BRIEF COMMUNICATIONS

PRE-EXPONENTIAL FACTOR FOR THE HYDROGEN ION DISCHARGE REACTION

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The present paper is devoted to a detailed analysis of the relation existing between the pre-exponential factors for conventional and barrier-less hydronium ion discharge, a problem basic to the theory of the elementary act of proton transfer [1].

The rate of ionic discharge on a free, homogeneous metallic surface (e.g., on a mercury cathode, in the case of hydrogen) can be described by the equation

$$i=kn_s\exp\left[-\frac{A_0+\alpha(\varphi-\psi_1)F}{RT}\right]. \qquad (1)$$

Here i is the discharge current density, k is a temperature-independent pre-exponential factor which includes the Faraday constant, a frequency factor characterizing classical subsystem motion, and a tunneling factor characterizing quantum subsystem motion, n_S is the concentration of ions in a plane representing an optimal approximation to the electrode surface [2] for ionic discharge, ψ_1 is the potential at the point occupied by the discharging ion, and the remaining terms have their usual significance.

Representing the surface concentration of water by n_{H_2O} and the mole fraction of H_3O^+ ions in the surface layer by x_S, one can write $n_S = n_{H_2O}x_S$. In reasonably dilute solutions, the H_3O^+ surface concentration can be described by a Henry isotherm with

$$x_s=xe^{\Delta S_a/R}e^{-\Delta H_a/RT}e^{-\psi_1 F/RT}, \qquad (2)$$

x being the mole fraction of H_3O^+ in the body of the solution and ΔS_a and ΔH_a, the respective entropy and enthalpy of specific adsorption. Introducing the overvoltage $\eta = \varphi_e - \varphi$ and drawing on the Nernst equation for the reversible potential

$$\varphi_e=\varphi^0+\frac{RT}{F}\ln x, \qquad (3)$$

one finally obtains

$$i=kn_{H_2O}e^{\frac{\Delta S_a}{R}}x^{\beta}e^{-\frac{\Delta H_a+A_0+\alpha\varphi_e{}^0F}{RT}}e^{-\frac{\beta\psi_1 E}{RT}}e^{\frac{\alpha\eta F}{RT}}. \qquad (4)$$

Although ΔH_a and A_0 can be considered as constant, in a first approximation, the temperature dependence of the standard potential $\varphi_e{}^0$ cannot be neglected. If $\varphi_e{}^0F$ is expressed as a difference of standard chemical potentials, and the latter, in turn, expressed in terms of partial molar enthalpies and entropies, one obtains

$$i=kn_{H_2O}e^{\frac{\Delta S_a}{R}}e^{\frac{\alpha\Delta S_e{}^0}{R}}x^{\beta}e^{-\frac{\Delta H_a+A_0+\alpha\Delta H_e}{RT}}e^{-\frac{\beta\psi_1 F}{RT}}e^{\frac{\alpha\eta F}{RT}}, \qquad (5)$$

where $\Delta H_e = H_{H_3O^+} - H_{H_2O} + H_e - {}^1/_2 H_{H_2}$ and $\Delta S_e{}^0 = S_{H_3O^+}{}^0 - S_{H_2O}{}^0 - S_e - {}^1/_2 S_{H_2}{}^0$, and the expressions for the charged-particle partial molar enthalpies are free of electrical terms.

For barrier-less discharge: $\alpha = 1$, $\beta = 0$, and one has

$$i_{(b)}=k_{(b)}n_{H_2O}e^{\frac{\Delta S_a}{R}}e^{\frac{\Delta S_e{}^0}{R}}e^{-\frac{\Delta H_a+A_0'+\Delta H_e}{RT}}e^{\frac{\eta F}{RT}}. \qquad (6)$$

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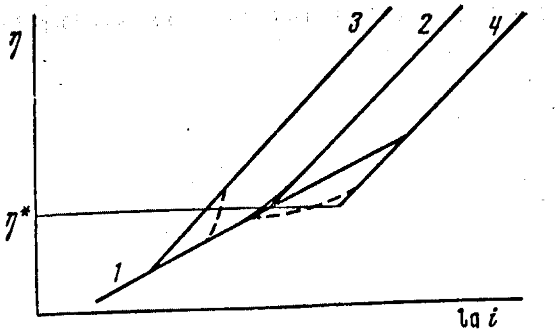

Fig. 1. Schematic representation of polarization curves in the region of passage from conventional to barrier-less discharge.

Here a prime has been attached to the A_0 to emphasize that the pre-exponential factors for barrier-less discharge and conventional are not the same.

