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The Fundamental Step in Electrode Reactions

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The modern quantum-mechanical theory of the fundamental step in electrode reactions, which takes into account the necessity for the reorganisation of the polar medium and the qualitative difference between the behaviour of classical and quantum-mechanical degrees of freedom, is briefly reviewed. The experimental studies on the influence of various factors on the pre-exponential factor, the kinetic isotope effect, and the activation energy for the evolution of hydrogen have demonstrated a satisfactory agreement with the predictions of the quantum theory and a qualitative contradiction with the Horiuti-Polanyi model, which postulates the extension of the O-H bond in the activation process.
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I. INTRODUCTION

Reviews dealing with the theory of the fundamental step in electrode reactions[1] and certain experimental studies in this field[2] were published ten years ago in the issue of this journal devoted to the 70th birthday of Academician A. N. Frumkin. Since then the problem as a whole has developed very significantly, new ideas have been put forward, justified theoretically, and proved experimentally. In principle, these have permitted a theoretical analysis of any complex reaction involving charge transfer becoming possible.

II. THE QUANTUM THEORY OF THE FUNDAMENTAL STEP IN ELECTRODE REACTIONS

At the beginning of the 1960s only the simplest electron transfer reactions, unaccompanied by the dissociation, formation, or rearrangement of covalent bonds, could be treated theoretically. These studies revealed the decisive role of the reorganisation of the polar medium, i.e. the reorientation of the solvent dipoles in the course of such reactions. Electron transfer takes place after the molecules of the medium have attained a configuration (intermediate between the equilibrium initial and final configurations) as a result of thermal fluctuations for which the energies of the initial and final states are equal. These ideas were then extended to any charge-transfer reaction in the course of which not only the medium but also the reactants undergo rearrangement.

The principal ideas in the quantum chemistry of the fundamental step of electrochemical reactions will be described using as an example the discharge of hydrogen ions. This reaction was chosen, firstly, because it is apparently one of the electrochemical processes which have been investigated in greatest detail and, secondly, this reaction constitutes the simplest instance where the fundamental step involves the dissociation of a single covalent bond and the formation of another covalent bond. Finally, as will be seen below, the difference between the quantum theory and the theory of absolute reaction rates in relation to the mechanism of the fundamental step is manifested most clearly in proton transfer processes.

One of the first microscopic models used to describe the fundamental step in the electrochemical proton transfer process was proposed by Horiuti and Polanyi[3]. This study played a major role in the development of the theory of the kinetics of the fundamental step in chemical reactions, since it explained correctly for the first time a number of phenomenological relations. According to this theory, the proton is transferred from the AH^+ species to the electrode via a gradual extension of the $A-H^+$ bond, which corresponds to the excitation of the high vibrational levels in the AH^+ molecule. Subsequently, in order to account for the isotope effect, it was suggested that some tunnelling can occur near the top of the barrier (see, for example, Bell's review[4]). It is important to emphasise that, both in the initial study by Horiuti and Polanyi and in subsequent investigations based on the ideas of the theory of absolute reaction rates, the dynamic role of the polar medium in the fundamental step was completely ignored.

Dogonadze and coworkers[5,6] made the first attempt to consider proton transfer, within the framework of an extremely simplified model, on the basis of a fully quantum-mechanical calculation without any *a priori* hypothesis concerning the reaction pathway on the potential energy surface. Subsequently it was possible to improve significantly, on the one hand, the quantitative model used to describe the polar medium[7-9] and, on the other hand, to examine a more realistic model of the ion undergoing discharge, taking into account the possible changes in the intramolecular configurations of the reactants[10]. The method for calculating the rate of the fundamental step developed in these studies was in principle applicable not only to proton transfer reactions but to reactions of virtually any type. The modern quantum theory of chemical and electrochemical reactions in a condensed phase has been reviewed[11-15]. In the present survey we shall describe only some results of this theory and shall discuss qualitatively the overall features of the fundamental step.

In chemical kinetics the mechanism of the fundamental reaction step is usually treated with the aid of the potential energy surfaces of the initial state $U_i(Q)$ and the final state $U_f(\zeta)$. Here we denote by the symbol Q the entire set of coordinates of the degrees of freedom which are altered in the course of the reaction, and exert a dynamic influence on the fundamental step. Thus Q includes the set of coordinates R defining the configuration of the molecule (dipoles) of the medium and the set of coordinates r defining the intramolecular configuration of the reactants.

Quantum-mechanical calculation has shown (see, for example, Dogonadze and Kuznetsov[14]) that the probability of the transition per unit time from the initial potential energy surface $U_i(Q)$ to the potential energy surface of the final state $U_f(Q)$ can be formulated as follows†:

$$w_{if} = \text{const} \cdot L_{if}(Q^*) \cdot \Phi_i(Q^*, 1-\Theta^*) \cdot \Phi_f(Q^*, \Theta^*), \quad (1)$$

where $\Phi_i(Q, 1-\Theta)$ is the quantum-statistical distribution function for the coordinates in the initial state calculated for an effective temperature $T/(1-\Theta)$, $\Phi_f(Q,\Theta)$ is similarly the distribution function for the coordinates in the final state calculated for a temperature T/Θ, Θ is an auxiliary variable the physical significance of which will be explained below, $2L_{if}$ is the resonance splitting of the U_i and U_f surfaces in the vicinity of their intersection and is determined by the electronic exchange integral, Q^* are the coordinates of the "transition" configuration, and Θ^* is the value of Θ in the transition state; it is identical with α—the transfer coefficient or the symmetry factor in the Brønsted relation.

