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THEORY AND APPLICATIONS OF ELECTRON TRANSFERS AT ELECTRODES AND IN SOLUTION

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ABSTRACT

The theory of simple electron transfers at electrodes and in solution is reviewed, and various thermal fluctuations of coordinates leading to electron transfer are described. A simplified derivation is given of the free energy of such fluctuations. Implications of the theoretical equations for experiment are described, some of t relevant results having been summarized recently in Dahlem Konferenz Phys. Chem. Sci. Res. Rept., 1(1975)477. They include relations between rate constants of cross-reactions and self-exchange reactions, between rates of reactions at electrodes and those in solution, nonspecific solvent effects, chemiluminescence, and other properties. Approximate equations of the BEBO type are also given for Tafel slopes, Bronsted slopes and rates of cross-reactions, for systems involving rupture and formation of bonds.

INTRODUCTION

The theory of reactions at electrodes has much in common with that of reactions in solution. The electrode behaves as one large reactant, one with special properties: it has numerous electronic energy levels and the energy of those levels is controllable by the electrode potential. Just as one reactant in solution may bind the other, the electrode may adsorb the other reactant.

In the present paper we shall be concerned principally with simple electron transfer reactions at electrodes and in solution, reactions which involve no rupture or formation of chemical bonds. Elsewhere [1] we have discussed reactions involving rupture of a chemical bond at an electrode M, e.g., Eqs. [1]-[2], and for brevity omit a discussion of this topic here.

$$H_3O^+ + M(e) \rightarrow H_2O + H - M \qquad [1]$$

$$H_3O^+ + H - M \rightarrow H_2O + H_2 + M^+ \qquad [2]$$

A simple electron transfer reaction at an electrode can be written as

$$A_1(ox) + M(ne) \rightarrow A_1(red) + M \quad , \qquad [3]$$

while a simple electron transfer between species A_1 and A_2 in solution is represented as

$$A_1(ox) + A_2(red) \rightarrow A_1(red) + A_2(ox) \quad , \qquad [4]$$

where (ox) and (red) denote the oxidized and reduced forms of the two chemical species A_1 and A_2. The ionic charges on these reactants are usually about one to three, though sometimes as high as four and sometimes as low as zero. The solvation energies are therefore very large and their fate during the course of the reaction must be analyzed carefully.

POTENTIAL ENERGY CURVES, SURFACES, FLUCTUATIONS, AND RATES

It is useful to examine first the vibrational motion within the reactant in Eq. [3], considering initially the case of one vibrational coordinate q. (The same plot suffices for Eq. [4] also.) A plot of the potential energy U versus q for the system on the left hand side of Eq. [3] is labelled R in Fig. 1, and a plot of U versus q for the system on the right hand side of Eq. [3] is labelled P [2,3].

There are many electronic states of the metal--a continuum of them. Thus, Fig. 1 for the reaction in Eq. [3] should consist of many parallel curves, vertically displaced from each other, one for each electronic state. However, one can show [3,4] that the electrons donated from the electrode M to A(ox) in Eq. [3] come from levels near the Fermi level, and most of them donated from A(red) to M in the reverse reaction go into levels near the Fermi level. Thus, it suffices to confine our attention for the present purposes to the two curves in Fig. 1 and take the energy level of the electron in the metal as the Fermi level. The following analysis then applies equally well to reactions [3] and [4].

Several facts are noted:

(1) The minima of the two curves occur at different values of q, reflecting the fact that the equilibrium bond length in A_{ox} is different (usually shorter in the case of transition metal ions and a metal-ligand bond) from that in A_{red}.

