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ON THE NATURE OF ELECTRON TRANSFER REACTIONS IN SOLUTION

By

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Abstract

In this paper, the two models of activation, thermal and electrostatic, are compared in their application to proton discharge at electrodes. The assumption of the insufficiency of thermally activated states for the bonds for which $h\omega_i \gg kT$ to sustain the reaction has been proved to be wrong in the case of the activation of O-H^+ bond. Recent spectroscopic evidence has been given to show the existence of the continuum of energy states for OH^+ stretching.

A detail calculation has been made to estimate the probability of having the activation energy (20 kcal/mole) by electrostatic fluctuation of the solvent. This probability of fluctuation is found negligible and also the energy of activation contribution from the inner solvation shell insignificant. From the electrostatic fluctuation the number of activated H_3O^+ states has been calculated to be much less than the required amount to sustain the reaction.

I. Introduction

Two different approaches are present in the literature concerning the activation mechanism for electron transfer reactions. The thermal approach originated from GURNEY[1] and was developed by BUTLER[2], GERISCHER[3], CHRISTOV[4] and BOCKRIS and MATTHEWS[5]. The vibration-rotation levels are assumed to be continuous and sufficient in number to allow reaction. An approach, in terms of dielectric continuum theory, originated by WEISS[6], and by PLATZMANN and FRANCK[7]. It was assumed that the energy of activation arises from "some movements" in a continuum solvent. It was developed by MARCUS[8]. DOGONADZE[10] suggests specifically that fluctuations in electrostatic energy arising from the libratory movement of solvent dipoles outside the solvation sheath, cause the activation of the ion. Detailed discussion of both models has recently appeared[9,11].

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One of the difficulties of distinction between the two approaches is that the solvent fluctuation approach has been formulated mainly in terms of continuum theory[10]. The equations in terms of a molecular model have not been solved.

In this paper, the models are compared in their application to proton discharge at electrodes.

II. Considerations of the Thermal Approach

In the thermal approach, the following assumptions are made[11]:

(a) The excited vibrational-rotational levels of the H_3O^+ ion from the activated state, where the condition for the radiationless electron transfer from the metal to the H_3O^+ ion is satisfied.

(b) A continuum distribution of the vibrational-rotational levels exists because interactions between the H_3O^+ ion and surrounding solvent smear out existing (rotation-vibration) levels.

Objections to these assumptions have been made[10]. It is claimed[10] that, for any bond for which $h\omega_1 \gg kT$, the occupancy of higher vibration-rotation levels is small. Thus, it is suggested[9] that there may be too few to play a significant part in the activation process. A continuous distribution of states between each vibrational level has been rejected, too, it being argued that there is no translation of the solvent in solution, and hence no collisional activation.

For the proton discharge reaction:

$$H_3O^+ + e(M) \longrightarrow H_{ads} + H_2O \qquad (1)$$

one has:

$$i = F\kappa \frac{kT}{h} C_{H_3O^+} e^{\Delta S^*/R} e^{-\Delta H^*/RT} e^{-\beta \Delta \phi_r F/RT}, \qquad (2)$$

where i is the rate expressed as a current density; κ, the transmission coefficient; $C_{H_3O^+}$ is the concentration of H_3O^+ ion at the O.H.P. per cm^2; ΔS^* is the entropy of activation; ΔH^* is the energy of activation, and $\Delta \phi_r$ is the Galvani potential difference at equilibrium at the metal solution interface. The absolute value of $\Delta \phi_r$ is not known experimentally. But we can write:

$$\Delta \phi_r = -\frac{\Delta G^0}{F} = -\frac{\Delta H^0}{F} + T\frac{\Delta S^0}{F}, \qquad (3)$$

where ΔG^0 standard free energy change of the single electrode reaction

$$H_3O^+ + e(M) \rightleftharpoons \frac{1}{2} H_2 + H_2O .$$

Introducing (3) in (2) yields :

$$i = F \frac{kT}{h} C_{H_3O^+} e^{(\Delta S^* - \beta \Delta S^0)/R} e^{-(\Delta H^* - \beta \Delta H^0)/RT} , \qquad (4)$$

where :

$$\Delta S^* = \Delta S^* - \beta \Delta S^0$$

and

$$\Delta H^* = \Delta H^* - \beta \Delta H^0$$

can be defined as the apparent activation entropy and energy respectively. With a transmission coefficient $\kappa = 1$ (for an adiabatic reaction), equation (4) reduces to :

$$i = F \frac{kT}{h} C_{H_3O^+} e^{\Delta S^*/R} e^{-\Delta H^*/RT} . \qquad (5)$$

A value of ΔS^* can be estimated (Appendix I) by assuming the applicability of the thermal model, and from an Arrhenius type plot. The values are -10.5 and -15 eu respectively.

