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## ON QUANTUM ELECTROCHEMICAL KINETICS

By

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### Abstract

In this article, a critical estimation is made of the theory of electrochemical kinetics in terms of two models of activation, thermal and electrostatic. It has been shown that the electrostatic model cannot predict the linearity of a Tafel line and also the constancy of symmetry factor  $\beta$  with overpotential and the relation of rate constants,  $k_{\text{hom}}$  and  $k_{\text{het}}$  does not diagnostically support the electrostatic model.

A quantum mechanical derivation is given to show the consistency of the time dependent perturbation theory with the GAMOW equation for the time dependent barrier concerned in charge transfer.

### I. Historical

Few examples<sup>1,2,3)</sup> are available where an attempt has been made to investigate the quantum mechanical aspects of reaction rates, even in the gas phase. However, quantum mechanical aspects of electron transfer reaction in solution were first discussed by GURNEY<sup>4)</sup> in 1931: it was one of the first topics in Chemistry to receive quantal discussion.

The GURNEY<sup>4)</sup> theory was developed by BUTLER<sup>5)</sup>, CHRISTOV<sup>6)</sup>, GERISCHER<sup>7)</sup> and BOCKRIS *et al*<sup>8)</sup>.

The basic aspect of this type of model is that there is a thermal equilibrium between the solvated ions and the solution. A BOLTZMANN distribution is assumed to give a population of excited vibrational states of the ion, and the rate of the electron transfer reaction is the product of the probability of a quantum mechanical transition (usually of an electron) and that of the probability of finding a suitable acceptor (or donor) level in the ion. This model will be referred to as the *thermal activation model*.

Another model originates with LIBBY<sup>9)</sup>, who suggested that, in a redox reaction, the energy change during electron transfer could be expressed as the difference between the BORN solvation energies of the initial and final

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states. (But see ref. 10). WEISS (1954)<sup>11)</sup>, followed by HUSH (1968)<sup>12)</sup> and MARCUS (1959)<sup>13)</sup> developed a view in which the optical polarisation associated with a fast electron transition was the principal part of an expression for the heat of activation. In 1965 MARCUS<sup>14)</sup> developed a more detailed model, which took into account contributions to activation from the inner solvation sheath. The former approach, —that based on the BORN equation, —has continued to be developed by LEVICH<sup>15)</sup>, with DOGONADZE<sup>16)</sup> and KUZNETSOV<sup>17)</sup>, with explicit stress upon the validity of the application of the BORN equation and the rejection of contributions by the inner shell of activation. This latter model (that which stresses the BORN equation) will be referred to here as the *continuum electrostatic approach*.

Until 1970, the physical meaning of the continuum electrostatic view was not differentiated from that of WEISS<sup>11)</sup>, HUSH<sup>12)</sup> and MARCUS<sup>13)</sup>. It did not contain a molecular-level description of how energy was transferred from the solvent to the entity to receive charge, (which must exist in an activated state at the moment of transition). In 1970, LEVICH<sup>18)</sup> suggested a molecular model which sought to rationalise the continuum electrostatic view in terms of fluctuation theory.

In this article, we would like to make a comparison of the two models\*.

## II. The Two Models

### 1. Description of the Models

The following is common to both models :

(a) A radiationless electron transfer is assumed. Therefore, one calculates a condition for setting up equal electronic energy states on the electrode and the solution side of the barrier, so that electron transition can occur from the state  $E_p$ , the FERMI level in the electrode, to a state of the same energy in the solution.

(b) As with the consideration of the quantum mechanical transitions in reactions, the BORN-OPPENHEIMER approximation is invoked to separate the fast moving electronic co-ordinate and the co-ordinates of the heavy particle, *e.g.*, at  $H_3O^+$  ion, or the solvent.

(c) In considering the hydrogen evolution reaction, both approaches consider the quantum mechanical aspect of a proton leaking through the barrier. But in the continuum electrostatic approach, the transfer of a heavy particle is pictured as occurring by means of a "quantum mechanical transi-

\* Importance of the field gains because many biophysical reactions probably involve interphasial charge transfer<sup>19)</sup>.

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tion" of the whole system. In the development of the thermal view the transfer of heavier particles over the barrier is taken into account.

We now describe the differences.

(i) **Thermal Model**

The model assumes that the  $\text{H}_3\text{O}^+$  ion is in thermal equilibrium with the surrounding solvent and there is a BOLTZMAN distribution of electronic energy levels in the ion and its solvent shell which provides a distribution of levels to correspond to the varying electronic level which occurs as the potential of the electrode is changed. Therefore, there must be some states in the  $\text{H}_3\text{O}^+$  ion which possess an energy to match the FERMI level of electrons in the electrode. It is to these states that electron transfer from the metal occurs without gain or loss in energy.

In this approach, the permeability of the barrier to protons is taken into account. Depending upon the energy level in the proton, at penetration, there is a probability of electrons being in the same level in the metal, whereupon a transition of the electron to the penetrated protons occur. Some protons will also go over the barrier. For heavy ion transfer, all the transitions will be over the barrier. For these, the quantal character of the electrode reaction will be (effectively) restricted to the electronic transition.

An electrostatic contribution to the energy of the initial state (ion in the double layer and electron in the metal) was made explicit by PARSONS and BOCKRIS<sup>20)</sup> and CONWAY and BOCKRIS<sup>21)</sup>. They took into account the electrostatic energy of the ion in defining the electron energy level in the initial state. These energy contributions were divided into chemical, ion-dipole and BORN terms. They were thought of as contributions to the energy of the system at equilibrium. Vibrations of the inner solvation sphere will, however, change the radius term in the BORN equation and can produce a *continuum* electrostatic fluctuation, in addition to whatever other fluctuations may arise in the electronic energy of the ion due to the librations of nearest neighbour dipoles.

(ii) **Electrostatic Continuum Model**

This model differs radically from the basic model used in the theory of activation in kinetics, where the small number of *excited* bonds are the medium of the reaction. In the electrostatic continuum model, for a bond for which  $h\nu \gg kT$ , the occupancy of the level (in the thermal distribution) is too small at room temperature that it does not play a part in the reaction. But species have to be excited. To achieve this, the reacting ion is pictured as existing in a dielectric continuum, and dielectric polarization fluctuations

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in the continuum are suggested as the cause of fluctuations in the energy of the reacting species.

LEVICH<sup>18)</sup> suggests that the fluctuating particles are water molecules, *i. e.* dipoles, undergoing librations in solution. They have a frequency of about  $10^{11} \text{ sec}^{-1}$ , so that for these  $\frac{h\nu}{kT} \ll 1$ , and they behave classically at room temperature\*. These librators produce longitudinal polarization waves and give rise to electrostatic fluctuations in the energy of the ion. Since a large number of librators are needed for the activation\*\* process, it is necessary that these longitudinal waves are in phase, *i. e.*, the oscillators librate in phase to create a standing wave, for, otherwise, sufficient energy can not be transferred to the ion. Thus, the concept of the polaron theory developed for solid crystals is used to describe the activation process. In this way (though not explicitly), it is suggested that energy pulses of the order of 1 ev. reach the ion, placing it thus momentarily at an energy level at which radiationless transfer can occur.

Second-order time-dependent perturbation theory is used to solve for the quantum mechanical transition probability of the electron and for the proton in the hydrogen evolution reaction.

## 2. The Rate-Overpotential relation according to both Models†

Both the models start off from the fundamental equation, which gives the rate of an electron transfer reaction as††:

$$i = eC_s \int_x \int_x n(\epsilon_f) \rho(\epsilon_f) W_{if}(\epsilon_f) d\epsilon_f dx \quad (1)$$

\*  $10^{-11} \text{ sec}$  is the DEBYE relaxation time in water. This has been attributed to water dipole librations by LEVICH<sup>15,16,18)</sup>.

\*\* LEVICH<sup>18)</sup> calculates the approximate number in the following manner: If  $E_a$  be the activation energy, and each dipole has the capacity of contributing an amount of energy not exceeding its own energy  $\hbar\omega_0$ , then if  $N$  dipole takes part in creating the reaction situation, the value of  $N$  is given as:

$$N \geq E_a / \hbar\omega_0$$

For  $E_a \sim 0.5 \text{ ev}$ , the  $N \geq 10^3$ .

However, using  $\omega_0 = 10^{11}$ , the frequency quoted by LEVICH for the librators in water,  $\hbar\omega_0 \approx \frac{1}{100} kT$ . Thus, the majority of librators would possess about 100 quanta, in which case the number of particles needed for activation would be about 10. Whether a continuum polaron concept can be applied to this small number must be questioned.

† For list of symbols, see end.

†† The double integral is annulled in the following simple treatment by taking the electrons only from the FERMI level and the distance of the acceptor states at the outer HELMHOLTZ plane.

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where  $i$  is the current per sq. cm, and gives in fact the rate of the electron transfer reaction.

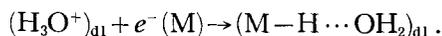
The main difference in approach is in the calculation of the transition probability,  $W_{ef}(\epsilon_f)$ . We will examine the methodology in a simplified way to show the essence of each model.

**(a) The Thermal Approach**

One may consider that electron transfer reactions are adiabatic, *i. e.*, the electronic motions are faster than the motions of the heavy particles (the ions). The probabilities of electron transfer ( $P_T$ ), and of attaining suitable acceptor states ( $P_{H_3O^+}(\epsilon)$ ), are hence independent. The transition probability (taken here, for simplicity, as occurring only from the FERMI level) is:

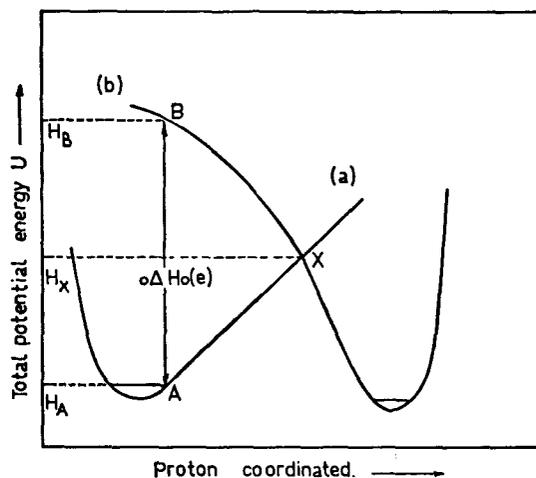
$$W_{ef}(\epsilon_f) = P_T P_{H_3O^+}(\epsilon) \quad (2)$$

The problem is to evaluate these two probabilities separately. For the hydrogen evolution reaction, the rate-determining step may be chosen for the sake of discussion as that corresponding to:

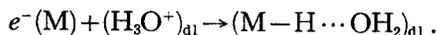


The potential energy profile will be as shown in Fig. 1.