The transition configuration Q^* and the transfer coefficient Θ^* are determined in the following way according to the quantum theory[10,11]. For a fixed arbitrary value of Θ, we initially seek a maximum in the function $L_{if}(Q)\cdot\Phi_i(Q, 1-\Theta)\cdot\Phi_f(Q,\Theta)$ with respect to Q; then, having found $Q^*(\Theta)$, we determine Θ^* from the condition for the maximum in the function $L_{if}[Q^*(\Theta)]\cdot\Phi_i[Q^*(\Theta), 1-\Theta]\cdot\Phi_f[Q^*(\Theta), \Theta]$ with respect to Θ. Having found Θ^*, we find the transition configuration $Q^* = Q^*(\Theta^*)$.

The formula of the theory of absolute reaction rates can be easily found from Eqn. (1). For this purpose, it is sufficient to suppose that motion is classical for all degrees of freedom. Then the classical Boltzmann distribution function[19,20] should be used as the distribution function with respect to coordinates:

$$w_{if}^{cl} = \text{const} \cdot L_{if}(Q^*) \cdot \exp\left[-(1-\Theta^*)\frac{U_i(Q^*)}{kT} - \Theta^*\frac{U_f(Q^*)}{kT}\right]. \quad (2)$$

The system of equations for Q^* and Θ becomes under these conditions

$$(1-\Theta)\frac{\partial U_i(Q)}{\partial Q_k} + \Theta\frac{\partial U_f(Q)}{\partial Q_k} = kT\frac{\partial \ln L_{if}(Q)}{\partial Q_k}, \quad (3)$$

$$U_i[Q^*(\Theta)] = U_f[Q^*(\Theta)]. \quad (3')$$

Condition (3′) implies that the transition from the surface U_i to U_f proceeds via the intersection surface, where U_i is equal to U_f. This condition corresponds fully to the classical features of the transition adopted in the theory of absolute reaction rates.

In analysing Eqn. (3), one should bear in mind that the exchange integral L_{if} depends virtually only on the intermolecular coordinates R of the reactants. For this reason, in determining the transition configuration with respect to the intramolecular coordinates r^* and the coordinates of the molecules of the medium q^*, the right-hand side of Eqn. (3) can be replaced by zero. In other words, for fixed intermolecular coordinates R of the transition configuration, a saddle point on the surface of intersection of U_i and U_f corresponds to r^* and q^*. Eqn. (3) for the coordinates R^* makes it possible to find the optimum distance between the reactants and their optimum mutual orientation. The existence of this optimum is a consequence of the fact that L_{if} decreases sharply with increase of the distance between the reactants, while for short distances the probability of the mutual approach of the reactants $e^{-U_i/kT}$ diminishes sharply.

Taking into account condition (3′), formula (2) can be rewritten as follows:

$$w_{if} = \text{const}\, L_{if}(Q^*)\exp\left[-\frac{U_i(Q^*)}{kT}\right]. \quad (4)$$

Here $U_i(Q^*)$ plays the role of activation energy and const. contains a number of factors which determine the transmission coefficient and the frequencies of the fluctuations leading to the formation of the transition state (the entropy term).

Together with the classical limit, which formally occurs when sufficiently high temperatures ($T \to \infty$) are considered, it is of interest to examine the opposite limiting case of low temperatures ($T \to 0$). Here the behaviour of the system is determined by purely quantum-mechanical factors and the distribution function for the coordinates is equal to the square of the modulus of the wave function for the system in the ground state Ψ_0.[19,20] Above we pointed out the formal criterion for the classical ($T \to \infty$) and quantum-mechanical ($T \to 0$) behaviour of the system. In order to obtain the real quantitative criterion in terms of temperature, we shall consider the case, which is of practical interest, where the system is described by a set of harmonically vibrating oscillators. Denoting by $Q_k^{(i)}$ and $\omega_k^{(i)}$ the normal coordinates and frequencies in the initial state and by $Q_k^{(f)}$ and $\omega_k^{(j)}$ the normal coordinates and frequencies in the final state, Eqn. (1) can be rewritten as follows[19]:

$$w_{if} = \text{const}\, L_{if}(Q^*)\prod^{k}\exp\left[-(Q_k^{*(i)})^2\tanh\frac{\hbar\omega_k^{(i)}(1-\Theta^*)}{2kT} - (Q_k^{*(f)})^2\tanh\frac{\hbar\omega_k^{(f)}\Theta^*}{2kT}\right]. \quad (5)$$

Eqn. (5) becomes identical with Eqn. (2), corresponding to the classical limit, when all the hyperbolic tangents are replaced by their arguments, which is possible for arguments much smaller than unity. Thus we arrive at the following criterion of classical behaviour of the system‡:

$$\hbar\omega_k^{(i)}(1-\Theta^*) \ll 2kT, \qquad \hbar\omega_k^{(f)}\Theta^* \ll 2kT. \quad (6)$$

Since the transfer coefficient $\alpha = \Theta^*$ lies in the range zero to unity[2,11,13], it is sufficient for classical behaviour of the system that the energy of the vibrational quantum $\hbar\omega$ should be small compared with the energy of thermal motion $2kT$.

