the potential function can be represented as a surface in a many-dimensional space. For the case of two dimensions the projection of this surface, $V(x_1, x_2)$, on the plane x_1, x_2 is represented by drawing several lines of constant energy[9-11]. The reaction is described in a familiar way[11] by the translational motion of a representative mass-point from an initial region (R) to a final region (P), corresponding to configurations of reactants and products, respectively.

From the view point of classical mechanics the most probable reaction path is usually that along the line of lowest energy**, the so called »reaction coordinate« which normaly passes through a »saddle-point« S determining the »transition state« of the system. This state is not required to be considered

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** A deviation from that line may be caused by centrifugal effects[13].

in the usual sense as a relatively stable »activated complex«[11]. The reaction coordinate is in general curvilinear, although, in some cases it may be represented by a straight line to a good approximation. The energy profile along that line has a maximum just at the saddle-point (Fig. 1). According to quantum
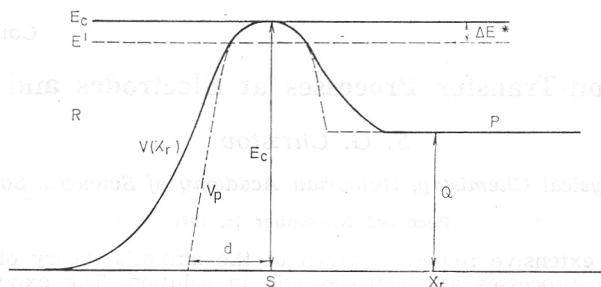

Fig. 1. $V(x_r)$ — Energy profile along the reaction coordinate x_r; E_c — classical activation energy; Q — heat of reaction at T = 0; $E' = E_c - \Delta E^*$ (see Eq. 2a); V_p — parabolic barrier approximation in the energy range $E > E'$; d — half-width of the parabolic barrier V_p; R — reactants region; P — products region.

mechanics transitions by »tunneling« in the energy range below the saddle-point are possible which leads to a departure of the most probable path from the classical reaction coordinate, when it represents the common case of curve line.

On the basis of a general quantum-statistical treatment[10] the rate constant of any reaction can be expressed without restrictions by equation

$$V = \varkappa \chi \; \frac{kT}{h} \; \frac{Z^*}{Z_1 Z_2} \; e^{-E_c/kT}$$

$$\varkappa = \chi^{-1} \int_{-E_c}^{\infty} \Sigma \Sigma \varkappa_{n\,n}{}'(\varepsilon) \; \frac{g_n \, e^{-E_n/kT}}{Z^*} \; e^{-\varepsilon/kT} \frac{d\varepsilon}{kT} \qquad Z^* = \Sigma_n g_n \, e^{-E_n/kT} \tag{1}$$

Here E_c is the »classical« activation energy, i. e. the height of he saddle-point referred to the minimum potential energy of reactant (Fig. 1); Z_1 and Z_2 are the full partition functions of reactants; Z^* is a sum over all quantum states of reactants excluding the motion along the reaction coordinate, E_n and g_n being the energy and the statistical weight factor for a particular quantum state n, respectively. The factor $\varkappa$ is the »tunneling correction« ($\varkappa \geq 1$) defined as a mean value of the transition probability $\varkappa_{nn}$, from an initial state n to a final state n', summation being over all initial and final states consistent with the total energy conservation and integration is over the translational energy ε along the reaction coordinate measured relative to the saddle-point energy (E_c). The factor χ represents the »transmission coefficient« ($\chi = 1$ for adiabatic reactions and $\chi < 1$ for nonadiabatic reactions).

