

CALCULATION OF THE TUNNELING FACTOR FOR THE ELECTROCHEMICAL DESORPTION OF HYDROGEN

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The quantum-mechanical calculation of the tunneling factor for the elementary act of the reaction for the electrochemical desorption of hydrogen, which takes place according to the scheme $AH^+ + H_{ads} + e^- \rightarrow A + H_2$, is of interest in studying the isotope effect in electrochemical kinetics [1]. In addition, as was shown in [2], by analyzing the concentration of the ortho and para modifications of hydrogen it is possible to make a number of interesting conclusions about the mechanism for the course for the elementary act of the electrode reaction. In this work the tunneling factor will be calculated for a simplified model, according to which: 1) The internal structure of the acceptor A does not change in the course of the reaction; 2) the valence bond of the particle AH^+ is oriented perpendicularly to the electrode's surface; 3) two of the deformation frequencies of the proton coincide and are equal to ω_{id} in the AH^+ particle and ω_{ad} for the adsorbed hydrogen; 4) the hydrogen molecule rotates freely and the center of gravity R moves in a classic effective field $U(P)$. Within the framework of the given model the proton's potential energy can be written in the following form with an accuracy up to an arbitrary constant in the initial $[U_i(P)]$ and final $[U_f(P)]$ states:

$$U_i^{(p)} = \frac{1}{2} \{ m_i \omega_{iv}^2 (x_i - x_{i0})^2 + m_i \omega_{id}^2 [(y_i - y_{i0})^2 + (z_i - z_{i0})^2] + m_a \omega_{av}^2 x_a^2 + m_a \omega_{ad}^2 (y_a^2 + z_a^2) \}; \quad (1a)$$

$$U_f^{(p)} = \frac{1}{2} m_f \omega_f^2 \{ [(x_i - x_a)^2 + (y_i - y_a)^2 + (z_i - z_a)^2]^{1/2} - r_0 \}^2 + U(R), \quad (1b)$$

where ω_{iv} and ω_{av} are the frequencies of the valence vibrations in the particles AH^+ and H_{ads} (x_{i0} , y_{i0} , z_{i0}) are the equilibrium coordinates for the proton in the AH^+ particle (the system of coordinates was chosen so that the equilibrium coordinates of the proton of the H_{ads} particle would be equal to zero: $x_{a0} = y_{a0} = z_{a0} = 0$). In order that the results obtained below could be used to study the isotope effect, different masses m_i and m_a were introduced into the formulas in (1) for different isotopes of hydrogen which are present in the discharging particle AH^+ and in the adsorbed particle H_{ads} , and $m_f = m_i m_a / (m_i + m_a)$. Finally, in Eq. (1b), the vibration frequency and the equilibrium bond length for the hydrogen molecule are designated by ω_f and r_0 .

In calculating the tunneling factor, we will proceed from the general quantum-mechanical theory for the elementary act of a chemical reaction which takes place in the condensed phase (see, for example [3]). According to [3], the probability of a transition can be written in the form

$$W_{if} = \frac{\beta}{i\hbar} |L_{if}|^2 e^{\beta F_i} \int_{-\infty}^{\infty} d\theta \text{Sp} \{ \rho_i (1 - \theta) \rho_f(\theta) \}, \quad \beta = \frac{1}{kT}, \quad (2)$$

where L_{if} is the exchange integral for fixed electronic states at the beginning (i) and end (f) of the reaction, F_i is the free energy of the system in the initial state (for the condition that the electronic state i is fixed), $\rho_i(1-\theta)$ is the density matrix for the system in the initial state, calculated for a temperature $T/(1-\theta)$, analogously $\rho_f(\theta)$ is the density

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matrix for the final state at the temperature T/θ . As has been shown in the general theory (see [3, 4]) the integral with respect to θ in Eq. (2) can be calculated with good accuracy by the crossover method, in which case the point of crossover θ^* will lie on the real axis and will coincide, in value, with the symmetry factor in Bronsted's relationship, i.e., with the derivative of the free activation energy with respect to the heat effect. In this work we will assume that the integral with respect to θ in Eq. (2) has already been taken and we will consider θ^* as a phenomenological parameter. In calculating the spur in Eq. 2, the density matrix can in reality be replaced by the quantostatistical function for the coordinate distribution. This is related with the fact that the dependence of the density matrix on the difference in the arguments in the coordinate representation has a δ -shaped character with a very sharp maximum. For this reason, in this work, by tunneling factor for the protons we will mean the value