We shall use criterion (6) to elucidate the problem of the quantum-mechanical or classical behaviour of the proton in chemical and electrochemical reactions. We shall assume initially that the reaction proceeds in the normal region of thermal excitation where $\alpha \simeq 0.5$. According to condition (6), the parameter $\gamma \simeq \hbar\omega/4kT$ should be estimated in this case. If $\omega \simeq 6\times10^{14}$ s^{-1} is adopted as the vibrational frequency, then we obtain $\gamma \simeq 3.75$ at room temperature. Since $\tanh 3.7 \simeq 0.999 \simeq 1$, we obtain the

† Eqn. (1) is valid for non-adiabatic processes when the transmission coefficient κ is less than unity. Adiabatic processes have been examined in a number of studies[16-18]. Since $\kappa \ll 1$ for proton transfer reactions, as shown by studies on the isotope effect, in the present review we shall consider only non-adiabatic reactions.

‡ Together with condition (6), another condition, namely the requirement that the subsequent terms of the expansion of the tangent be small, follows from Eqn. (5). It has been shown[10] that this condition does not usually alter significantly Eqn. (6).

following distribution function for the coordinates of the proton:

$$\Phi(Q) = \frac{1}{\sqrt{\pi}} e^{-Q^2} \equiv |\Psi_0(Q)|^2, \quad (7)$$

where $\Psi(Q)$ is the wave function of the ground vibrational state of the proton. Thus the distribution function of the proton coordinates at room temperature is determined by purely quantum-mechanical laws. In particular, the coordinates $Q > 1$, which are located in the inaccessible region according to the classical theory, can be realised only by virtue of the tunnel effect. Finally, we may note that, according to Eqn. (7), the distribution function for the proton coordinates is independent of temperature, like that for any quantum-mechanical particle.

We shall now consider the region of barrierless reactions, i.e. highly endothermic processes [2,11-15]. In this case the transfer coefficient Θ^* is close to unity and, according to condition (6), when $\hbar\omega(1-\Theta^*) \ll 2kT$, the behaviour of the proton in the initial state is classical. The physical significance of this result is that in highly endothermic processes a preliminary excitation of the proton to a high vibrational level, where its behaviour becomes virtually classical, is necessary. In particular, one may say that, in the formation of the transition state, the chemical bond involving the proton undergoes classical "extension". Evidently [this also follows from formula (6) according to which $\hbar\omega\Theta^* \gg 2kT$ for the proton in the barrierless region], after the rearrangement of the electronic state in the transition region, the proton is in the vibrational ground state. In this sense, one may say that the classical degree of freedom of the proton is converted into the quantum-mechanical degree of freedom in the course of the reaction. A completely analogous treatment has shown that, in reactions without activation energy, i.e. in highly exothermic processes, where Θ^* is close to zero, the proton passes from its ground vibrational state to a highly excited vibrational state.

One must emphasise that the conclusion concerning the virtually classical behaviour of the proton in a barrierless discharge is valid only for very high activation energies, i.e. far from the region of transition from normal discharge to barrierless discharge. The existing theory, which provides a qualitatively correct explanation of the variation of α from 1/2 to 1, does not describe the transition region quantitatively. In particular, it is not yet been possible to account for the expérimental observation of a sharp variation of α over a very narrow range of potentials [2]. Certain estimates, carried out using Morse potentials, have shown that in the transition region the lowest excited levels of the proton make an appreciable contribution together with its ground vibrational level, but the behaviour of protons still remains significantly of the quantum-mechanical type [11].

The scheme described above leads to the following physical picture of the transition from the initial to the final state. On the potential energy surface for the initial state, a classical fluctuation takes place initially in accordance with the Boltzmann Law along the degrees of freedom for which the first condition (6) holds. The extension of the length of these classical degrees of freedom depends significantly on the behaviour of the given degree of freedom after the reaction: if it remains classical also after the reaction, the transition configuration is determined by Eqn. (3), but, when there is a change from a classical to a quantum-mechanical (quantised) degree of freedom as a result of the reaction, the extension is virtually a maximum, since in the final state the system must be at the zero-point level, i.e. must be localised near the equilibrium configuration of the final state.