Eq. (1) is derived[10] without making the usual assumption of the activated complex theory[11] that there exists thermal equilibrium between initial and transition states of the system. This equation contains the classical approximation as a limiting case in which $\varkappa = 1$. The conditions at which this approximation is justified may be determined[2,7] by introducing a characteristic

temperature T_k at which the number of systems passing over the barrier $(E > E_c)$ is just equal to that of the system tunneling through the barrier $(E < E_c)$. Expression[3,6,7,12]

$$T_k = \frac{h}{2\pi^2 k} \sqrt{\frac{f^*}{\mu^*}} = \frac{h\nu^*}{\pi k} \tag{2}$$

for T_k is derived, where f^* is the absolute value of curvature of the barrier profile along the reaction path just at the saddle point, μ^* is the effective mass of the system and ν^* is the frequency of a harmonic vibration with a force constant f^*. The magnitude[6,10]

$$\Delta E^* = k T_k = \frac{h\nu^*}{\pi} \tag{2a}$$

represents a characteristic energy for the system in consideration. At temperatures higher than about $T_k/2$ most of the systems pass through and over the barrier in the energy range

$$E > E' = E_c - \Delta E^*$$

in which the barrier profile along the reaction coordinate may be well approximated by a parabolic function (Fig. 1)

Then expression[6,7,9,10,12]

$$\varkappa = \frac{(\pi/2)(T_k/T)}{\sin[(\pi/2)(T_k/T)]} \tag{3}$$

represents a good approximation for the tunneling correction if $T > (2/3)T_k$ as shown using both one-dimensional[2,6,11] and two-dimensional barrier models[9,10]. In the region of moderate tunneling (i. e. $T > T_k/2$) we obtain from this formula $\varkappa$-values between 1 and 7; especially we have $\varkappa = 1.57$ for $T = T_k$, and $\varkappa = 1.1$ for $T = 2 T_k$. In the region of large tunneling ($T < T_k/2$) $\varkappa$ may be much greater than unity[6].

Recent calculations[9] with two-dimensional barrier models indicate that reactions of the type $AX^+ + B = A + X^+B$ occur at the ordinary temperatures above or only somewhat below $T_k/2$ if X^+ is a proton and A and B are heavy atoms or atomic groups as is always the case of proton-transfer processes in solution. These calculations also show that the usual one-dimensional treatment of the classical reaction path gives only somewhat higher values for the tunneling factor $\varkappa$ than does the two-dimensional treatment. The $\varkappa$-values are of the order of several units. These results justify the use of one-dimensional barrier models[1-8,14,15] for approximate estimates of the tunneling corrections. Taking into account the interactions between reacting particles and solvent molecules leads to an effective potential to be added in order to obtain the total potential energy of the system. On the other hand, an increase of the effective mass of the system is to be expected because the free motion of the reacting complex $A - H^+ - B$ is strongly restricted in solution. Therefore, it is likely that proton-transfer processes in solution normally occur in the region of moderate tunneling. As far as transitions of other ions are concerned some minor role of tunneling at ordinary temperatures is possible only for light metal ions such as Li^+ and Be^{++}. Far below room

temperature, however, tunneling may play a significant role in all ion-transfer processes.

There are several ways to discover the role of tunneling by experiment. The first one is to investigate the temperature dependence of reaction rate at low temperatures. From the basic rate Eq. (1) we obtain the expressions[7]

$$E_a' = E_a - k \frac{\delta \ln K}{\delta (1/T)} - k \frac{\delta \ln \varkappa}{\delta (1/T)} \tag{4a}$$

$$K' = \varkappa \cdot K \cdot e^{(E_a' - E_a)/kT} \tag{4b}$$

for the experimental activation energy E_a' and frequency factor K' defined by

$$E_a' \equiv - k \frac{\delta \ln v}{\delta (1/T)} \qquad\qquad K' \equiv v\,e^{E_a'/kT}$$

in order to represent the reaction rate constant in the form of Arrhenius equation:

$$v = K' \cdot e^{-E_a/kT}$$

In Eq. (4) E_a' is the barrier height including zero-point energies and K is the corresponding factor in the rate equation

