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SOME COMMENTS ON THE DEVELOPMENT OF THE THEORY OF PROTON TRANSFER IN SOLUTION

By

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Abstract

The bond stretching model and the solvation barrier model for proton transfer in solution and their relations to the author's work are considered. The essential results of that work are shown to be quite independent of any assumption about the relative role of the bond-stretching and the solvent reorganization in the proton transfer. Some misinterprations of the above treatment are discussed.

In a recent paper of DOGONADZE and KUZNETSOV[1] two different approaches to the calculation of the probability of proton transfer in polar media have been compared. The first one, originating from the work of HORIUTI and POLANYI[2], takes into account only for the stretching of the chemical bond $A-H^+$ of a molecule AH^z in a solution due to the chemical excitation of the vibrational states in the course of reaction. The other approach, used by DOGONADZE et al.[3,4], consideres the primary role of the solvent polarization which changes during the proton transfer process, according to an idea suggested first by LIBBI[5] and developed further by MARCUS[6], HUSH[7], LEVICH and DOGONADZE[8] for election transfer processes. A similar comparison between the two approaches is also made in a paper of KRISTALIK, TSIONSKY and TITOVA[9]. Surprisingly, in both papers, as well as in some earlier papers of the same authors[10], my work[11,12] is quoted as a treatment of proton transfer reactions in which the role of the solvent is "entirely ignored" as in the bond-stretching model of HORIUTI-POLANYI[2] used by other authors[13]. This statement is, however, completely incorrect, which is easily seen if one reads more carefully my papers[11,12].

The choice of a model to describe a physical process depends largely on the purpose of investigation. The model may be adequate to reality in some respect and not adequate in an other respect. Thus, in 1935 HORIUTI

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and POLANYI described the proton transfer reaction $AH^+ + B \rightarrow A + H^+B$ in terms of a potential barrier obtained by the intersection of two curves representing the electronic energies of the bond to be brocken $(A-H^+)$ and the bond to be formed (H^+-B) as functions of the corresponding internuclear distances. This barrier model leads to a relationship between classical activation energy E_c and reaction heat Q of the form

$$E_c = E_c^0 + \beta_c Q, \qquad E_c - Q = E_c^0 - \alpha_c Q \qquad (1)$$

where β_c and $\alpha_c = 1 - \beta_c$ are the "transfer coefficients" assumed to be constants. These relations permit to derive the BRÖNSTEDT equations for acid-base catalysis which relate the rate constants to the dissociation constants of the acid and the base. In a similar way one can obtain, as pointed out by FRUMKIN[14] the TAFEL equation in electrode kinetics. It is easily seen that these conclusions follow from the geometric properties of the potential barrier and *not* from the assumption that the barrier represents the electronic energy of the system $A-H-B$. This model explains also the influence of the nature of the metal on the hydrogen evolution reaction. The theory of HORIUTI-POLANYI[2] is consistent in the framework of the classical model assumed. However, this model is not adequate since the calculations show that at the actual internuclear distances the quantum-mechanical tunneling of the proton plays a dominant role[*]. This suggests that the solvent effects are important in proton transfer processes.

DOGONADZE *et al.*[3,4] have used a harmonic oscillator model[6,8] to describe the dynamical role of the solvent in proton transfer reactions. The general approach is based on a separation of variables using either a harmonic approximation for the proton vibration or a double adiabatic approximation, which means to include the proton energy into the electronic energy to obtain an effective potential for the motions of solvent molecules. This procedure implies that a solvent fluctuation is necessary to make possible the proton transfer by a tunneling process from the initial ground state to the final ground state of vibration. Thus, no any change of the $A-H$ bond-length takes place, so that the activation energy is entirely determined by the solvent reorganization. In the framework of this model a consistent quantum-mechanical theory is used to calculate the proton transfer probability, which is essentially based on the assumption that the FRANCK-CONDON approximation is valid (*i. e.* the proton tranfer occurs at fixed positions of the solvent molecules). A more careful examina-

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[*] The possibility of proton tunneling was first assumed by POLANYI[15] who stimulated the calculations of BAWN and OGDEN[16]. Similar calculations have been performed by BELL[17], CHRISTOV,[11a,18] CONWAY[19], DOGONADZE *et al.*[4]

tion of this assumption seems to be necessary[*]. In any case, the model of DOGONADZE *et al.* is convenient to describe, at least qualitatively, the role of the solvent in proton transfer processes. This model is, however, incomplete as far as the translation-rotation motions of solvent molecules are disregarded[6]. It implies, moreover, that the solvent fluctuation takes place at a fixed distance between reactants. A justification of this adiabatic approximation is desirable. The model may be also not adequate, because it neglects completely the stretching of the A−H bond in all proton-transfer reactions[**].

