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SOME ASPECTS OF THE THEORY OF PROTON-TRANSFER PROCESSES

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Abstract

The paper represents a critical survey of the present situation of several basic problems of the kinetics of proton-transfer processes and includes also some new considerations and elucidations.

First, the difficulties of the complete quantum-mechanical evaluation of the reaction rates on the basis of the transition state theory are discussed. It is emphasized that the familiar methods for the theoretical construction of potential-energy barriers are not reliable and cannot constitute a solid base for quantitative studies of chemical kinetics. The usual one-dimensional approximation is shown to be relevant for the estimation of a lower limit of tunnelling corrections. For this purpose the experimental data related to the kinetic isotope effects can be used under certain conditions.

Second, some important points of the theory of proton-transfer reactions in solution are considered. It is concluded that the non-equilibrium solvation of the proton probably does not play a significant role when the proton transition occurs along a hydrogen bond. A theoretical foundation of the Brönsted relation is proposed which accounts for the possibility of both moderate and large proton tunnelling. The proportionality relationship between activation energy and reaction heat is shown to be not equivalent to the proper Brönsted relation if the tunnelling correction is depending on reaction heat. Some recent results of the quantum theory of proton-transfer processes at electrodes are subjected to critical consideration. The inconsequency of previous studies in which the actual energy-barrier is confused with the apparent barrier related to the experimental activation energy, is stressed.

1. Introduction

The purpose of the present paper is to consider some problems of the kinetics of proton (or hydrogen atom) transfer reactions, which have been subject to discussions in recent time. In the first place these are some basic assumptions of the activated complex theory concerning to the same extent both the processes of proton transfer in gas phase and in solution. We will consider the methods for theoretical construction of potential-energy barriers and those for evaluation of the quantum corrections to reaction rates, related to the kinetic isotope effects too.

For the theory of proton-transfer processes in solution the study of the influence of the solvent on the reaction rate is of great importance. This refers to homogenous reactions, including acid-base catalysis, as well as to heterogeneous proton-transfer processes, such as electrolytic hydrogen evolution at various metals and semiconductors. The role of the solvent for both types of reactions has been often underestimated in current theories and only in recent time its significance has been particularly emphasised. We shall consider some points of this problem, too.

2. General Considerations

A reaction of proton (or hydrogen atom) transfer can be written in the form,

$$\mathrm{AH}+\mathrm{B}=\mathrm{A}+\mathrm{HB}\,, \tag{1}$$

where A and B are atoms or atomic groups (molecules or radicals). Supposing an adiabatic course of the process we can treat separately the movements of nuclei and electrons (principle of Born-Oppenheimer). The potential energy of the system $V(x_1, y_1, z_1, x_2, y_2, z_2, \cdots)$ will then be a function of the coordinates x_i, y_i, z_i of all the nuclei and could be represented as a surface in a multidimensional configuration space. The reaction may be described as a translational movement of a representative point, with an effective mass μ, along the line of the lowest energy (reaction coordinate), passing through the saddle point (transition state) of the potential surface. In the theory of the absolute rate of the processes[1] one usually assumes, that this movement obeys the laws of classical mechanics. A further assumption in this theory is the existence of thermal equilibrium between the initial and transition states. Under the above conditions the usual statistical treatment leads to the familar expression for the reaction rate (or rate constant),

$$v=\frac{kT}{h}\frac{Z^{\ddagger}}{\prod Z_i}e^{-E/kT}\,, \tag{2}$$

where E is the barrier height (classical activation energy), Z_i—the partition functions for the reactants and $Z^{\ddagger}$—the partition function for the activated complex (transition state) in which the factor corresponding to motion along the reaction path is excluded. Both Z_i and $Z^{\ddagger}$ contain a factor accounting for the vibrations in the initial and transition state, respectively. These are usually treated as small harmonic vibrations. The quantum mechanical consideration then gives the expression,

$$v = \frac{kT}{h} \frac{\prod \mathcal{X}_s^{\ddagger}}{\prod \mathcal{X}_i} \frac{Z_c^{\ddagger}}{\prod Z_{c,i}} e^{-E/kT}, \tag{3}$$

where Z_c are the "classical" partition functons, including the vibrational factor $Z_{v,c} = \prod (4kT/h\nu_k)$, and

$$\mathcal{X}_k = \frac{\frac{1}{2}u_k}{\sinh\frac{1}{2}u_k}, \qquad u_k = h\nu_k/kT, \tag{4}$$

is the quantum correction factor for a vibration with a frequency $\nu_k = (1/2\pi) \times \sqrt{f_k/\mu_k}$ (f_k—force constant, μ_k—reduced mass).

The motion of the system along the reaction coordinate near the saddle-point may be described as an instable harmonic vibration with an imaginary frequency $\nu_r^{\ddagger} = i\nu_t^{\ddagger}$. Then, the quantum correction for this motion can be represented as shown by BELL[2] also by expression (4), *i. e.*

$$\mathcal{X}_t = \frac{\frac{1}{2}u_t}{\sin\frac{1}{2}u_t}, \qquad u_t = h\nu_t^{\ddagger}/kT. \tag{5}$$

This correction accounts for the possibility of barrier penetration or tunnelling in the saddle-point region.

Inclusion of the factor $\mathcal{X}_t$ in the product $\prod \mathcal{X}_s^{\ddagger}$, refering to the real vibrations of the activated complex, gives the full expression for the quantum correction of the classical rate constant in Eq. (3). This expression is a generalization of the Wigner[3] correction

$$\prod \mathcal{X}_s^{\ddagger} = 1 - \frac{1}{24} \sum (u_s^{\ddagger})^2, \qquad u_s^{\ddagger} = h\nu_s^{\ddagger}/kT, \tag{5 a}$$

which is only a first approximation. Therefore, Eqs. (3–5) represent an exact quantum mechanical solution of the kinetic problem for the case of harmonic (stable and unstable) vibrations.

Let us consider the basic assumptions under which this general solution is obtained in view of the possibility of its practical application. First of all, the adiabatic principle is strictly valid only if all the nuclei move much more slowly than the electrons. For protons this is surely the case at very small velocities, especially when the proton vibrations occur near the equilibrium positions in the initial and final state. However, during reaction, the system passes through exited states in which the relatively light proton should have a high velocity. That is why, it appears doubtfull, whether the adiabatic assumption is justified enough for proton transfer processes. Fortunately, in principle, it is possible to account for the incomplete separation of the movements of protons and electrons by replacing the electronic energy $V(x_n)$ with an *effective* potential energy $V'(x_n)$ which is also a continuous function of the positions of the nuclei. This was shown by DAUDEL and BRATOZ[4] in supposing weak interaction between the movements of nuclei and electrons. However replacement of $V(x_n)$ by $V'(x_n)$ leads to complications of the problem for theoretical construction of the potential-energy surface, which is the basis for complete evaluation of the rate constant.

There exists also some doubt concerning the legitimacy of the current procedure of evaluation of the partition functions for the activated complex. Because of the very short lifetime $\Delta\tau$ of this complex the uncertainty in the energy determination $\Delta\varepsilon \sim h/\Delta\tau$ becomes comparable with the energy value ε itself, so that according to KASSEL[5] the quantization of the vibrational energy cannot be considered as justified. It has been remarked[6] that this objection is less valid for the zero-point energy, which is a direct consequence of the uncertainty principle. This is inasmuch true as from the relation $\Delta p \Delta x \sim h$ we conclude that the momentum p cannot be equal zero, because the vibrations occur in a restrected space region near the saddle-point ($\Delta p \neq 0$ when $\Delta x \neq \infty$). There results, indeed, the *existence* of some zero-point energy but its value ε_0 remains undeterminable within the range $\Delta\varepsilon \sim h/\Delta\tau$. Therefore, if $\Delta\tau$ is a short time*) so that $\Delta\varepsilon \sim \varepsilon$, the whole vibrational energy spectrum will have an intermediate position between a strong quantized and a continuous one. In this case it seems doubtfull, whether the stationary quantum-mechanical treatment of the real vibrations in the transition state would always give better results than the classical approximation.