$$v = \varkappa \cdot K \cdot e^{-E_a'/kT} \tag{5}$$

obtained from the basic expression (1). In the region of moderate tunneling ($T > T_k/2$), using Eqs. (3) and (4a, b) we get[5,14]

$$E_a' = E_a - kT\,(1 - \pi u/2 \cot \pi u/2) \tag{6a}$$

$$K' = K\varkappa \exp\left[-(1 - \pi u/2 \cot \pi u/2)\right] \tag{6b}$$

where $u = T_k/T$, if the slight temperature dependence of K is neglected. These expressions predict deviations from the empirical Arrhenius law which have been really observed in several proton-transfer processes in solution[14,15] thereby giving evidence for a significant role of the tunnel effect.

However, a more sensitive indication on tunneling is given by the isotopic separation factor for which an expression of the form[7]

$$S \equiv \frac{v_H}{v_D} = \frac{\varkappa_H\,K_H}{\varkappa_D\,K_D}\,e - (E_H - E_D)/kT \tag{6}$$

is obtained, say, for H/D separation, where K_H/K_D is near to unity.

Assuming that proton-transfer processes occur in the region of moderate tunneling we can estimate the tunneling corrections[3-5] using Eqs. (5) and (6) on the basis of experimental data for the kinetic parameters E_a', K' and S. Thus the characteristic temperature T_k can be calculated by means of Eqs. (3) without knowledge of the potential-energy surface. Inversely, we may estimate the dimensions of an effective one-dimensional barrier, which is equivalent to the real many-dimensional barrier. Such calculations have been made independently for several catalytic acid-base reactions[14,15] and for the electrolytic hydrogen evolution[3,5]. In this way, as expected, values for $\varkappa$ between 1 and 7 have been found thereby confirming the rule of a moderate role of tunneling in proton-transfer processes in solution.

However, it is not excluded that certain reactions of this type may proceed near or somewhat below $T_k/2$ *i. e.* they fall already in the temperature region of large tunneling. Then, the tunneling factor $\varkappa$ will depend, in general, on the heat of reaction Q as shown by analytical calculations[1,2,5,6] for simple one-dimensional barrier models. Thus, for example, in the simplest case of an asymmetrical parabolic barrier (Fig. 1) one obtains[2]:

$$\varkappa = \frac{\pi u/2}{\sin(\pi u/2)} - \frac{u/2}{1 - (u/2)} \, e^{(u-2)\,\delta_0\,(E_c - Q)}, \qquad (u < 2), \qquad (7a)$$

$$\varkappa = 2\,\delta_0\,(E_c - Q)\,[1 + 1/2\,e^{(u-2)\,\delta_0\,(E_c - Q)} - \ldots], \quad (u \simeq 2), \qquad (7b)$$

$$\varkappa = \frac{u/2}{(u/2) - 1}\, e^{(u-2)\,\delta_0\,(E_c - Q)}, \qquad (u > 4) \qquad (7c)$$

where $u = T_k/T$ and $\delta_0 = \pi^2 d \sqrt{2\,\mu\,E_0}/h\,E_0$; here 2 d is the width of the barrier and E_0 its height when Q = 0 (symmetric barrier).

In electrode reactions we have $Q = \varepsilon\,(\varphi - \varphi_0)$ and $E_c - Q = E_0 - \alpha\varepsilon\,(\varphi - \varphi_0)$ where φ is the electrode potential (φ_0 corresponds to Q = 0) and ε is the ion charge ($\alpha < 1$). Hence, the tunneling factor $\varkappa$ will generally decrease with the increase of φ[2,7]. If $T > (2/3)\,T_k$, ($u < 3/2$), the second term in (7a) may be neglected so that Eq. (3) is obtained which is now independent on Q (φ). It results, that the electrolytic separation factor according to Eq. (6) should decrease with the increase of electrode potential when $T < (2/3)\,T_k$ ($u > 3/2$) and it remains constant when $T > (2/3)\,T_k$ ($u < 3/2$). These predictions seem to be the unique explanation of the experimentally observed strong potential dependence of the H/T separation factor in acid solutions[16] and its potential independence in basic solutions[17]. In the first case because of the attraction of the H_3O^+-ion by the cathode the transfer distance of the proton is certainly smaller than in the second case when a proton from the neutral H_2O-molecule is discharged[17]. Hence, the effective barrier width for the proton transfer in acid solutions will be smaller than in basic solutions, so that it is likely that if in the first case the reaction occurs at $T \approx T_k/2$ ($u \simeq 2$) it may proceed in the second case in the region $T > (2/3)\,T_k$ ($u < 3/2$)*.