On the basis of the above assumptions the theory of DOGONADZE *et al.*[3,4] provides a detailed picture of the molecular mechanism of charge transfer in solution and, in particular, of proton transfer at electrodes. The consequences of this theory agree qualitatively with the experimental facts concerning both the influence of the cathode nature on the proton discharge and the so called barrierless and activationless hydrogen evolution reactions[9]. However, the isotope effects are explained only by a change of the preexponential factor K in the ARRHENIUS equation

$$v = Ke^{-E_a/kT},\tag{2}$$

since the activation energy E_a is assumed to depend entirely on the solvent properties. This conclusion is not in accordance with the observation that in many proton transfer reactions[21], including proton discharge[32], the isotope substitution affects both K and E_a[21]. Furthermore, the theory of DOGONADZE *et al.*[3,4] is not able at present to justify a fundamental equation of chemical kinetics—the TAFEL relation

$$\eta = a + b\ln i\tag{3}$$

which is shown to be valid for the hydrogen evolution in a wide range of overvoltage η ($\sim$1 V and more) and several orders of magnitudes with respect to the current density i.

Thirty years ago (1945–1948), my first work on the theory of metal ion discharge[22 a] was stimulated by GURNEY[23] who was the first to introduce the concepts of quantum mechanics in electrochemistry. The potential barrier is assumed to be a result of the intersection of two curves which describe the interactions of the ion with the polar solvent and the metal

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[*] See footnote on p. 41.

[**] Calculations with two dimensional models for the gas phase reaction AH+B→ A+HB, where A and B are heavy particles (or atomic groups), show[20] that the most probable configuration A-H-B at which the H-atom transfer occurs, involves a considerable stretching of the A-H bond.This might be the situation in the case of proton transfer in solution too.

lattice, respectively. This model implies a slow motion of the ion and an adiabatic adjustment of the motions of the solvent molecules and the electron cloud in the metal. Subsequently[22 b], a similar picture was used to describe the proton discharge: "We can represent the energy barrier for the proton transfer by a potential curve in the metal-electrolyte boundary region, obtained by combination of two separate curves representing the potential energy of the proton in hydrated and adsorbed state, respectively. The first curve will have a deep well because of the large hydration energy of the proton, due to the considerable Coulomb forces acting between it and the electric dipoles of the water molecules, which are related to the small radius of the proton. The potential curve for adsorbtion has the same form as that for adhesion of metal ions to the lattice of the same or an other metal" (Ref. (22 b), pp. 67–68). Clearly, this is *not* the HORIUTI-POLANYI bond-stretching model in which the interaction of the proton with the solvent is completely ignored but, in contrary, this is a model which neglects entirely the bonding between the proton and the water molecule. This is certainly an oversimplification of the real situation, which is, however, allowed for the purpose of the investigation considered.

The problem was to derive the relationship between current density and electrode potential taking into account for the possibility of nuclear tunneling. For the purpose it is necessary to solve the SCHRÖDINGER equation

$$\frac{\hbar^2}{2\mu}\,\Delta\phi+\left(E-V(x)\right)\phi=0 \qquad\qquad (4)$$

in order to calculate the transition probability through and over the potential barrier $V(x)$. The solutions $\phi(x)$ depend only on the shape of the barrier and *not* on the nature of the potential energy involved. Using an arbitrary (one-dimensional) barrier model a current expression of the form

$$i = \mathcal{X}_t(Q,\,T)\,K^{cl}\mathrm{e}^{-E_c(Q)/kT} \qquad\qquad (5)$$

has heen derived[22], where the classical activation energy E_c is expressed as a function of reaction heat $Q=Q_r+\varepsilon\eta$, or overvoltage η, by

$$E_c = E_c^r-\alpha_c\varepsilon\eta\,. \qquad\qquad (6)$$

In (5) $\mathcal{X}_t(Q,\,T)$ is the tunneling correction to the classical TAFEL equation

$$i^{cl} = K^{cl}\mathrm{e}^{-E_c(Q)/kT} = i_0^{cl}\mathrm{e}^{\alpha_c\varepsilon\eta/kT}\,.$$

This correction depends on the geometrical properties of the barrier, the mass of the ion, the temperature and is generally a function of reaction

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heat Q (or overvoltage η). Therefore, in the general case, expression (5) does not represent the TAFEL equation (3). The conditions at which $\mathscr{X}_t(\eta, T)$ may be independent of η have been also discussed in that time[22].