(2) The relative height of the two minima ΔU^0 depends on the electrostatic potential, the P curve being lowered vertically

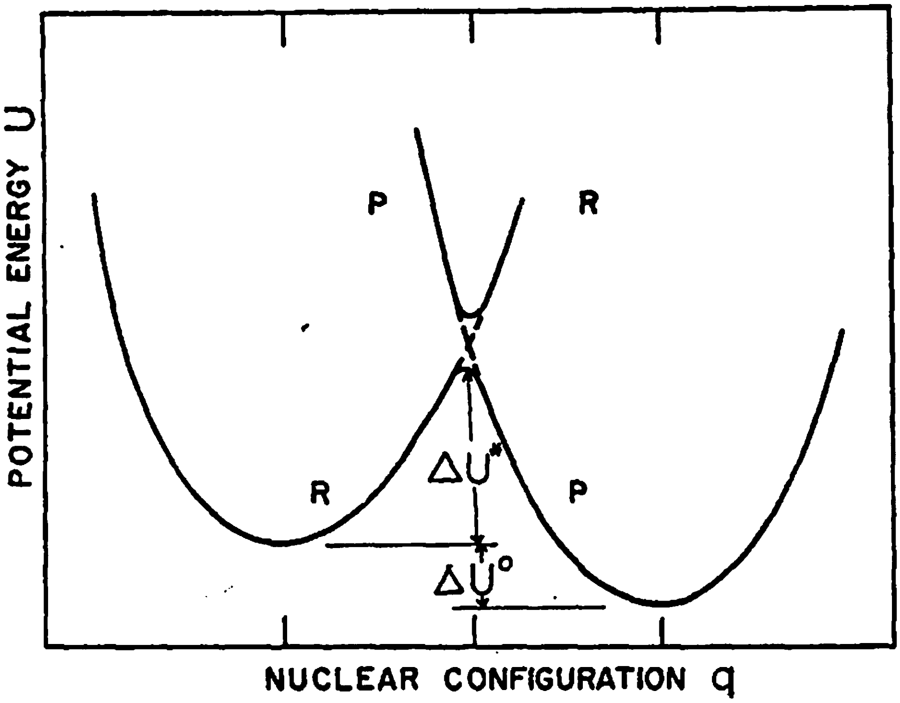

Fig. 1. A plot of the potential energy U of the system consisting of reactants plus solvent (R), along some coordinate q, and of the system consisting of products plus solvent (P), holding all other coordinates fixed, for reaction [3] or [4].

relative to the R curve by making the electrode more negative, i.e., by decreasing $e(\varphi_M - \varphi_S)$ where the φ's represent the potentials of the metal and solution.

(3) When the difference of equilibrium bond lengths Δq^0 is less, for a given ΔU^0, the barrier height ΔU^* is less.

(4) When the P curve is lowered relative to the R one, the barrier height ΔU^*, corresponding to the intersection of the R and P curves, is reduced.

The two curves have further properties: When the reactant is far from the electrode the appropriate curves in Fig. 1 merely cross in the intersection region (dotted lines there). When the reactant is close to the electrode, the electronic interaction of the orbitals of the reactant and the electrode perturbs the dotted line curves, particularly near the point of intersection. At that point the unperturbed R and P electronic quantum states are degenerate, and the degeneracy is broken by the interaction. The new curves are the solid curves. The energy of the maximum of the lower solid curve is less than that at the intersection by an electronic interaction energy ε_{12}, the "resonance energy."

When ϵ_{12} is zero (e.g., large separation distance between electrode and reactant) a system having a potential energy curve R will undergo thermal fluctuations of the vibrational coordinate q, but not transfer to the P curve even on passing through the intersection region. When ϵ_{12} is nonzero, there is a coupling of the electronic orbitals of the reactant and the electrode, and there is a nonzero probability κ of going from the R curve to the P curve when the system passes through the intersection region. When ϵ_{12} is small the reaction has a small κ and the reaction is termed nonadiabatic. When κ is of the order of unity the reaction is adiabatic. The electronic factor κ can be calculated by the Landau-Zener-Stueckelberg formula [5], or by a more numerical quantum mechanical computation [6], if ϵ_{12} and the properties of the R and P curves are known.

One notes from Fig. 1 that a fluctuation of coordinate q is needed for the electron transfer to occur: Not only must the reactant-electrode distance, or in Eq. [4] the reactant-reactant distance, become sufficiently small for electronic orbital overlap to occur but also the transfer does not occur at the equilibrium value of q for the R-curve. Only by absorption of light could the system move from the R curve to the P curve at this q. Otherwise the vibrational momentum p, given by $\sqrt{2m(E-U)}$, would not be conserved during the electronic transition and thus the Franck-Condon principle would be violated. However, at the crossing point this momentum p is substantially conserved, so the transfer from the R curve to the P curve can occur.