Conventional discharge can be best handled by considering separately the two simplest limiting cases. In sufficiently concentrated solutions $\psi_1 = 0$, and one has

$$i = kn_{\mathrm{H_2O}} e^{\frac{\Delta S_a}{R}} e^{\frac{\alpha \Delta S_e{}^\circ}{R}} x^\beta e^{-\frac{\Delta H_a + A_0 + \alpha \Delta H_e}{RT}} e^{\frac{\alpha \eta F}{RT}}. \qquad (7)$$

In dilute solutions of pure acids, $\psi_1 \simeq -B(RT/F)\ln x$, the constant B being possibly temperature dependent. In a first approximation $B \simeq (RT/F)\ln x_0$, the constant x_0 being taken as ~0.03 [3]. The corresponding substitutions into (5) give

$$i = kn_{\mathrm{H_2O}} e^{\frac{\Delta S_a}{R}} e^{\frac{\alpha \Delta S_e{}^\circ}{R}} x_0{}^\beta e^{-\frac{\Delta H_a + A_0 + \alpha \Delta H_e}{RT}} e^{\frac{\alpha \eta F}{RT}}. \qquad (8)$$

Equation (8), and Eq. (10) which will eventually follow from it, are not as well suited as the preceeding equations for the treatment of experimental data since the quantity x_0 may show a marked temperature dependence.

The last two terms in Eqs. (6)-(8) vary exponentially with the reciprocal temperature, the coefficient in the one exponent being the apparent real activation energy [4];* the remaining terms, taken together, represent the real pre-exponential factor K_p [5], a quantity which can be evaluated experimentally.

Comparison of the pre-exponential factors for barrier-less and conventional discharge is of primary interest since the ratio of tunneling probabilities, i.e., actually, the ratio K_b/K, can thereby be determined. Combining (6) and (7), and (6) and (8), one obtains

$$\frac{K_b}{K} = \frac{K_p^{(6)}}{K_p^{(7)}} x^\beta e^{-\beta \frac{\Delta S_e{}^\circ}{R}} \qquad (9)$$

$$\frac{K_b}{K} = \frac{K_p^{(6)}}{K_p^{(8)}} x_0{}^\beta e^{-\beta \frac{\Delta S_e{}^\circ}{R}} \qquad (10)$$

It is a well-known fact that ΔS_e, the change in entropy for the single-electrode reaction, cannot be determined thermodynamically. We have shown, however, that it can, in principle, be estimated from kinetic data [6]. In fact the value of ΔS_e can be obtained from the real activation energies for barrier-less and conventional discharge and the value of the overvoltage corresponding to passage from the one mechanism to the other, the last determined from the point of intersection of the respective Tafel curves. The figures in question here are: $\Delta S_e{}' = -12.1$ e.u., $S_{\mathrm{H_3O^+}}{}^0 = 20.3$ e.u. ($S_{\mathrm{H^+}}{}^0 = S_{\mathrm{H_3O}}{}^0 - S_{\mathrm{H_2O}}{}^0 = 3.5$ e.u.).† All of the calculations of [6] were based on the conventional standard state of the H_3O^+ ion, namely 1 mole/liter. Since the concentrations of the earlier equations were expressed in mole fractions, $\Delta S_e{}^0$ differs from

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* The apparent activation energy (measured at constant bulk H_3O^+ concentration) differs from the true activation energy (measured at constant surface concentration) by the quantity ΔH_a. A_0 is the ideal activation energy measured at zero total potential difference φ. The real activation energy differs from the ideal by the term αq, $q = T\Delta S$ being the latent heat of the electrode reaction at the potential in question [4]. In a solution in which the reversible potential difference φ_e is zero, $\Delta H_e = T\Delta S_e$. From this it is clear that it is the apparent real activation energy which appears in the exponents of Eqs. (6)-(8). This quantity does not vary with the solution composition, at least in the ideal case, as can be seen convincingly from the term plots recommended by Temkin for calculating real activation energies [4].

† The figures cited in [6] differ by 3.5 e.u. The calculations of [6] were based on data for the 0.25 N H_2SO_4 + 1.0 N Na_2SO_4 system which had been reported by Iofa and Mikulin [7]. The figures presented above were also calculated by the method of [6], but are based on data on the 0.1 N HCl + 0.9 N KCl system reported in [8]. In comparison with the sulfate system, the chloride system has the advantage of requiring no correction for incomplete dissociation of the acid.

$\Delta S_e'$ by $+R \ln 1/56 = -8$ e.u., the mole fraction of H_3O^+ ions in a one-molar solution being 1/56. On introducing numerical values for the various constants, one obtains

$$\frac{K_b}{K} = \frac{K_p^{(8)}}{K_p^{(7)}} x^{1/2} \cdot 10^{+2.2}. \tag{9a}$$

It is quite likely that the error inherent in entropy determinations by the method of [6] would amount to several entropy units. Other methods of estimating $S_{H^+}^0$ give a value which is more negative by ~8-9 e.u. [9].