This consideration does not concern the translational motion along the reaction path which is not quantized with respect to energy but can be considered quantum-mechanically with respect to the transition probability through the barrier. However, there are other difficulties in calculating tunnel-effect corrections. The motion along the reaction coordinate may be described as an unstable harmonic vibration only in the vicinity of the saddle-point where we can consider the small vibrations in different directions as independent

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*) Calculations for simple activated complex models give frequencies between $9 \cdot 10^{12}$ and $9 \cdot 10^{13}\ \mathrm{sec}^{-1}$, while according to KASSEL[5] the frequency uncertainly is $\Delta\nu = \frac{1}{\Delta\tau} \simeq 2 \cdot 10^{13}$ sec^{-1}, therfore $\Delta\varepsilon/\varepsilon = \Delta\nu/\nu \gtrsim 1$.

from one another. JOHNTSON[7] proposed as criterion for the separability of the reaction coordinate that the region Δ in which the reaction path near the saddle-point may be replaced by a parabola, is much longer than the De-Broglie wave length λ, associated with the motion of the system from the initial to the final state. Under this condition ($\lambda < \Delta$) it is legitimate to treat the motion in the transition region as a tunnelling through an one-dimensional parabolic barrier. This means that the application of BELL's tunnel-effect corrections is justified enough only for moderate tunnelling, occuring entirely in the uppermost part of the reaction path profile.

If the above conditions are not fulfilled, the reaction is to be treated as an n-dimensional tunnelling problem. A general solution of this problem is not given at present time. Under certain conditions an approximate method, proposed by JOHNSTON and RAPP[8] may be applied for calculating the tunnelling correction for the case $n=2$.

3. Construction of the Potential-Energy Barrier

Besides of the difficulties in applying the adiabatic principle to the proton transfer processes, there are no exact mathematical methods for evaluating the electronic energy $V(x_k)$ as a function of the coordinates x_k of all nuclei. In the case of a three-center reaction of type (1) *via* a linear activated complex (A···H···B), one sometimes constructs a two-dimensional barrier $V(x)$ by intersecting two Morse potential curves for the diatomic molecules AH and BH. This approximation is justified when A and B are heavy atoms (or atomic groups), which remain at a fixed distance $r_{AB} = r_{AH} + r_{HB}$ during the proton transfer from A to B, provided that their repulsion is negligible. If A and B are light atoms (atomic groups) a three-dimensional energy-surface $V(r_{AH}, r_{HB})$, determined by two independent distances r_{AH} and r_{HB}, is to be constructed. For this purpose the half-empirical method of EYRING–POLANYI,[1] based on LONDON's theory and the application of Morse curves, is often used. A modification of this method has recently been proposed by SATO.[9] To compare these methods a detailed analysis of the vibrations in the transition state and an account for the tunnel-effect correction $\mathscr{X}_t$ is necessary.

Using the Sato potential and BELL's tunnelling expression (5), for the interaction $H + H_2 \rightarrow H_2 + H$, WESTON[10] obtained strong temperature dependence of $\mathscr{X}_t$, *i. e.* a considerable deviation from Arrhenius law, not observed experimentally. He concluded that the Sato potential gives too thin a barrier profile or, perhaps expression (5) for $\mathscr{X}_t$ over-estimates the tunnelling.

JOHNSTON and RAPP[8] investigated in detail the kinetic isotope effect for the reaction,

$$H_3C + H\text{-}CR \longrightarrow CH_4 + CR\,, \tag{7}$$

considering the unreacting groups as mass points. A similar investigation for the reaction

$$F_3C + H\text{-}CD_3 \longrightarrow F_3C\text{-}H + CD_3 \tag{8}$$

was carried out by SHARP and JOHNSTON.[11a)] In both works the Sato method was used for constructing the potential energy surface for the linear triatomic group C–H–C. The tunnelling correction was calculated by applying an approximate two-dimensional method (see Sec. 4). In this way a good agreement between the calculated and the experimental values of the isotopic ratio v_H/v_D of rate constants has been found. For the case of reaction (8), a comparison between the methods of SATO and EYRING–POLANYI has been made by JOHNSTON *et al.*,[11b)] who believe that the advantage of the Sato method as well as the necessity of a considerable tunnelling correction is evident from their calculations.

It seems, that the success in such calculations is due to a great extent to compensating the inaccuracy of LONDON's potential expression by a favorable choice of variable parameters in both half-empirical methods.*) The above discussed conceptual difficulties in the quantum-mechanical treatment of the activated complex vibrations must also be taken into account in estimating the results of these calculations.

The evaluation of the electronic energy for more complicated, manyatomic interactions is impossible without very rough approximations, especially for reactions in solution, where the solvation effects also play a very important role.

We conclude, that the available theoretical methods for constructing potential barriers are rather imperfect to serve as a basis for quantitative studies of the kinetics of proton transfer reactions.

4. Estimation of the Tunnelling Correction

An exact solution of the tunnelling problem is as yet possible only in one-dimensional approximation. The BELL's correction factor for a symmetrical parabolic barrier has been first generalised for the unsymmetrical one.[12)] Recently[13)] a solution was found for a rather general barrier type (generalised Eckart potential) which can be represented by the expression,[14)]

$$V(x) = B\left(\frac{e^{2ax/l}}{(1+e^{2ax/l})^2} - C\right) + \mu A\left(\frac{e^{2ax/l}}{1+e^{2ax/l}} - D\right) \tag{9}$$

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*) The ratio of coulombic to total bond-energy in the method of EYRING–POLANYI and the overlapping integral in the Sato method are such adjustable parameters.

$$C=\frac{e^{2a}}{(1+e^{2a})^2}\,,\quad \mu=\frac{(e^{a}+e^{-a})^2}{e^{2a}-e^{-2a}}\,,\quad D=\frac{1}{1+e^{2a}}\,,\quad B=4E_s\left(\frac{e^{2a}+1}{e^{2a}-1}\right)^2,$$

where A and E_s are constants, and the parameter a varies from 0 to ∞. In the special case $a=\pi(C\simeq 0, D\simeq 0, \mu\simeq 1)$ this expression practically coincides with the Eckart potential[15] and in the limiting case $a=0(B=\infty)$ it represents an asymmetrical parabolic barrier. The maximum value of function (9) (the barrier height) is given by

$$E=E_s+bA\,,\qquad b=\frac{1}{2}+\frac{A}{16E_s}\,, \tag{10}$$

where E_s is the barrier height for $A=0$ (symmetric barrier).

The tunnelling correction factor for the asymmetrical parabolic barrier $(a=0, A\neq 0)$ is represented by the expression,[12]

$$\mathscr{X}_t=\frac{\pi\gamma/\delta}{\sin(\pi\gamma/\delta)}-\frac{\gamma/\delta}{1-(\gamma/\delta)}e^{-(\delta-\gamma)\omega}\,, \tag{11}$$

$$\gamma=E_s/kT\,,\qquad \delta=2\pi^2 l\sqrt{2\mu E_s}\,,\qquad \omega=(E-A)/E_s\,,$$

where $2l$ is the barrier width and μ the mass transferred. This formula is valid under the condition $\delta>\gamma$ (moderate tunnelling).

If $(\delta-\gamma)\omega>2$ the second term in Eq. (11) may be neglected. Then Eq. (11) turns to Eq. (5), having in view that $\pi\gamma/\delta=u_t/2$. In this case it can also be written as

$$\mathscr{X}_t=\frac{(\pi/2)(T_k/T)}{\sin[(\pi/2)(T_k/T)]}\,, \tag{12}$$

where

$$T_k=\frac{h\sqrt{L_m}}{\pi^2 k\sqrt{2\mu}}=\frac{2E_s}{k\delta}\,,\qquad L_m=-\left(\frac{\partial^2 V}{\partial x^2}\right)_{x=x_m} \tag{13}$$

is a characteristic temperature,[16,14] determined by the barrier curvature $L_m=2E_s/l^2$.

It can be shown[16] that at the temperature $T=T_k$ just the half of the incident particles (systems) tunnel through the barrier while the other half pass over it.[*] This is also nearly valid for an arbitrary barrier which may be approximated in the top region by a parabola and especially for the barrier

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[*] In Ref. 16) this conditions is used both for the definition of T_k and for the analytical derivation of expression (13) for T_k. Essentially the same result was obtained by JOHNSTON and RAPP,[8] using numerical methods for the calculation of transition probability. This situation is shown to be nearly valid for the Eckart barrier[16,8] and for the Schottky image potential barrier.[17]

(9) when $a>0$; in this case L_m is the barrier curvature at the top $(x=x_m)$.

If $a>0$, the tunnelling correction for the barrier (9) can be evaluated analytically for $A=0$ (symmetric barrier).[13] This solution includes the Eckart barrier $(a=\pi)$, for which a numerical computation has aslo been made by JOHNSTON and RAPP.[8]

These results are immediately applicable with a good approximation to all reacting systems of three colinear atoms A–H–B if A and B are too heavy and remain stationnary during the transition of H from A to B, so that the reaction may be described in one dimension by the coordinate $x_{\mathrm{AH}}=r_{\mathrm{AH}}$ (or r_{BH}). The reduced mass transferred through (over) the barrier is then the mass of a proton $(\mu=m_{\mathrm{H}})$.