The vertical transition (see Fig. 1) AB corresponds to the process:



**Fig. 1.** Potential energy-distance profile for h.e.r.;  $H_A$  is the ground state energy level of the reactants; curves (a) and (b) show the variation of potential energy with internuclear separation for  $M(e^-) \cdots H^+ - OH_2$  and  $M-H \cdots OH_2$ , respectively;  ${}_0\Delta H_0(e)$  is the standard enthalpy of reaction for reactants in their ground state.

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*i. e.*, of taking an electron from the FERMÍ level of the metal to an  $H_3O^+$  ion in its ground rotation-vibration state, with no change in the proton-coordinate,  $d$ . The energy change of the system for this vertical process is, say,  ${}_0\Delta H_0(e)$ , (Fig. 1). Such a transition for an  $H_3O^+$  ion not in its ground state will be accompanied by an energy change  $\Delta H_0(e)$ . Eventually, at the intersection point  $X$  of curves "a" and "b" in Fig. 1,  $\Delta H_0(e)=0$  and electron tunneling from the metal to the proton becomes possible\*.

Since the thermal model assumes that a BOLTZMAN distribution exists between the various vibrational-rotational energy states of the  $H^+-OH_2$  ion, the probability of finding the  $H^+-OH_2$  ion sufficiently activated, so that its energy will correspond to the intersection point  $X$  of fig. 1, is given by\*\*:

$$P_{H_3O^+}(\varepsilon) = \exp\left[-\frac{\Delta\varepsilon}{kT}\right]. \quad (3)$$

From Fig. 1,  $\Delta\varepsilon$  is a fraction of  ${}_0\Delta H_0(e)$ ,

$$\Delta\varepsilon = \beta_0 \Delta H_0(e)$$

where  $0 < \beta < 1$ .

Hence:

$$P_{H_3O^+}(\varepsilon) = \exp\left[-\frac{\beta_0 \Delta H_0(e)}{kT}\right]. \quad (4)$$

Since:

$$\left[{}_0\Delta H_0(e)\right]_{d\phi} = {}_0\Delta H_0(e) + e\Delta\phi$$

we have

$$P_{H_3O^+}(\varepsilon) = \exp\left[-\frac{\beta_0 \Delta H_0(e)}{kT}\right] \exp\left[-\frac{\beta e \Delta\phi}{kT}\right]. \quad (5)$$

The tunneling probability, assuming a square barrier† is:

\* For the h. e. r., the r. d. s. of which is  $(H_3O^+)_{d1} + e^-(M) \rightarrow (M-H \cdots OH_2)_{d1}$ , the point  $X$  in Fig. 1, is the point where the equality  $I+L-\phi=R+A$  is satisfied (see BOCKRIS and MATTHEWS<sup>8b</sup>). Rewriting the above equality in the form  $\phi=I+L-R-A$  shows that at the point  $X$  the radiationless electron tunneling condition is also satisfied (see GURNEY<sup>4</sup>).

\*\* The presentation is heuristic. The quantum mechanical properties of the proton are suppressed, for the sake of simplicity in the presentation of principles. Such properties have been taken into account<sup>8b</sup>).

† Again, the barrier has been taken here as the simplest for heuristic purposes. CHRISTOV<sup>6</sup>, and BOCKRIS and MATTHEWS<sup>8b</sup>) discussed the quantum mechanical properties of the proton in terms of Eckart barriers.

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$$P_T = A \exp \left[ -\frac{4\pi l}{h} \left\{ 2m(E_X - E_F) \right\}^{1/2} \right]. \quad (6)$$

Hence, the total current, using equation (6), is\* :

$$\begin{aligned} i_{d\phi} &= 2eC_s \frac{4\pi m(kT)^2}{h^3} \exp \left[ -\frac{4\pi l}{h} \left\{ 2m(E_X - E_F) \right\}^{1/2} \right] \\ &\times \exp \left[ -\frac{\beta(\Delta H_0(e) + e\Delta\phi_e)}{kT} \right] \exp \left[ -\frac{\beta e\eta}{kT} \right] \\ &= i_0 \exp \left[ -\frac{\beta e\eta}{kT} \right]. \end{aligned} \quad (7)$$

This is TAFEL's law.

**(b) The Electrostatic Approach**

As mentioned in Sec. IV, the electrostatic approach makes an initial *assumption* in contrast to theories of activation in collisional kinetics that bonds for which  $h\nu/kT \gg 1$  do not take part in the reaction. The activation

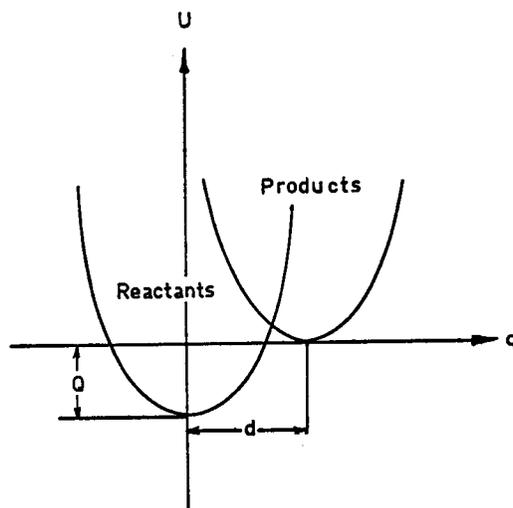


Fig. 2. Potential energy-distance profile using harmonic oscillators.

\*  $E_F$  varies linearly with overpotential. However,  $E_X$  also varies linearly with overpotential. Thus, as the overpotential changes, the state in  $H_3O^+$  to which an electron is transferred changes by the same amount and the height of the *electron* transfer barrier remains independent of potential. There will be a change in *field* strength in the double layer as a function of overpotential. However, the expected changes (say, a doubling of field strength) can be shown<sup>(8c)</sup> to have a negligible effect on the shape and height of the electron transfer barrier.

is effected by *classical* degrees of freedom. Moreover, the ion-solvent interaction in the inner solvation sheath gives rise to the inequality  $h\nu \gg kT$ . Thus, the number of particles in the higher energy states is few. This is usual in any reaction kinetic situation. In the present theory, it is assumed that there are too few of such higher energy bonds to be of interest in the process. The suggestion is that classical harmonic librations in the bulk of the solvent produce (by means of long range electrostatic interactions) fluctuations in the electronic energy levels of the ion, to give it its required energy for a quantum mechanical transition.

Thus, the potential energy profile in the initial and final state are essentially produced from the intersection of two *harmonic* potential wells, as shown in Fig. 2.

Corresponding to the heuristic presentation given of the thermal model, we regard the transition probability as the product of the electron transfer probability and the probability of the acceptor state attaining the level where a radiationless electron transfer takes place. Thus:

$$W_{if}(\epsilon_f) = P_T P(\Delta\epsilon) \quad (8)$$

where  $P_T$  now is the transmission coefficient, or electron transfer probability, and  $P(\Delta\epsilon)$  is the probability that the acceptor state is in its activated configuration ready to accept an electron. To evaluate  $P(\Delta\epsilon)$ , consider the *PE* profile of Fig. 2. Putting the equation of the parabolas in the form<sup>24)\*</sup>:

$$\text{and } \left. \begin{array}{l} U = k(q-d)^2 \\ U-Q = kq^2 \end{array} \right\} \quad (9)$$

where  $k$  is a force constant. For the purpose of simplification, we have set the  $k$ 's for the two parabolas to the same.

At the intersection point, we can therefore write:

$$kd^2 - kdq' - Q = 0. \quad (10)$$

A reorganizational energy,  $E_s$ , can be defined as the energy difference between the ground state of the reactant and the point corresponding to its displacement  $q$  to overlap the ground state of the other oscillator. Hence, by definition (Fig. 2):

$$E_s = kd^2. \quad (11)$$

\* The assumption of simple harmonic behaviour arises because the displacement of each oscillator involved in contributing to the activation of the ion is only about  $10^{-3}$  ev.

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Therefore, from equation (10):

$$E_s + Q + 2kq'd = 0$$

or

$$q' = -\left(\frac{E_s + Q}{2kd}\right).$$

Hence,

$$E_{\text{act}} = kq'^2 = \frac{(E_s + Q)^2}{4E_s}. \quad (12)$$

Since the potential energy profiles are made up of *classical* oscillations, the BOLTZMAN distribution is valid.

Therefore:

$$P(\Delta\varepsilon) = \exp\left[-\frac{E_{\text{act}}}{kT}\right] = \exp\left[-\frac{(Q + E_s)^2}{4E_s kT}\right]. \quad (13)$$

Thus,

$$\begin{aligned} i &= eC_s \rho_0 P_r \eta(\varepsilon_f) \exp\left[-\frac{(Q + E_s)^2}{4E_s kT}\right] \\ &= A \exp\left[-\left(\frac{E_s}{4kT} + \frac{Q}{2kT} + \frac{Q^2}{4E_s kT}\right)\right]. \end{aligned} \quad (14)$$

The potential dependent part is lumped in  $Q$ , since:

$$Q = J_{in} - J_{fn}$$

where  $J_{in}$  and  $J_{fn}$  are the ground state energies of the initial and final states. Therefore, we can write:

$$Q = Q_0 + e\eta.$$

If, in equation (14),  $Q^2 \ll 4E_s kT$ , then:

$$\begin{aligned} i &= A \exp\left[-\left(\frac{E_s}{4kT} + \frac{Q_0}{2kT} + \frac{e\eta}{2kT}\right)\right] \\ &= A' \exp\left[-\frac{e\eta}{2kT}\right]. \end{aligned} \quad (15)$$

Thus, we obtain the TAFEL equation.