As a result of the classical fluctuation, all the zero-point (ground) energy levels of the quantum-mechanical subsystem, satisfying conditions which are the opposite of conditions (6) in both the initial and final states, are equalised in the initial stage. In fact we are dealing here with the general Franck–Condon principle, according to which the rearrangement of the state of the fast subsystem (in our case the quantum-mechanical subsystem) can occur only when the energies of the initial and final states are equal, since the slow subsystem (in our case the classical subsystem) cannot change (because of the considerable inertia) its coordinates and momenta, in order to compensate the difference between the energies of the fast subsystem.

In the second stage quantum fluctuation, i.e. tunnelling of the quantised degrees of freedom, begins for fixed coordinates of the classical subsystem. For a certain configuration of the quantised degrees of freedom, corresponding to the inaccessible region according to the classical theory, the energies of the initial and final states of the electronic subsystem are equalised. Thus at this stage the condition of the usual Franck–Condon principle is fulfilled; according to this principle, the change of state of the electronic (fast) system takes place for fixed coordinates and momenta of the nuclear (slow) subsystem. After the Franck–Condon barrier to the electronic subsystem is removed in the second stage, in the third stage there is electron tunnelling from the initial to the final state, after which there is an initial relaxation of the quantised and then the classical degrees of freedom of the system.

Cases are in principle possible (and probably extremely common) where the electronic subsystem follows adiabatically the motion of the remaining quantised subsystems, for example protons. In this case the second and third stages described above in fact merge into one and the only transition under the barrier is the one executed by the quantised subsystem of the nuclei. For such processes, which are adiabatic with respect to electrons and non-adiabatic with respect to other quantised degrees of freedom, L_{if} in Eqn. (1) can be understood as, for example, the proton exchange integral and no longer the electron exchange integral.

It is interesting to consider one of the characteristics of the reactions in the course of which a classical degree of freedom is converted into a quantised degree of freedom. If the conditions

$$\frac{2kT}{\hbar\omega^{(f)}} \ll \Theta^* \ll 1, \quad (8)$$

hold in the system, then the right-hand side of the inequality ensures that the reaction proceeds virtually without activation energy, while the left-hand side of the inequality implies that the given degree of freedom can be treated as virtually of the quantum-mechanical type in the final state (see Dogonadze et al.[6]). This implies that, although the process as a whole occurs almost without activation energy (in the sense that Θ^* is close to zero), it follows from the picture of the transition described above that there will be preliminary activation along the given degree of freedom from the initial equilibrium configuration to the final equilibrium configuration. Processes in which $\Theta^* \simeq 0$ but the activation energy is non-zero and constant (independent of the heat change) have come to be called quasi-non-activated processes. Quasi-barrierless processes, where $\Theta^* \simeq 1$ but the activation energy differs from the heat change by a constant amount, can be treated similarly [21,22].

On passing from simple potential energy surfaces, having the form of multi-dimensional paraboloids, to more complex surfaces, the qualitative picture of the transition naturally does not change. Only the form of the criterion of the quantum-mechanical or classical behaviour of the given degree of freedom is altered: instead of condition (6), we have a more complex condition. The new feature introduced into the qualitative picture by the anharmonicity of the potential energy curves is that, along different sections of the potential energy curve, there can be a change from the classical to the quantum-mechanical (tunnel) motion of the particle or conversely. For example, when the vibrational frequency near the minimum satisfies the condition of classical behaviour ($h\omega \ll 2kT$), the behaviour of the system far from the minimum can be nevertheless of the quantum-mechanical type if the potential energy curve rises very steeply in consequence of the marked repulsion from another particle. The opposite situation can also arise when the vibrational frequency near the minimum satisfies the condition for quantum-mechanical behaviour ($h\omega \gg 2kT$) and yet the motion of the particle is classical at a sufficient remove from the minimum where the potential energy curve acquires a low slope.

However, one should remember that the motion of the particle becomes classical in a state very close to dissociation. For example, numerical calculation of the quantum-statistical distribution function for the proton coordinates using the Morse potential curve with the parameters D (dissociation energy) = 172.5 kcal mole^{-1} and ω (frequency near the minimum) = 4×10^{14} s^{-1} has shown that the motion of the proton becomes classical when it departs from the minimum by a distance of about 4 Å. Such extension of the bond requires an energy consumption of the order of 100 kcal mole^{-1}, i.e. much greater than the experimental activation energies (< 20 kcal mole^{-1}). Therefore under real experimental conditions the classical behaviour of the proton in the highest state is unlikely.

III. EXPERIMENTAL STUDY OF THE FUNDAMENTAL STEP IN ELECTRODE REACTIONS

We shall consider the possibility of an experimental comparison of two fundamentally different models of the fundamental step in the discharge of a proton donor—the model involving a gradual extension of the O–H bond and the model postulating a rearrangement of the solvent structure with a subsequent quantum jump of the proton from the initial to the final state. Both give virtually the same explanations of the majority of the known experimental facts. This is not surprising, since, for a semi-quantitative treatment of the majority of observations, it is sufficient that certain simple phenomenological relations, associated with the existence of an energy barrier, are maintained regardless of the causes responsible for the barrier. Therefore, in order to choose between the two models, it is necessary to seek relations for which they would give rise to qualitatively different predictions.