A simple calculation provides an estimate of the barrier height ΔU^* in Fig. 1: It will be assumed that the resonance energy ϵ_{12} is small enough that the height of the crossing-point is approximately that of the maximum of the lowest solid curve in Fig. 1. We let the potential energy of the R and P curves be approximated by

$$U^r(q) = \frac{1}{2} k(q-q_0{}^r)^2 \qquad [5]$$

$$U^p(q) = \frac{1}{2} k(q-q_0{}^p)^2 + \Delta U^0 \quad , \qquad [6]$$

where $q_0{}^r$ and $q_0{}^p$ are the equilibrium bond lengths for the A(ox) and A(red), respectively. ΔU^0 is negative in Fig. 1, and is a linear function of $ne(\varphi_m-\varphi_s)$ in the case of reaction [3]. At the intersection of the dotted curves we have

$$U^r = U^p \quad , \qquad [7]$$

an equation which can be solved for the value of q, $q^{\ddagger}$ at the intersection. Introducing this $q^{\ddagger}$ into Eq. [5] one obtains ultimately

$$\Delta U^{*} = (\lambda_i/4)[1 + (\Delta U^{0}/\lambda_i)]^2 \quad , \qquad [8]$$

where

$$\lambda_i = \frac{1}{2}\, k(\Delta q^{0})^2 \quad , \qquad \Delta q^{0} = q^{0p} - q^{0r} \quad . \qquad [9]$$

$\lambda_i/4$ is actually the barrier height when the ΔU^{0} in Fig. 1 is zero.

The rate constant k_r would be given by the collision frequency Z per unit area of electrode per unit time in the electrode case and per unit concentration per unit time in the homogeneous case, multiplied by the Boltzmann factor $\exp(-\Delta U^{*}/RT)$, by a Boltzmann factor $\exp(-w^r/RT)$ for bringing the reactant to the electrode, and by κ:

$$k_r = \kappa\, Z \exp[-(w^r + \Delta U^{*})/RT] \quad . \qquad [10]$$

Here, w^r is the work term, if any, required to bring the reactants together to some separation distance R. When such work terms occur, the ΔU^{0} in Eq. [8] is replaced by $\Delta U_R^{\,0}$, the ΔU at that separation distance R. Thus, Eq. [8] is replaced by

$$\Delta U^{*} = (\lambda_i/4)[1 + (\Delta U_R^{\,0}/\lambda_i)]^2 \qquad [11]$$

$$\Delta U_R^{\,0} = \Delta U^{0} + w^p - w^r \quad , \qquad [12]$$

where ΔU^{0} is the ΔU at infinite separation and w^p is the work to bring the products together to the separation distance R.

The above calculation of ΔU^{*} is classical, and indeed classical mechanics is commonly used nowadays to treat reactive collisions, by calculating the trajectories of all the atoms of a reacting molecule or pairs of molecules during a collision. However, for some problems a quantum mechanical treatment is needed, for example for treating a protonic vibration in Eq. [1]. A quantum treatment is given in Refs. [7,8], other approximations being introduced as well.

The results in Eqs. [10]-[12] were derived for the case of one vibration. The derivation can be extended to all the vibrations of the reactant(s) in Eq. [3] or [4]. The potential energy curves of Fig. 1 are replaced by potential energy surfaces, plotted as a function of all the q's in the system rather than just one. If there are N q's, the intersection which is a point in Fig. 1 becomes a hypersurface of N-1 dimensions in the N-dimensional case. The coordinate q in Fig. 1 then represents some path in the N-dimensional q-space and the R- and P-curves are profiles of the actual potential energy surfaces plotted along that path.