$$T = \int dr_i \int dr_a \Phi_i^{(p)}(r_i, r_a; 1-\theta^*) \Phi_f^{(p)}(r_i, r_a; \theta^*), \quad (3)$$

where $\Phi^{(p)}$ is the coordinate distribution function for the protons, i.e., the diagonal element of the density matrix. The approximation for $U_f^{(p)}$ used in Eq. (1b), allows us to write $\Phi_f^{(p)}(\theta^*)$ in the form of the product of three distribution functions:

I. $\Phi_{ft}^{(p)}(R; \theta^*)$, which describes the spatial distribution for the center of gravity of the hydrogen molecule [$R = (m_1 r_1 + m_a r_a) / (m_1 + m_a)$];

II. $\Phi_{fr}^{(p)}(n, \theta^*)$, which describes the orientation distribution [$n = (r_1 - r_a) / |r_1 - r_a|$];

III. $\Phi_{fv}^{(p)}(|r_1 - r_a|; \theta^*)$, which describes the distribution of the bond length.

By assuming that the movement of the center of gravity has a classic character, we get

$$\Phi_{ft}^{(p)} = [M / (2\pi\hbar^2\beta\theta^*)]^{3/2} \exp\{-\beta\theta^* U(R)\}, \quad M = m_1 + m_a. \quad (4)$$

By making use of the properties of the spherical functions $Y_{lm}(n)$ for $\Phi_{fr}^{(p)}$, it is not difficult to get the following expression:

$$\Phi_{fr}^{(p)} = \frac{1}{4\pi} \sum_{l=0}^{\infty} (2l+1) \exp\{-\beta\theta^* B l(l+1)\}, \quad B = \frac{\hbar^2}{2m_f r_0^2}. \quad (5)$$

Finally, for $\Phi_{fv}^{(p)}$, according to Blokh's formula [5] we have

$$\Phi_{fv}^{(p)} = \frac{1}{r_0^2} \left(\frac{m_f \Omega_f}{4\pi\hbar \text{sh}^{1/2} \beta\theta^* \hbar\omega_f} \right)^{1/2} \exp\left\{ -\frac{m_f \Omega_f [|r_1 - r_a| - r_0]^2}{\hbar} \right\}. \quad (6)$$

$\Omega_f = \omega_f \text{th}^{1/2} \beta\theta^* \hbar\omega_f.$

For all six of the vibrational degrees of freedom of the free protons in the initial state, we will have a formula which is analogous to (6).

The calculation of the integral in Eq. (3) can be greatly simplified if we make use of the auxiliary relationship

$$\exp\{2\gamma_f r_0 |r_1 - r_a|\} = \sqrt{\frac{\gamma_f r_0^2}{\pi}} \int_L \frac{d\tau}{\tau^{1/2}} \exp\left\{ -\frac{\gamma_f r_0^2}{\tau} - \gamma_f |r_1 - r_a|^2 \tau \right\}; \quad (7)$$

where the contour L passes in sequence through the points 0, +1, i, -1, -i, +1, $+\infty$, and $\gamma_f = m_f \Omega_f / \hbar$. After substituting Eq. (7) into Eq. (3), it can be integrated precisely with respect to r_1 and r_a , as the result of which we get

$$T = \frac{\gamma_f \Gamma_d \sqrt{\Gamma_0}}{32(4\pi)^2 r_0^2} \left(\frac{M}{2\pi\hbar^2\beta\theta^*} \right)^{3/2} \text{sh}^{-1} \frac{\beta\theta^* \hbar\omega_f}{2} \prod_{\alpha=1}^6 \text{sh}^{-1} \frac{\beta(1-\theta^*) \hbar\omega_\alpha}{2} \sum_{l=0}^{\infty} (2l+1) \exp\{-\beta\theta^* [U(R^*) + B l(l+1)]\} \cdot I; \quad (8)$$

here the following designations are introduced:

$$\Omega_a = \omega_a \text{th} \frac{\beta(1-\theta^*)\hbar\omega_a}{2}, \quad \Gamma_d = \frac{m_a m_i \Omega_{ad} \Omega_{id}}{m_f \Omega_f (m_a \Omega_{ad} + m_i \Omega_{id})},$$