Now, we can rewrite (5) as :

$$i = A C_{H_3O^+} e^{-\Delta H^*/RT} ,$$

where

$$A = F \frac{kT}{h} e^{\Delta S^*/R} .$$

$C_{H_3O^+} e^{-\Delta H^*/RT}$ is the concentration of protons in the activated state needed to sustain the reaction with the observed i. Taking $i = 10^{-11}$ amp/cm^2 for proton discharge reaction on Hg, $\Delta S^* \simeq -10$ eu, we get :

$$C_{H_3O^+} e^{-\Delta H^*/RT} = \frac{ih}{FkT} e^{-\Delta S^*/R} = 9.6 \times 10^{-4} \text{ molecules/cm}^2 .$$

ΔH^* for the proton discharge reaction[12] is 20 kcal/mole. For the O–H$^+$ bond in the H_3O^+ ion[13], $h\nu = 3600$ cm^{-1}. Thus, if the excited vibrational levels form the activated state, we must have the O–H$^+$ bond in the second vibrational level. The probability of having an O–H$^+$ bond in the second vibrational level is :

$$P_{H_3O^+} = e^{-2h\nu/kT} = 10^{-15} .$$

Also:

$$C_{H_3O^+} = 2rNC_{H_3O^+},$$

where r is the radius of H_3O^+ ion and $C_{H_3O^+}$ is the bulk concentration of H_3O^+. For a molar solution of H_3O^+ ion we have:

$$C_{H_3O^+} = 1.7 \times 10^{13} \text{ molecules/cm}^2.$$

Hence:

$$C_{H_3O^+} P_{H_3O^+} = 0.01 \text{ molecules/cm}^2.$$

Thus, there are 0.01 molecules/cm^2 of H_3O^+ ion in the second vibrational level in excess of the number needed ($\sim 9.6 \times 10^{-4}$ molecules/cm^2) to sustain the reaction at the observed rate. The assumption of the insufficiency of thermally activated states to sustain the reaction is, thus, unsound*.

The most important fact[14,15] observed in the spectroscopy of H_3O^+ ion in water is the large band-width for the stretching region of the order of 400 cm^{-1} compared to the extremely small band-width of the same stretching band in ice (28 cm^{-1}). The hydrogen in ice is much fuller than that in liquid water. Thus, hydrogen bonding cannot explain the breadth of these bands in liquid water.

Alternatively, SCHIFFER and HORNIG[14] (cf. also WALL and HORNIG[15]) explain the O–H band width in terms of lateral collisions in solution. A Maxwellian distribution of velocities exists among free molecules in liquid water. We may therefore expect a Maxwellian distribution of environments and therefore $\nu_{OH's}$, one for each collision of different strength. This Maxwellian distribution of $\nu_{OH's}$ gives rise to the Gaussian distribution of the band seen in the spectra**. The model explains both the observed band width in the liquid and the enhanced FERMI resonance in liquid water over that in certain hydrates.

Analogous arguments can be made for the H_3O^+ ion. Hence, a continuous distribution of acceptor level would exist. FALK and GIGUERE[16]

* Similar arguments are also valid for the same reaction occurring on platinum where $i_0 \simeq 10^{-3}$ amp/cm^2 and $\Delta H^{\neq} \simeq 5$ kcal/mole. Thus, for Pt, using the above equations, the number of particles in the excited vibrational level is approximately 10^6 molecules/cm^2, whereas the amount of activated particles needed to sustain the reaction at the observed rate is approximately 10^4 molecules/cm^2.

** The Maxwellian distribution gives rise to a Gaussian distribution for the intensity as a function of the frequency because the intensity depends also on the EINSTEIN absorption coefficients (which is also frequency dependent when collisional broadening occurs), which are themselves a function of frequency, as well as on the number of particles with the particular frequency.

for H_3O^+ has shown that there is spectroscopically a continuum of energy states from low frequencies in the intermolecular libration H-bond stretching and bending regions (60 to 1000 cm^{-1}) up to higher frequencies (broad bands centred at 3628 and 3444 cm^{-1}) for OH^+ stretching, *i.e.*, OH vibration-rotation activation. Similar conclusions follow from the recent spectroscopic studies of O'FERRALL *et al*[13].