In effect, λ_i becomes a sum of terms of the type in Eq. [9], summed over all vibrations, i.e.,

$$\lambda_i = \frac{1}{2}\Sigma_i k_i(\Delta q_i{}^0)^2 \quad , \qquad [13]$$

and k_i is related to the force constants of a bond $k_i{}^r$ and $k_i{}^p$ in the oxidized and reduced forms [3]. A somewhat more sophisticated treatment of λ_i is given in Ref. [3], leading to k_i being a certain average of $k_i{}^r$ and $k_i{}^p$.

There remain the solvent fluctuations outside of the inner coordination shell of the reactant in Eq. [3] or reactants in Eq. [4]. Here, the potential energy functions do not depend on the solvent coordinates (orientations, translations) in the simple quadratic fashion in Eqs. [5] and [6] and of Fig. 1. The treatment of the solvent coordinates is correspondingly more complicated. However, one feature is immediately clear: Just as a thermal fluctuation of vibrational coordinates was needed to reach the intersection region in Fig. 1, a suitable thermal fluctuation of solvent orientation coordinates or reactant's vibrations also permits the system to reach the N-1 dimensional hypersurface (the intersection region). A statistical mechanical treatment of the free energy associated with these fluctuations is given in Ref. [3]. Dielectric continuum theory also permits an estimate of the latter to be made, and was first given for the homogeneous reaction case in 1956 [9], and in ONR Technical Report No. 12 (presented elsewhere in this volume) in 1957 for the electrode reaction, Eq. [3].

The intersection region in Fig. 1, now for a generalized coordinate q and a many-dimensional configuration space, is reached by a thermal fluctuation of coordinates q from their most probable values. Such a fluctuation produces a corresponding thermal fluctuation in the solvent dielectric polarization function. In the intersection region this polarization is appropriate neither to the charges of the reactants nor to those of the products but rather to some compromise, which depends on ΔU^0 or more generally on a free energy of reaction $\Delta G^{0\prime}$ or in the electrode case on a half-cell potential E minus the standard potential $E^{0\prime}$, $E-E^{0\prime}$. This dielectric polarization was termed nonequilibrium polarization [9] and indeed the original dielectric continuum (nonstatistical mechanical) derivation [9,10] was concerned with fluctuations in solvent dielectric polarization.

It is instructive to give a somewhat simpler derivation of the free energy change needed to reach the intersection region by these fluctuations of solvent dielectric polarization. This derivation is given in the next section.

SIMPLIFIED DERIVATION OF NONEQUILIBRIUM POLARIZATION EXPRESSION

We consider the homogeneous reaction system Eq. [4] first and then indicate the modification for the electrode case Eq. [3]. We denote the charges by e_i and radii by a_i for reactants 1 and 2 ($i = 1,2$), and add a superscript p to the e_i to denote charges of the products. The static dielectric constant of the solvent medium is denoted by D_s and the square of the refractive index (the "optical dielectric constant") by D_{op}. The separation distance is denoted by R.

A nonequilibrium dielectric polarization of the medium can be produced in a reversible manner by a two-step charging process. Since each step is reversible, the free energy of formation of this nonequilibrium system, i.e., the free energy of this polarization fluctuation, can be calculated in a relatively straightforward manner. The two-step charging process is the following, at a given separation distance R.

(1) Change the charge of each reactant i from e_i to e_i', e_i' being so chosen to produce the desired orientational-vibrational dielectric polarization.

(2) Change the charge of each particle i back from e_i' to e_i, holding the above orientational-vibrational dielectric polarization fixed.

The details of the calculation are as follows, where the electrostatic potential in the solvent medium at any point $\underset{\sim}{r}$ is denoted by $\psi(\underset{\sim}{r})$.

Step 1

The value of e_i and $\psi(\underset{\sim}{r})$ at any stage ν of the charging process are denoted by e_i^ν and $\psi^\nu(\underset{\sim}{r})$, respectively. They are given by

$$\psi^\nu(\underset{\sim}{r}) = \frac{e_1^\nu}{D_s r_1} + \frac{e_2^\nu}{D_s r_2} \tag{14}$$

$$e_i^\nu = e_i + \nu(e_i'-e_i) \quad , \tag{15}$$

where r_i is the distance from the field point $\underset{\sim}{r}$ to the center of ion i. ν varies from 0 at the beginning of the charging process to 1 at the end, and e_i^ν can be written, thereby, as in Eq. [15].

