where A is the Warburg constant, V is the molar volume of S-1, $\delta$ is the degree of deviation of S-1 from stoichiometry (this characterizes the concentration of silver dissolved in S-1), $\kappa_i$ is the ionic conductivity of S-1, $\kappa_e$ is the electronic conductivity of S-1, and R, T, and F have their generally accepted significance.

The partial conductivity components contained in Eq. (4) were obtained by dc and ac measurements and construction of a coulometric titration curve using the same experimental technique as in [1, 2].

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# ACTIVATION ENERGY OF HYDROGEN ION DISCHARGE IN LIGHT AND HEAVY WATER


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The activation energies of hydrogen evolution from light water and deuterium evolution from heavy water at mercury cathodes differ by 0.8 kcal [1]. This difference was explained in terms of the Horiuti–Polanyi model as difference in the zero-point energies of the O–H and O–D bond. Ample experimental data have accumulated by now which show that the model of gradual bond stretching does not apply to the hydrogen evolution reaction [2]; it has become necessary, therefore, to discuss the isotope effect in the activation energies in terms of modern quantum-mechanical theory, which describes the elementary act of proton donor discharge as a process of solvent reorganization with subsequent tunneling of the proton (or other hydrogen isotope) from the initial to the final ground state [3].

We start our analysis of the experimental data by observing that the activation energies being determined experimentally, and in particular the values found in [1], are real energies, i.e., they are found at constant overpotential rather than at constant potential drop [4]. Temkin has shown [4] that the real activation energy differs from the ideal one by an amount $\alpha q$, where q is the latent equilibrium heat of the overall electrode reaction, which in the present case is the reaction

$$H_3O^+ + \bar{e} = {}^1/_2H_2 + H_2O.$$

In constructing the potential energy diagrams from which one can calculate the real activation energy, one must shift the potential energy curve of the initial state by an amount q, and for the equilibrium potential in particular, one must superimpose its minimum with the energy level of ${}^1/_2H_2 + H_2O$. Turning now to a comparison of the cathodic process in light and heavy water we see that the energy levels of ${}^1/_2H_2 + H_2O$ and ${}^1/_2D_2 + D_2O$ are different. The minima of the potential energy curves of the initial states accordingly are displaced relative to each other by the difference of the corresponding zero-point energies (Fig. 1). The energy levels of the discharge products, $H_{ads} + H_2O$, differ by similar quantities. As a result, the heat effect, $\Delta I$, of the elementary act for $D_3O^+$ discharge is larger by an amount ${}^1/_2(E_{H_2}^\circ - E_{D_2}^\circ) + E_{MD}^\circ - E_{MH}^\circ$. The zero-point energies of the $H_2$ and $D_2$ molecule are 6.20 and 4.41 kcal, respectively [5]. From the Hg–H bond energy, which is 29 kcal, we estimate the value of $E_{MN}^\circ$; this is 2.56 kcal. Reckoning that $E_{MD}^\circ = E_{MH}^\circ/\sqrt{2}$ we find $E_M^\circ = 1.88$ kcal (here deformation vibrations are included as well) [6]. Thus, the real heat effect


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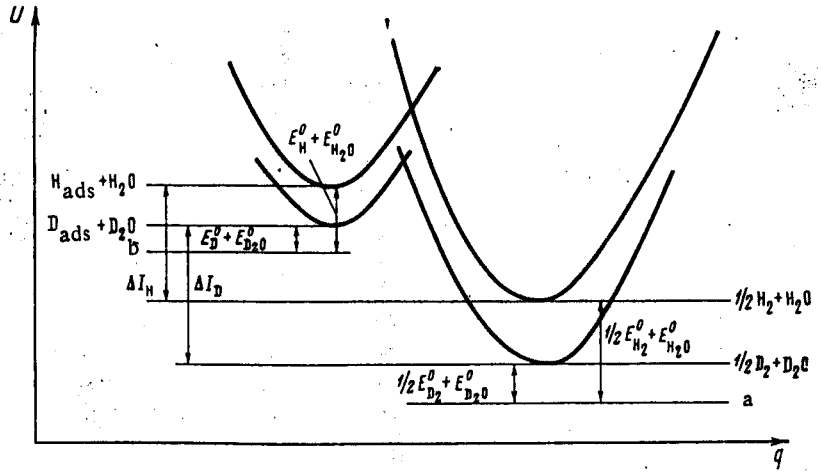


Fig. 1. Energy levels, and the scheme of potential energy curves for calculating the real activation energy of $H_3O^+$ ($D_3O^+$) discharge at the equilibrium potential. a) The energy levels of the systems $^1/_2H_2(D_2) + H_2O(D_2O)$ disregarding the zero-point energy, b) the energy levels of the systems $H_{ads}$ ($D_{ads}$) + $H_2O(D_2O)$ disregarding the zero-point energy. The U(q) curves show the system's potential energy as function of generalized solvent coordinate q.

for the discharge of $D_3O^+$ in $D_2O$ is 0.22 kcal higher than for $H_3O^+$ in $H_2O$. For $\alpha = {}^1/_2$ this yields an excess activation energy of 0.11 kcal.