However, to obtain this result  $Q^2 \ll 4E_s kT$ . This is not usually true. Thus, the electrostatic continuum model does not give a linear TAFEL line. There are no regions on the overpotential-log current relation which should be linear, in contradistinction to experiment.

### 3. Differences between the Two Models

The main difference between the two models is in the mode of energy communication between the solvent and the ion.

In the electrostatic continuum view, vibration-rotation levels due to the thermal equilibrium of the reacting species are neglected. Electrostatic fluctuations from long range interactions of a large number of dipoles (see footnote on page 156) are envisaged. The electrostatic contribution from librations of the inner solvation shell is neglected.

The reason put forward<sup>18)</sup> for the neglect of vibrations of the inner solvation sheath, is that, since the ion-solvent interaction of the ion is large, the thermal movements of the solvent molecules in the inner solvation sheath  $h\omega/kT \gg 1$ . It seems to be suggested that, because of the small excited to higher states, the effect of vibrational activation of the inner solvent sheath can be neglected. (See Section IV).

The other main difference between discussions in terms of thermal and electrostatic activation is in the treatment of the transition probability. In the electrostatic continuum view, the treatment has not been explicitly made, but it is suggested that it be made by means of time-dependent perturbation theory. In the thermal view, a WKB approximation is applied to obtain a one-dimensional probability of passage through a barrier, (Section IV).

## III. Comparison with Experiment

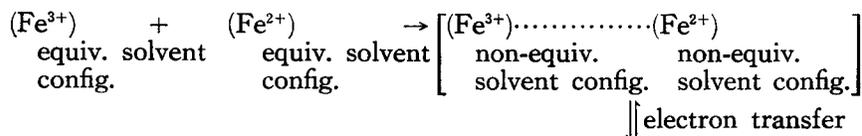
### 1. Relation between $k_{\text{het}}$ and $k_{\text{hom}}$ .

An argument which has been used to support the continuum electrostatic theory<sup>25,13)</sup> is that the rate constant for the heterogeneous reaction can be predicted from the rate constant for the homogeneous reaction. The prediction is:

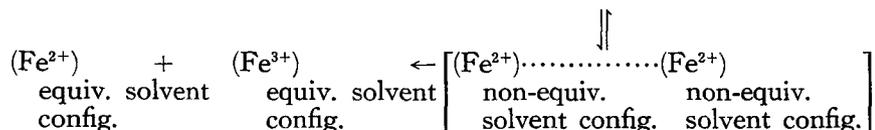
$$\left(\frac{k_{\text{hom}}}{z_{\text{hom}}}\right)^{1/2} = \left(\frac{k_{\text{het}}}{z_{\text{het}}}\right) \quad (16)$$

where  $k_{\text{hom}}$  and  $k_{\text{het}}$  are the rate constants for the exchange reaction in solution (*e.g.*  $\text{Fe}^{3+} + \text{Fe}^{2+} \rightarrow \text{Fe}^{2+} + \text{Fe}^{3+}$ ) and at an electrode (*e.g.*,  $\text{Fe}^{3+} + e(\text{M}) \rightarrow \text{Fe}^{2+}$ ). Let us derive this equation from the most general assumptions.

Consider the homogeneous reaction  $\text{Fe}^{3+} + \text{Fe}^{2+} \rightarrow \text{Fe}^{2+} + \text{Fe}^{3+}$  as proceeding along the path:



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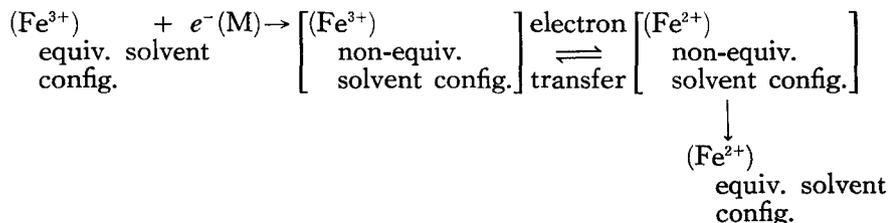


The free energy of activation may then be written as :

$$\Delta F_{\text{hom}}^* = \left[ (\Delta F_{(\text{Fe}^{3+})_{\text{nesc}}} + \Delta F_{(\text{Fe}^{2+})_{\text{nesc}}}) - (\Delta F_{(\text{Fe}^{3+})_{\text{esc}}} + \Delta F_{(\text{Fe}^{2+})_{\text{esc}}}) \right] \quad (17)$$

where  $(\Delta F_{(\text{Fe}^{3+})_{\text{nesc}}} + \Delta F_{(\text{Fe}^{2+})_{\text{nesc}}})$  is the free energy of the activated state and  $(\Delta F_{(\text{Fe}^{3+})_{\text{esc}}} + \Delta F_{(\text{Fe}^{2+})_{\text{esc}}})$  is the free energy of the initial state.

For the corresponding heterogeneous reaction  $(\text{Fe}^{3+} + e^-(M) \rightarrow \text{Fe}^{2+})$ , proceeding according to the path :



The activation free energy for the forward and backward reaction can then be written as :

$$\vec{\Delta F}_{\text{het}}^* = \frac{1}{2} (\Delta F_{(\text{Fe}^{3+})_{\text{nesc}}} + \Delta F_{(\text{Fe}^{2+})_{\text{nesc}}}) - \Delta F_{(\text{Fe}^{3+})_{\text{esc}}} \quad (18)$$

and

$$\overleftarrow{\Delta F}_{\text{het}}^* = \frac{1}{2} (\Delta F_{(\text{Fe}^{3+})_{\text{nesc}}} + \Delta F_{(\text{Fe}^{2+})_{\text{nesc}}}) - \Delta F_{(\text{Fe}^{2+})_{\text{esc}}} \quad (19)$$

where  $\frac{1}{2} (\Delta F_{(\text{Fe}^{3+})_{\text{nesc}}} + \Delta F_{(\text{Fe}^{2+})_{\text{nesc}}})$  is the free energy of the activated state and  $\Delta F_{(\text{Fe}^{3+})_{\text{esc}}}$  and  $\Delta F_{(\text{Fe}^{2+})_{\text{esc}}}$  are free energies of the initial state.

The two activated states are in resonance and have equal energies.

Hence :

$$\frac{1}{2} (\Delta F_{(\text{Fe}^{3+})_{\text{nesc}}} + \Delta F_{(\text{Fe}^{2+})_{\text{nesc}}}) = \frac{1}{2} \times 2 \Delta F_{(\text{Fe}^{3+})_{\text{nesc}}} = \Delta F_{(\text{Fe}^{3+})_{\text{nesc}}} .$$

Similarly,

$$\frac{1}{2} (\Delta F_{(\text{Fe}^{3+})_{\text{nesc}}} + \Delta F_{(\text{Fe}^{2+})_{\text{nesc}}}) = \Delta F_{(\text{Fe}^{2+})_{\text{nesc}}} .$$

Hence :

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$$\left. \begin{aligned} \overrightarrow{\Delta F}_{\text{het}}^* &= \Delta F_{(\text{Fe}^{3+})_{\text{nesc}}} - \Delta F_{(\text{Fe}^{3+})_{\text{esc}}} \\ \overleftarrow{\Delta F}_{\text{het}}^* &= \Delta F_{(\text{Fe}^{2+})_{\text{nesc}}} - \Delta F_{(\text{Fe}^{2+})_{\text{esc}}} \end{aligned} \right\} \quad (20)$$

Moreover, at the equilibrium potential, and equal concentration of reactants and products :

$$\overrightarrow{\Delta F}_{\text{het}}^* = \overleftarrow{\Delta F}_{\text{het}}^* \quad (21)$$

Now, we can rewrite equation (17) as :

$$\begin{aligned} \Delta F_{\text{hom}}^* &= \Delta F_{(\text{Fe}^{3+})_{\text{nesc}}} - \Delta F_{(\text{Fe}^{3+})_{\text{esc}}} + \Delta F_{-(\text{Fe}^{2+})_{\text{nesc}}} - \Delta F_{(\text{Fe}^{2+})_{\text{esc}}} \\ &= \overrightarrow{\Delta F}_{\text{het}}^* + \overleftarrow{\Delta F}_{\text{het}}^* . \end{aligned} \quad (22)$$

So, at the equilibrium potential,

$$\Delta F_{\text{hom}}^* = 2\Delta F_{\text{het}}^* . \quad (23)$$

But :

$$\left. \begin{aligned} k_{\text{hom}} &= z_{\text{hom}} \exp \left[ -\frac{\Delta F_{\text{hom}}^*}{RT} \right] \\ \text{and} \\ k_{\text{het}} &= z_{\text{het}} \exp \left[ -\frac{\Delta F_{\text{het}}^*}{RT} \right] . \end{aligned} \right\} \quad (24)$$

Hence :

$$\left( \frac{k_{\text{hom}}}{z_{\text{hom}}} \right) = \exp \left[ -\frac{\Delta F_{\text{hom}}^*}{RT} \right] = \exp \left[ -\frac{2\Delta F_{\text{het}}^*}{RT} \right] = \left( \frac{k_{\text{het}}}{z_{\text{het}}} \right)^2 .$$

Thus :

$$\left( \frac{k_{\text{hom}}}{z_{\text{hom}}} \right)^{1/2} = \left( \frac{k_{\text{het}}}{z_{\text{het}}} \right) .$$

No assumptions or models have been used in this derivation. Thus, relation (16) does not support particularly the continuum electrostatic view.

## 2. Predictions of the Free Energies of Activation from a Continuum Electrostatic Theory.

The free energy of activation,  $\Delta F_{\text{calc}}^*$  is given according to the continuum electrostatic view<sup>18)</sup> by :

$$\Delta F_{\text{calc}}^* = \frac{(E_s + Q)^2}{4E_s} \quad (25)$$

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where

$$E_s = \left( \frac{1}{2a_1} + \frac{1}{2a_2} - \frac{1}{r} \right) \left( \frac{1}{\epsilon_{\text{opt}}} - \frac{1}{\epsilon_{\text{stat}}} \right) (ne)^2.$$

$\Delta F_{\text{calc}}^*$  were computed for 52 reactions, including both the electron exchange (*e.g.*,  $\text{Fe}^{*2+} + \text{Fe}^{3+} \rightarrow \text{Fe}^{*3+} + \text{Fe}^{2+}$ ) and usual electron transfer (*e.g.*,  $\text{Fe}^{2+} + \text{Ce}^{3+} \rightarrow \text{Fe}^{3+} + \text{Ce}^{2+}$ ) reactions. They were made for various ligands as well.