The expressions for one-dimensional tunnelling correction are generally not applicable to the curve-linear reaction path of a multi-dimensional potential barrier. However, in all cases they may be very useful in the study of the general character of the dependences between kinetic parameters and tunnelling degree. As far as the characteristic temperature T_k is concerned, it can always be used as an approximative criterion for the relative role of the tunnel effect, if L_m in Eq. (13) is expressed by the curvature of the barrier profile at the saddle-point. This is possible because at $T=T_k$ only half of all the systems tunnel just the very top of the barrier, where the separation of the reaction coordinate is justified. Thus, we can determine in which cases tunnelling is significant $(T<T_k)$ and in which it can be completely neglected $(T>2T_k)$.[12,13,16]

For $T\gtrsim T_k$ the tunnelling correction can always be calculated in harmonic approximation from Eq. (12) (or 5).*) This expression may also be valid for $T<T_k$, if the barrier profile is sufficiently thin, so that the separation of the reaction coordinate would be possible in a larger region near the saddle-point. This seems to be the case for reaction (8), for which from the data of SHARP and JOHNSTON[11a] for the parameters of the three-dimensional barrier we find, that formula (12) for $\varkappa_t$ applies well for $T\gtrsim 0{,}7\,T_k$ ($T_k=1090$°K for H and $T_k=770$° for D).

JOHNSTON *et al.*[8,11] treated the reactions (7) and (8) as a two-dimensional problem in evaluating the potential energy of the linear three-center model A–H–B as a function of two distances r_{AH} and r_{HB} by means of the SATO

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*) From Eq. (12) one finds $\varkappa_t=1{,}57$ for $T=T_k$ and $\varkappa_t=1{,}12$ for $T=2T_k$. In the temperature region $T\gtrsim T_k$ Eq. (12) can be replaced by

$$\varkappa_t=1+\frac{1}{2}\left(\frac{T_k}{T}\right)^2. \tag{12 a}$$

This relation nearly coincides with Wigner tunnel-effect correction[3] which is included in expression (5 a). It results indeed, that for $T<T_k$ the tunnelling correction must be taken into account and for $T>2T_k$ it is completely negligible.[12,13,16] method. Then the reduced mass for motion through the saddle-point, corresponding to an unsymmetrical vibration $\overleftarrow{\mathrm{A}}\cdots\overrightarrow{\mathrm{H}}\cdots\overleftarrow{\mathrm{B}}$, is

$$\mu=\frac{1}{2}m_{\mathrm{H}}\frac{m_{\mathrm{A}}+m_{\mathrm{B}}}{m_{\mathrm{H}}+m_{\mathrm{A}}+m_{\mathrm{B}}}\,. \tag{14}$$

It is $\mu\simeq m_{\mathrm{H}}/2$ because A and B are much heavier than H. Since in this case the distance $r_{\mathrm{AB}}=r_{\mathrm{AH}}+r_{\mathrm{HB}}$ remains constant during the proton transfer, the reaction coordinate has a slop of $-45°$ at the saddle-point. According to the approximate method of Johnston and Rapp[8] the two-dimensional tunnelling correction is calculated (using numerical integration) as a sum of the one-dimensional tunnelling corrections for a series of parallel cuts at $-45°$, approximating the energy profiles by the Eckart potential.

In this way it has been found, that at low temperatures the one-dimensional approximation, based on the extended reaction path, leads to considerably higher values of tunnelling correction than does the two-dimensional consideration. This conclusions is drawn from a comparison with the same value of the reduced mass in both cases. However, if A and B are heavy atoms or atomic groups, one commonly uses the one-dimensional method taking $\mu=m_{\mathrm{H}}$, while the two-dimensional procedure of Johnston-Rapp implies that $\mu\simeq m_{\mathrm{H}}/2$. A comparison with these different reduced masses leads to the inverse conclusion, namely that the one-dimensional treatment gives lower values for tunnelling corrections than does the two-dimensional one. For example, from the data of Sharp and Johnston[11a] we find that a parabolic barrier with the same height as the real barrier ($E=7{,}82$ kcal) and the same curvature as the energy profile at the saddle-point has a width of $2d=0{,}452$ Å, so that one obtains for the tunnelling factor (with $\mu=m_{\mathrm{H}}$) $\mathscr{X}_t=14{,}6$.[*] The application of an Eckart barrier (with the same height and the same curvature at the top) gives (with $\mu=m_{\mathrm{H}}$) $\mathscr{X}_t\simeq 10$. The one-dimensional approximation based on the extended reaction path, would obviously give a lower value for $\mathscr{X}_t$ (<10). On the other hand by means of the two-dimensional method of Johnston-Rapp one obtains (with $\mu=0{,}4945\,m_{\mathrm{H}}$) $\mathscr{X}_t=18{,}4$ ($T=300$°K).[11a] Thus, we conclude, that the one-dimensional approximation gives a *lower* limit for the tunnelling correction, if we take the transferred mass to be equal to the proton mass.

Of course, using the familiar method for constructing a two-dimensional barrier, $V(x)$ ($x=r_{\mathrm{AH}}$), by the intersection of the potential curves for A–H and B–H, we do not obtain just the profile of the extended reaction path of

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[*] In this case $\gamma>\delta$ ($\gamma=13.1$, $\delta=12.8$) and Eq. (11) is not valid. The value $\mathscr{X}_t=14.6$ is found, using Eq. 25 (with $\omega=1$) which holds for $\gamma\simeq\delta$.

a three-dimensional barrier $V(r_{AH}, r_{BH})$. However, in the considered case of heavy atoms (atomic groups) A and B, a two-dimensional treatment is really not necessary, inasmuch the *change* of potential energy for the linear complex A–H–B is in fact only a function of the proton position between the fixed centres A and B. Although the repulsion between A and B may significantly contribute to the total (classical) energy of activation, the barrier profile for the proton transfer itself remains the same, as in the case of negligible repulsion.*) Under this condition it is legitimate to calculate the tunnel-effect correction in one-dimensional approximation assuming $\mu = m_H$.

5. Tunnel Effect and Kinetic Isotope Effect

Because of the difficulties in a theoretical construction of the potential barrier, attempts have been made by BELL[19] and CHRISTOV[20,23] to estimate tunnelling correction by determining the barrier parameters from experimental data, related to the kinetic isotope effect.

The Arrhenius equation,

$$v = K' e^{-E'/kT} \tag{15 a}$$

gives the experimental values of the activation energy E' and the frequency factor K', which may also be calculated from Eq. (3) (including the tunnelling correction) by rewriting the latter in the form,

$$v = \mathscr{X}_t \frac{kT}{h} \frac{Z'^{\ddagger}}{\prod Z'_i} e^{-E_0/kT}, \qquad E_0 = E + \Delta\varepsilon_0^{\ddagger}, \tag{15 b}$$

where E_0 is the "true" activation energy, $\Delta\varepsilon_0^{\ddagger} = \varepsilon_0^{\ddagger} - \varepsilon_0$ is the difference between the zero-point energies in the transition and the initial state while the partition functions Z' includes the vibrational factors $Z'_{v,q} = \prod (1 - e^{-h\nu/kT})$. From Eq. (15 a) and (15 b) we obtain

$$\left.\begin{aligned} E' &= E_0 - k\frac{d \ln K}{d(1/T)} - k\frac{d \ln \mathscr{X}_t}{d(1/T)}, & \text{(16 a)} \\ K' &= \mathscr{X}_t K e^{(E'-E_0)/kT}, & \text{(16 b)} \end{aligned}\right\} \quad K = \frac{kT}{h} \frac{Z'^{\ddagger}}{\prod Z'_i}$$

The second term in Eq. (16 a) is small in general, so that $E' - E_0$ and K'/K depend essentially on the tunnelling correction $\mathscr{X}_t$ and its temperature change.

The kinetic isotope effect is determined by the expression,

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*) The repulsions between the *proton* and the atoms (atomic groups) A and B are always negligible,[18] so that the course of the two separate potential curves for A–H and H–B will not change, if we bring A and B together at a finite distance, to obtain an intersection of the curves. However, if a hydrogen *atom* is transferred, the repulsions between H and A(B) must be taken into account.

$$\frac{v_{\mathrm{H}}}{v_{\mathrm{D}}} = \frac{\mathscr{X}_{\mathrm{H}}}{\mathscr{X}_{\mathrm{D}}} \frac{K_{\mathrm{H}}}{K_{\mathrm{D}}} e^{-(E_{0,\mathrm{H}}-E_{0,\mathrm{D}})/kT}, \quad E_{0,\mathrm{H}}-E_{0,\mathrm{D}} = \varDelta\varepsilon^{\ddagger}_{0,\mathrm{H}} - \varDelta\varepsilon^{\ddagger}_{0,\mathrm{D}}, \quad (17)$$

resulting from Eqs. (15 a) and (15 b). For reaction (1) we obtain $2 > K_{\mathrm{H}}/K_{\mathrm{D}} > \frac{1}{2}$*) so that $K_{\mathrm{H}}/K_{\mathrm{D}}$ is near to unity. This means that the isotope effect depends essentially on the difference of the zero-point energies and on the ratio between the tunnelling corrections of the two isotopes, H and D.