The problem has been treated again more extensively in a later period (1958–1963), using different one-dimensional models for the potential barrier (such as the asymetric ECKART and parabolic potentials[11 a,18]). In this way it has been possible to estimate the tunneling correction $\mathscr{X}_t = i/i^{cl}$ by both numerical and analytical calculations. The quantum-mechanical justification of the TAFEL equation (3) is given for the first time in 1958, when considering a large amount of tunneling ($\mathscr{X}_t \simeq 300$) through an ECKART barrier[11 a]. A general treatment of the problem in a closed analytical form, including any possible tunneling degree, has been done using an asymetric parabolic barrier[24 a]. This allows to determine the conditions of validity of TAFEL equation and to derive expressions for the TAFEL slopes[18 b] $b = d\eta/d\ln i$. Formulas for the classical transfer coefficients β_c and α_c have been also obtained[11,24]. For an arbitrary potential barrier $V(x)$

$$\beta_c = \frac{1}{2}\left(1 + \frac{\gamma^2 Q}{4E_c^0}\right), \qquad \alpha_c = 1 - \beta_c, \qquad Q = \varepsilon(\varphi - \varphi_0), \qquad (7)$$

where E_c^0 is the barrier height at the electrode potential $\varphi = \varphi_0$ ($Q = 0$) and $\gamma \leq 1$ (for a parabolic barrier $\gamma = 1$).

The temperature dependence of the current as well as the kinetic isotope effects have been also investigated by means of the same simple barrier models[18 a,b]. A characteristic temperature was introduced[11 a] as a very useful criterion for determining the role of nuclear tunneling. The simple expression[25]

$$T_k = \frac{h\nu^{\ddagger}}{\pi k}, \qquad \nu^{\ddagger} = \frac{1}{2\pi}\sqrt{\frac{f^{\ddagger}}{\mu^{\ddagger}}} \qquad (8)$$

was derived for any simple continuous barrier, where $\nu^{\ddagger}$ is the frequency of an imaginary vibration with a force constant $f^{\ddagger}$ equal to the absolute value of curvature just at the barrier top, $\mu^{\ddagger}$ being the effective mass transferred. In the temperature range $T > T_k/2$ the tunneling correction can be estimated by the formula[24 a,25 c]

$$\mathscr{X}_t = \frac{(\pi/2)(T_k/T)}{\sin[(\pi/2)(T_k/T)]} - \frac{1/2(T_k/T)}{1 - 1/2(T_k/T)}$$
$$\times \exp\left[\left(\frac{T_k}{T} - 2\right)\delta_0(E_c - Q)\right]. \qquad (9)$$

The second term may be neglected for $T > 2/3\,T_k$. At $T = T_k$, by defini-

tion[11a,25a], the probability for tunneling is just equal to the probability for hopping over the barrier. For $T > 2T_k$, $\mathscr{X}_t \simeq 1$, *i. e.* the nuclear motion practically obeys the laws of classical mechanics. For $T < T_k/2$ tunneling largly prevails and quantum mechanics is absolutely necessary to describe the reaction course.

Evidently, the general results from these investigations are independent of the assumptions concerning the nature of interactions determining the barrier potential. No any statement is made anywhere in my work that the potential energy should be necessarily related to the bond stretching as in the Horiuti-Polanyi model[*]. In contrary, it is claimed quite definitely that "the potential energy conditioned by the interactions of ion with all the surrounding particles in the metal and the solution passes through a maximum determining the height of the energy barrier for this process" (Ref. (18c), p. 724). It is only the *existence* of the barrier a necessary condition for the derivation of the current-potential relationship (5) and for several other general conclusions concerning the temperature dependence of the current, the Bröndstedt relations, the isotope effects *etc.*[11,22,24~26] The restriction to a one-dimensional potential barrier is not essential for the purposes of a *qualitative* description which incorporates the nuclear tunnel effect in the theory of proton transfer processes. It is, however, in general, not adequate to the real situation, where the potential energy is a function of all nuclear coordinates of the system, including reactants and solvent molecules. Therefore, a more complete description of reaction requires a multi-dimensional treatment using a potential energy surface $V(x_1 x_2 \cdots)$ instead of a potential curve $V(x)$.