There are few electron transfer reactions for which the temperature dependence of the rate has been studied. One can calculate an "experimental" value for free energy of activation by equating the rate constant (experimentally determined to  $Z_{bt} \exp\left[-\frac{\Delta F_{\text{exp}}^*}{RT}\right]$ , where  $Z_{bt}$  is the *bi*-molecular collision number\* of the two uncharged species in solution per unit volume, per unit time and is given as<sup>(14)</sup>:

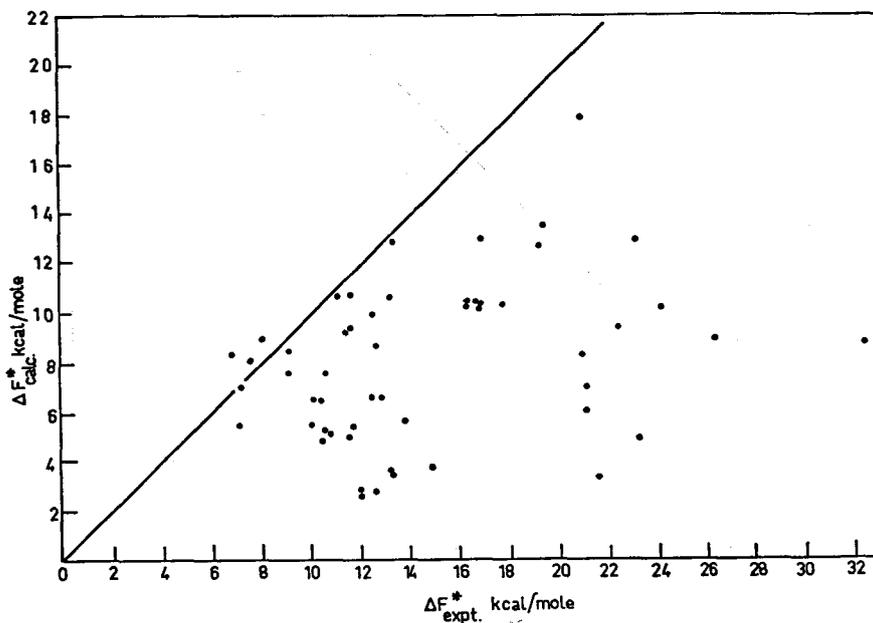


Fig. 3. Plot of  $\Delta F_{\text{calc}}^*$  (from electrostatic approach) against  $\Delta F_{\text{expt}}^*$  for electron transfer reactions.

\* The equation (26) used for  $Z_{bt}$  is valid only for gas kinetic collisions. Application to solutions would be a drastic approximation. Let us derive a crude  $Z_{bt}$  for solutions. Assume a quasi lattice model for a liquid, each reactant *A* and *B* being surrounded by *N* nearest neighbours in a hexagonal array. The time for a reactant to jump to a nearest lattice site is:

$$t(r_{AB}) = \frac{r_{AB}^2}{6D_{AB}}.$$

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$$Z_{bt} = \left( \frac{8\pi kT}{m^*} \right)^{1/2} r^2. \quad (26)$$

Using  $10^{11}$  for  $Z_{bt}$  and the experimentally determined  $k$  (the rate constant), the experimental  $\Delta F_{\text{expt}}^*$  can be obtained<sup>†</sup>.

The  $\Delta F_{\text{calc}}^*$  is plotted against the experimental  $\Delta F^*$  value in Fig. 3.

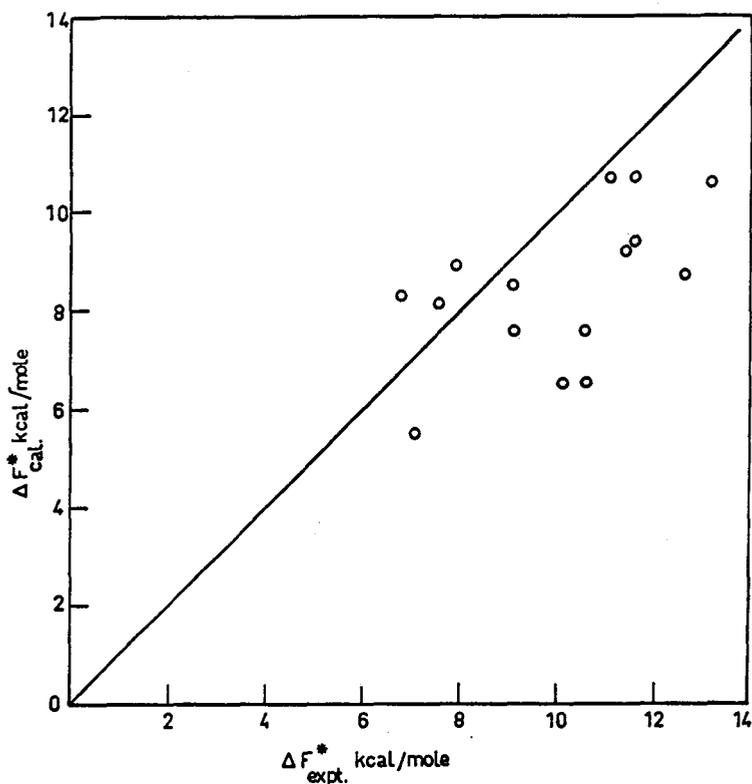


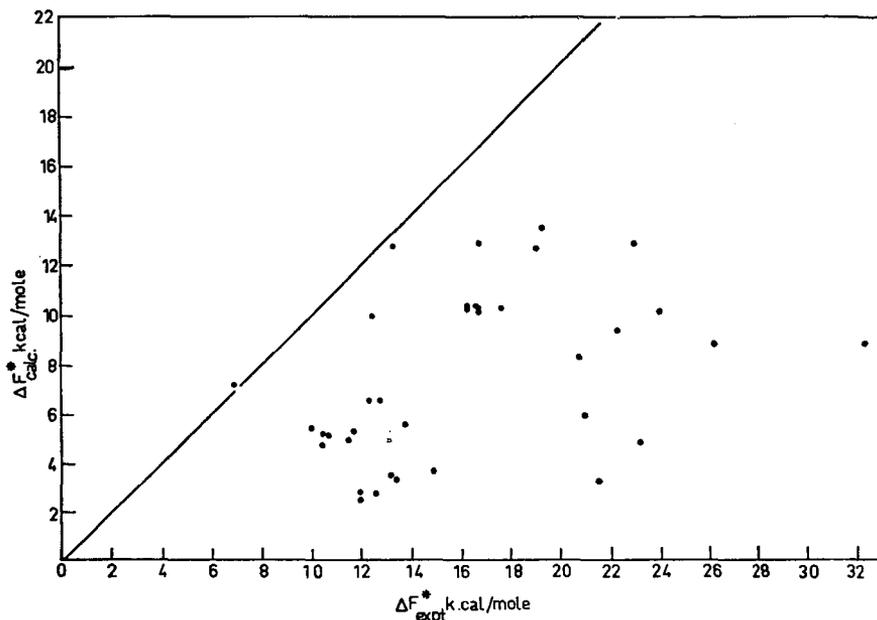
Fig. 4(a). Plot of  $\Delta F_{\text{calc}}^*$  (from electrostatic approach) against  $\Delta F_{\text{expt}}^*$  for reactants with ligands other than water or ammonia.

† The rate at which a reactant encounters new neighbours in solution is given by:

$$\frac{N}{2} = 3 \frac{ND_{AB}}{r_{AB}^2}.$$

The frequency at which reactant  $A$  will meet reactant  $B$  is  $\frac{N_B}{N_S}$ , where  $S$  denotes the solvent,  $\frac{1}{N_S}$  = volume per solvent molecule =  $\alpha r_{AB}^3$ . So  $Z_{AB} = 3N\alpha r_{AB}D_{AB}$ . This quantity evaluated for  $D_{AB} = 2 \times 10^{-5}$  cm<sup>2</sup>/sec and  $r_{AB} = 4A^0$  gives  $Z_{AB} = 6 \times 10^9$  litres/mole sec. The value of  $Z_{bt}$  from the equation (26) is  $10^{11}$  litres/mole sec. The difference is not great enough to affect the comparison of trends. Similar remarks concerning oversimplification would apply to the values of  $Z_{\text{het}}$ .

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**Fig. 4(b).** Plot of  $\Delta F_{\text{calc}}^*$  (from electrostatic approach) against  $\Delta F_{\text{expt}}^*$  for reactants involving water and ammonia ligands.

There is no general correlation between the prediction of the electrostatic continuum view and experiment. A few points lie close to the theoretically expected line. An attempt was made to categorize the reactions on the basis of the nature of ligands and reconstructed the plots as shown in Fig. 4a and 4b. In Fig. 4a redox couples with  $\text{CN}^-$ ,  $\text{Br}^-$ ,  $\text{Cl}^-$  and  $\text{O}^-$  as ligands give results near to those predicted, whereas poor agreement is obtained with ligands like  $\text{H}_2\text{O}$ ,  $\text{NH}_3$ , dipy, Phen.

The most likely cases in which the electrostatic continuum view would have applicability would be for ions of largest radius. There, a set of water molecules oriented around the ion and remaining attached to it for times much longer than the ions jump time in diffusion "primary solvation", would be unlikely<sup>26)</sup>. The continuum viewpoint might be more correct. Hence, a plot of  $\frac{\Delta F_{\text{calc}}^*}{\Delta F_{\text{expt}}^*}$  should tend to unity with increasing radius. Such a test is shown in Fig. 5, and shows the theory to be inconsistent with this test.