The first group of phenomena for which significant differences between the conclusions reached on the basis of the two theories may be expected is associated with the pre-exponential factor, namely with the influence on the latter of the probability of a tunnel transition of the proton through the barrier. The correction for tunnelling within the framework of the bond extension model has been estimated in a number of studies. Without going into their analysis, we may note the common and most significant feature of all these investigations—in this model tunnelling is determined by the same barrier as the activation energy—the barrier along the proton coordinate. On the other hand, within the framework of the quantum-mechanical theory, the activation energy is determined by the barrier on the classical coordinate, describing the orientation of the solvent dipoles, and the probability of the transition under the barrier is determined by the energy profile along the proton coordinate. Thus in the first model the activation energy and the pre-exponential factor are linked by a definite relation, while in the second model they can in principle vary independently.

The existence of barrierless electrode processes, in particular the barrierless discharge of the hydrogen ion, for which the activation energy is equal to the heat of the fundamental step (see Krishtalik's review [2]), was demonstrated previously. In the bond extension model the barrierless process involves the absence of a barrier on the path followed in the motion of the proton and hence the absence of a tunnell effect. The implication is that in this model κ for the barrierless discharge should be unity, while in the usual discharge $\kappa < 1$. In the quantum-mechanical model the energy profile along the solvent coordinate is barrierless, while the barrier along the proton coordinate is retained. Thus this theory leads to the conclusion that values of $\kappa < 1$ are of similar order of magnitude for both the barrierless and the usual discharges§.

Theoretical calculation of the pre-exponential factor, particularly for electrode processes, by the method of the theory of absolute reaction rates involves certain difficulties concerning the estimation of the entropy of the activated state [24,25]. However, for a barrierless discharge all these difficulties disappear, because here the activated state is identical with the final state. This permits a fairly rigorous calculation of the theoretical value of the pre-exponential factor for the barrierless discharge [26]. The theoretical value $\lg k = 5.7$ (the pre-exponential factor k is expressed in A cm^{-2}) is much higher than the experimental value $\lg k = 3.0$. This discrepancy indicates a significantly non-adiabatic process ($\kappa = 10^{-2.7}$), i.e. a fairly low probability of proton transfer below the barrier. As shown above, $\kappa \ll 1$ for a barrierless discharge can be hardly explained by assuming that the extension of the O–H bond determines the activation process, but it can be naturally accounted for within the framework of the quantum-mechanical theory.

A similar conclusion can be reached also by comparing the pre-exponential factors for the barrierless and the usual discharges. In order to compare the tunnelling probabilities, it is necessary to compare ideal rather than real pre-exponential factors, i.e. a correction must be introduced for the change in the entropy of the electrode process and account must be taken of the concentration dependence of the pre-exponential factor. Such a calculation has been made [27] and showed that the tunnelling probabilities for the barrierless and the usual discharges are similar (the difference between them is within the

§ Since the experiments are performed at potentials close to the transition region, the possibility of a change from the quantum-mechanical to the classical motion of the proton discussed above need not as yet be taken into account here. The involvement of the first excited vibrational levels in the barrierless process together with the ground level can lead to an increase of κ.

limits of experimental error). This result also agrees with the quantum-mechanical theory, but is difficult to explain on the basis of the bond extension model.

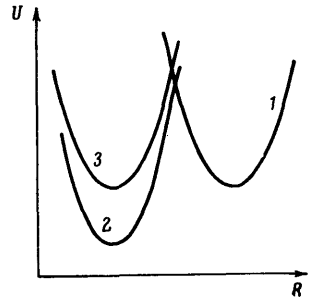


Figure 1. Schematic potential energy curves: 1) component describing the O–H bond; 2) and 3) components describing the M–H bond ($E_{M_2} > E_{M_3}$).

We shall consider the influence of the nature of the metal on the probability of proton tunnelling[28]. From the standpoint of the bond extension model (Fig. 1), the higher the energy of the M–H bond ($E_{M\text{-}H}$) the lower the height of the barrier for tunnelling and the narrower the barrier (the potential curve rises more steeply for a more rigid bond). Consequently Fig. 1 leads to the conclusion that tunnelling by the proton is facilitated by higher values of $E_{M\text{-}H}$. In the quantum-mechanical model the probability of the transition below the barrier increases with increased overlap of the wave functions of the proton in the initial and final states. The more rigid the bond the more highly localised the proton and the less effective the overlapping of the wave functions (Fig. 2). Therefore, within the framework of the given model, one may expect a decrease of tunnelling probability with increase of $E_{M\text{-}H}$. Fig. 3 shows that experiment agrees with this conclusion.

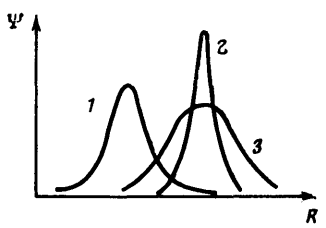


Figure 2. Wave functions of the proton in OH (curve *1*) and MH (curves *2* and *3*) ($E_{M_2} > E_{M_3}$).