The way for a generalization of the theory in this direction has been discussed in details already in Ref. (26). The first step is to relate the reaction to the classical motion of a configuration point along the line of minimum energy on the potential surface as made in the transition state theory. The second step is to include a factor $\mathscr{X}_t$ which takes into account for the non-classical behaviour of nuclei for motion along the reaction path. Assuming this motion to be entirely separable from the other motions (vibrations and rotations) we can calculate the tunneling correction in the usual way to obtain an equation of the form (5). This is the reason for

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*) This model has been used sometimes[11a,18b,24] for qualitative discussions emphasizing, however, its shortcomings rather than its advantages. Thus, it is claimed that "in the presence of pure electrostatic interactions one can put some objections towards this model" (Ref. (24a), p. 847).

the statement: "It is necessary to underline that the relation (7)*) and the conclusions derived from there have rather general character. This follows from that, that the one-dimensional barrier can be considered as a profile along the "reaction path" on the surface of the many-dimensional barrier" (Ref. (26), p. 1557). A complete separation of the reaction coordinate is possible, for instance, if one treats the motions of reactants and products (including solvent molecules) as harmonic vibrations. This is just the model used by DOGONADZE *et al.*[3,4] in their treatment of electrotn and proton transfer processes. Therefore, many results of my previous investigations, based on an one-dimensional barrier potential, can be applied to this model, without any restrictions concerning the tunneling degree**).

The main shortcomings of the oscillator model, as mentioned above, is the neglect of the translation-rotation motions of reactants and solvent molecules. In particular, inclusion of the relative translation of reactants would lead to a curvelinear reaction coordinate as in gas phase reactions. This coordinate is dynamically non-separable except in reactants (products) region and transition state, *i. e.* the saddle on the potential surface. This restricts the applicability of one-dimensional calculations for *quantitative* estimates of tunneling corrections to relatively high temperatures, at which tunneling occurs mainly in an area around the saddle-point, *i. e.* near the top of the barrier along the reaction coordinate. Thus, in the region of moderate tunneling $(T > T_k/2)$ a corrected transition state theory expression for the rate constant

$$v = \mathscr{K}_{ac} \frac{kT}{h} \frac{Z_{ac}^{\ddagger}}{Z} e^{-E_c/kT} \tag{10}$$

applies, where $\mathscr{K}_{ac}$ is given by the first term in (9), $Z_{ac}^{\ddagger}$ is the partition function of the "activated complex" (transition state) and Z is the full partition function of reactants, both including the surrounding solvent molecules. This is just the expression discussed in my papers Ref. 11 b) and (26). Introducing (6), (7) and (9) into (10) gives a current-voltage relation of the type (5). The resulting expression is more general than (5) as far as *all* degrees of freedom of the over-all system (reactants + solvent) are included into the multi-dimensional potential surface, however, it is restricted to the temperature range $T > T_k/2$, while equation (5) applies for all temperatures.

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*) It corresponds to Eq. (5) of the present paper.
**) This has been recently done using the harmonic oscillator model for the solvent in the framework of a complete theory of electron-transfer processes[27]. A similar treatment is possible to a large extent for proton-transfer processes[27 b].

An important consequence from (10) is that the TAFEL equation is always valid in the range of moderate tunneling $(T > T_k/2)$ where the second term in (9) only slightly depends on reaction heat Q (*i. e.* on electrode potential η) provided the classical transfer coefficient (7) is nearly constant, which requires that $r^2 Q/4E_c^0 \ll 1$. This justifies the conclusions derived earlier[18 b,24] by means of an one-dimensional treatment of ion (proton) transfer processes.

A more general treatment of these processes has been proposed on the basis of a new formulation of chemical kinetics[28], which leads to an equation of the form

$$v = \mathscr{X} \frac{kT}{h} \frac{Z^{\#}}{Z} \, e^{-E_c/kT} \tag{11}$$

where $Z^{\#}$ is a partition function of *reactants* in which the motion along the reaction coordinate is excluded and $\mathscr{X}$ is a suitably defined quantum correction factor. The derivation of (11) is based on an exact quantum-mechanical expression in which the notion of an "activated complex" is avoided, *i. e.* no use is made of the hypothesis that the transition state represents a stationary state configuration being in thermal equilibrium with reactants. A formal generalization of activated complex theory in which $\mathscr{X}_{ac}$ in (10) represents an *exact* quantum correction was more recently proposed[28 b]. A comparison between the classical limits of (10) and (11) then shows, that if $\mathscr{X}_{ac} = 1$ equation (10) corresponds to the extreme case of a *very slow* motion along the reaction coordinate and when $\mathscr{X} = 1$ expression (11) refers to the other extreme case of a *very fast* motion along the classical reaction path. These general formulations of the reaction rate theory allow a reconsideration of all previous investigations of ion transfer processes[*]. In this way, as already shown in Ref. (12), a justification of many earlier results on the basis of an exact quantum-mechanical theory becomes possible.