### 3. Variation of $\beta$ with overpotential and the TAFEL relationship from both the approaches.

The continuum electrostatic theory predicts that for the h.e.r. in the normal overvoltage region, the transfer coefficient is given as:

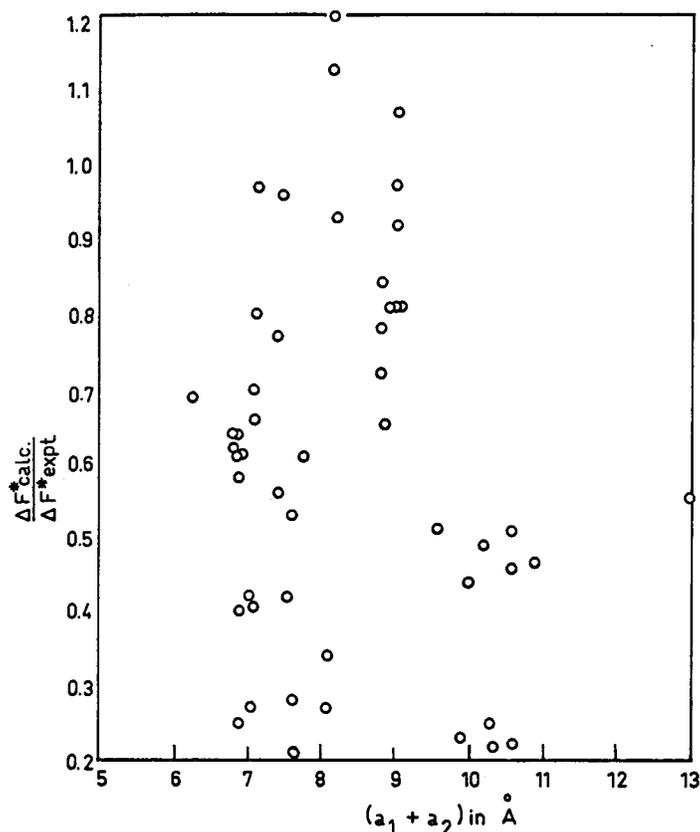
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Fig. 5. Plot of  $\frac{\Delta F_{\text{calc}}^*}{\Delta F_{\text{expt}}^*}$  against the distance of closest approach for the two reactions.

$$\beta^* = \frac{1}{2} + \frac{J_{fn'} - J_{in}^0}{2E_s} - \frac{e\eta}{2E_s}. \quad (27)$$

Experimentally, it has been found<sup>27,28)</sup> that for h.e.r. the transfer coefficient remains constant over more than 1 ev. From equation (27) this would be so only if  $J_{fn'} - J_{in}^0$  (heat of reaction at the reversible potential) =  $e\eta$ . In Fig. 6 the transfer coefficient  $\beta^*$ , calculated according to the electrostatic continuum theory, varies linearly with overpotential. Using these values of the transfer coefficients for  $E_s = 2$  ev, the predicted TAFEL line is shown in Fig. 7. There is markedly no linear region at variance with the experimental line.

In the thermal model,  $\beta$  is:

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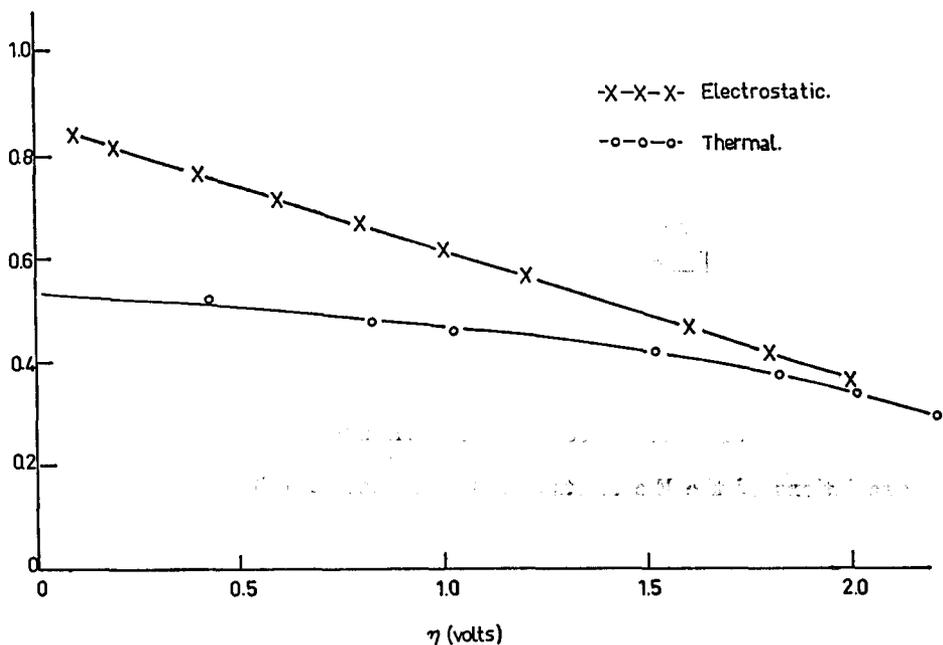


Fig. 6. Variation of transfer-coefficient with potential.

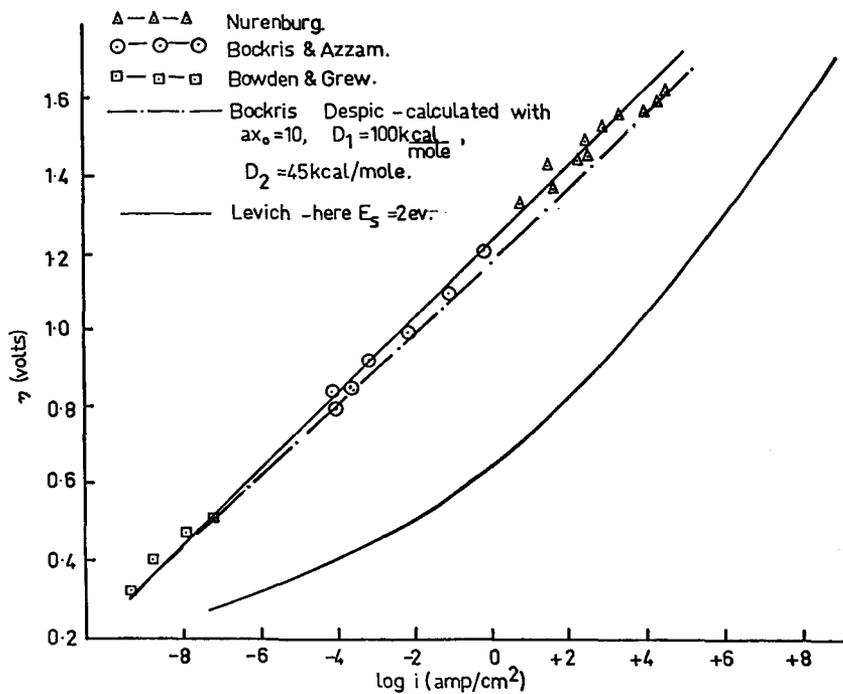


Fig. 7. Tafel lines from thermal and electrostatic approaches compared with experiment.

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$$\beta_c = \frac{1}{2} - \frac{1}{2ax_0} \frac{[1 - \{(\langle \Delta H_i^* \rangle - (1-\beta)F\eta)/D\}^{1/2}]}{[1 - \{(\langle \Delta H_i^* \rangle - A_0 + \beta F\eta)\}^{1/2}]} \quad (28)$$

The variation with potential is shown in Fig. 6. The agreement is good.

Using these  $\beta$  values the TAFEL line was evaluated using the expression:

$$i = C_{H^+} \left( \frac{\pi r_H^2}{3} \right) \left( \frac{4\pi m_e e_1 kT}{h^3} \right) \bar{w}_e \int_{-\infty}^{+\infty} \left[ 1 + \exp \frac{[E - E_1]}{RT} \right]^{-1} \\ \times \exp \left[ -\beta_c (E_{O^-} - E)/RT \right] dE. \quad (29)$$

The equation was derived by BOCKRIS and MATTHEWS<sup>8)</sup> and solved numerically using a digital computer. The theoretical and experimental lines are shown in Fig. 7. The  $\beta$  stays constant over a wide range of potential, and the TAFEL line obtained agrees with experiment quite well.

#### 4. Predictions of the Electrostatic (*E*) and Thermal (*T*) Models

Test	Symbolic Representation	Comments
1. (a) The current density is exponentially proportional to the overpotential.	$i = Ae^{\beta\eta}$	<i>T</i> predicts experiment. <i>E</i> shows continuous curvature. Fig. 7.
(b) Variation of $\beta$ with overpotential.	$(\beta)_{\eta \rightarrow \infty} \rightarrow 0$	<i>T</i> gives negligible variation over 1.5 V for h.e.r. <i>E</i> shows continuous variation. Fig. 6.
2. Magnitude of separation factor on different metals.	$S_{H^+/T} = 3-20$	No calculation done on <i>E</i> model. <i>T</i> model reproduces experiment for high $\eta$ .
3. Variation of the separation factor with potential.	$S_{H^+/T} = f(\eta)$	<i>T</i> reproduces $dS/d\eta$ better than <i>E</i> . Fig. 8.
4. For reaction which involves adsorbed intermediates, the current is a function of the heat of adsorption of one of the intermediates involved in the rate-determining step.	$(\log i)_\eta \propto f(\Delta H)_{\text{ads}}$	For h.e.r. both models are consistent with experiment. Fig. 9.
5. The rate is a function of the solvent dielectric constant.	$(\log i)_\eta = f(\epsilon)$	Predicted well by <i>T</i> model; and not by <i>E</i> model. Fig. 10.
6. The current density is a function of light.	$(i)_\eta = \kappa(v - v_0)^{5/2}$	Not yet diagnostic <sup>30)</sup> .
7. Plot of $\Delta F_{\text{expt}}^*$ vs. $\Delta F_{\text{calc}}^*$ .	$\Delta F_{\text{expt}}^*$ vs. $\Delta F_{\text{calc}}^*$	No correlation on <i>E</i> theory. Fig. 3.