$$\Gamma_v = \frac{m_a m_i \Omega_{av} \Omega_{iv}}{m_f \Omega_f (m_a \Omega_{av} + m_i \Omega_{iv})}, \quad (9)$$

$$I = \int \frac{d\tau}{\tau(\tau+1+\Gamma_d) \sqrt{\tau(\tau+1+\Gamma_v)}} \exp \left\{ -(1+\tau) \left[\frac{\Gamma_v x_{0i}^2}{\tau+1+\Gamma_v} + \frac{\Gamma_d (y_{0i}^2 + z_{0i}^2)}{\tau+1+\Gamma_d} + \frac{r_0^2}{\tau} \right] \gamma_f \right\}, \quad (10)$$

where the different values $\Omega_1, \Omega_2, \dots, \Omega_6$ correspond to $\Omega_{iv}, \Omega_{id}, \Omega_{id}, \Omega_{av}, \Omega_{ad}, \Omega_{ad}$. Being given the numerical values of the parameters which enter into I, the integral can be calculated by the crossover. As a concrete example, the results are given below for the calculation of I in various limiting cases.

1) The case of linear "collision," i.e., when $y_{0i} = z_{0i} = 0$ leads to the following value for the crossover point: $\tau^* = -r_0(1+\Gamma_v)/(r_0 + x_{0i}\Gamma_v)$. In this case we find for I

$$I = \left[\frac{i(r_0 + x_{0i}\Gamma_v)(r_0 + x_{0i}\Gamma_d)^2}{(1+\Gamma_v)(1+\Gamma_d)^2(x_{0i}r_0)^{3/2}\Gamma_v^{1/2}\Gamma_d} \right] \exp \left\{ -\frac{\gamma_f \Gamma_v (r_0 - x_{0i})^2}{1+\Gamma_v} \right\}. \quad (11)$$

2) In the case in which the valence and deformation frequencies are the same ($\Gamma_v = \Gamma_d \equiv \Gamma$) for τ^* and I we have

$$\tau^* = -\frac{r_0(1+\Gamma)}{r_0 + R_0\Gamma}, \quad I = \frac{i(r_0 + R_0\Gamma)^3}{(1+\Gamma)^3(r_0 R_0\Gamma)^{3/2}} \exp \left\{ -\frac{\gamma_f \Gamma (R_0 - r_0)^2}{1+\Gamma} \right\}, \quad (12)$$

where $R_0^2 = x_{0i}^2 + y_{0i}^2 + z_{0i}^2$.

3) In the case for which $\Omega_{av} = \Omega_{ad} \equiv \Omega_a$ and $\Omega_a \ll \Omega_{iv}, \Omega_{id}$ we get $\Gamma_d = \Gamma_v \equiv \Gamma = m_a \Omega_a / (m_f \Omega_f)$ and Eq. (12) is valid. If, in this case, $\Omega_a \ll \Omega_f$, then we get

$$I = \frac{(r_0 m_f \Omega_f + m_a \Omega_a R_0)^3 i}{(m_f \Omega_f)^{3/2} (r_0 R_0 m_a \Omega_a)^{3/2}} \exp \left\{ -\frac{m_a \Omega_a (R_0 - r_0)^2}{\hbar} \right\}. \quad (13)$$

4) If the electrochemical desorption takes place without activation, i.e., $\theta^* \rightarrow 0$, then $\Omega_f \rightarrow 0$ and $\tau^* = -r_0/R_0$ and we get the following for I

$$I = \frac{i R_0^3}{r_0^{3/2} [(1+\Gamma_v)R_0 + r_0]^{3/2} [(1+\Gamma_d)R_0 + r_0]} \exp \left\{ -\frac{\theta^* m_f \omega_f^2 (R_0 - r_0)^2}{2kT} \right\}. \quad (14)$$

5) Finally, let us consider the last case for which $r_0 \ll R_0$. In this case we get for I

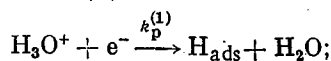
$$I \sim \exp \left\{ -\gamma_f \left[\frac{\Gamma_v x_{0i}^2}{1+\Gamma_v} + \frac{\Gamma_d (y_{0i}^2 + z_{0i}^2)}{1+\Gamma_d} + r_0 \sqrt{\frac{\Gamma_v^2 x_{0i}^2}{(1+\Gamma_v)^2} + \frac{\Gamma_d^2 (y_{0i}^2 + z_{0i}^2)}{(1+\Gamma_d)^2}} \right] \right\}. \quad (15)$$