The probability of tunnelling by the proton influences significantly another quantity susceptible to measurement—the isotope separation factor S. The experimental value is determined by kinetic isotope effects for two irreversible stages—discharge (S_d) and electrochemical desorption (S_{ed})[35,36]:

$$S = \frac{2S_dS_{ed}}{S_d + S_{ed}}. \qquad (9)$$

Electrochemical desorption on mercury and similar cathodes is highly exothermic, so that its activation energy should become zero[2,22,37].¶ If the activation process consists of the extension of the bond, then the non-activated electrochemical desorption should proceed at the same rate for all hydrogen isotopes, since there is no barrier to tunnelling by the proton and since, by virtue of the zero activation energy, the effect of the difference between the zero-point energies disappears. In other words, in this model $S_{ed} = 1$. But this implies that $S = 2S_d/(S_d + 1) \leqslant 2$. This conclusion is completely inconsistent with experimental data—as will be shown below, fairly large effects can be observed on mercury and similar metals ($S_{H/T}$ varies from 3 to 17). On the other hand, in the new quantum-mechanical theory this difficulty does not arise, because the non-activated process is associated solely with the absence of a barrier on the coordinate for the solvent dipoles, while the barrier persists along the proton coordinate[28].

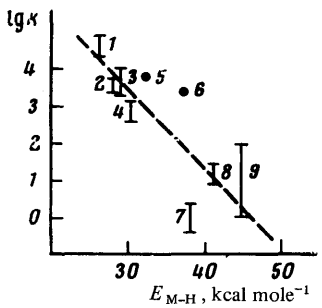


Figure 3. Variation of the pre-exponential factor for the hydrogen evolution reaction in acid solutions with the M–H bond energy: 1) 40.6 at.% thallium amalgam[29]; 2) lead[30]; 3) mercury[25,26,31]; 4) 60.3 at.% indium amalgam[32]; 5) gallium–16.4 at.% indium[31]; 6) gallium[31]; 7) silver (0.1 *N* HCl)[33]; 8) silver (0.1 *N* H_2SO_4);[33] 9) indium[34].

Within the framework of the bond extension model, the metal of the cathode influences S mainly because of its influence on the isotope effect at the discharge stage, since it affects S_{ed} much less (and in non-activated desorption not at all). If one considers the nature of the overlap of the proton wave functions in the initial and final states, it is seen that the change in the M–H bond energy acts in the same direction on tunnelling probability both in the discharge and in electrochemical desorption, i.e. both on S_d and on S_{ed}. The influence of the nature of the metal on tunnelling probability was considered above from the standpoint of both the models discussed. In agreement with the quantum-mechanical model and the experimental pre-exponential factors for the reaction, it was found[28] that an increase of the M–H bond energy, which hinders proton transfer under the barrier, increases the kinetic isotope effect.

¶ The conclusion that the electrochemical desorption of hydrogen from metals of the same type as mercury proceeds without activation energy is confirmed by the results of Rotenberg, Pleskov, and coworkers[38] (see below).

Experimental data indicate a significant lowering of the isotope separation factor with increase of the potential[28,39]. Within the framework of the bond extension model, this type of relation can be explained by a decrease of the activation barrier with increase of the potential and, accordingly, by the facilitation of tunnelling by the proton[40]. The new theory leads to the conclusion that there is no direct relation between the activation energy (barrier on the coordinate of the solvent dipoles) and the probability of proton tunnelling. The decrease of S with increase of the potential can be explained from this standpoint by the larger overlap of the wave functions for the initial and final states because of the approach of the hydronium ion to the electrode under the influence of the electric field. The validity of this explanation is evident from a comparison of the isotope effects in acid and alkaline solutions. In the latter the uncharged water molecule, which is naturally attracted to the electrode much less strongly than the H_3O^+ ion, serves as the proton donor. Its distance from the electrode hardly changes with potential and therefore there is no dependence of the isotope effect on the potential (Fig. 4).[28,41]

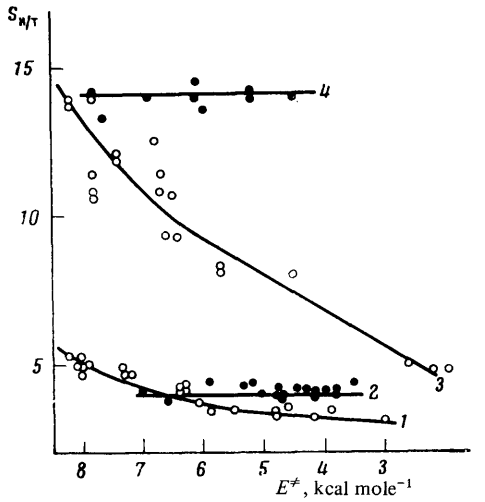


Figure 4. Variation of the separation factor for protium (H) and tritium (T) with activation energy: 1) mercury, acid[28,42]; 2) mercury, alkali[28,42]; 3) gallium, acid[28,41]; 4) gallium, alkali[41].