Thus, in the formulation of rates of proton transfer, the entire vibration-libration spectrum of H_3O^+ in liquid water[16] should be taken into account, including levels above kT. The rate must be calculated by integrating contributions from closely spaced vibration-rotation (libration) states. The continued formulation of the discharge of ions in terms of a frozen or ice-like crystal lattice model[10] (*e.g.*, using polaron theory) is a simplification so gross that it becomes qualitatively crippling.

III. Considerations of the Electrostatic Approach

(a) Calculation of the Probability of Energy Fluctuation:

Consider an ion of radius* r_i and charge +e is surrounded by N water dipoles in a random manner. The interaction between the ion and the dipole is:

$$E = -\frac{e\mu \cos\theta}{R^2}, \tag{6}$$

where μ is the dipole moment, θ the angle the dipole makes with the field direction, and R is the distance between the ion and the dipole.

The number of dipoles in a shell at R and $R+dR$ from the ion is:

$$n = \frac{4\pi R^2 dR}{\frac{4}{3}\pi r_\omega^3} = \frac{3R^2 dR}{r_\omega^3}. \tag{7}$$

Let r_∞ be the radius of a circular area around the ion containing the N dipoles. Then:

$$N = \int_{r_i}^{r_\infty} \frac{3}{r_\omega^3} R^2 dR = \frac{3}{r_\omega^3}\left(\frac{r_\infty^3}{3} - \frac{r_i^3}{3}\right). \tag{8}$$

Since $r_\infty \gg r_i$,

$$r_\infty = (N)^{1/3} r_\omega. \tag{9}$$

* The radius r_i includes the radius of the ion and the diameter of a water molecule, since in this first calculation we assume that the inner solvation sheath does not play any part in the activation process and thus is considered to be part of the ion.

If the N-dipoles are non-interacting, the number of dipoles $dN(\theta, R)$ between R and $R+dR$ from the ion having an angle between θ and $\theta+d\theta$ is:

$$dN(\theta, R) = \frac{4\pi R^2 dR}{\frac{4}{3}\pi r_\omega^3} \exp\left(\frac{e\mu \cos\theta}{\varepsilon_{\text{stat}} R^2 kT}\right) \frac{2\pi \sin\theta d\theta}{4\pi}$$

$$= \frac{3}{2r_\omega^3} \exp\left(\frac{e\mu \cos\theta}{\varepsilon_s R^2 kT}\right) R^2 dR \cdot \sin\theta \cdot d\theta . \tag{10}$$

Therefore, the probability that a dipole has an angle between θ and $\theta+d\theta$ with an ion at a distance between R and $R+dR$ from the ion, is:

$$P_i = \frac{dN(\theta, R)}{N} = \frac{\frac{3}{2r_\omega^3} \exp\left(\frac{e\mu \cos\theta}{\varepsilon_s R^2 kT}\right) R^2 dR \sin\theta d\theta}{\int_0^\pi \int_{r_i}^{r_\infty} \frac{3}{2r_\omega^3} \exp\left(\frac{e\mu \cos\theta}{\varepsilon_s R^2 kT}\right) R^2 dR \sin\theta d\theta} . \tag{11}$$

Equation (11) is for non-interacting dipoles. However, following KIRKWOOD's[17] treatment of the dielectric properties of liquid water, we represent water as a system of non-interacting dipoles having the effective dipole moment μ_{eff} given as:

$$\mu_{\text{eff}} = (1 + g \overline{\cos\gamma}) , \tag{12}$$

where g is the number of neighbour water molecules around a water molecule, and $\overline{\cos\gamma}$ is the average cosines of the angles between dipole moments of the central water molecule and those of its neighbours. In evaluating $g\overline{\cos\gamma}$, KIRKWOOD[17] considered the nearest neighbours, but POPLE[18] extended KIRKWOOD's[17] treatment and considered the contribution of first and second layers of water molecules, obtaining $\mu_{\text{eff}} = 1.53\mu_\omega$ as the effective dipole moment of water in water.