If A and B are heavy groups, when treating the problem in one dimension, one sees that for a given barrier shape the tunnelling correction $\mathscr{X}_t$ will depend on the height E and the width $r_0 = 2l$ of the barrier and on the proton (deuteron) mass $m_{\mathrm{H}}(m_{\mathrm{D}})$. However, in replacing E with E_0, we can consider $\mathscr{X}_t$ as a function of E_0, l and m.21),23) Under these conditions the isotope effect is determined by three unknowns $E_{0,\mathrm{H}}$, $E_{0,\mathrm{D}}$ and $r_0 = 2l$, if we assume that $r_{0,\mathrm{H}} = r_{0,\mathrm{D}} = r_0$. For the calculation of these unknowns the theory offers three equations, expressing three experimentally determinable magnitudes E'_{H}, E'_{D} and $K'_{\mathrm{H}}/K'_{\mathrm{D}}$ (or $v_{\mathrm{H}}/v_{\mathrm{D}}$) by means of Eqs. (16 a, b) and (17).

By this approach the true barrier profile is replaced by two barriers with the same width r_0, but with different heights $E_{0,\mathrm{H}}$ and $E_{0,\mathrm{D}}$ for the two isotopes. In this way the influence of the tunnelling on the isotope effect will not be overestimated as far as generally $\varDelta\varepsilon_0^{\ddagger} < 0$, *i. e.* $E_0 < E$, so that $\mathscr{X}(E_0, r_0) < \mathscr{X}(E, r_0)$24) Further, $\varDelta\varepsilon^{\ddagger}_{0,\mathrm{H}} > \varDelta\varepsilon^{\ddagger}_{0,\mathrm{D}}$ in general, so the $E_{0,\mathrm{H}} < E_{0,\mathrm{D}}$.19) Therefore $\mathscr{X}_{\mathrm{H}}/\mathscr{X}_{\mathrm{D}}$ will have a lower value than in the case of $E_{0,\mathrm{H}} = E_{0,\mathrm{D}}$.

The method for estimating the tunnel corrections described accounts for the influence ofthe real vibrations in the transition state :24) I) by replacing E with E_0 which leads to the result $E_{0,\mathrm{H}} \leq E_{0,\mathrm{D}}$; II) by accounting for the limits of variation of $K_{\mathrm{H}}/K_{\mathrm{D}}$.20~23) BELL *et al.* take $K_{\mathrm{H}}/K_{\mathrm{D}} = 1$18),19) and CHRISTOV assumes $K_{\mathrm{H}}/K_{\mathrm{D}} = \sqrt{2}$ which is the upper limit in the simple collision theory. However we could also take $K_{\mathrm{H}}/K_{\mathrm{D}} = 2$. This way seems possible for finding a lower limit of the *net* tunnelling correction, excluding a cancellation by the contribution of the zero-point energies in the transition state.24)

The value or r_0, calculated in the manner described, depends on the

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*) These limits are obtained18),19) if A = R–H and AH = R–X–H so that not only the stretching vibration $\overset{\rightarrow}{\mathrm{X}}-\overset{\leftarrow}{\mathrm{H}}$ but also the doubly degenerate bending vibration $\underset{\downarrow}{\mathrm{R}}-\overset{\uparrow}{\mathrm{X}}-\underset{\downarrow}{\mathrm{H}}$ in the initial state is taken into account. The activated complex is assumed to be (A···H···B) (if R is an atomic group, its inner vibrations are almost unaffected by the substitution of H by D so that in this case $K_{\mathrm{H}}/K_{\mathrm{D}}$ is near to unity, too18)). If, however, the activated state is treated as (R–X···H···B) one obtains $2\sqrt{2} > K_{\mathrm{H}}/K_{\mathrm{D}} > 1/2$ where the factor $\sqrt{2}$ arises from the asymmetrical streching vibration $\overset{\leftarrow}{\mathrm{R}}-\overset{?}{\mathrm{X}}\cdots\overset{\rightarrow}{\mathrm{H}}\cdots\overset{\leftarrow}{\mathrm{B}}$ which is recently considered to be important for isotope effects.6)

barrier shape assumed and is in general not equal to the real barrier width. In changing the barrier shape by variation of parameter a in Eq. (9), we obtain different values for $r_0=2l$.[20~23)] In this way one can calculate and compare the tunnelling corrections for various forms of the barrier with respect to a better fitting to the experimental data.*)

In the one-dimensional consideration the value found for E_0 will represent the barrier height, which the proton has to overcome, only if the repulsion between A and B is negligible. Otherwise, the contribution of this repulsion to the total barrier height will lead to overestimation of the tunnelling. However, the results of the procedure of calculation discussed may also be interpreted in terms of a two-dimensional consideration, provided that the tunnelling occurs essentially in the saddle-point region where a separation of the reaction coordinate is possible. Then E_0 is to be related to the total barrier height $E=E_0-\varDelta\varepsilon_0^{\ddagger}$ and the tunnelling correction may be calculated from Eq. (12) in which $\mathscr{X}_t$ appears as a function of E_0 and $l\sqrt{\mu_\mathrm{H}}$.[26)] Thus, by determining the three unknowns $E_{0,\mathrm{H}}$, $E_{0,\mathrm{D}}$ and $\beta_\mathrm{H}=l\sqrt{\mu_\mathrm{H}}$ **) from experimental data, as explained above, it is possible to estimate the tunnel-effect correction without any special assumptions about the values of μ_H and l. If tunnelling occurs mainly outside the region of separability of the reaction coordinate, the value of $\mathscr{X}_t$ may be overestimated using Eq. (12). In this case we can find at least a lower value for the characteristic temperature T_k by means of expression (13) for both H and D to decide whether the tunnelling is appreciable or may be disregarded.

6. Proton Transfer Processes in Solution

Calculation of the potential-energy surface for reactions in solution is complicated by the effect of solvation of the interacting particles. These effects are usually taken into account only by approximate estimates of the solvation energy of both the initial and the activated state in assuming equilibrium configuration of the surrounding solvent molecules. Under this con-

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*) The statement of BOCKRIS and MATHEWS[25)] that CHRISTOV identifies the width of a parabolic barrier model with the real barrier width is fully incorrect as easily seen from the fact that different *equivalent* values for r_0 were found by CHRISTOV for various barrier models (see the explanations in writer's papers[20~24)]).

**) In this interpretation l is the half-width of a parabolic barrier with height E_0. Assuming $l_\mathrm{H}=l_\mathrm{D}$ we find from Eq. (14) that the ratio $\beta_\mathrm{H}/\beta_\mathrm{D}=\sqrt{\mu_\mathrm{H}/\mu_\mathrm{D}}$ changes very slowly with variation of m_A and m_B, so that if A and B are heavy atoms (atomic groups) we can take $\beta_\mathrm{H}/\beta_\mathrm{D}=\sqrt{m_\mathrm{H}/m_\mathrm{D}}=0.707$ (In the limit case when A=H and B=H we have $\beta_\mathrm{H}/\beta_\mathrm{D}=0.817$). Thus β_D is determined by β_H, which is the only independent unknown related to the reduced mass transferred.

dition it is possible to describe reaction (1) in one dimension, provided that A and B are heavy atoms (atomic groups), and neglect the repulsion between them. However, an accurate analysis of the vibrations in the transition state, requiring the construction of a multidimensional energy surface, seems impossible at present.