The above inspection shows that the *essential* results of my work on the theory of ion-transfer processes are not related with the bond-stretching model of HORIUTI–POLANYI[2] nor with the recent solvation barrier model of DOGONADZE *et al.*[3,4] For the purposes of my investigations no *a priori* assumptions have been made about the part played by the bond-stretching or the solvent reorganization, because, in principle, *both* are included in

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[*] This was first presented at the *Electrochemistry meeting in Moscow*, April, 1971 as well as at the *22nd Meeting of the International Society of Electrochemistry*, Dubrovnik, Yugoslavia, September 1971, followed by the *International School of Quantum Electrochemistry*, Ohrid, Yougoslavia, September, 1971. See Ref. (12).

the potential barrier.

Therefore, there is a large misinterpretation of the results of my work as presented in the papers of DOGONADZE *et al.*[1] and KRISTALIK *et al.*[9] This can be immediately seen just in my papers refered to by those authors. Thus, for example, it is stated: "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 configurations of the unreacting atoms or no considerable departure from the equilibrium polarization of the solvent occur during the proton transition. In the last case a multi-dimensional 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 ($\mu^{\#} \neq m_{\mathrm{H}}$)" (Ref. (11 b), p. 182). This statement concerns a semi-empirical approach for estimating the parameters of an *effective* one-dimensional barrier using experimental data for isotope effects which has been used independently by BELL[29] and myself[18]. The results of such calculations are usually interpreted[29,30] by means of the bond-stretching model as parameters of the actual barrier for the proton transfer. The above interpretation in terms of a many-dimensional barrier, including motions of reactants and solvent molecules, has been first proposed by myself in Ref. (26). According to this interpretation "using experimental values for the kinetic parameters one can estimate the barrier height E_t and the product $l\sqrt{\mu}$, *i.e.* determine $\mathscr{X}_t$ without knowledge of the effective mass μ. If we assume $\mu = m_{\mathrm{H}}$ we can calculate the width $2l$ of a parabolic barrier which approximates the top region of the effective one-dimensional barrier for the proton discharge. The one-proton approximation is, however, not a necessary condition for estimating the role of the tunnel effect in the above manner" (Ref. (26), p. 1558). Repeatedly, it is stated: "Assuming that proton-transfer processes occur in the region of moderate tunneling we can estimate the tunneling corrections 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 Eq. (3) without knowlege of the potential energy surface. Inversely, we may estimate the dimensions of the 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 $\mathscr{H}_t$ between 1 and 7 have been found thereby confirming the rule of a moderate role of tunneling in proton-transfer processes in solution" (Ref. (12), p. 70).

I believe, it is not necessary to give more references to show that the general approach in my work is based on the idea that, *a priori*, bond-stretching and solvent reorganization play equally important roles in the kinetics of proton transfer processes. Consequently, the statements of DOGONADZE *et al.*[1] that I treat the proton-transfer only "as the process of movement of the system on two-dimensional potential energy surface" and "this approach ignores entirely the rearrangement of the solvent molecules in the course of the reaction" are quite misleading.

Actially, the two-dimensional considerations in Ref. (11 b) concern only the simple gas phase reactions of the type AH+B→A+HB, where A and B are heavy atoms or atomic groups, for the purpose of comparing with the results of the usual one-dimensional treatment of the reaction coordinote. The comparison shows that this treatment overestimates the tunneling corrections not to much if the reaction proceeds in the region of moderate tunneling ($T > T_k/2$) or somewhat in the region of large tunneling ($T \lesssim T_k/2$) as is usually the case at room temperatures. The same conclusions are recently drawn in an undoubted way on the basis of exact two-dimensional calculations[28 b]. These conclusions agree with the results of the above semiempirical approach of estimating tunneling corrections for proton transfer in solutions[18,29], which actually imply, as discussed above, a multi-dimensional potential surface including all motions of reactants and solvent molecules[11 b,26]. At $T \gtrsim T_k/2$ the most probable reaction path crosses the saddle point of the surface very near to the classical reaction coordinate[20], which allows an approximate estimation of the tunneling correction using the energy profile along that coordinate. In particular, in the temperature range $T > 2/3 T_k$, the first term of formula (9) represents a quite good approximation, provided T_k is calculated by (8) with the corresponding value of the *effective* mass $\mu^{\ddagger}$. Taking $\mu^{\ddagger}$ to be equal to the proton mass ($\mu^{\ddagger} = m_H$) leads to lower values of the tunneling corrections[11 b,20]. These conclusions are valid not only for two-dimensional but also for arbitrary many-dimensional potential surfaces[*].