The potential at the surface of ion 1 due to the medium and to ion 2 is obtained by replacing r_1 by a_1 in Eq. [14]. Φ_1^ν, the potential there minus the self-potential, is obtained by subtracting e_1^ν/a_i from [14]:

$$\Phi_1^\nu = \frac{e_2^\nu}{D_s r_2} + \frac{e_1^\nu}{a_1}\left(\frac{1}{D_s} - 1\right) \quad . \qquad [16]$$

The average of Φ_1^ν over the surface of ion 1 is denoted by $\bar{\Phi}_1^\nu$ and is found to be

$$\bar{\Phi}_1^\nu = \frac{e_2^\nu}{D_s R} + \frac{e_1^\nu}{a_1}\left(\frac{1}{D_s} - 1\right) . \qquad [17]$$

The average leading from Eq. [16] to [17] will be recognized as the well-known electrostatic result [11] that the average value of a $1/r_2$ potential from a uniform distribution over a sphere is $1/R$.

When $\bar{\Phi}_1^\nu$ is multiplied by an increment of charge $d(e_1^\nu)$, i.e., $(e_1'-e_1)d\nu$, and integrated over ν from 0 to 1 and when the same integration is performed for ion 2, and both terms summed we obtain the work term W_I required in charging step 1:

$$W_I = \int_0^1 \bar{\Phi}_1^\nu (e_1'-e_1)d\nu + \int_0^1 \bar{\Phi}_2^\nu (e_2'-e_2)d\nu \quad . \qquad [18]$$

Eqs. [17]-[18] yield immediately

$$W_I = \frac{e_1\Delta e_2 + e_2'\Delta e_1}{D_s R} + [e_1\Delta e_1 + \tfrac{1}{2}(\Delta e_1)^2]\left(\frac{1}{D_s} - 1\right)\frac{1}{a_1} + [e_2\Delta e_2 + \tfrac{1}{2}(\Delta e_2)^2]\left(\frac{1}{D_s} - 1\right)\frac{1}{a_2} \qquad [19]$$

where

$$\Delta e_i = e_i' - e_i \quad . \qquad [20]$$

When e_1 and e_2 are both zero, the $1/R$ term becomes the usual coulomb repulsion $e_2'e_1'/D_s R$, the $1/a_1$ term the well-known Born charging term for ion 1 $(e_1'^2/2a_1)[(1/D_s)-1]$, and the $1/a_2$ term the Born charging term for ion 2.

Step 2

The charges are now given by Eq. [21], where ν goes from 0 to 1.

$$e_i^\nu = e_i' + \nu(e_i - e_i') \quad . \qquad [21]$$

If $\psi_I(\underset{\sim}{r})$ denotes the potential at the end of step 1 and $\psi^\nu(\underset{\sim}{r})$ the potential at any state ν of step 2, the change of potential during step 2, for any ν, is $\psi^\nu(\underset{\sim}{r})-\psi_I(\underset{\sim}{r})$. Since the medium responds to a change of charge

δe_i^{ν} only via the optical dielectric constant D_{op}, now, we have during step 2

$$\delta\psi^{\nu}(\underset{\sim}{r}) = \frac{\delta e_1^{\nu}}{D_{op}r_1} + \frac{\delta e_2^{\nu}}{D_{op}r_2} \quad . \tag{22}$$

Writing δe_i^{ν} as $\nu(e_i - e_i')$ and $\delta\psi^{\nu}$ as $\psi^{\nu} - \psi_I$ we have

$$\psi^{\nu}(\underset{\sim}{r}) = \psi_I(\underset{\sim}{r}) + \frac{\nu(e_1 - e_1')}{D_{op}r_1} + \frac{\nu(e_2 - e_2')}{D_{op}r_2} \tag{23}$$

where

$$\psi_I(\underset{\sim}{r}) = \frac{e_1'}{D_s r_1} + \frac{e_2'}{D_s r_2} \quad . \tag{24}$$