The one-dimensional treatment would be unjustified for quantitative studies in the case of significant deviations from the equilibrium solvation. Such deviations are possible in certain reactions in polar liquids, in which the time involved in the proton transfer is probably less than the dielectric relaxation time of the solvent.[6)] This is possibly the reason that many proton transfer reactions occur more slowly in D_2O than they do in H_2O. However, in other cases the effect of non-equilibrium solvation might be quite unimportant. This is probably the case of electrolytic hydrogen evolution on metals from aqueous solutions as could be concluded from the measurments of BARKER *et al.*[27)] at mercury by very fast methods up to high rate constants. From this data, assuming a distance of 0.5 Å for the proton transfer, one obtains an equivalent time from 10^{-4} sec to $6 \cdot 10^{-12}$ sec for the whole range of measurments including 7 powers of ten in the rate constant (from $5 \cdot 10^{-5}$ cm/sec to $8 \cdot 10^{2}$ cm/sec), while the dielectric relaxation time for water is about $9 \cdot 10^{-12}$ sec.[*)] This suggests that the reorientation of water molecules follows the proton transfer without relaxation, so that a minimum of the potential energy of the system is assured during the transition. This situation is probably valid for other proton transfer reactions in water solution too, but the relative significance of the non-equilibrium reorientation of water molecules is to be investigated for each special case separately.

There are several reasons[30,31)] for believing that solvent reorganization does not play an important role in many proton transfer reactions in contrast to the case of electron transfer processes[29)] between hydrated ions. Proton transition normally occurs along a hydrogen bond, *i. e.* over a distance which is much smaller than the electron transfer distance, so that the surrounding solvent molecules will be much less affected by the proton transfer than by the electron jump.[30)] The fact that the activation energies for proton transfer reactions differ considerably from those for electron transfer processes[30)] supports this conclusion. Also, the well known relation between activation energy and heat of reaction (Brönsted relation) could hardly be understood if we assume

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[*)] The highest extrapolated value of the rate constant is $2 \cdot 10^4$ cm/sec and the corresponding equivalent time is $2.5 \cdot 10^{-13}$ sec. According to an estimate of NÜRNBERG[28)] the effective rotation time for H_2O molecule is $1.62 \cdot 10^{-13}$ sec., so that the reorientation of water molecules is not affecting the proton transfer up to the highest rate constant measured at the time.

that the solvent barrier determines essentially the rate constant.

Estimations of the role of proton tunnelling in solutions have been made by BELL,[18,19] CHRISTOV[20~23] and other authors[32,33] using the above explained half-empirical method. BELL *et al.*[18,19] investigated three reactions of catalytic bromination of 2-carbetoxy-cyclopentanone (R–H): I. $RH+D_2O$; II. $RH+CH_2ClCO_2^-$; III. $RH+F^-$. It has been found that the ratio between the pre-exponential factors in equation (15 a) for the two isotopes H and D is $K'_H/K'_D < 1/2$, this beeing an indication of considerable tunnelling. For reaction (III) this conclusion is confirmed by the significant departure from Arrhenius law by low temperatures ($-20°C$)[32] due to the temperature dependence of the tunnelling factor $\mathscr{X}_t$ in Eq. (15 b). Using the parabolic barrier model one obtains from Eq. (16 a) that the ratio E'_H/E varies between 0.80 and 0.90 and a barrier width $r_0=2l$ from 1.17 to 1.26 Å is calculated. CHRISTOV[20~23] has carried out such estimations for the hydrogen evolution reaction at mercury cathode, using the experimental data of POST and HYSKEY,[34] by means of the parabolic, Eckart and the generalised Eckart potential (9). Similar results have been obtained by HULETT[32] and CALDIN *et al.*,[33] using a parabolic barrier for a series of reactions.

It is obvious that the absolute values of the barrier parameters, calculated on the basis of special one-dimensional models, cannot be of great importance, if we have not sufficient reasons to believe that no changes in the electronic configuration of the unreacting atoms*) or no considerable departure from the equilibrium polarisation of the solvent occur during the proton transition. In the last case a multidimensional interpretation of the results of such calculations, as discussed above, is necessary. Especially then it is not permissible to take the reduced mass of the system equal to the proton mass, so that the effective (one-dimensional) barrier width will depend on the choice of this magnitude ($\mu \neq m_H$).

7. Acid-Base Catalysis. The Brönsted Relation

If reaction (1) occurs in solution, AH will represent an acid (proton donor) and B a base (proton acceptor). For the study of the acid-base catalysis of basic importance is the wellknown Brönsted relation[18]

$$v_1 = C_1 K_{AH}^{\beta}, \qquad v_2 = C_2 K_{BH}^{\alpha}, \tag{18}$$

where v_1 and v_2 are the rate constants for both directions of reactions (1),

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*) For example, according to CALDIN and KASPARIAN[33] the activation energy for the reaction $HF+C_6H_2(NO_2)_3CH_2^-$ is assotiated in large part with changes in the substrate molecule.

$K_{\mathrm{AH}}(K_{\mathrm{BH}})$ is the electrolytic dissotiation constant of AH(BH), $C_1(C_2)$ and $\beta(\alpha)$ are constants for a series of acids (bases) of the same type.

A simple theoretical interpretation of relation (18) was first proposed by HORIUTI and POLANYI[35] on the basis of the relation between activation energy $E(E-Q)$ and heat of reaction Q:

$$\varDelta E=\beta \varDelta Q\,,\qquad \varDelta(E-Q)=-\alpha \varDelta Q\,,\qquad (\alpha+\beta=1)\,, \tag{19}$$

obtained by graphical represantation of the potential-energy barrier resulting from the intersection of the potential curves for the covalent bonds A–H and B–H. The derivation of the Brönsted relation (18) from Eq. (19) implies that $\beta(\alpha)$ is a constant. However, this assumption remains unjustified in the frame of the above treatment. Moreover, the possibility of proton tunnelling is also disregarded in the usual consideration of relations (18) and (19) and their connection.

Recently considerable deviations from the linear relationship (19) have been observed by BELL,[18] EIGEN[36] a. o. in several cases, in which the coefficient $\beta(\alpha)$ varies from 0 to 1 for a series of related compounds. These facts give rise to a new discussion of the conditions under which the Brönsted relation is valid.[36] The problem has already been considered in some detail for a more specific case by the author.[37] A more general treatment will be presented elsewhere. Here, we shall discuss only the essential points of this treatment in terms of the potential function (9) which represents a rather general expression for the energy profile of the reaction path in acid-base catalysis, too.

From Eq. (10) one obtains (with $A=Q$)

$$\beta\equiv\frac{dE}{dQ}=\frac{1}{2}\left(1+\frac{Q}{4E_s}\right),\quad \alpha\equiv-\frac{d(E-Q)}{dQ}=\frac{1}{2}\left(1-\frac{Q}{4E_s}\right). \tag{20}$$

Both β and α varies between 0 and 1, $(\alpha+\beta=1)$, the limiting values corresponding to $Q=-4E_s$ for $\beta=0$ $(\alpha=1)$ and $Q=4E_s$ for $\beta=1$ $(\alpha=0)$. For these values Eq. (10) gives $E=0$, $E-Q=-Q=4E_s$ for $\beta=0$ $(\alpha=1)$ and $E=Q=4E_s$, $E-Q=0$ for $\beta=1\,(\alpha=0)$, which means that the barrier disappears for the one direction of reaction while for the inverse direction it is equal to the heat of reaction.

In the following we will consider the one direction of reaction (1) (from left to right) assuming $Q>0$ (endothermic direction). In expanding the function $E=f(Q)$ in Taylor series about a given value $Q=Q_0$ we obtain from Eq. (10)

$$\begin{gathered}E=E_{Q_0}+\beta(Q_0)(Q-Q_0)+\frac{1}{2}\left(\frac{\partial\beta}{\partial Q}\right)_{Q=Q_0}(Q-Q_0)^2\,,\\ \beta(Q_0)=\frac{1}{2}\left(1+\frac{Q_0}{4E_s}\right),\quad \left(\frac{\partial\beta}{\partial Q}\right)_{Q=Q_0}=\frac{1}{8E_s}\,,\end{gathered} \tag{21}$$

all higher order terms been equal to zero. The third term can be neglected under the condition,

$$\frac{1}{2}\,\frac{Q-Q_0}{4E_s+Q_0} \ll 1\,. \tag{22}$$

Then, Eq. (21) will represent the proportionality relationship (19) between $\varDelta E = E - E_{Q_0}$ and $\varDelta Q = Q - Q_0$ with $\beta = \beta(Q_0)$.

Let us first assume that the tunnel effect may be neglected, *i.e.* in Eq. (16) we take $\mathscr{X}_t = 1$, $E' = E_0 \simeq E$. Then using the expression for the equilibrium constant,

$$K_{\mathrm{C}} = K_{\mathrm{AH}}/K_{\mathrm{BH}} = Ce^{-Q/kT}, \tag{23}$$

we easily derive the Brönsted relation (18) from Eqs. (16 a) and (21) under the condition (22) with $\beta = \beta(Q_0)$. If this condition is not satisfied, in both Eqs. (18) and (19) β cannot be regarded as a constant, but will vary between 0 and 1 according to expression (20).