From the standpoint of the O–H bond extension model, there is no fundamental difference between the discharge of H_3O^+ and H_2O—in both cases the potential barrier is lowered with increase of the overvoltage and facilitation of tunnelling is to be expected. Fig. 4 shows that, for the same activation energies in acid and alkaline solutions, there is a significant difference between the variation of S with potential. This shows that, in full agreement with the new quantum-mechanical theory, there is no direct relation between the activation energy and the probability of tunnelling by the proton†.

The above explanation of the variation of S with potential presupposes that, with increase of the electric field, the pre-exponential factor for the discharge of the hydrogen ion should increase. In the study of the temperature dependence of the rate of this reaction over the usual, fairly narrow range of potentials this effect lies at the limit of experimental error (a weak tendency to change has been observed[31]), but it has been shown[44] that, on a silver cathode for potentials in the region of 1 V, the pre-exponential factor increases at least by two orders of magnitude.

The much weaker attraction of water molecules to the electrode compared with the H_3O^+ ion must result in a greater distance between the initial and final positions of the proton and hence in a smaller tunnelling probability. This conclusion has been fully confirmed experimentally—the ratio of the tunnelling probabilities for H_3O^+ and H_2O, found from the pre-exponential factors, is $10^{5\cdot6}$ for gallium and $10^{4\cdot8}$ for the indium–gallium alloy[31].

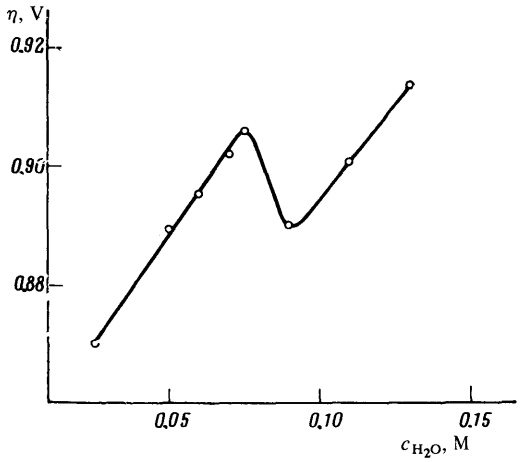


Figure 5. Variation of the hydrogen overvoltage (for $\log i = -4.0$) in 0.01 N $HClO_4$ solution in acetonitrile with the concentration of water.

Another approach to the study of the mechanism of the fundamental step in hydrogen evolution consists of employing a medium with properties significantly different from those of water. We chose the aprotic weakly basic solvent

† Christov[43] drew attention to the fact that, for certain parameters of the barrier on the proton coordinate, the optimum region for tunnelling is located at some distance from the top of the barrier, so that the tunnelling probability is independent of activation energy. This factor might explain, within the framework of the bond extension model, the constancy of S in alkaline solutions, but, on the one hand, there is no evidence that the real parameters of the barrier correspond to conditions necessary for this and, on the other hand, even with the aid of these additional hypotheses it is still impossible to account for the above data concerning the barrierless and non-activated processes and the influence of the nature of the cathode metal.

acetonitrile as a medium of this kind[45]. In anhydrous acetonitrile the hydrogen overvoltage of the mercury cathode in an acid solution is lower by about 150 mV than in water. After the addition of small amounts of water, which is a much stronger base than acetonitrile, hydronium ions are formed and the concentration of acetonitrilonium ions, which are the main proton donors, decreases. This leads to a corresponding increase of the overvoltage (Fig. 5). At a fairly high concentration of water the fraction of H^+ ions bound to the solvent becomes vanishingly small and hydronium ions become the main source of protons. From this instant, further addition of water decreases the overvoltage because the concentration of H^+ ions bound to water becomes virtually constant, while the concentration of the electrode reaction product (free water) increases. This results in a maximum on the curve in Fig. 5.

The hydronium ion can exist in acetonitrile both in the H_3O^+ form and as its association complex with one, two, or three water molecules (the last form predominates in aqueous solutions). Calculation based on Kolthoff and Chantooni's data[46] showed that, near the maximum on the curve in Fig. 5, the dominant species are $H_3O^+.H_2O$ and H_3O^+. This implies that the ion undergoing discharge is surrounded mainly by acetonitrile molecules. On the other hand, at a higher water concentration the fraction of $H_3O^+.2H_2O$ and $H_3O^+.3H_2O$ ions increases, i.e. the immediate coordination sphere of the H_3O^+ ion becomes increasingly similar to that in aqueous solution, which gives rise to a new increase of overvoltage. Although the mole fraction of water under these conditions is only 0.007 and the macroscopic properties of the medium have still not been able to change significantly, the micromedium near the hydronium ion becomes more "water-like" by virtue of the selective formation of hydrates and this has a significant influence on the kinetics of the discharge of the hydronium ion. Thus the influence of the change in the properties of the medium under the conditions of a virtually unchanged type of bond dissociation process are clearly manifested in these experiments.

Pre-exponential factors and activation energies.