Equation (11) becomes:

$$P_i = \frac{\frac{3}{2r_\omega^3} \exp\left(\frac{e\mu_{\text{eff}} \cos\theta}{\varepsilon_s R^2 kT}\right) R^2 dR \sin\theta d\theta}{\int_0^\pi \int_{r_i}^{r_\infty} \frac{3}{2r_\omega^3} \exp\left(\frac{e\mu_{\text{eff}} \cos\theta}{\varepsilon_s R^2 kT}\right) R^2 dR \sin\theta d\theta} . \tag{13}$$

The average value of the interaction energy between the ion and the dipole is thus:

$$[E] = \frac{\int_0^\pi \int_{r_i}^{r_\infty} \frac{3}{2r^3} \left(-\frac{e\mu_{\text{eff}} \cos\theta}{\varepsilon_s R^2 kT}\right) R^2 dR \exp\left(\frac{e\mu_{\text{eff}} \cos\theta}{\varepsilon_s R^2 kT}\right) \sin\theta d\theta}{\int_0^\pi \int_{r_i}^{r_\infty} \frac{3}{2r_\omega^3} \exp\left(\frac{e\mu \cos\theta}{\varepsilon_s R^2 kT}\right) R^2 dR \sin\theta d\theta} . \tag{14}$$

The integral in the denominator can be seen to be equal to N. Hence:

$$[E]=\frac{1}{N}\int_0^{\pi}\int_{r_i}^{r_\infty}\frac{3}{2r_\omega^3}\left(-\frac{e\mu\cos\theta}{\varepsilon_s R^2}\right)R^2dR\exp\left(\frac{e\mu\cos\theta}{\varepsilon_s R^2kT}\right)\sin\theta d\theta\,. \quad (15)$$

We can expand the term in the exponential provided $\frac{e\mu_{\text{eff}}\cos\theta}{\varepsilon_s kTR^2}\ll 1$. It is so for $R>4$ Å. (For a discussion of the first layer of water molecules, see Section III **d**).

$$[E]=\frac{1}{N}\int_0^{\pi}\int_{r_i}^{r_\infty}\frac{3}{2r_\omega^3}\left(-\frac{e\mu_{\text{eff}}\cos\theta}{\varepsilon_s R^2}\right)R^2dR\left(1+\frac{e\mu_{\text{eff}}\cos\theta}{\varepsilon_s R^2kT}\right)\sin\theta d\theta\,. \quad (16)$$

Integrating R, and using the condition $r_i\ll r_\infty$

$$[E]=\frac{1}{N}\int_0^{\pi}\frac{3}{2r_\omega^3}\left(-\frac{e\mu\cos\theta}{\varepsilon_s}\right)\left(r_\infty+\frac{e\mu_{\text{eff}}\cos\theta}{\varepsilon_s r_i kT}\right)\sin\theta d\theta\,. \quad (17)$$

Now integrating over θ

$$[E]=\frac{1}{N}\frac{3r_\infty e\mu_{\text{eff}}}{2r_\omega^3\varepsilon_s}\int_0^{\pi}\cos\theta\sin\theta d\theta-\frac{3}{2Nr_\omega^3}\left(\frac{e^2\mu^2}{\varepsilon_s^2 r_i kT}\right)\times\int_0^{\pi}\cos^2\theta\sin\theta d\theta\,. \quad (18)$$

Now $\int_0^{\pi}\cos\theta\sin\theta d\theta=0$, and $\int_0^{\pi}\cos\theta\sin\theta d\theta=\frac{2}{3}$.

Hence:

$$[E]=-\frac{1}{N}\cdot\frac{e^2\mu_{\text{eff}}^2}{\varepsilon_s^2 r_\omega^3 r_i kT}\,. \quad (19)$$

The total interaction energy is then:

$$[u]=N[E]=-\frac{e^2\mu_{\text{eff}}^2}{\varepsilon_s^2 r_\omega^3 r_i kT}\quad\text{(energy per ion)} \quad (20)$$

$$=-3.3\ \text{kcal}\ (\text{g}\cdot\text{ion})^{-1}\,.$$

Now, for the theory of fluctuation, we want to evaluate the average of the square of the energy. This is:

$$[E^2]=\frac{1}{N}\int_0^{\pi}\int_{r_i}^{r_\infty}\frac{e^2\mu_{\text{eff}}^2\cos^2\theta}{\varepsilon_s^2 R^4}\cdot\frac{3}{2r_\omega^3}R^2dR\exp\left(\frac{e\mu_{\text{eff}}\cos\theta}{\varepsilon_s R^2kT}\right)\sin\theta d\theta\,. \quad (21)$$