When the proton tunnelling is not negligible ($\mathscr{X}_t > 1$), we obtain essentially the same results only if the tunnelling correction $\mathscr{X}_t$ is independent of the reaction heat. In such a case it follows from Eq. (16 a) (neglecting the small second term and the contribution of the zero-point energies) that $\varDelta E' = \varDelta E$ (althought $E' \neq E$). Therefore in the relation,

$$\varDelta E' = \beta' \varDelta Q \tag{24}$$

between experimental activation energy E' and heat of reaction Q the coefficient $\beta' = \beta$ will be the same as in the Brönsted relation (18). This result is realized in the region of moderate tunnelling if expression (12) for $\mathscr{X}_t$ is valid. For a parabolic barrier this is the case under the condition $(\delta - \gamma)\omega > 2$ under which Eq. (12) is derived from the more general expression (11).

The situation is quite different, if the tunnelling correction depends on the reaction heat. For simplicity, we shall first consider a parabolic barrier profile, *i.e.* Eq. (9) for $a \to 0$ in the special case $\gamma \simeq \delta$ in which[12]

$$\mathscr{X} = \delta\omega \left[1 + \frac{1}{2}(\gamma - \delta)\omega - \frac{1}{6}\delta(\gamma - \delta)^2 \omega^3 + \cdots \right]. \tag{25}$$

Then from Eq. (16 a) we obtain the expression,

$$E' = E - \frac{1}{2}\,\frac{E_s \delta \omega^2}{\mathscr{X}},$$

which for $\gamma = \delta$ reduces to $E' = (E+Q)/2$. Using Eq. (21) for E under condition (22) gives

$$\Delta E' = \beta'\Delta Q\,, \qquad \beta' = \frac{1+\beta(Q_0)}{2}\,, \tag{26}$$

while from Eqs. (16 a), (21) and (23) under the same condition one derives a relation of the form (18) with $\beta=\beta(Q_0)$.

In the case of very large tunnelling we can apply expression,[12]

$$\varkappa = \frac{\gamma}{\gamma-\delta}\,e^{(\gamma-\delta)\omega} \tag{27}$$

which holds for a parabolic barrier if $(\gamma-\delta)\omega>2$.[13] In this case Eq. (16 a) gives

$$E' = E-kT\left(1-\frac{\gamma}{\gamma-\delta}+\gamma\omega\right)$$

from which, for $\gamma\gg\delta$, we find $E'=Q$, *i.e.* Eq. (24) with $\beta'=1$, while Eqs. (16 a), (21) and (23) lead to relation (18) with

$$\beta = 1-\frac{\delta kT}{2E_s}\left(1-\frac{Q}{8E_s}\right). \tag{28}$$

Similar results are obtained using potential function (9) with an arbitrary value of $a>0$. In this more general case, provided that tunnelling is very large, $E'=Q$, *i.e.* $\beta'=1$ and

$$\beta = 1-\frac{\delta kT}{aQ}\left(\sqrt{\frac{K+Q}{E_s}}-\sqrt{\frac{K+(1-\mu)Q}{E_s}}\right),^{*)} \quad K=BC+\mu AD. \tag{29}$$

It is obvious that in the case of very large tunnelling the reaction in the inverse (exothermic) direction occurs without any activation ($E'-Q=0$).

We see in general that Eqs. (18) and (24) cannot be considered, as usually accepted, as two equivalent expressions of the Brönsted relation because when the tunnelling correction depends on the reaction heat coefficients β and β' in both expressions may be quite different. This difference can be regarded as an indicative of extensive tunnelling which would be expected if proton transfer occurs along a hydrogen bond. However, it seems that this is not

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*) For $a\to 0$ (parabolic barrier) Eq. (29) turns to Eq. (28) and for $a=\pi$ (Eckart barrier) it leads to

$$\beta = 1-\frac{\delta kT}{\pi\sqrt{E_s}\,\sqrt{Q}}\,. \tag{29'}$$

This result differs from the expression found by WEISS[38] by a factor of 1/2 in the second term. This difference is due to the fact that WEISS uses a symmetric Eckart barrier ($A=0$) with constant height E having no relation to the reaction heat Q, while according to Eq. (10) the height E of the asymmetric barrier, used in the above calculation, is a function $A=Q$.

always the case in proton transfer reactions.[39]

Although the above conclusions are based on one-dimensional barrier models, they are certainly qualitatively valid in the more general case where a multi-dimensional representation of the process is necessary.

8. Electrolytic Hydrogen Evolution Reactions

As first pointed out by FRUMKIN[40] electrode reactions of the type,

$$H_2O\text{-}H^+ + Me^- \longrightarrow H_2O + H\text{-}Me \qquad (30)$$

can be treated as a special case of acid-base proton-transfer processes in which the hydroxonium ion H_3O^+ is the acid while the metal Me^- plays the role of the base. Then, by means of relationship (19), in which $\Delta Q = \varepsilon\Delta\varphi$ (ε is the proton charge), one derives from Eq. (15 b) an expression for the rate of hydrogen evolution or current density i as a function of electrode potential φ:

$$i = Ae^{-\alpha\varepsilon\Delta\varphi/kT}. \qquad (31)$$

This expression leads to the Tafel relation,

$$\eta = a + b\lg i, \qquad (32)$$

in which $\eta = \Delta\varphi = \varphi_r - \varphi$ is the overpotential (φ_r-reversible electrode potential), only under the condition that $b = 2.3kT/\alpha\varepsilon$ and $a = \lg A$, *i. e.* α and A in Eq. (31) are independent of φ.

HORIUTI and POLANYI's interpretation[35] of the Brönsted relation in terms of potential-energy curves includes also a theoretical foundation of Tafel equation (32). A more general theory is given by CHRISTOV,[12,21,37,41,42] accounting for the potential dependence of both the symmetry factor $\alpha = 1 - \beta$, and the preexponential factor A in Eq. (31). This theory allows determining the conditions of validity of the Tafel equation. The classical treatment of the motion of protons leads to a constant A and to a potential dependent α*) while the quantum-mechanical consideration predicts variation of A with electrode potential.**)

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*) The potential dependence of α was first derived analytically by CHRISTOV,[12,21,42] using the Eckart barrier[42] and the parabolic barrier.[12] Later DESPIC and BOCKRIS[43] treated the problem, following HORIUTI and POLANYI[35] but no explicit relation between α and φ has been obtained. In more general form the theory of the symmetry factor and its potential dependence has been developed by the author in Ref. 37).

**) A possibility of proton tunnelling in reaction (30) was first assumed by POLANYI[44] who stimulated the work of BAWN and OGDEN[45] on the relation between tunnel effect and isotope effect. A quantum-mechanical foundation of the current-potential relation (31) on this basis was first given by CHRISTOV.[41,42] Full references can be found in previous works.[12,20~24]

From standpoint of the classical theory, the Tafel relation is valid under condition (22), in which we can set $Q-Q_0=\varepsilon\eta$ in relating E_s and Q_0 to the reversible potential φ_r. This is shown[31] to be the case of hydrogen evolution on mercury in a range for $\eta=\varphi_r-\varphi$ of more than 1 volt (from 1 to 2 volts) in agreement with the experiment.

The quantum-mechanical theory leads to the conclusion[41] that factor A in Eq. (31) (including the tunneling correction $\mathscr{X}_t$ from Eq. (15 b)) is in general a function of electrode potential φ depending parametrically on the barrier shape and dimensions and on the mass of the ion (H^+ or D^+), too. The relation between A (or $\mathscr{X}_t$) and φ has been investigated by the author[21~23,42] using various one-dimensional barrier models of type (9). It is shown that in the region of weak and moderate tunnelling ($T>T_k/2$) factor A (*i.e.* $\mathscr{X}_t$) in Eq. (31) is practically independent of φ which leads to Tafel equation (32) with almost constant values of a and b. In the case of a parabolic barrier, *i.e.* Eq. (9) with $a\rightarrow 0$, the following simple relations[21] were found:

$$\begin{array}{lll} b/b^{\mathrm{Cl}} \simeq \gamma/\delta & \text{for } \gamma>\delta, & \\ & & (b^{\mathrm{Cl}}=2.3kT/\alpha\varepsilon). \qquad (33) \\ b/b^{\mathrm{Cl}} \simeq 1 & \text{for } \gamma<\delta, & \end{array}$$