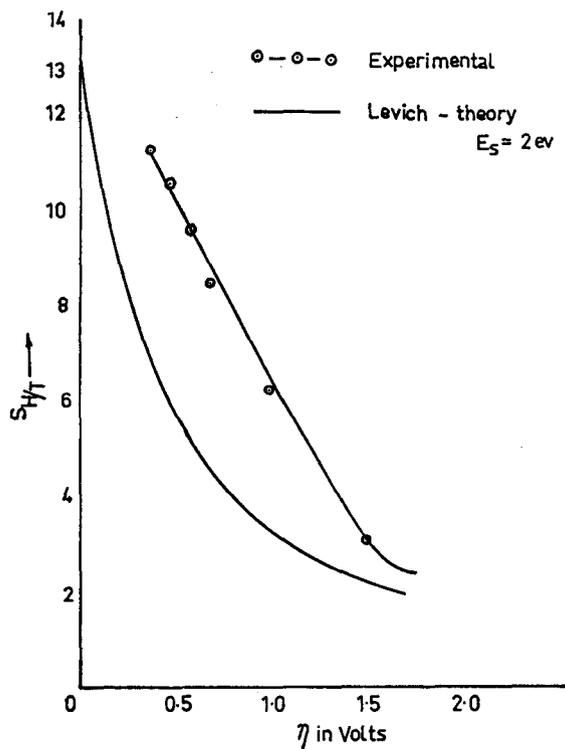


Fig. 8(a). Variation of the separation factor with potential-electrostatic approach.

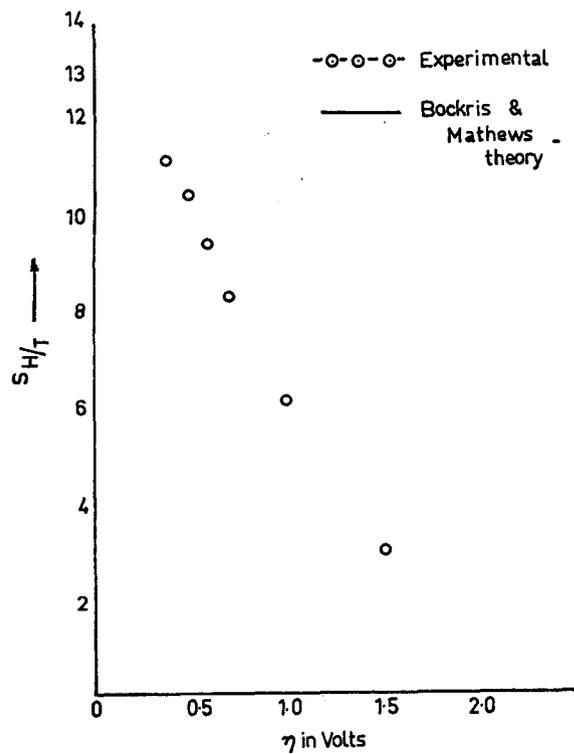


Fig. 8(b). Variation of the separation factor with potential-thermal approach.

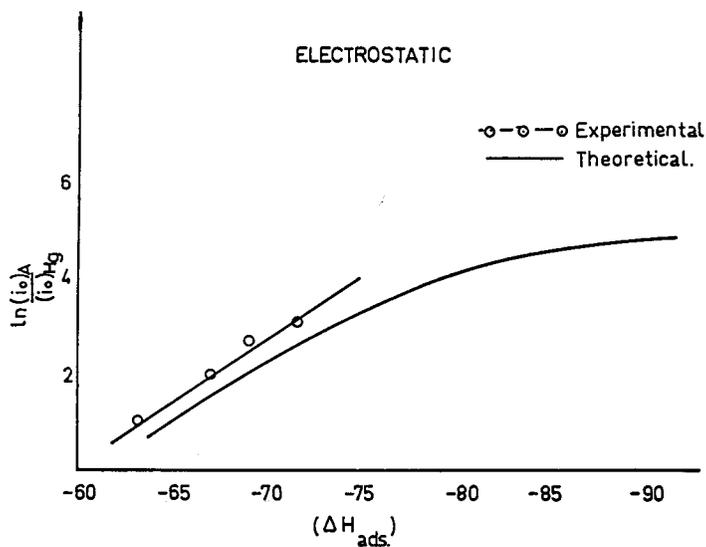
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Fig. 9(a). Variation of  $\ln \frac{(i_0)_A}{(i_0)_{Hg}}$  with the heat of adsorption in the electrostatic approach.

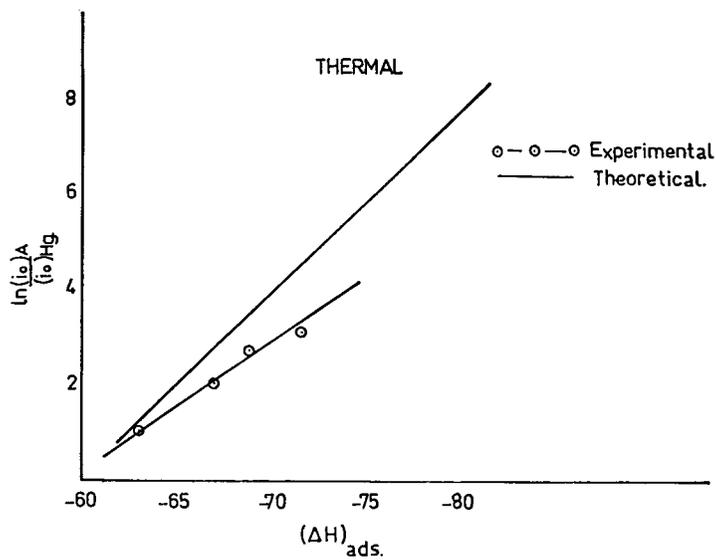
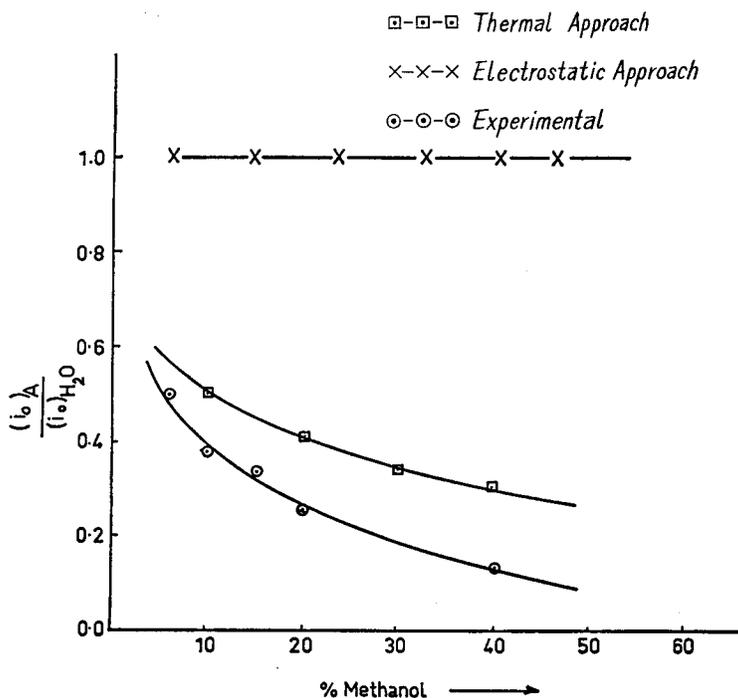


Fig. 9(b). Variation of  $\ln \frac{(i_0)_A}{(i_0)_{Hg}}$  with heat of adsorption for thermal approach.

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**Fig. 10.** Variation of  $\ln \frac{(i_0)_A}{(i_0)_{H_2O}}$  with the variation of methanol concentration.

The thermal activation model gives a better agreement with experiment than the continuum electrostatic view, particularly in respect to the tests (1a), (1b), (5) and (7). However, this may arise from approximations at present used in the electrostatic continuum model. It is therefore desirable to discuss the likelihood of the models themselves.

#### IV. Critical Consideration of both Approaches

##### 1. The Activation Mechanism

The poor current potential relationship obtained from the electrostatic approach arises from the parabolic nature of the potential energy profile. The small perturbations in libratory oscillations of the solvent molecules, far away from the ion, must be harmonic. Since these oscillations activate the ion, the potential energy profile must be harmonic, too. A source of anharmonicity could be the vibrations and librations of the inner sphere dipoles, where there is strong interaction between the ion and the dipole.

However, this source of activation is specifically rejected in the continuum electrostatic approach<sup>18)</sup>.

The mode of activation envisaged by the electrostatic approach involves the fluctuations of about a 1000 dipoles (see Section II) "in phase". If the librations were not in phase, the large number of dipoles needed could not transfer energy to the ion additively at the same instance. Polaron theory in solids, where a system of interacting oscillators are coupled to one another, has postulated such fluctuation<sup>46)</sup>. It does not seem to be unreasonable in a solid. However, in a liquid without appreciable periodicity, it is questionable whether the principles of polaron theory can be applied at all<sup>31)</sup>. Thus, NEMETHY and SCHEREGA<sup>32)</sup> showed that in water at any instant the percentage of free water ranges between 20~50%. It is doubtful that such a liquid will produce a significant probability of oscillators in phase.

Even if there is a group of some 1000 dipoles librating in phase and contributing their energy additively to the ion, there would be another (and another) group of 1000 dipoles librating together but in a different phase. The effects would cancel.

Such a model might be modified to be applicable where there is a highly oriented secondary solvation sheath extending to about 20 Å from the ion. In such a case, librations of the dipoles in the secondary solvation sheath might be in phase, and if it extends to about 20 Å from the ion, the possibility of 1000 dipoles taking part is not unreasonable. However, a recent calculation by BOCKRIS and SALUJA<sup>26)</sup> shows that entropy and heat calculations are difficult to bring into consistency with the experimental values if the water structure is broken past two layers from the ion. AMIS<sup>33)</sup> has discussed a large structure broken secondary layer. The evidence for it, however, is ambiguous for it rests upon the values obtained for "solvation numbers" from various methods, which are of such ill defined significance.

Coming to thermal contributions to activation from the inner layer, the reason for their neglect (see Section II) was that the vibrational levels were far apart ( $h\omega_i \gg kT$ ), so that there would be discontinuity in the TAFEL line.