Expanding the term in the exponential as before, we get:

$$[E^2] = \frac{1}{N}\int_0^{\pi}\int_{r_i}^{r_\infty} \frac{e^2\mu_{\text{eff}}^2 \cos^2\theta}{\varepsilon_s^2 R^4} \cdot R^2 dR \frac{3}{2r_\omega^3}\left(1+\frac{e\mu_{\text{eff}}\cos\theta}{\varepsilon_s R^2 kT}\right)\sin\theta\, d\theta$$

$$= \frac{1}{N}\int_{r_i}^{r_\infty} \frac{3}{2r_\omega^3} \cdot \frac{e^2\mu_{\text{eff}}^2}{\varepsilon_s^2 R^2} dR \int_0^{\pi} \cos^2\theta \sin\theta\, d\theta$$

$$+ \frac{1}{N}\int_0^{\pi}\int_{r_i}^{r_\infty} \frac{e^2\mu_{\text{eff}}^2 \cos^2\theta}{\varepsilon_s^2 R^2} \frac{3}{2r_\omega^3} \frac{e\mu_{\text{eff}}\cos\theta}{\varepsilon_s R^2 kT} \times \sin\theta\, d\theta\, dR\,. \qquad (22)$$

Since as before $\int_0^{\pi}\cos^2\theta\sin\theta\,d\theta = \frac{2}{3}$ and $\int_0^{\pi}\cos^3\theta\sin\theta\,d\theta = 0$ we can rewrite equation (23) as:

$$[E^2] = \frac{1}{N}\int_{r_i}^{r_\infty} \frac{e^2\mu_{\text{eff}}^2}{\varepsilon_s^2 r_\omega^3} R^{-2} dR$$

$$= \frac{1}{N} \cdot \frac{e^2\mu_{\text{eff}}^2}{\varepsilon_s^2 r_\omega^3 r_i}\,.$$

Thus:

$$[u^2] = N[E^2] = \frac{e^2\mu_{\text{eff}}^2}{\varepsilon_s^2 r_\omega^3 r_i}\,. \qquad (23)$$

Therefore, the mean square deviation in the fluctuation of the energy can be written as:

$$\sigma^2 = [u^2] - [u]^2$$

$$= \left(\frac{e^2\mu_{\text{eff}}^2}{\varepsilon_s^2 r_\omega^3 r_i} - \left(\frac{e^2\mu_{\text{eff}}^2}{\varepsilon_s^2 r_\omega^3 r_i kT}\right)^2\right) \qquad (24)$$

$$\simeq 0.01 \times 10^{-24} \text{ ergs per ion.}$$

Thus, since σ^2 is very much smaller than $[u]^2$, we can use the Gaussian distribution to evaluate the possibility of the fluctuation[19], which can be expressed as:

$$P_{H_3O^+} = A \exp -\frac{(u-[u])^2}{2\sigma^2}\,, \qquad (25)$$

where $(u-[u])=0$, $P_{H_3O^+}=A$, *i.e.*, A is the probability of the system having an energy corresponding to the average energy and in the electrostatic continuum approach, it is considered to be almost equal to unity. Thus, we can set $A \simeq 1$. The fluctuation we need is $E=(u-[u])=20$ kcal/mole$=1.39\times10^{-12}$ ergs/molecule. Thus, using equation (25) we get $P_{H_3O^+} \simeq 10^{-41}$ *.

* In one calculation the probability of having a fluctuation is independent of the number of molecules. That is so because we are considering N to be extremely large and the ion-dipole interaction energy completely dies down. If N Were sufficiently small so that I/r_∞ was not negligible compared to I/r_i we would have a probability depending on N, the number of dipoles considered.

Now, we have shown before (see Section II) that the number of activated particles needed to sustain the reaction to be equal to 10^{-3} molecules/cm^2. From electrostatic fluctuation the number of activated particles present will be:

$$C_{H_3O^+} \cdot P_{H_3O^+} = 1.686 \times 10^{-28} \text{ molecules/cm}^2$$

far less than the amount required at $\eta = 0$.

(b) Estimation of the accuracy of the calculation:

There are two approximations in the calculation. They are: (1) The neglect of ion-quadropole and other interaction between the ion and the water molecules, and (2) the estimated value of the entropy.

The ion-quadropole and other effects on the energy are about one-tenth in order of magnitude compared to the ion-dipole energy since they die off very rapidly.

A positive entropy of activation of the order of 60 eu. would make the electrostatic fluctuation effective. However, such a value of the entropy of activation seems unlikely (TEMKIN[20], Appendix I). Surface reactions have a negative entropy of activation. Thus, even if we assume $\Delta S^{\ddagger}$ for $H_3O^+ + e(M) \rightarrow H_2O + H_{ads}$ to be zero, $P_{H_3O^+}$ from the fluctuation is still extremely small compared to the states available thermally.