An other important conclusion[7] concerns the relation between experimental activation energy E_a' and reaction heat Q (or electrode potential φ in electrode kinetics). According to Polanyi there is a linear dependence

$$E_a' = E_0' + \beta'\,Q, \qquad E_a' - Q = E_0' - \alpha'\,Q \qquad (8)$$

between these quantities for both directions (endothermic and exothermic) of reaction, α' and β' being the corresponding »transfer coefficients«. However, from theoretical point of view these magnitudes are, in general, not constant and moreover, the each of them is different and depends on reaction heat in a different manner by quantum-mechanical and classical treatment of reactions.

From Eq. (4a) we obtain

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* The possibility of large tunneling ($T \ll T_k/2$) is to be excluded because it leads to abnormal high Tafel slopes (see below). Thus, the potential dependence of $\varkappa$ according to Eqs. (7a, b) is consistent with the classical (practically constant) Tafel slopes in the corresponding region $T \geq T_k/2$.

$$\beta' = \beta + kT^2 \frac{\delta^2 \ln \varkappa}{\delta T \, \delta Q}$$

$$\alpha' = \alpha - kT^2 \frac{\delta^2 \ln \varkappa}{\delta T \, \delta Q}$$

(8')

where

$$\beta' \equiv \frac{\delta E_a{}'}{\delta Q}, \qquad \alpha' \equiv -\frac{\delta (E_a{}' - Q)}{\delta Q}$$

$$\beta \equiv \frac{\delta E_a}{\delta Q}, \qquad \alpha \equiv -\frac{\delta (E_a - Q)}{\delta Q}$$

so that $\alpha' + \beta' = 1$ and $\alpha + \beta = 1$.

Evidently, α and β are the »classical« transfer coefficients. In the region of moderate tunneling $(T > T_k/2)$, where the tunneling correction is almost independent on reaction heat, β' and β (α' and α) practically are equal, however in the region of large tunneling $(T < T_k/2)$ they may differ largely[7] (see below). This difference could be detectable also when the temperature is somewhat above $T_k/2$.

It is important to stress that both β' and β (α' and α) are, in general, different from the coefficient $\bar{\beta}$ and $\bar{\alpha}$ in the Brönstedt relations

$$v_1 = C_1 K_{AH}^{\bar{\beta}}, \qquad v_2 = C_2 K_{BH}^{\bar{\alpha}}$$

(9)

where v_1 and v_2 are the rate constants for both (endothermic and exothermic) directions of an acid-base proton-transfer reaction; K_{AH} and K_{BH} are the electrolytic dissociation constants of the acid (AH) and base (BH), respectively. These equations can be derived from Eqs. (5) and (8) using the expression for the equilibrium constant

$$K_c = K_{AH}/K_{BH} = C \, e^{-Q/kT}$$

In this way we find that $\bar{\beta} = \beta' = \beta$ when the reaction occurs in the region of the moderate tunneling just at conditions that $\varkappa$ is independent on Q, i. e. Eq. (3) is valid $(T > (2/3) T_k)$. The difference between $\bar{\beta}$, β' and β when $T \simeq T_k/2$ or $T < T_k/2$ can be demonstrated by one-dimensional calculations[7]. Thus using the simple asymmetrical parabolic barrier, for which expressions (7) for $\varkappa$ apply, we find for $u \simeq 2$ $(T \simeq T_k/2)$

$$E_a{}' = 1/2 \, (E_a + Q), \qquad E_a = E_0 + \frac{Q}{2} \left(1 + \frac{Q}{8 E_0} \right)$$

and

$$\beta' = 1/2 \, (\beta + 1), \qquad \bar{\beta} \simeq \beta = 1/2 \left(1 + \frac{Q}{4 E_0} \right)$$