A relationship of the form $b/b^{\mathrm{Cl}}=f(\gamma/\delta)$ is also obtained[21] for the Eckart barrier, *i.e.* Eq. (9) for $a=\pi$. It may be concluded that such a relation exists for the generalized potential barrier (9) for any value of parameter a, the form of function $f(\gamma/\delta)$ varying with a but always $f(\gamma/\delta)\simeq 1$, if $\gamma/\delta<1$. Therefore, the inequality $\gamma<\delta$ (or $T>T_k/2$) is to be considered a sufficient condition for the practical validity of the Tafel equation (32) with $b\simeq b^{\mathrm{Cl}}$ as far as the "classical" dependence of α on φ is disregarded. However, Eq. (32) irrespective of the barrier shape could also be valid, to a certain limit, for $\gamma>\delta$ ($T<T_k/2$), *i.e.* in the region of large tunnelling, provided that $a\gg 1$ (for example $a=\pi$, *i.e.* Eckart barrier).[42]

In the general relationship $b/b^{\mathrm{Cl}}=f(\gamma/\delta)$ are included all the dependences of the Tafel slopes on barrier shape and dimensions and temperature, found in special cases by CHRISTOV,[21,41,42] CONWAY *et al.*[46,47] and BOCKRIS *et al.*[48~50] There follows from it not only $b\geq b^{\mathrm{Cl}}$ but also $b_{\mathrm{H}}\geq b_{\mathrm{D}}$, so that for $\gamma>\delta$ ($b_{\mathrm{H}}>b_{\mathrm{D}}$) the isotope separation factor $S=i_{\mathrm{H}}/i_{\mathrm{D}}$ will decrease with increasing overvoltage. This is clearly the case when $\gamma/\delta\gg 1$ (large tunnelling) as first shown by CONWAY[46] for a single Eckart barrier (for which $\gamma/\delta\simeq 6$). However, if $\gamma/\delta\sim 1$, the tunnelling correction $\mathscr{X}$ as well as the ratio $\mathscr{X}_{\mathrm{H}}/\mathscr{X}_{\mathrm{D}}$ in Eq. (17) could also vary noticeably with overpotential, so that the separation factor may be found as potential dependent although $b_H \simeq b_D \simeq b^{Cl}$.[*]

The influence of proton tunnelling on the isotopic separation by electrolysis has first been treated by Bawn and Ogden[45] without any relation to current-potential dependence. They obtained very high values for the separation factor ($S \sim 100$) which have never been confirmed by experiment. The reasons for these incorrect results have been discused previously.[20b,21][**] In more recent time the problem was treated again by Christov[20] and Conway.[46]

Christov[20,23] calculated the barrier dimensions for the hydrogen evolution on mercury at $\eta=0$ from the experimental data of Post and Hiskey[34] by means of potential function (9). The value $E_0=1.6\cdot 10^{-12}$ erg was found for the barrier height and for the barrier width: $2l=4.7$ Å for $a=\pi$, $2l=1.65$ Å for $a=0$ and $2l=2.1$ Å for $a=1$. The tunnelling correction factor was found to be $\mathscr{K}_H=3.33$. These results are consistent with the experimental values of all kinetic parameters (E'_H, E'_D, K'_H, K'_D and $S=i_H/i_D$) meseared by Post and Hiskey.[34]

Conway[46] used an Eckart barrier with a height $E_0=1.25\cdot 10^{-12}$ erg and a width $2l=0.5$ Å, corresponding to the calculations of Parsons and Bockris.[55] The high Tafel slopes ($b_H > b_D > b^{Cl}$) and strong potential dependence of the separation factor, obtained by Conway, are in contradiction with the experiment.

In investigating experimentally the hydrogen evolution on mercury in a metanol solution of HCl at low temperatures Conway and Salomon[47] have not observed the expected deviation from Arrhenius law. They concluded that the tunnel-effect could not be significant for reaction (30) on Hg. However, this negative conclusion is unnecessary because when the tunnel-effect plays a moderate role ($\mathscr{K} \sim 2$–10) no observable departure from the Arrhenius plot is to be expected.[21] This seems to be the case in Conway and Salomon's investigations[47] in which a considerably lower activation energy in a methanol solution as compared to a water solution has been measured, so

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[*] The variation of $\mathscr{K}=i/i^{Cl}$ with η under the condition $b \simeq b^{Cl}$ was first shown by Christov[42] for an Eckart barrier for which $\gamma/\delta \simeq 1.5$. Later a similar result was obtained by Bockris and Mathews[49] for $\gamma/\delta \approx 0.9$.

[**] The statement of Conway and Salomon[51] that the work of Bawn and Ogden[45] "does not appear to have been mentioned by Christov" is quite incorrect. It is very surprising, as Christov's papers[20a,21] in which the results of Bawn and Ogden have been discussed in detail, are quoted by Conway and Salomon.[47] A series of the authors papers of the period 1946–1959 have actually not been mentioned in the earlier works of Conway.[46,52] However, it is very gratifying that these works are already refered to in more recent papers of Conway and al.[47] About the chronological facts on electrochemical proton tunnelling, see Christov.[24b] See also Bockris[53] and Schuldiner.[54]

that the effect of temperature decrease is compensated by the lowering of the barrier.[24b]

The disagreement between the theoretical calculations of CONWAY[46] and the experimental facts are not surprising, having in view that these calculations are based on a barrier model which is supposed to represent the true potential energy barrier for reaction (30). According to TEMKIN[56] in electrode processes the height of this barrier does not coincide with the experimental activation energy as assumed by CONWAY. There exists a relation,

$$E'_r = E'_i - \alpha q\,, \qquad q = -\varepsilon T \frac{\partial \varphi_r}{\partial T} \tag{34}$$

between the "real" (experimental) and "ideal" (true) activation energies E'_r and E'_i, where q is the heat of reaction (30) at the reversible electrode potential φ_r which, in principle, can not be determined from experimental data.

If we negelect the tunnel-effect (and zero-point energies), E'_r and E'_i will nearly be equal to the height, E_r and E_i, of the "real" and "ideal" barrier, respectively. Then, following TEMKIN,[56] we obtain the "ideal" barrier from the "real" one, using the construction of HORIUTI and POLANYI,[35] with a vertical shift of the potential curve for the H^+-OH_2-bond at distance q, so that the barrier height change is $E_i - E_r = \alpha q$ while the barrier shape and width remain unchanged. However, if the tunnelilng is not negligible, this procedure would lead to a variation of the tunnelling correction from $\mathscr{X}_i$ to $\mathscr{X}_r$ ($\mathscr{X}_r > \mathscr{X}_i$ if $E_r > E_i$). To obtain the "real" barrier with the same value of $\mathscr{X}$ ($\mathscr{X}_r = \mathscr{X}_i$), it is necessary to change not only the height but also the shape and width of the "ideal" barrier in a convenient manner. Under these conditions TEMKIN's relation[34] will be valid, if we express both E'_r and E'_i by Eq. (16 a) with the respective values E_r and E_i for $E_0 \simeq E$ but with the same value for $\mathscr{X}$ ($\mathscr{X}_r = \mathscr{X}_i$). We conclude that in fitting the parameters of a given barrier model to the experimental data one cannot expect a coincidence with the parameters of the true ("ideal") barrier.[42] In this way it is possible to explain the difference between the above given values for the width of the "real" barrier[20~23] and the width of the true barrier (0.5–0.8 Å) usually assumed.

CONWAY and SALOMON[47] give the following argument against significant proton tunnelling in reaction (30) on Hg. From Eqs. (15) and (34) we find

$$\frac{K'_{i,\mathrm{H}}}{K'_{i,\mathrm{D}}} = \frac{K'_{r,\mathrm{H}}}{K'_{r,\mathrm{D}}}\, e^{\alpha(q_\mathrm{H} - q_\mathrm{D})/kT}\,, \qquad q_\mathrm{H} - q_\mathrm{D} = \varepsilon T \frac{\partial(\varphi_{r,\mathrm{D}} - \varphi_{r,\mathrm{H}})}{\partial T}\,. \tag{35}$$

From the data of POST and HISKEY[34] $K'_{r,\mathrm{H}}/K'_{r,\mathrm{D}} = 0.48$ and from the thermodynamical calculations of CONWAY and SALOMON[47] one obtains $\partial(\varphi_{r,\mathrm{H}} - \varphi_{r,\mathrm{D}})/\partial T$