(c) Life time of the states produced by fluctuations:

The maximum life time can be obtained using:

$$\Delta E \Delta t = h .$$

Since $\Delta E \simeq 20$ kcal/mole

$$\Delta t = h/\Delta E = 4.7 \times 10^{-15} \text{ sec} .$$

Thus, these states last for a time in which electron transfer can occur.

(d) Inner sphere librating fluctuation:

We have shown in the previous section that at least for the hydrogen-evolution reaction the outer sphere electrostatic fluctuation does not produce enough activated particles to sustain the reaction at the observed rate. But there might be a probability that the inner sphere dipoles may librate and increase the energy of the reacting species. Let us therefore see what contribution to the activation energy comes from the librations of the inner sphere dipoles.

Let us consider an ion and a dipole near it rotating with thermal energy. There will be two forces operating on it. One is the rotational force due to the kinetic energy of the dipole which would induce the dipole to rotate

near to the ion and the other force is the ion-dipole force which would tend to keep it oriented.

The force of rotation then can be written as:

$$F_r = I\left(\frac{d^2\theta}{dt^2}\right), \tag{26}$$

where I is the moment of inertia of the particle, and $\frac{d^2\theta}{dt^2}$ is the angular acceleration.

The energy due to the ion-dipole interaction, u, is

$$u = -e\mu\cos\theta/\varepsilon_s R^2 . \tag{27}$$

Hence, the force due to ion-dipole attraction which tries to keep the dipole oriented is:

$$F_d = \frac{dt}{d\theta} - e\mu\cos\theta/\varepsilon_s R^2 = \frac{e\mu}{\varepsilon_s R^2}\sin\theta . \tag{28}$$

At the point where the two forces become equal, the particle stops and starts retracing its path. Thus, at that point:

$$I\left(\frac{d^2\theta}{dt^2}\right) = \frac{e\mu}{\varepsilon_s R^2}\sin\theta . \tag{29}$$

Multiplying both sides by $2(d\theta/dt)$ and integrating we get:

$$I\left(\frac{d\theta}{dt}\right)^2 = 2B\cos\theta + C , \tag{30}$$

where C is the integration constant. When $\theta=\theta_0$, $\left(\frac{d\theta}{dt}\right)_{\theta=\theta_0} = 0$.

So: $C = -2B\cos\theta_0$.

Hence:

$$\frac{1}{2}I\left(\frac{d\theta}{dt}\right)^2 = 2B(\cos\theta - \cos\theta_0) . \tag{31}$$

Now $\frac{1}{2}I\left(\frac{d\theta}{dt}\right)^2$ is the kinetic energy of rotation and thus by the equipartition theorem should be equal to $\frac{1}{2}kT$.

So: $\cos\theta - \cos\theta_0 = \frac{kT}{2B}$.

So when $\theta=0$:

$$1-\cos\theta_0=\frac{kT}{2B}$$

$$\cos\theta_0=0.97$$

We have assumed free rotation of the dipole. Thus, the value of θ we have obtained is the maximum limit. Hence, the total change in energy of the ion due to librations of the dipoles of the inner sphere will be less than:

$$u=4\frac{3}{\varepsilon R^2}(1-\cos\theta_0)$$

$$\simeq 1.5 \text{ kcal/mole.}$$

Thus, electrostatic fluctuation from the inner sphere is negligible.

(e) **Tafel line from electrostatic fluctuation model**:

In the electrostatic fluctuation model, the activation energy is $(u-[u])$. Thus, we can write, following the usual procedure:

$$\left(u-[u]\right)=(\Delta H_0^*+\beta\eta F), \tag{32}$$

where ΔH_0^* is the activation energy at the reversible potential. Thus, the rate of the reaction can be written as:

$$i=\text{constant } C_{H_3O^+}P_eP_{H_3O^+}, \tag{33}$$

where P_e is the probability of quantum mechanical electron transfer and $P_{H_3O^+}$ is the probability of the H_3O^+ ion being in the activated state. Assuming the reaction to be adiabatic, we can set $P_e\simeq 1$. Hence:

$$i=\text{constant } C_{H_3O^+}P_{H_3O^+}. \tag{34}$$

$P_{H_3O^+}$ is then given by equation (25). Thus:

$$i=\text{constant } C_{H_3O^+}\exp\left(-\frac{(u-[u])^2}{2\sigma^2}\right). \tag{35}$$