(10)

If $Q/4 E_0 \ll 1$, we have $\bar{\beta} \simeq \beta = {}^1\!/_2$ and $\beta' = {}^3\!/_4$. For $u > 4$ $(T < T_k/4)$ one obtains

$$E_a{}' = Q, \qquad E_a = E_0 + \frac{Q}{2} \left(1 + \frac{Q}{8 E_0} \right)$$

and

$$\beta' = 1, \qquad \beta = 1/2 \left(1 + \frac{Q}{4 E_0} \right), \qquad \bar{\beta} = 1 - \frac{T}{T_k} \left(1 - \frac{Q}{8 E_0} \right)$$

(11)

If $Q/4 E_0 \ll 1$, one gets $\beta = 1/2$ and $\bar{\beta} \geq 3/4$ $(T/T_k \leq 1/4)$. Similar results are obtained using more general (one-dimensional) models for the potential barrier[7].

The quantum-mechanical transfer coefficients α' and β' can be determined experimentally on the basis of Eqs. (8) independently from the Brönstedt coefficients $\bar{\alpha}$ and $\bar{\beta}$ in Eq. (9). Therefore, a comparison between β' and $\bar{\beta}$ (α' and $\bar{\alpha}$) could serve, in principle, as a criterion for determination of the role of tunneling in chemical and electrochemical reactions, a possible difference between them indicating a rather large tunneling degree. As far as to my knowledge no experimental data are available for that purpose in literature, it will be certainly of great interest to do investigation in this direction.

The transfer coefficients β, β' and $\bar{\beta}$ are, in general, not constant but depend on reaction heat as seen from Eqs. (10) and (11) for the asymmetrical parabolic barrier. For a more general barrier shape the following expressions for the classical transfer coefficients have been derived[2c]

$$\beta = \frac{1}{2}\left(1 + \frac{\gamma^2 Q}{4 E_0}\right), \quad \alpha = \frac{1}{2}\left(1 - \frac{\gamma^2 Q}{4 E_0}\right), \tag{12}$$

where γ is a factor of the order of unity which depends on the barrier shape (for a parabolic barrirer $\gamma = 1$). In general, γ is also a slowly varying function of Q which remains practically constant when the change of Q is not too large. The variations of β (α) between 0 and 1 as predicted by these relations have been really observed in many protolytic reactions in solution[14,18] which probably occur in the region of moderate tunneling where $\beta' \simeq \beta \simeq \bar{\beta}$. However, a possibly detectable difference between β' and β indicating some more tunneling should be also taken into account when interpreting these experimental results.

These general conclusions can be immediately applied to all electrode processes in which the discharge is the rate determining step. We have to express only the reaction heat Q in terms of the electrode potential $\varphi : Q = \varepsilon (\varphi - \varphi_0)$, or the overvoltage $\eta = \varphi - \varphi_r : Q = Q_r + \varepsilon\eta$, where φ_r and Q_r are the reversible potential and the corresponding reaction heat. The current density is determined by the difference of reaction velocities in two opposite directions (discharge and ionization)

$$i = \varepsilon (\overrightarrow{v} - \overleftarrow{v});$$

for each of them Eq. (1) or (5) is to be applied by replacing E_c by

$$E_c = E_r + \lambda\beta\varepsilon\eta \quad \text{and} \quad E_c - Q = (E_r - Q_r) - \lambda\alpha\varepsilon\eta,$$

respectively, where E_r is the classical activation energy at the reversible potential and λ is the fraction of the total potential drop across the double layer corresponding to the ion-transfer distance r ($\lambda = r/R$, C, (R is the double layer thickness). In this way we can derive a current potential relationship of the general form[1,2].