$= -1.48\cdot 10^{-4}$ V/°C, therefore $K'_{i,\mathrm{H}}/K'_{i,\mathrm{D}} = 1.1$. This result does not support the theoretical expectation that in presence of considerable tunnelling $K'_\mathrm{H}/K'_\mathrm{D}$ could be much less than unity. However, the condition $K'_\mathrm{H}/K'_\mathrm{D} \leq 1/2$ is only sufficient but not a necessary one for a significant tunnelling degree.[24b)] In fact, one obtains for the region of very large tunnelling ($T < T_k/2$), $K'_\mathrm{H}/K'_\mathrm{D} > 1$[20b)] and this relation is also possible in the region of moderate tunnelling. We obtain, indeed, from Eq. (16 b)

$$\frac{K'_\mathrm{H}}{K'_\mathrm{D}} = \frac{\mathscr{X}_\mathrm{H}}{\mathscr{X}_\mathrm{D}} \frac{K_\mathrm{H}}{K_\mathrm{D}} \exp\left[(E_{0,\mathrm{D}} - E'_\mathrm{D}) - (E_{0,\mathrm{H}} - E'_\mathrm{H})\right], \tag{36}$$

where $E_{0,\mathrm{D}} - E'_\mathrm{D} < E_{0,\mathrm{H}} - E'_\mathrm{H}$ if $\mathscr{X}_\mathrm{H}/\mathscr{X}_\mathrm{D} > 1$. $K_\mathrm{H}/K_\mathrm{D}$ varies between 1/2 and 2 if reaction (30) is described as

$$(\mathrm{H_2})\text{-O-H}^+ + \mathrm{Me}^- \longrightarrow \left[(\mathrm{H_2O})\cdots\mathrm{H}^+\cdots\mathrm{Me}^-\right] \longrightarrow \mathrm{H_2O} + \mathrm{HMe}\,,$$

$(\mathrm{H_2})$ and $(\mathrm{H_2O})$ being considered as pseudoatoms. However, in the more justifiable picture

$$(\mathrm{H_2})\text{-O-H}^+ + \mathrm{Me}^- \longrightarrow \left[(\mathrm{H_2})\text{-O}\cdots\mathrm{H}^+\cdots\mathrm{Me}^-\right] \longrightarrow \mathrm{H_2O} + \mathrm{HMe}$$

we obtain the wider limits $1/2 < K_\mathrm{H}/K_\mathrm{D} < 2\sqrt{2}$.*) At any rate, the values $K_\mathrm{H}/K_\mathrm{D} \gtrsim 2$ and therefore $K'_\mathrm{H}/K'_\mathrm{D} \gtrsim 1$ are not excluded. For example for a barrier of type (9) with a height of $E_{0,\mathrm{H}} = E_{0,\mathrm{D}} = 3.2\cdot 10^{-13}$ erg (4.6 kcal) and a width from 0.8 Å (for $a=0$) to 1 Å for ($a=\pi$) we obtain $\mathscr{X}_\mathrm{H} = 2.27$, $\mathscr{X}_\mathrm{D} = 1{,}45$, $(E'_\mathrm{H} - E'_\mathrm{D})/kT = -1{,}19$ so that $K'_\mathrm{H}/K'_\mathrm{D} = 0.47\, K_\mathrm{H}/K_\mathrm{D}$ which gives $K'_\mathrm{H}/K'_\mathrm{D} \simeq 1$ if $K_\mathrm{H}/K_\mathrm{D} \simeq 2$. Therefore, CONWAY's argument against considerable tunnelling through the "ideal" barrier in the case of proton discharge on Hg cannot be considered as unrejectible. Anyway this argument does not concern the necessity of a tunnelling correction in considering the "real" barrier for reaction (30) which follows from the experimental fact that $K'_\mathrm{H}/K'_\mathrm{D} = 0.48$ inasmuch as in absence of tunnelling $K_\mathrm{H}/K_\mathrm{D} > 0.5$.

In a recent paper of SALOMON, ENKE and CONWAY[57)] an attempt has been made to estimate the true barrier height for reaction (30) on the basis of JOHNSTON's empirical method of bond orders,[7,58)] by neglecting the electrostatic interactions of the proton with the polar solvent molecules. It is found to be $E = 29.1$ kcal ($E_0 = 25.5$ kcal), *i. e.* $E_i > E' = 21.7$ kcal. The discharge is treated as a simple proton transfer, as in acid-base reactions, without formation of an atom as supposed prevoiusly by CHRISTOV.[41,42)] However, this mechanism cannot explain the absence of considerable tunnelling as assumed by SALOMON *et al.*[57)] Inversely, because of the very high barrier ($E_i > E_r$)

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*) See note on p. 179.

we should expect a large tunnelling correction ($\mathscr{X}_i > \mathscr{X}_r$). Thus, the inverse situation ($E_i < E_r$) seems to be more consistent with the experimental facts.

BOCKRIS, SRINIVASAN and MATHEWS[25,48~50] have calculated the separation factors H/D and H/T for reaction (30) on the basis of the potential-energy surface of the pseudo-triatomic system (H_2O)–H–Hg, constructed by the EYRING–POLANYI's method. In these calculations both the bending and stretching vibrations (the latter neglected by KEII and KODERA[59]) have been taken into account. The values found for H/D and H/T separation factors, tunnelling excluded, are less than the experimental ones, which leads to the conclusion that a tunnelling correction is necessery. This correction was estimated using an Eckart barrier model with a height $E = 1.5 \cdot 10^{-12}$ erg (at $\eta = 0$) and a width of 4 Å, both found by fitting to the experimental data. With these parameters (for which $\gamma/\delta \simeq 0.9$) one obtains a significant variation of the tunnelling factor $\mathscr{X}_t$ with the electrode potential which confirms the results of earlier calculations of CHRISTOV[42] for nearly the same barrier parameters. The value of $\mathscr{X}_{\mathrm{H}} \simeq 3$ calculated by BOCKRIS *et al.* is also near to the one found by CHRISTOV.[20,21]

The main contribution in the work of BOCKRIS *et al.*[48~50] is the very probable explanation proposed for the experimentally established strong dependence of the H/T separation factor on overpotential which seems not to be interpretable in any other way. As far as the numerical results and their agreement with earlier estimates[20,21,42] are concerned, the importance of this fact is not to be overestimated. The method used by BOCKRIS *et al.* is, indeed, not very reliable. The well known inaccuracy of the calculations of potential-energy surfaces has already been discussed in Secs. 2, 3, 5. The height of the "ideal" barrier (4–6 kcal) found by BOCKRIS *et al.*, is not unreasonable but the results for the frequencies of vibration in the transition state cannot be accepted as relevant. The argument[48~50] that these frequencies are slightly affected by large variations of the ratio $\rho = Q_{jk}/E_{jk}$ between the coulombic and total bond energy is also valid for the imaginary frequency $\nu_t^{\ddagger}$ related to the curvature of the energy profile along the reaction path at the saddle-point. According to the data of BOCKRIS *et al.* this frequency is very low ($\nu_t^{\ddagger} = 50 - 90i$), which means that the tunnel-effect should be completely negligible for the "ideal" (true) barrier and therefore the calculated separation factor ($S_{\mathrm{HD}} = 2.4$) would be lower than the ones observed ($S_{\mathrm{HD}} \simeq 3.1$–$3.4$). Application of the SATO method would surely give more tunnelling[11b] than the method of EYRING–POLANYI used by BOCKRIS *et al.* but the interactions of the proton with the water dipole molecules must be also taken into account in exact calculations.[24c]

To estimate the tunnelling correction BOCKRIS *et al.*$^{25,48\sim50)}$ chose a barrier height near to the experimental activation energy at random. Thus the stable vibrations of the activated complex are derived from the properties of the "ideal" barrier while the instable vibration, *i. e.* the profile of the reaction path is related to the "real" barrier. This inconsequence is the main disavantage of the method used by BOCKRIS *et al.*. That is why it can be affirmed that the writer's method which refers only to the "real" barrier, is more relevent[*] although the difficult problem of the proton tunnelling through the "ideal" barrier remains undecided in the frame of this consideration.

All results above have been obtained on the basis of a one-dimensional consideration of the proton transfer in the discharge reactions (30). The reasons for this approximation have already been discussed (Sec. 6) as the possibility of a multi-dimensional interpretation of the numerical results if the conditions of such an approximation would not be strictly fulfilled. Qualitatively, many of the general conclusions, concerning the electrochemical proton discharge, should be the same in both one-dimensional and many-dimensional treatment. It should be emphasized though that the remarkable constancy of the symmetry factor α over a range of about 2 volts in the case of hydrogen evolution on mercury$^{27,28)}$ would hardly be explained if we supposed that non-equilibrium solvation of the proton played an essential role for the rate of the process. Thus, the one-dimensional approximation receives further support for electrode reactions of type (30).

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[*] The affirmation of BOCKRIS *et al.*$^{25)}$ that the zero-point energies are neglected in this method, is incorrect as explained in Sec. 5. In this way the conceptual difficulties in the quantum-mechanical calculation of the partition functions of the activated complex (Sec. 2) are also removed.

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