σ^2 can be written as follows:

$$\sigma^2=\left(\frac{\partial^2 F}{\partial u^2}\right)_{u=[u]}RT$$

$$=BRT.$$

Thus:

$$i=\text{constant } C_{H_3O^+}\exp\left(-\frac{(\Delta H_0^*+\beta\eta F)^2}{2BRT}\right)$$

$$=\text{constant } C_{H_3O^+}\exp\left(-\frac{(\Delta H_0^*)^2}{2BRT}-\frac{2\Delta H_0^*\beta\eta F}{2BRT}-\frac{(\beta\eta F)^2}{2BRT}\right).$$

Hence :

$$i = \text{constant } C_{H_3O^+} \exp\left(-\frac{\beta C\eta F}{RT} - \frac{(\beta\eta F)^2}{2BRT}\right). \tag{36}$$

Thus, we get a linear Tafel line only if $(\beta\eta F)^2 \ll RT$.

IV. Relative Contributions of Thermal and Electrostatic Fluctuation to the Activation Energy

We have estimated the probability of having a thermal and the electrostatic fluctuation type of activation at the reversible potential, *i.e.*, $\eta = 0$. However, it is most important to estimate how these probabilities vary as the overpotential changes. For the hydrogen evolution reaction, the activation energy at any overpotential is given as :

$$\Delta H^* = (\Delta H^*)_{\eta=0} - \beta\eta F. \tag{37}$$

Thus, we know the variation of the activation energy with overpotential is know. Thus, we can estimate the thermal probability using a Boltzmann distribution and the fluctuational probability using a Gaussian distribution. The results are tabulated in Table 1. The ratio of the two probabilities are plotted in Fig. (1). In most of the experimentally accessible overpotential, the probability of obtaining a suitable state by means of an energy fluctuation is negligible compared with the probability of existence of the same state as a result of thermal equilibrium of the ion with the solvent.

TABLE 1.

Volts	ΔH^* in kcal/mole	Probability thermal	Probability Fluctuational	Probability ratio (T/F)	log (T/F)
0	20	10^{-14}	10^{-42}	10^{28}	28
0.2	17.7	$10^{-12.4}$	$10^{-32.8}$	10^{20}	20
0.4	15.4	10^{-11}	10^{-25}	10^{14}	14
0.6	13.1	$10^{-9.5}$	$10^{-17.8}$	$10^{8.3}$	8.3
0.8	10.8	$10^{-8.1}$	$10^{-12.1}$	$10^{4.3}$	4.3
1.0	8.5	$10^{-6.7}$	$10^{-7.6}$	$10^{1.4}$	1.4
1.2	6.2	$10^{-4.5}$	$10^{-4.2}$	$10^{0.2}$	0.2
1.4	3.9	$10^{-3.0}$	$10^{-1.68}$	$10^{-0.9}$	−0.9
1.6	1.4	$10^{-0.9}$	$10^{-0.4}$	$10^{-0.5}$	−0.5

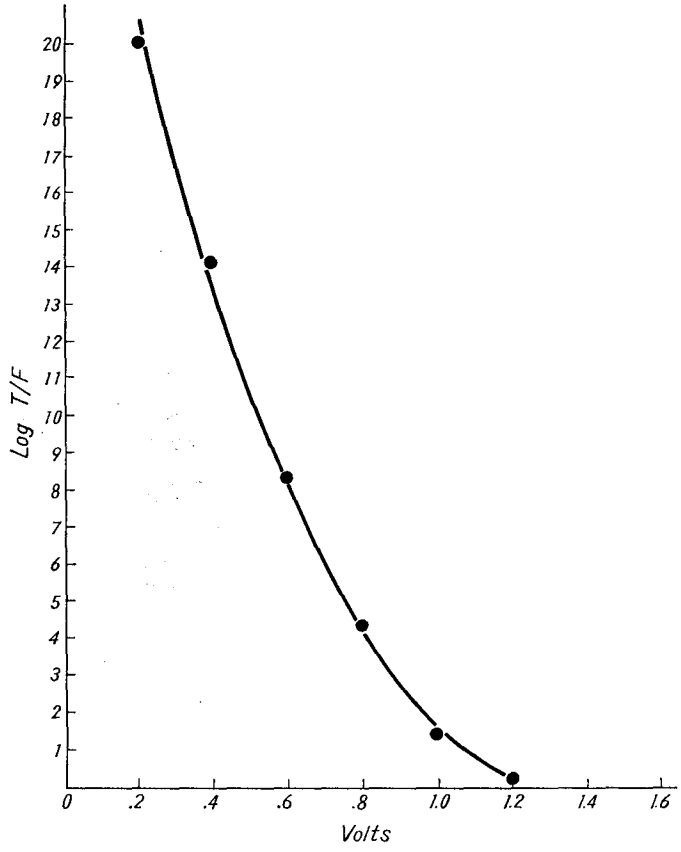

Fig. 1. Log of fluctuational probability-*vs.* volts.