However, this is at variance with knowledge of the energy levels associated with, for example, aq.  $H_3O^+$  and, by implication, other solvated ions. According to FALK and GIGUERE<sup>23)</sup>, and FALK<sup>34)</sup> for liquid  $H_2O$ , there is a continuum of energy states from 60 to 3444  $cm^{-1}$ . Similar conclusions follow from O'FERRALL *et al*<sup>22)</sup>.

Thus, classical (continuous) modes of heat transfer are available in water and, in particular, aq.  $H_3O^+$ . The appreciable partial molar heat capacity ( $C_p$ ) at room temperature for  $H_3O^+$ , indicates a broad range of frequencies

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giving classical  $C_p$  contributions and provides compelling evidence for the above conclusions.

By analogy to the gas phase, where translational energy is converted into vibrational energy (after collisions), it is reasonable to assume that the same process occurs in liquid water. The translational energy of free waters obeys a BOLTZMAN distribution of energy and is in equilibrium with the  $H_3O^+$  ion in solution. The vibration-rotational energy levels of the  $H_3O^+$  ion will also have a BOLTZMAN distribution (at least up to a certain energy level). There will be sufficient activation of O-H bonds to sustain the reaction over the rates observed on various metals\*.

The above arguments presuppose that  $H_3O^+$  ion does not upset the equilibrium distribution among the levels by a permeation of the barrier to the electrode. This might be the case where the barrier thickness for proton transfer is assumed<sup>18)</sup> to be  $0.5 \text{ \AA}$ . It is difficult to accept such a thickness, if one is to accept a model of hydrated ions in the double layer in which the double layer capacitance is independent of ionic radius. On this basis, the minimum width of the barrier for proton transitions is  $\sim 2.8 \text{ \AA}$ .

A compelling piece of evidence that an oriented primary solvated ion solvent plays a role in the activation process for electron transfer reactions, comes from the study of hydrated electrons. The absorption spectrum of the hydrated electron shows a strong adsorption in the uv region, which is attributed to the  $1s-2p$  transition. JORTNER<sup>36)</sup> calculated  $h\nu_e$  using the LANDAU Hamiltonian (that used in the continuum electrostatic model), and FUEKI *et al*<sup>37)</sup> considered a layer of oriented water dipoles around the electron plus the LANDAU contribution. The results of these two calculations, as well as the experimental value, is summarized in Table 1.

This calculation does show that the inner sphere changes between the  $1s$  and  $2p$  states of the hydrated electron is large. There must, therefore,

---

\* For an electrochemical reaction :

$$\frac{i_0}{nF} = \frac{kT}{h} C_s e^{-\Delta H^*/RT}.$$

Taking  $\Delta H^* = 15 \text{ Kcal/mole}$  and  $i_0 = 10^{-11} \text{ amp/cm}^2$ ,  $C_s$  comes out to be  $\sim 10^{-3} \text{ molecules/cm}^2$ . Thus we need  $10^{-3} \text{ molecules/cm}^2$  in the activated state for the reaction to go. Assuming a BOLTZMAN distribution, the number of particles in higher vibrational levels is given as :

$$N = N_0 e^{-\frac{n h \nu}{kT}}$$

for  $n=1$ ,  $N$  comes out to be  $10^4 \text{ molecules/cm}^2$ , and for  $n=2$  the value comes out to be  $10^{-2} \text{ molecules/cm}^2$ . Thus, we have plenty of molecules in higher vibrational states to sustain the above rate.

$N_0$  is taken to  $10^{13} \text{ molecules/cm}^2$  as usual.

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TABLE 1.

Model	$(\Delta H)_{\text{sol. calc.}}$	$h\nu_{\text{calc}}$	$(\Delta H)_{\text{sol. exp}}$	$h\nu_{\text{exp}}$
Continuum	0.91 ev	0.93 ev	1.7 ev	1.73 ev
Semi-Continuum	1.95 ev	1.86 ev		

be some rearrangement of the inner sphere (thermal or electrostatic) before the electron transfer can occur.

Moreover, if the inner spheres of the reactant and product are different, there must be inner sphere activation to satisfy the FRANCK-CONDON restriction of the electron transfer process<sup>9</sup>). Thus, the reactant and product activated state, must be in resonance and identical. If the inner sphere is different, activation must occur in it before the right activated state can be obtained. The explicit omission of the inner sphere<sup>18</sup>) implies that the inner spheres for reactant and product are the same. Applied to  $\text{H}_3\text{O}^+ + e^-(M) \rightarrow \text{H}_{\text{ads}} + \text{H}_2\text{O}$ , such a concept is unreasonable, and quantum mechanical treatment based on such a model is so far from reality that its consideration loses interest.

The applicability of employing the BORN-LANDAU Hamiltonian for treating electrons in a polar medium is unlikely<sup>36</sup>), apart from considerations made above. The BORN-LANDAU Hamiltonian arises when the electronic adiabatic approximation is used to treat the problem of an electron trapped in a polar solvent. This approximation can be applied if the binding energy of the trapped electron is much smaller than the binding energy of the medium electrons. This is a reasonable approximation in a polar crystal where the electron binding energy is low. With polar liquids, the situation is different. The binding energies are higher, 1~2ev. This energy is comparable to the binding energy of the medium electrons (4~5 ev); the electronic adiabatic approximation is not valid. To calculate the binding energy of electrons in polar crystals, JORTNER<sup>36</sup>) suggests that the additional electron and the medium electron should be treated as an equal basis and uses the independent particle treatment better known as the self-consistent field scheme. The basic difference between these results and those obtained with the electronic adiabatic approximation is due to the fact that in the self-consistent field scheme the electronic polarisation does contribute to the binding energy of the electron. Thus, the potential then becomes of the form  $\frac{e^2}{2r} \left(1 - \frac{1}{\epsilon_s}\right)$  instead of the  $\frac{e^2}{2r} \left(\frac{1}{\epsilon_{\text{op}}} - \frac{1}{\epsilon_{\text{stat}}}\right)$  involved in the expression derived from the electronic adiabatic approximation. Thus, the reorganisational energy would not be given by the BORN-LANDAU equation. It would, correspondingly,

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not be given by the time-average BORN energy, but by an equation for the change in the *orientation* energy on ejection of a charge in a polar dielectric.

## 2. The Quantum Mechanical Transition Probability

There are two ways whereby one can calculate the transition probability of electrons or protons between two states of equal energies<sup>40</sup>. (a) from Perturbation theory; (b) from Tunneling theory. Most authors<sup>33,34</sup> have treated the transition via tunneling theory. In respect to electrochemical kinetics, CHRISTOV<sup>6</sup>) and BOCKRIS and MATTHEWS<sup>8</sup>), following the work of BELL<sup>38</sup>) and JOHNSTON<sup>39</sup>), have made numerical calculations of the transition probability using tunneling theory and barriers of various shape. LEVICH<sup>18</sup>) has criticized this approach, not only with respect to the electrochemical situation, but in all chemical reactions. The barrier created by solvent fluctuations is time-dependent. At time  $t=0$ , the system is in its initial state and that part of the barrier connected with the presence of an adsorbed hydrogen does not exist. Similarly, at  $t=t$  the system is in its final state, and the first part of the barrier does not exist. It is only the finite time interval ( $t$ ) that the barrier forms and disappears as the transition occurs. The tunneling theory assumes that the barrier is fixed and independent of time and does not change during the course of transition. This latter approximation puts into doubt the use of the WKB approximation and the GAMOW equation in calculating tunneling probability.

Consider the situation in Fig. 11. When we apply time-dependent perturbation theory, we assume initially the electron is in region (I) and after an interval of time, due to the action of a time-dependent perturbation (which results in the formation of the square barrier), the electron finds itself in region (III). There is no obvious way of

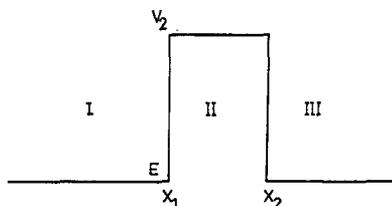


Fig. 11. Tunneling through a square barrier.

introducing a small perturbation term in the Hamiltonian. However, for treating such problems, BARDEEN<sup>41</sup>) has suggested a different approach. Instead of looking for exact solutions of an approximate Hamiltonian, we introduce approximate solutions of the exact Hamiltonian. Therefore, we select the following wave functions for the electron inside the barrier (Fig. 11).

$$\left. \begin{aligned} \Psi_i(x) &= a_{2i} e^{-k_2 x} & x \geq x_1 \\ \Psi_f(x) &= a_{2f} e^{+k_2 x} & x \leq x_2 \end{aligned} \right\} \quad (30)$$

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Here,  $\Psi_f(x)$  has to be matched to the correct solution for  $x \geq x_2$ , and will decay in the region  $x \leq x_1$ . On the other hand,  $\Psi_i(x)$  has to be matched to the correct solution for  $x \leq x_1$ , and decay in the region  $x \geq x_2$ .