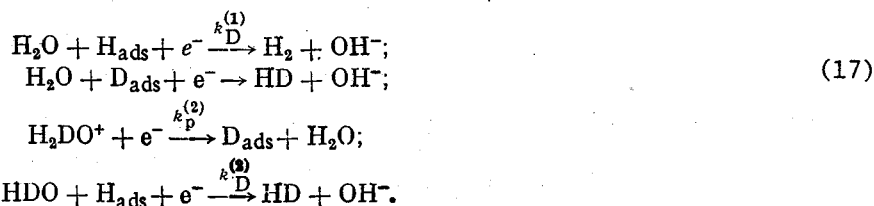
The isotope effect for the process of hydrogen evolution in acid solutions is determined by the ratio for the rates of evolution of H_2 and HD (the concentration of the heavy hydrogen is assumed to be small so that the formation of D_2 is ignored):

$$S = \frac{v_{H_2} [H_2DO^+]}{v_{HD} [H_3O^+]}, \quad (16)$$

$[H_2DO^+]$ and $[H_3O^+]$ are the volume concentrations in the solution.

The process for hydrogen evolution from acid solutions consists of the following main steps:





For the quasisteady course of the process, the isotope effect S is determined by both the discharge stage and the stage for electrochemical desorption of the atomic hydrogen from the surface:

$$1/S = 1/S_p + 1/S_D; \quad S_p = k_p^{(1)} / k_p^{(2)}; \quad S_D = (k_D^{(1)} / k_D^{(2)}) (K_{\text{H}_2\text{DO}^+} / K_{\text{H}_3\text{O}^+}); \tag{18}$$

Here $K_{\text{H}_2\text{DO}^+}$ and $K_{\text{H}_3\text{O}^+}$ are the dissociation constants for H_2DO^+ and H_3O^+ with the stripping of the proton H^+ . Below only the ratio of the rate constants for the desorption stage will be studied, which is determined mainly by the ratio for the corresponding tunneling factors:

$$k_D^{(1)} / k_D^{(2)} \simeq T^{(1)} / T^{(2)} \simeq C \cdot I^{(1)} / I^{(2)}, \tag{19}$$

$$C = \frac{\Gamma_d^{(1)} \sqrt{\Gamma_v^{(1)}} \Omega_f^{(1)} \text{sh}^{-1/2} \beta \theta^* \hbar \omega_f^{(1)} \prod_{\alpha=1}^6 \text{sh}^{-1/2} \beta (1 - \theta^*) \hbar \omega_{\alpha}^{(1)} \sum_{l=0}^{\infty} (2l+1) \exp\{-\beta \theta^* B^{(1)} l(l+1)\}}{\sqrt{6} \Gamma_d^{(2)} \sqrt{\Gamma_v^{(2)}} \Omega_f^{(2)} \text{sh}^{-1/2} \beta \theta^* \hbar \omega_f^{(2)} \prod_{\alpha=1}^6 \text{sh}^{-1/2} \beta (1 - \theta^*) \hbar \omega_{\alpha}^{(2)} \sum_{l=0}^{\infty} (2l+1) \exp\{-\beta \theta^* B^{(2)} l(l+1)\}}; \tag{20}$$

here all of the parameters Ω_{α} and Γ are determined by the relationships in (9) where the following substitutions should be made: $m_f^{(1)} = \frac{1}{2}m$, $m_1^{(1)} = m_{\alpha}^{(2)} = m$, $m_f^{(2)} = \frac{2}{3}m$, $m_{\alpha}^{(2)} = m$, $m_1^{(2)} = 2m$, $\omega_f^{(2)} = (\sqrt{3}/2)\omega_f$, $\omega_{\alpha}^{(2)} = \omega_{\alpha}$, $\omega_1^{(2)} = \omega_1 / \sqrt{2}$.

All of the results obtained above were not based on a priori assumptions about the quantum or classical movement of the protons. As we can see from Eq. (9), in the normal region ($\theta^* \approx 0.5$) the behavior of the proton can be considered as quantum.

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