This is the basis of the explanation of the isotope effects in hydrogen

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[*] WIGNER[31] has shown that for a $n+1$ dimensional energy surface the tunneling correction is given to a first approximation by $\mathscr{H}_t = 1 + h\nu^{\ddagger}/24\,kT$. This result may be obtained by a series expansion of the first term in (9) if only the first two terms of the series are considered.

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evolution I proposed in Ref. (12). There, the above formula (9) for the tunneling correction was used, which implies a parabolic approximation of the potential along the *reaction coordinate* in the vicinity of the saddle point of the many-dimensional potential surface (See Fig. 1 in Ref. (12)). Although, quantitatively, this formula is sufficiently accurate only for $T > 2/3 \, T_k$, it is quite suitable for qualitative purposes also for $T \gtrsim T_k$[*]. It follows from it that "the tunneling factor $\mathcal{X}_t$ will generally decrease with the increase of (the electrode potential) φ[2,7]. If $T > 2/3 \, T_k$ the second term in (7 a) may be neglected so that Eq. (3) is obtained, which is now independent of $Q(\varphi)$. It results that the electrolytic separation factor according to (6) should decrease with the increase of electrode potential, when $T < 2/3 \, T_k$ and it remains constant when $T > 2/3 \, T_k$. These predictions seem to be the unique explanation of the experimantally 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 $T \approx T_k/2$ it may proceed in the second case in the region $T > 2/3 \, T_k$" (Ref. (12), p. 71).

KRISHTALIK *et al.*[9] have misinterpreted the above explanation when claiming that in it the "proton coordinate" is concerned. Actually, in Ref. (12) T_k is defined by the above Eq. (8) for a many-dimensional energy surface and at $T \gtrsim T_k/2$ the formula (9) for $\mathcal{X}_t$ refers to tunneling along the reaction coordinate in the saddle-region. It is *not* the proton, but a configuration point with an effective mass $\mu^{\ddagger}$ which tunnels through the barrier along that coordinate. Both the motions of the proton and the solvent molecules, which are not separable in the saddle-region[27 b], are included in this description of the tunneling process (although practically the quantum behaviour of the system is determined by the proton motion only). Isotope substitution ($H \rightarrow D$) affects T_k and $\mathcal{X}_t$ through the corresponding change of the effective mass. Any change of the barrier along the "proton coordinate", which facilitates tunneling of the proton, will increase the tunneling of the system-point along the *reaction coordinate,* too. This situation can be described also in terms of the change of an *effective*

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[*]) Formulas for $T \lesssim T_k/2$ and $T \ll T_k/2$ are also given in Ref. (12) (Eqs. 7 a, b, c). See also Ref. (24 a).

barrier for the proton tunneling, in the sense discussed above. This is the meaning of the explanation of the isotope effects in electrolytic hydrogen evolution proposed in Ref. (12). Evidently, it is not related with the bond-stretching model at all, as incorrectly claimed by KRISHTALIK *et al.*[9] Evidence that the parameters of the many-dimensional barrier considered fit the conditions $T \gtrsim T_k/2$ was also given by stating that "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 $\mathscr{X}_t$ according to (7 a, b) is consistent with the classical (practically constant) TAFEL slopes in the corresponding region $T \gtrsim T_k/2$" (Ref. (12), footnote p. 71).

It should be stressed that in this way it is possible to explain the experimental fact[32] that in hydrogen evolution both the apparent activation energy E_a and the pre-exponential factor K in the empirical ARRHENIUS equation (2) change due to the isotope substitution. This fact contradicts the consequences of the model of DOGONADZE *et al.*[3,4], that E_a remains the same and only K is affected by that substitution.

There are no any difficulty, in principle, to explain the barrierless and activationless processes, as well as the influence of the nature of metal cathode on the proton discharge, by means of the concept of a potential surface including all interactions with the solvent and the metal. The formulas (7) for the classical transfer coefficients

$$\beta_c \equiv \frac{\partial E_c}{\partial Q}, \qquad \alpha_c = 1 - \beta_c, \tag{12}$$

can be easily derived[24 a,b] using the parabolic approximation of the barrier potential along the *reaction coordinate* near the saddle point. The quantum transfer coefficients defined by[11 b,12]

$$\beta \equiv \frac{\partial E_a}{\partial Q}, \qquad \alpha = 1 - \beta, \tag{13}$$

where E_a is the experimental activation energy, can be related to the classical ones by the equation[12,28 a]

$$\beta = \beta_c + kT^2 \frac{\partial^2 \ln \mathscr{X}}{\partial T \partial Q} \tag{14}$$

which follows from (10) or (11). We have $\beta = 1$ $(\alpha = 0)$ for barrierless and $\beta = 0$ $(\alpha = 1)$ for activationless processes, hence