Appendix I.

Estimation of the Entropy of Activation

Considering the proton-discharge reaction, the rate-determining step of which is:

$$H_3O^+ + e(M) \rightleftharpoons H_2O \cdots H^+ \cdots M \rightarrow M\text{-}H + H_2O \qquad \text{(i)}$$

we can then write, according to the absolute reaction rate theory

$$k' = \frac{kT}{h} \cdot \frac{f^*}{f_{in}} e^{-E_0/RT} = \frac{kT}{h} \cdot \kappa^{\pm}, \qquad \text{(ii)}$$

where k' is the specific rate constant and f's are the partition functions of

the activated and initial state and E_0 is the zero point energy term. Thus:

$$\kappa^{+} = \frac{f^{*}_{tr} f^{*}_{vib} f^{*}_{rot}}{f^{in}_{tr} f^{in}_{vib} f^{in}_{rot}} e^{-E_0/RT}. \qquad \text{(iii)}$$

SALUJA[22] argued that the solvated ion, since it finds itself surrounded by water molecules, consequently has very little translational freedom. Moreover, the activated complex has been considered to be immobile. Thus, $f^{*}_{tr}/f^{in}_{tr}=1$. We also consider that the activated complex has no rotational properties either. Thus, $f^{*}_{rot}=1$. Moreover, f^{in}_{rot} should be replaced by the vibrational partition function of the ion f^{in}_{lib}. Thus, we can now write:

$$\Delta F^{*} = -RT \ln \left(\frac{f^{*}_{vib}}{f^{in}_{vib} f^{in}_{lib}} \right) + E_0 \qquad \text{(iv)}$$

and

$$\Delta S^{*} = -RT \frac{\partial \ln (F^{*}_{vib})}{\partial T} + RT \frac{\partial \ln (f^{in}_{vib})}{\partial T} + RT \frac{\partial \ln (f^{in}_{lib})}{\partial T}. \qquad \text{(v)}$$

Since $f^{*}_{vib}=(f^{*}_{vib})_s (f^{*}_{vib})_b$, where the subscripts "$s$" and "$b$" denote stretching and bending. Using ν_s and ν_b to be 2900 cm^{-1} (BOCKRIS, SRINIVASAN and MATTHEWS[22]) and 1200 cm^{-1} (CONWAY and SALOMON[23]), the vibrational partition was evaluated. The vibration (f^{in}_{vib}) and the librational partition function (f^{in}_{lib}) of the initial state were evaluated using ν_{vib} equal to 3600 cm^{-1} [13] and ν_{lib} equal to 600 cm^{-1} [13]. Using equation (v), then to evaluate ΔS^{*} gives a value of -3 eu.

The apparent entropy of activation, $\Delta S^{\neq}$ is given as:

$$\Delta S^{\neq} = \Delta S^{*} - \beta \Delta S.$$

ΔS has been estimated[24] to be 15 eu. Thus, $\Delta S^{\neq} = 10.5$ eu.

On the other hand, TEMKIN[20] has shown that entropy of the activated state is given as:

$$\Delta S^{*} = \beta S^{0}_{H_3O^{+}}.$$

Hence:

$$\Delta S^{*} = S^{*} - S^{0}_{in}$$
$$= (\beta - 1) S^{0}_{H_3O^{+}} = 2.5 \text{ eu}.$$

Thus:

$$\Delta S^{\neq} = -5.0 \text{ eu}.$$

Using the data of POST and HISKEY[25] and MATTHEWS[26], if we plot ln i *vs* $1/T$, the pre-exponential factor A comes out to be 10^4 amp/cm^2.

Hence, using the relationship:

$$A = F\frac{kT}{h} C_{H_3O^+} e^{\Delta S^{\ddagger}/R}$$

we get $\Delta S^{*} \simeq -15$ eu. in good agreement with both the above mentioned theoretical calculations.

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