$$i = A (\varphi, T) (e^{\alpha^* \varepsilon\eta/kT} - e^{-(1-\alpha^*) \varepsilon\eta/kT}),$$

$$A (\varphi, T) = \varkappa (\varphi, T) K e^{-E_r/kT} e^{(\alpha^* - \alpha_r^*) \varepsilon \varphi_r/kT} \tag{13}$$

where $\alpha^* = \lambda\alpha$. It is seen that the preexponential $A(\varphi, T)$ is, in general, potential dependent through the tunneling factor $\varkappa(\varphi, T)$ and through the classical transfer coefficient $\alpha^* = \lambda\alpha(\varphi)$ ($\alpha_r^* = \lambda\alpha_r$ refers to the reversible potential). In the case of ion discharge and dissolution α^* is conveniently expressed by the relation[2]

$$\alpha^* = \alpha_r^* \frac{\varkappa^2 \gamma^2 \varepsilon \eta}{8 E_r} \tag{14}$$

On the basis of Eqs. (13) and (14) the conditions of validity of the Tafel equation

$$\eta = a + b \lg i$$

can be determined both from standpoint of quantum and classical mechanics. An expression of this form is obtained from Eq. (13) when $\varepsilon\eta/kT \gg 1$, however, a and b will be constant only if $\varkappa$ and α are practically independent on electrode potential φ (or overvoltage η). This will be certainly in the region of moderate tunneling where Eq. (3) for $\varkappa$ applies if the second term in Eq. (14) is so small that $\alpha^* \simeq \alpha_r^*$ ($\alpha \simeq \alpha_r$). Then the Tafel slope $b = d\eta/d\lg i$ is given by the classical expression

$$b_{cl} = \frac{kT}{2.3\, \alpha_r^* \varepsilon}$$

In general $b > b_{cl}$. Using one-dimensional barrier models it has been shown[5] that the ratio $(b/b_{cl})_{\eta \to 0}$ is an increasing function of the dimensionless quantity T_k/T (which is a measure for the tunneling degree):

$$b/b_{cl} = f(T_k/T) \tag{15}$$

For $T_k/T \ll 1$ we have $f(T_k/T) = 1$. The form of function $f(T_k/T)$ depends on the barrier shape, however, practically

$$b/b_{cl} = f(T_k/T) > 1 \quad \text{for} \quad T < T_k/2$$
$$b/b_{cl} = 1 \quad \text{for} \quad T > T_k/2 \tag{15a}$$

For the simplest case of an asymmetrical parabolic barrier using Eqs. (7abc) we find the simple formula[5]

$$b/b_{cl} = 1/2\,(T_k/T) \quad \text{for} \quad T < T_k/2$$
$$b/b_{cl} = 1 \quad \text{for} \quad T > T_k/2$$

It seems that proton-discharge processes at metals and semiconductors usually occur in the region of moderate tunneling. Thus, the tunneling factor for hydrogen evolution on mercury is estimated[5] to be about $\varkappa = 3.3$, hence the Tafel slope should have its classical value ($b = b_{cl}$)*. Moreover, it follows from Eq. (14) that b will be constant over a potential range of 1—2 volts, because owing to the large activation energy ($E_r = 21.7$ kcal/mol) the potential dependent term is very small so that $\alpha^* = \alpha_r^* \pm 0.02$. These conclusions excellently agree with the well known experimental facts[19].

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* It has been shown[2,5], however, that in some cases depending on the barrier shape relation $b/b_{cl} \simeq 1$ may be valid also in the region of large tunneling ($\varkappa \simeq 300$!).