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$$\beta_c = 1 - kT^2 \frac{\partial^2 \ln \mathscr{X}}{\partial T \partial Q}, \qquad \text{barrierless}$$

$$\beta_c = kT^2 \frac{\partial^2 \ln \mathscr{X}}{\partial T \partial Q}, \qquad \text{activationless}. \qquad (15)$$

These relations are quite general and independent on any hypothesis about the detailed machanism of the reaction. Eqs. (13) and (14) show that only if the quantum correction $\mathscr{X}$ is independent of reaction heat Q (or electrode potential φ), then, $\beta = \beta_c$ $(\alpha = \alpha_c)$. This is certainly the case when the reaction proceeds in the region of moderate tunneling $(T > T_k/2)$ where the second term in (9) may be neglected. In the region of large tunneling $(T < T_k/2)$ however, in general, $\beta \neq \beta_c$ $(\alpha \neq \alpha_c)$. This is, in particular, the situation when barrierless and activationless processes occur for which according to (15) $\beta_c < \beta = 1$ and $\beta_c > \beta = 0$, respectively. These general conclusions have been illustrated using simple (one-dimensional) models for the barrier along the reaction coordinate assumed to be separable[11 b].

Another definition of the transfer coefficients

$$\beta_k \equiv -kT \frac{\partial \ln v}{\partial Q}, \qquad \alpha_k = 1 - \beta_k, \qquad (16)$$

closely related to the BRÖNSTEDT equation (TAFEL equation), should be distinguished from (13). We obtain, indeed, from (10) or (11) the relation

$$\beta_k = \beta_c - kT \left(\frac{\partial \ln \mathscr{X}}{\partial Q} + \frac{\partial \ln K}{\partial Q} \right) \qquad (17)$$

where $K = \frac{kT}{h} \frac{Z^{\neq}}{Z}$, which generally differs from (14). As pointed out in Ref. (12), p. 73, only when both the quantum correction $\mathscr{X}$ and the partition function ratio $Z^{\neq}/Z$ are independent of reaction heat, we obtain $\beta_k = \beta = \beta_c$. Therefore, a possibly detectable difference between β_k and β may give us evidence for a large degree of tunneling[12] and should be taken into account when interpreting the barrierless and activationless processes too[27 b]. This detailed discussion is obviously overlooked by KRISHTALIK *et al.*[9]

The general trend of my investigations has been to avoid possibly all unnecessary assumptions which may restrict the validity of the relations derived. Such assumptions are, for instance, that only the bond-stretching or only the solvent reorganization are responsible for the proton transfer. In the general case, the activation process involves approaching of reactants, changes of chemical bonds and rearrangement of solvent molecules. The relative role of each of these processes may vary to a large extent with the variation of reactants and solvent nature. Therefore, a general

theory of reactions in solution should take into account *a priori* in an equal way for all degrees of freedom of reactants and solvent[12].

The way to the generalization of a theory is not always easy and straightforward. Different ways are often followed by different investigators. In chemical kinetics the solvent effects have been frequently neglected[2] or underestimated when applying transition state theory, account being taken usually by approximate estimates of the solvation energy of reactants and activated complexes in assuming equilibrium configuration of the solvent molecules[33]. In the first period of my own work[22,24] a such reversible solvation during the ion transfer has been also implicitly assumed, however, without using activated complex theory. The dynamical role of the solvent was first taken into account in electron-exchange reactions. For the purpose MARCUS[6] and HUSCH[7] used transition state theory in treating adiabatic processes, while LEVICH and DOGONADZE[8] were concerned with a treatment of non-adiabatic reactions on the basis of the quantum-mechanical perturbation theory. The possibility of a similar consideration of proton transfer was first discussed by KUZNETSOV[34] in terms of the (not very clearly defined) notion of a "proton term". Independently, during the Faraday Discussion on "The Kinetics of Proton Transfer Processes" (1965) BELL[35] raised the question of a possible role of non-equilibrium solvation from point of view of the activated complex theory. This discussion[*] stimulated my work[11b,26] in the direction of a generalization of the theory to include both solvent-effects and quantum effects (nuclear tunneling) in a many-dimensional description of the (adiabatic) proton-transfer reactions. In the same time DOGONADZE, KUZNETSOV and LEVICH[3] applied the harmonic oscillator model for the solvent to the proton discharge, introducing the concept of an "electron-proton term" in a well defined way. This model is very useful for an application of perturbation theory to describe the irreversible solvent polarization in non-adiabatic processes, but it might overestimate the role of the solvent in the proton transfer. In the subsequent development of the theory by DOGONADZE *et al.*[4] the adiabatic processes are also considered by introducing additional criteria for a separation of the proton motion from that of solvent molecules in the transition