Initially, the electron is in the state represented by  $\Psi_i(x)$  and we have to compute the transition probability for the electron to go into the state  $\Psi_f(x)$ . Let us form a time-dependent solution as a linear combination of  $\Psi_i(x)$  and  $\Psi_f(x)$  by the usual method. We write:

$$\Psi = C(t) \Psi_i(x) e^{-iE_i t} + d(t) \Psi_f(x) e^{-iE_f t}. \quad (31)$$

Substitution of equation (31) in the time-dependent Schrödinger equation gives us finally<sup>(42)</sup> the effective matrix element for tunneling as:

$$T_{if} = \int \Psi_f^* (H - E_i) \Psi_i dx. \quad (32)$$

This, after manipulation, can be expressed in the form:

$$|T_{if}|^2 = \frac{\hbar^4 \kappa_2^2}{m^2} |b_{2f}^*|^2 |a_{2i}|^2. \quad (33)$$

In Fig. 11 the wave function in the regions I and III can be represented as:

$$\Psi_I = a_{1i} e^{ik_1 x} + b_{1f} e^{-k_1 x}$$

$$\Psi_{III} = a_{3f} e^{ik_3 x} + b_{3f} e^{-k_3 x}$$

One can therefore obtain  $b_{2f}$  in terms of  $a_{3f}$  and  $a_{2i}$  in terms of  $a_{2i}$  by solving the standard matching problem<sup>(43)</sup> at  $x_1$  and  $x_2$  of Fig. 11. Introducing these results in equation (33), one obtains:

$$|T_{if}|^2 = \frac{\hbar^4 \kappa_2^2}{m^2} \cdot \frac{16k_1^2 k_3^2 |a_{1i}|^2 |a_{3f}|^2 e^{-2\kappa_2 a}}{(k_1^2 + \kappa_2^2)(k_3^2 + \kappa_2^2)}. \quad (34)$$

Using the FERMI golden rule of second-order perturbation theory, the transmitted current can be written as:

$$j_f = \frac{2\pi}{h} |T_{if}|^2 \frac{dn}{dE_f} \quad (35)$$

where  $\frac{dn}{dE_f}$  is the density of states without spin in the transmitted wave and is given as<sup>(43)</sup>:

$$|a_{3f}|^2 \frac{dn}{dE_f} = \frac{m}{2\pi \hbar^2 k_3} \quad (36)$$

(where  $|a_{3f}|$  is the coefficient of the wave function for the transmitted wave).

The incident current is:

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$$j_i = \left( \frac{\hbar k_1}{m} \right) |a_{1i}|^2. \quad (37)$$

Thus, the transmission coefficient is ;

$$P_T = \frac{j_T}{j_i} = \frac{16k_1^2 k_2^2 k_3^2}{k_1 k_3 (k_1^2 + \kappa_2^2) (k_3^2 + \kappa_2^2)} e^{-2\kappa_2 \omega} \quad (38)$$

where  $\omega = x_2 - x_1 =$  barrier thickness, and

$$\kappa_2 = \left\{ 2m(E_x - E_p) / \hbar^2 \right\}^{1/2}.$$

Equation (38) has the same form as GAMOW's equations. We have, therefore, been able to prove that the time-dependent perturbation theory treatment of a square barrier penetration problem does give the same from of solution as the WKB approximation. (It would break down only in a non-adiabatic process).

Another argument which might invalidate the use of GAMOW's equation, apart from that involving the change of the barrier during a transition, involves the fact that the top of the barrier fluctuates with time. Only if the tunneling time is less than the fluctuation time of the barrier, will the usual tunneling expression be valid. Consider the situation in Fig. 12. Due to the permeability of the barrier, there is a splitting in energy levels in the two wells.

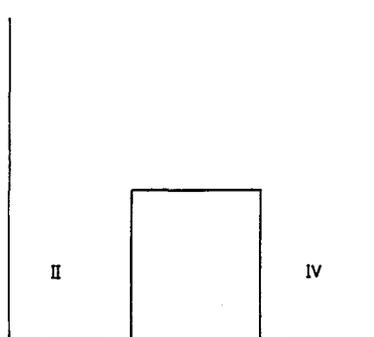


Fig. 12. Double well problem.

Let this splitting be  $\delta E$ . Let  $\Psi_{II}$  and  $\Psi_{IV}$  be the wave function in the wells II and IV. Then, we can say that,  $\Psi_{II} + \Psi_{IV}$  has the energy  $E_0 - \delta E$  and  $\Psi_{II} - \Psi_{IV}$  has the energy  $E_0 + \delta E$ .

Hence, using the time-dependent SCHRÖDINGER equation, we can solve that find :

$$\Psi = \exp[-iE_0 t / \hbar] \left\{ (\Psi_{II} + \Psi_{IV}) \exp[+i\delta E t / \hbar] + (\Psi_{II} - \Psi_{IV}) \exp[-i\delta E t / \hbar] \right\}$$

or

$$\Psi = 2 \exp[-iE_0 t / \hbar] \left\{ \cos \frac{\delta E t}{\hbar} \Psi_{II} + i \sin \frac{\delta E t}{\hbar} \Psi_{IV} \right\}. \quad (39)$$

We have chosen the phases such that the electron is in well (II) at  $t=0$ . At  $t = \hbar\pi / \delta E$ , the electron will be in well (IV). We define  $t = \hbar\pi / \delta E$  as the tunneling time. If  $\delta E = 0.1$  ev, then  $t = 10^{-14}$  sec.

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If the fluctuation time of the barrier is more than the tunneling time, GAMOW's equation is unaffected by this cause. For electron transfer reactions in aqueous solutions, the barrier is made up of vibrational or librational modes of the initial and final states. Since the vibrational and librational modes have a frequency about  $10^{13} \text{ sec}^{-1}$  and  $10^{11} \text{ sec}^{-1}$  respectively, the fluctuation time of the barrier should be greater than  $10^{-13}$ . Thus, the tunneling time is smaller than the fluctuation time, for  $\delta E = 0.1 \text{ ev}$ .

We have arbitrarily chosen the value of  $\delta E$  to be 0.1 ev. Physically, the value of  $\delta E$  is directly proportional to the interaction between the electron and the medium. For strong interaction,  $\delta E$  is generally of the order of  $0.1 \sim 0.3 \text{ ev}$ <sup>44,45</sup>. In our situation, the interaction between the electron and the polar media is strong, an estimate of 0.1 ev for  $\delta E$  is reasonable.

Thus, the solution of the barrier leakage problem, using perturbation theory, is the same as the one obtained by WKB approximation, and GAMOW's equation should give an accurate estimate of the electron tunneling probability.

## V. Summary

(1) Two models exist for activation in electrochemical reactions. In the first (thermal,  $T$ ) there is considered to be an equilibrium of vibrational-rotational levels with the translational energy of the solvent. These levels are the main source of acceptor and donor states for electrons. The other model (the continuum electrostatic,  $E$ ) discards the part played by such levels. Instead, the means of energy transfer from the solvent is a long-range electrostatic fluctuation which is to occur as a result of additivity of interaction between a large number of solvent molecules far from the ion.

(2) The rate-overpotential relation is deduced in a heuristic way on the basis of the two models.  $E$  does not predict a TAFEL-like law.

(3)  $E$  neglects the electrostatic interaction between the librators in the inner solvent shell. However, the ground state of these molecules involved librations which would seem to give rise to electrostatically originated fluctuations in the ion's energy.

(4) The relation of  $k_{\text{hom}}$  and  $k_{\text{het}}$  does not diagnostically support  $E$ , as previously claimed.

(5) The calculated free energy of activation at  $E$  is not parallel to the experimentally observed one in respect to extensive solution data (52 systems).

(6)  $T$  does give a reasonable account of the current-potential relation, both in the constancy of  $\beta$  over 1 volt and its reduction towards zero at sufficiently large overpotentials.

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(7)  $E$  does not reproduce the effect of change over solvent dielectric.

(8) The transfer of energy from the far out librators to the ion depends upon the applicability of polaron theory to solutions in water. However, the polaron theory loses its validity in structures in which there is no periodicity of the lattice.

(9) The assumption that there will be a large gap in energy between vibrational states in receptor ions, hence a discontinuous TAFEL line, on model  $T$ , is not acceptable. In solution, there is a continuum of energy states in, for example,  $\text{H}_3\text{O}^+$  over a large energy range.  $C_p$  for water is large at room temperatures: it shows the presence of classical modes.

(10)  $1s-2p$  transitions in hydrated electrons cannot be rationalised unless the energy of nearest neighbour water molecules (*i.e.*, not a continuum dielectric) is accounted for.

(11) The BORN-LANDAU equation, —the basis of  $E$ —, is applicable to polar crystals, but unlikely to be valid for electric charge transfer in liquids.

(12) Time-dependent perturbation theory is consistent with the GAMOW equation for time-dependent barriers concerned in charge-transfer.

(13) Electrostatic fluctuations contribute to the energy of ions undergoing transitions with electrons at interfaces. However, the origin of the energy of these fluctuations is in thermal equilibrium of the surrounding liquid into the nearest neighbour dipoles of the ions. Such an energy would add to the states in the electronic-vibrational and rotational levels of the ion, in addition to those which are present due to equilibrium between solvent and ion.

(14) Finally, the essential situation is a distinction between a kinetics in which collisional activation is the model and statistical mechanics gives the distribution of energy and quantum mechanics the probability of transfer; versus a mode in which the reaction is supposed to occur because *fluctuations* in energy. It is noteworthy that a considerable theory of reactions in solution exist, in terms of encounters and statistical mechanics. Either an entirely incorrect *type* of approach has been taken to solution kinetics, or the continuum electrostatic (fluctuation) theory is invalid.

**Glossary of Symbols**

$e$  = Electronic charge

$C_s$  = Surface concentration of reacting species

$n(\epsilon_f)$  = FERMI distribution

$\rho(\epsilon_f)$  = Density of states

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- $W_{ef}(\epsilon_f)$  = Transition probability for the whole system  
 $\Delta\epsilon$  = Difference between the energy of the activated state and ground state  
 $\beta$  = Transfer coefficient  
 $\Delta\phi$  = Potential difference across the electrode solution interface  
 $l$  = length of barrier  
 $m_e$  = mass of the electron  
 $E_X - E_F$  = barrier height  
 $\eta$  = overpotential  
 $E_{act}$  = activation energy  
 $\kappa$  = transmission coefficient  
 $k_{hom}$  = homogeneous rate constant  
 $k_{het}$  = heterogeneous rate constant  
 $Z_{hom}$  = Collision number for homogeneous reactions  
 $Z_{het}$  = Collision number for heterogeneous reactions  
 $J_{fn}$  = Energy of the final state  
 $J_{in}$  = Energy of the initial state  
 $r_1$  = radius of ion 1  
 $r_2$  = radius of ion 2  
 $r$  = distance of closest approach  
 $\epsilon_{opt}$  = optical dielectric constant  
 $\epsilon_{stat}$  = static dielectric constant  
 $D_{AB}$  = diffusion coefficient  
 $r_{AB}$  = nearest neighbour dipole  
 $a$  = Morse constant  
 $x_0$  = Equilibrium separation between the two Morse curves  
 $\langle \Delta H_i^\circ \rangle$  = activation energy for the cathodic reaction  
 $D_1$  = dissociation energy

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