Ion undergoing discharge	Medium	A_0, kcal mole^{-1}	lg k (A litre mole^{-1} cm^{-2})
CH_3CNH^+	CH_3CN	18.2	2.1
H_3O^+	CH_3CN	18.2	3.2
H_3O^+	H_2O	21.9	3.4

The influence of the medium and of the nature of the bond being ruptured is shown even more clearl y when the pre-exponential factors and the activation energies for the discharge of acetonitrilonium and hydronium ions are compared in acetonitrile and in water. All the pre-exponential factors in the Table have been recalculated for the same concentration of H^+ ions and for the same mole fraction of the conjugate base, which is unity (this correction, which is necessary to compare the data, was introduced for H_2O in the discharge of H_3O^+ in acetonitrile).

The Table shows that the discharge of the CH_3CNH^+ and H_3O^+ ions in acetonitrile solutions is characterised by significantly different pre-exponential factors and virtually the same activation energies, while the discharge of H_3O^+ in the two different media (water and acetonitrile) is characterised by virtually identical pre-exponential factors but different activation energies. Thus it has been found that the pre-exponential factor is determined mainly by the nature of the bond dissociated (N–H or O–H), while the activation energy depends on the solvent (acetonitrile or water). This conclusion is fully consistent with the predictions of the theory, according to which the activation energy is determined by the rearrangement of the structure of the medium and the pre-exponential factor is determined by the probability of tunnelling by the proton. On the other hand, from the standpoint of the bond-extension model, both the pre-exponential factor and the activation energy are determined by the bond undergoing dissociation, so that different relations are to be expected—similarity of the activation energies for the discharge of H_3O^+ ions in acetonitrile and water and different values of A_0 for the discharge of CH_3CNH^+ and H_3O^+ in acetonitrile. Thus different experimental data support a mechanism of proton transfer which relates the activation process only to a rearrangement of the structure of the medium without a significant extension of the bond between the proton and the proton donor.

Another aspect of the problem of the fundamental step in hydrogen evolution, which has been studied in the very last few years, is the nature of the rapid stage—the removal of adsorbed hydrogen. In their studies by the photoemission method Rotenberg, Pleskov, and coworkers[38] succeeded in determining the sum of the transfer coefficients for two reactions involving the removal of adsorbed hydrogen—electrochemical desorption and ionisation. For the mercury cathode in the range of potentials susceptible to investigation, it was found to be 0.5, which supported the hypothesis that one of the stages has no activation energy (most probably electrochemical desorption). On the other hand, for the bismuth cathode it was possible to attain potentials at which the above sum became zero, i.e. the possibility that both reactions can occur without activation energy was demonstrated.

Non-activated electrochemical desorption of hydrogen from metals of the same type as mercury was found to be fully irreversible (at least at overvoltages susceptible to measurement). This follows unambiguously from the isotope separation factor, which exceeds significantly the equilibrium constant for the isotope exchange between hydrogen and water[47].

The irreversibility of electrochemical desorption leads to the appearance of a new interesting phenomenon- a non-equilibrium ratio of the ortho- and para-modifications of hydrogen in the gas evolved on electrolysis at reduced temperatures[48,49]. A theory of this phenomenon was developed recently within the framework of the general quantum-mechanical theory of proton transfer[49].

In the hydrogen evolution reaction the species transferred (the proton) behaves significantly in accordance with the quantum-mechanical mechanism. Another situation arises in the transfer of heavy ions, linked by weaker bonds, i.e. their motion takes place in accordance with both the classical and quantum-mechanical mechanisms. As shown above, this feature of systems with heavy atoms leads to the occurrence of quasi-barrierless and quasi-non-activated processes characterised by $\alpha = 1$ and $\alpha = 0$ respectively. In this case the barrier disappears only for motion along the solvent coordinate, but remains on the heavy atom coordinate. However, the latter barrier does not change with the potential, so that α is determined only by the motion along the solvent coordinate.

The existence of quasi-barrierless processes was postulated previously for the chlorine evolution reaction on graphite and for the oxidation of azide on platinum [2]. The occurrence of quasi-barrierless and the reverse quasi-non-activated processes was recently demonstrated unambiguously for the evolution and ionisation of chlorine on ruthenium–titanium oxide anodes (RuO_2–TiO_2 solid solution). This process proceeds in stages:

$$Cl^- \overset{-e}{\rightleftarrows} Cl_{ad} \overset{-e}{\rightleftarrows} Cl^{+I} + Cl^- \rightleftarrows Cl_2.$$

The slow stage, involving the abstraction of the second electron, can be both of the usual type ($\alpha_a = 1/2$) and of the quasi-barrierless type ($\alpha_a = 1$), while in the opposite direction it is a quasi-non-activated process ($\alpha_c = 0$). If the slow stage were not of the quasi-barrierless type but simply of the barrierless type, i.e. if the abstraction of the second electron were not followed by the relaxation process involving a change in the heavy particle coordinate, then the second and third stages would have occurred as a single step and the reaction would have been of second order with respect to chloride ions. The experimental first order of the reaction demonstrates the quasi-barrierless nature of the electrode process [50].

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