Values of the real pre-exponential factor for barrier-less hydrogen ion discharge on the mercury cathode have been obtained for various solutions [10], the mean of these determinations being log $K_p = 3.0 \pm 1.0$ ($\pm$ 0.4).† For conventional H^+ ion discharge in a 0.1 N HCl solution containing excess salt, one finds that log $K_p^{(7)} = 3.9$ [8]; substitution into the corrected Eq. (9a) with $x = 0.1/56 = 10^{-2.75}$ then gives $K_b/K \simeq 10^{-0.07}$, thus indicating identical ideal pre-exponential factors for barrier-less and conventional discharge. It must be emphasized, however, that this conclusion cannot be considered as definitive. The situation here is that the value of the entropy of the hydrogen ion which was substituted into Eq. (9) was based on data which had been used earlier for estimating the real pre-exponential factors, and therefore rested, in essence, on an assumption of equality of K_b and K (see below). It can be shown that the value of the K_b/K ratio obtained from such calculations must faithfully reflect any assumptions concerning this ratio which may have been made in the course of estimating S_{H^+}. The above result therefore merely confirms the internal consistency of the data on which it was based.

It has been pointed out above that other, completely independent methods of evaluation lead to $S_{H^*}^0$ values which are not markedly different from that used in our calculation; from these it would follow that $K_b/K = 10^{+0.8}-10^{+0.9}$. Thus, it would seem that the difference between the pre-exponential factors for barrier-less and conventional ionic discharge should fall within the limits of experimental error.

A comparison of real values prompted an earlier suggestion on our part [1] that the pre-exponential factors for barrier-less and conventional discharge should be essentially identical. Strict treatment of tunneling probabilities would require comparison of ideal rather than real values. As pointed out above, however, this detail should not alter the final conclusion, the tunneling probabilities for conventional and barrier-less discharge being of the same order of magnitude.

It has been shown in [1] that this conclusion is more consistent with the new, quantum-mechanical theory of the elementary act of proton transfer [11, 12] than with the older Horiuti–Polanyi theory [13]. In the first of these theories one would expect essential equality of the tunneling factors for the two types of discharge, while the second would require a considerably higher probability for transfer in the case of barrier-less discharge where there is no impediment to proton movement.

It should be possible to calculate the real pre-exponential factor for barrier-less hydrogen ion discharge through the theory of absolute reaction rates, the only assumption required being that the transmission coefficient $\varkappa$ is equal to unity. The results of such calculation are entirely inconsistent with the experimental values, log K = 5.7 as compared to log K = 3.0 [10]. Thus, it can be concluded that absolute reaction rate theory is not applicable to this problem. This situation could not arise from a non-equilibrium distribution of energy over the various degrees of freedom of the activated complex, since one is dealing here with a very slow, liquid phase reaction.‡ What is more likely is that quantum effects play a vital role in the transfer process [12]. In other words, the fact that a $\varkappa$ value of the order of 10^{-3} would be required to account for the considerable difference between theoretical and experimental K values must be considered as an indication of proton tunneling. It is, however, difficult to fit quantum effects into the Horiuti–Polanyi model of the elementary act in barrier-less discharge where there is no barrier to impede proton transfer.

It was pointed out above that the method of [6] for calculating the entropy change associated with the electrode reaction essentially assumes equality of K_b and K. In fact this assumption must be made if one is to identify the voltage corresponding to intersection of curves 1 and 2 of Fig. 1 with η^*, the overvoltage corresponding to equality of the ideal activation energies for conventional and barrier-less discharge. If

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† The units for K_p are A/cm². The ± 1.0 indicates the maximum dispersion and the ± 0.4 the mean-square deviation.

‡ We discussed this possibility in [10], i.e., before the formulation of the quantum-mechanical theory of the elementary step.

the K_b/K ratio is greater or less than unity (curves 3 and 4, respectively), the voltage corresponding to intersection will be either less than, or greater than, η^* by the amount $(RT/\beta F)\ \ln (K_b/K)$. Since passage from barrier-less to conventional discharge must actually occur at η^*, the value of the pre-exponential factor could be expected to change markedly in the neighborhood of this particular value of the overvoltage, the polarization curves taking on the forms indicated by the broken lines of the figure. It is characteristic of these broken-line projections that each falls below one of the two intersecting lines. Experimentally, it is observed that the polarization curves have the form shown by the full lines of Fig. 1 in the transition region, thus suggesting that the difference between K_b and K cannot be great [14]. It is, of course, possible that there are two mutually compensating factors in operation in the transition region, each acting to bring about departures from linearity, namely, a nonlinear potential dependence of the activation energy, which would seem quite consistent with the theory of the elementary act [12], and a marked drift in the value of the pre-exponential factor. It is, however, very unlikely that these effects would exactly compensate, especially if neither were pronounced. The form of the polarization curves in the neighborhood of the transition point would therefore suggest that there is no marked change in the value of the pre-exponential factor, a conclusion fully consistent with the results of the earlier calculations.

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