In the case of electrodeposition and dissolution of metals at ordinary temperatures the tunneling factor is certainly near unity. However, because of the small values of the activation energies ($E_r = 5$—10 kcal) the classical Tafel slopes

$$b_{cl} = \frac{kT}{2.3 \, \alpha^* \, \varepsilon}$$

according to Eq. (14) are expected to be potential dependent. This is really observed[20] on silver where the ion discharge is found to be the rate determining step. We note that if the surface diffusion of adsorbed atoms is the limiting step, then in Eq. (14) for the transfer coefficient, λ is to be replaced by $1 - \lambda$ which is the corresponding fraction of the total potential difference between a kink site and the solution[21].

Anodic oxidation of the metals is another important case to be indicated especially as an example of electrochemistry of nonmetallic surfaces. The growth of homogeneous oxide layers on Al, Ta, Nb, Zr etc. is usually interpreted as a process of ion transitions over a potential barrier located either in the interior of the oxide or at the metal-oxide interface. The current flow is determined by the electric field in the oxide and can be expressed by equation of the form

$$i = A \, e^{-E_a (\xi)/kT} \tag{16}$$

where the activation energy E_a is usually taken to be a linear function

$$E_a = E_0 - a \, \varepsilon \, \xi \tag{17}$$

of the field strength ξ, E_0 being the activation energy at zero field ($\xi = 0$) and a is the activation distance (i. e. the distance from the point of minimum potential anergy to the position of barrier maximum). Eqs. (16) and (17) lead to an expression of Tafel type (Tafel-Frenkel equation) however, deviations from it have been observed on Ta, Nb and Al by several authors[22, 23].

The general theory of ion-transfer processes can be easily adapted to anodic oxidation of metals in order to explain the field dependence of Tafel slopes in this case[8]. Assuming again the tunneling factor to be $\varkappa = 1$, an expression for the activation energy

$$E_a (\xi) = E_a - a_0 \, \varepsilon \, \xi + \frac{\gamma_0^2 \, a_0^2 \, \varepsilon^2}{4 \, E_0} \, \xi^2 \tag{18}$$

has been derived[8] where a_0 is the activation distance at $\xi = 0$ and γ_0 is a factor of order of unity depending on the barrier shape (for a parabolic barrier $\gamma_0 = 1$). This factor is identical with γ in Eqs. (12) and (14) for $\xi = 0$.

Expressions (16) and (18) describe very well the experimentally observed current-field dependence on different film-forming metals[22,23]. Using these equations we can estimate on the basis of experimental data the barrier parameters E_0, a_0 and γ_0 for which reasonable values have been obtained[23, 24], especially the activation distance a_0 thus calculated is consistent with the lattice constant of the oxide.

We have reviewed some general results of the theory of ion-transfer processes which are independent on any special assumption about the particular mechanism of the process. In order to reveal the specific features of various types of electrochemical reactions, of course, more detailed considerations are needed. They concern the nature and location of the potential energy barriers, the role of the non-equilibrium solvent reorganization, the changes of electronic state during reaction and calculation of the transmission coefficients, the extent of electron localization in adsorption states of metal ions and protons *etc.* In many cases simplified models may be usefull to obtain at least a satisfactory qualitative description of different types of electrochemical reactions[1-10,16,24,25]. In this respect, however, a further extensive work is necessary for a complete understanding of all details of the kinetics of various homogeneous and heterogenous ion-transfer processes.