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*) During this discussion[36] I emphasized at many places the role of the solvent (reversible and irreversible polarization) in proton transfer processes. Thus, for instance, it is stated: "If we assume a barrier width of $r_0 \simeq$ 0.5–0.8 A (for an orientation of one H–O-bond normal to the electrode surface), which leads to large proton tunneling, it is again possible to explain the experimental facts by supposing a significant contribution of non-equilibrium solvation of the transitoin state to the activation energy" (Ref. (36), p. 255). See also p. 60, 263, 266.

configuration of the system[*]. Account is taken, in principle, also for the bond stretching, however, the primary role is ascribed to the reorganization of the solvent. In my recent work[28] the nonadiabatic processes were included in the general formulation of the theory. A detailed treatment of electron transfer reactions from this point of view, in which the restrictions of perturbation theory are avoided, was presented using the harmonic oscillator model for the solvent[27]. A similar treatment of proton transfer processes is also possible[27 b]. Thus, differet ways have been followed by DOGONADZE *et al.*[3,4] any myself to a more general theory of charge-transfer in solution.

The famous theory of HORIUTI and POLANYI[2] has played and plays also nowadays an important role by stimulating the development of chemical kinetics. The more recent theory of LEVICH and DOGONADZE,[8] further developed extensively by DOGONADZE *et al.*[4], is certainly an important contribution to the study of charge-transfar processes in solution. To recognize this does not mean at all that this is the unique consistent

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[*] The conditions for a separation of the motions of proton and solvent molecules was initially defined by[3]

$$\varDelta E = h\nu_p \gg h\nu_s \, (<kT) \tag{a}$$

where ν_p and ν_s are the vibration frequences of the proton and the solvent molecule, respectively. This implies, that both the electron and proton transfer probabilities are very small (completely non-adiabatic reactions), so that the electron-proton transfer takes place in a very small region of configuration space (including proton and solvent coordinates). If, however, the electron transfer probability is large (electronically adiabatic processes), then, there is a large transition region in configuration space in which the above condition of separability is not applicable.

Subsequently[4] an additional condition

$$\varDelta E_p^{\ddagger} = h\nu_p^{\ddagger} \gg kT \, (>h\nu_s) \tag{b}$$

for the transition region is introduced. Here $\nu_p^{\ddagger}$ is defined by (8) for a motion along the proton coordinate, so that the above condition is actually identical with $T \ll T_{\not k}^p \, (T < T_{\not k}^p/2)$, which means that the proton transfer occurs predominantly by tunneling. If, however,

$$\varDelta E_p^{\ddagger} = h\nu_p^{\ddagger} \lesssim kT$$

i. e. $T \gtrsim T_{\not k}^p \, (T > T_{\not k}^p/2)$, the proton motion in the transition region is a quasiclassical (or classical) one and cannot be separated from the motions of solvent molecules[27b]. The FRANCK-CONDON approximation (fixed positions of solvent molecules during the proton transfer) is not applicable in this situation, although $h\nu_p \gg h\nu_s$ in the initial and final state. The conditions (a) and (b) together justify the double adiabatic approximation used by DOGONADZE *et al.* The idea to include the energy of a fast vibration into the adiabatic potential of the system has been first proposed by HIRSCHFELDER and WIGNER[37] as an way for a justification of transition state theory. The work of DOGONADZE *et al.* is a successful application of this idea to nonadiabatic processes. This point will be discussed elsewhere[27b].

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quantum theory of these processes, nor that earlier or other simultaneous investigations in the same field should be overlooked or misinterpreted. Representing an older generation, I believe, it is necessary to quote all what has been done previously by other authors and to compare more carefully the results obtained by different methods. An objective information is needed for the history of the field and for the education of young people starting research in that field. It would be useful for everybody to know that any problem can be treated using different aproaches, each of them having some advantages and some shortcomings. Therefore, any attempt to treat the theory of charge transfer from an other point of view could contribute to a more complete understanding of these complicated chemical processes.

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