In the above calculation we disregarded the heats of adsorption of water and the hydroxonium ion (see, e.g., [2]). For $H_2O$, we are talking about a relatively small quantity, on the order of 1 kcal, so that the isotope effect will hardly be perceptible here. Any marked difference between the heats of adsorption of $H_3O^+$ and $D_3O^+$ also is unlikely (we are talking about adsorption in the ion's equilibrium position), although basically, somewhat larger differences are possible here, since we are concerned with ions that have penetrated into the first monolayer of water molecules [7]. The values of the $\psi_1$ potential in $H_2O$ and $D_2O$ will be somewhat different, because of the difference in the dielectric permittivities ($\varepsilon$) of these solvents. But this effect amounts to $(RT/F)\ln(\varepsilon_{D_2O}/\varepsilon_{H_2O}) = -0.2$ mV, i.e., can be neglected.

In addition to effects on the heat of the elementary act, one also must consider changes in solvent reorganization energy $E_S$. Using the values of the refractive index ($n_{H_2O}$ = 1.32741; $n_{D_2O}$ = 1.32696) and dielectric permittivity ($\varepsilon_{H_2O}$ = 78.54; $\varepsilon_{D_2O}$ = 78.25) [8] we find that the characteristic quantity $(1/\varepsilon_\infty - 1/\varepsilon_S)$ for $D_2O$ is merely 0.06% larger than for $H_2O$. Practically the same difference can be expected in the reorganization energies. Since $E_S \approx$ 20 kcal, we find that $\Delta E_S \approx 0.012$ kcal. The difference in the activation energies is about one fourth of this figure, i.e., 0.003 kcal. This estimate was based on the model of isotropic dielectrics, and is highly approximate. It shows nevertheless that the contribution of the change in reorganization energy is extremely small.

Thus, the factors examined produce a difference in activation energies of the order of 0.1 kcal, which is markedly less than the experimental value. However, the reasons for this discrepancy can be understood when taking into account that a substantial approach of the proton donor to the electrode is required during the elementary act. The proton would have to tunnel over distances on the order of 1.5 Å, were it to jump while the ion and the electrode are at equilibrium separation, i.e., at a distance on the order of the sum of the van der Waals radii. The proton's tunneling probability decreases very rapidly with distance (as $\exp(-ar^2)$ [9]). Hence some approach of the particles prior to tunneling should be advantageous. For such an approach, work must be expended against the repulsion forces, which reduces the probability of approach. The competition between these two trends leads to the existence of some optimum distance where by expenditure of some additional energy, a sufficiently high tunneling probability is attained. Other conditions being equal, the tunneling probability of deuterons is lower than that of protons, so that a closer approach is more advantageous for deuterium than for protium, but it is attained at the cost of higher additional activation energy.

For quantitative estimates one must know the exact dependence on distance of both the tunneling probability and the repulsive potential. The repulsion energy in proton donor—metal systems cannot be estimated directly from any independent data at the present time. However, such data obtained by studies of intermolecular interactions are available at the present time for pairs of saturated molecules. In conjunction with the harmonic-oscillator approximation, these data have been used to calculate optimum tunneling distances and additional contributions to the activation energy for CH—acid—base systems. The results of these calculations will not quantitatively characterize an electrode process, but should give a reasonable idea about the magnitude of the values involved. It was found that the elementary act of proton transfer is attended by a strong approach of the particles, viz., to a distance of about 0.4 Å; for deuterium transfer, this distance is substantially smaller (by about 0.06 Å). This approach is attained by the expenditure of additional activation energy (more than 7 kcal), and for deuterium, the additional activation energy is about 0.8 kcal higher. This effect matches the experimentally observed difference in the activation energies in order of magnitude. Thus, the basic reason for the larger energy of activation required in deuterium evolution from $D_2O$ is the need for closer approach of the $D_3O^+$ ion to the electrode, so as to compensate the lower tunneling probability of $D^+$ relative to $H^+$. Certain contributions are provided in addition by the other effects calculated here, and possibly also by the effect of a more difficult penetration of $D_3O^+$ into the first monolayer of $D_2O$ (as compared to the situation in light water), which cannot yet be estimated quantitatively.

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