REFERENCES

1. S. G. Christov, *Ann. Univ. Sofia, Fac. Phys. Math.* **42** (1945—46) 69; *ibid.* **43** (1946—47) 63; *C. R. Acad. Bulgare Sci.* **1** (1948) 43.
2. S. G. Christov, *Z. Elektrochem.* **62** (1958) 567; *ibid.* **64** (1960) 840; *Ber. Bunsenges. Phys. Chem.* **67** (1963) 117.
3. S. G. Christov, *Dokl. Akad. Nauk SSSR* **125** (1959) 141; *ibid.* **136** (1960) 663.
4. S. G. Christov, *Z. Physik. Chem.* (Leipzig) **212** (1959) 40; *ibid.* **214** (1960) 40.
5. S. G. Christov, *Electrochim. Acta* **4** (1961) 194, 306; *ibid.* **9** (1963) 575.
6. S. G. Christov, *Ann. Phys.* **12** (1963) 20; *ibid.* **15** (1965) 87; *Discussions Faraday Soc.* **39** (1965) 60, 254, 263.
7. S. G. Christov, *J. Res. Inst. Catalysis,* Hokkaido Univ. **16** (1968) 169.
8. S. G. Christov and S. Ikonopisov, *J. Electrochem. Soc.* **116** (1969) 56.
9. S. G. Christov and Z. L. Georgiev, *J. Phys. Chem.* **75** (1971) 1748.
10. S. G. Christov, *Ber. Bunsenges.* in print.
11. S. G. Christov, *Phys. Status Solidi* **17** (1966) 11; *ibid.* **21** (1967) 159; *ibid.* **42** (1970) 583; *ibid.* **7** (1971) 371.
12. S. Glasstone, K. J. Laidler, and H. Eyring, *The Theory of Rate Processes,* McGraw-Hill Book Co., Inc. New York, N. Y., 1941.
13. R. A. Marcus, *J. Chem. Phys.* **45** (1966) 4493; *ibid.* **41** (1964) 2614.
14. R. P. Bell, *The Proton in Chemistry,* Cornell University Press, Ithaca, New York, 1959; and *Trans. Faraday Soc.* **55** (1959) 1.
15. E. F. Caldin, *Discussions Faraday Soc.* **39** (1965) 62.
16. J. O'M. Bockris and D. B. Mathews, *Electrochim. Acta* **11** (1966) 143.
17. L. I. Krishtalik, private communication.
18. M. Eigen, *Angew. Chem.* **75** (1963) 489.
19. H. W. Nürnberg, *Discussions Faraday Soc.* **39** (1965) 52.
20. A. R. Despić and J. O'M. Bockris, *J. Chem. Phys.* **32** (1960) 389.
21. N. F. Mott and R. Watts-Tobin, *Electrochim. Acta* **4** (1961) 79.
22. L. Young and F. G. R. Zobel, *J. Electrochem. Soc.* **113** (1966) 277.
23. S. Ikonopisov and L. Andreeva, *Elektrokhimiya* **6** (1970) 1070; I. Nenov and S. Ikonopisov, *C. R. Acad. Bulgare Sci.* **24** (1971) 51.
24. R. A. Marcus, *Ann. Rev. Phys. Chem.* **15** (1964) 155; *Electrochim. Acta* **13** (1968) 995.
25. R. R. Dogonadze and A. M. Kuznetsov, *Elektrokhimiya,* Itochi nauki, Moskva, 1969.

IZVOD

Teorija procesa prijenosa iona na eletrodama i u otopini

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Prikazana je autorova kvantno-statistička teorija prijenosa iona na elektrodama i u otopini. Teorija opisuje osnovne procese, homogenog i heterogenog tipa, kao što su acido-bazna kataliza, razvijanje i otapanje vodika na elektrodama, izlučivanje i otapanje metala, te procesi anodičke oksidacije metala. U radu su prikazani svi opći rezultati teorije ionskog prijenosa, tj. oni koji ne zahtijevaju nikakve posebne pretpostavke o mehanizmu procesa. Sve specifičnosti različitih elektrokemijskih procesa, kao što su lociranje potencijalnih barijera, neravnotežna reorganizacija otapala, promjene u elektronskim stanjima u reakciji i proračun koeficijenata transmisije, lokalizacija elektrona u procesima adsorpcije metalnih iona ili protona, i niz drugih, mogu biti obuhvaćene aproksimacijama ili pojednostavljenim modelima. Ipak, potrebno je još mnogo rada na teoriji da bi postala dovoljno razrađena za razumijevanje kinetike raznih homogenih i heterogenih procesa.

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