$\bar{\Phi}_1^{\nu}$, the average potential on the surface of ion 1 minus the self-potential is obtained by subtracting e_1'/r_1 from Eq. [24] and $\nu(e_1 - e_1')/r_1$ from the last term but one in Eq. [23], then replacing r_1 in those equations by a_1 and averaging the $1/r_2$ in those equations over the surface of ion 1, thereby replacing $1/r_2$ by $1/R$. Thus

$$\bar{\Phi}_1^{\nu} = \frac{e_1'}{a_1}\left(\frac{1}{D_s} - 1\right) + \frac{e_2'}{D_s R} + \frac{\nu(e_1 - e_1')}{a_1}\left(\frac{1}{D_{op}} - 1\right) + \frac{\nu(e_2 - e_2')}{D_{op}R} \quad . \tag{25}$$

The work done during this step is W_{II},

$$W_{II} = \int_{\nu=0}^{1} \bar{\Phi}_1^{\nu} de_1^{\nu} + \int_{\nu=0}^{1} \bar{\Phi}_2^{\nu} de_2^{\nu} \quad . \tag{26}$$

One obtains

$$W_{II} = \left(\frac{\Delta e_1 \Delta e_2}{D_{op}} - \frac{e_2'\Delta e_1 + e_1'\Delta e_2}{D_s}\right)\frac{1}{R} + \left[\frac{1}{2}(\Delta e_1)^2\left(\frac{1}{D_{op}} - 1\right) - e_1'\Delta e_1\left(\frac{1}{D_s} - 1\right)\right]\frac{1}{a_1}$$
$$+ \left[\frac{1}{2}(\Delta e_2)^2\left(\frac{1}{D_{op}} - 1\right) - e_2'\Delta e_2\left(\frac{1}{D_s} - 1\right)\right]\frac{1}{a_2} \quad . \tag{27}$$

The net work done ΔG^r is the sum of W_I and W_{II} and is the free energy of this fluctuation. It is equal to

$$\Delta G^r = W_I + W_{II} = \left(\frac{\Delta e_1^2}{2a_1} + \frac{\Delta e_2^2}{2a_2} + \frac{\Delta e_1 \Delta e_2}{R}\right)\left(\frac{1}{D_{op}} - \frac{1}{D_s}\right) \quad , \tag{28}$$

where Δe_i is given by Eq. [20].

If $\Delta G_R^{0\prime}$ denotes the free energy change for unit concentration of reactants at a separation distance R, it is related to the same quantity at infinite separation $\Delta G^{0\prime}$ by an equation similar to Eq. [12], namely

$$\Delta G_R^{0\prime} = \Delta G^{0\prime} + w^p - w^r \quad . \tag{29}$$

On the intersection hypersurface of Fig. 1, the reactants and products have the same distribution of configurations (the same set values of $q^{\ddagger}$), and the same potential energy (cf Eq. [7]), averaged over a distribution of such configurations. Since the distribution of configurations (and momenta) are the same for the reactants and products on the intersection hypersurface, the entropy is also the same, and so the free energy of the reactants is the same as that for the products on the intersection hypersurface. It then follows that we can write

$$\Delta G^{r} - \Delta G^{p} = \Delta G_{R}^{0\prime} \quad , \qquad [30]$$

where ΔG^{r} is given by Eq. [28] and ΔG^{p} by the same expression with e_i replaced by e_i^{p}.

To find e_1' and e_2' one minimizes the ΔG^{r} in Eq. [28] subject to the constraint imposed by Eq. [30].

$$\delta\Delta G^{r} = (\partial\Delta G^{r}/\partial e_1')\,\delta e_1' + (\partial\Delta G^{r}/\partial\Delta e_2')\,\delta e_2' = 0 \qquad [31]$$

$$\delta\Delta G^{r} - \delta\Delta G^{p} = 0 \quad . \qquad [32]$$

Multiplying the second equation by a Lagrange multiplier m and adding to Eq. [31], introducing expressions such as Eq. [31] for $\delta\Delta G^{r}$ and $\delta\Delta G^{p}$ into Eq. [32], and setting the coefficients of $\delta e_1'$ and $\delta e_2'$ equal to zero, one finds

$$e_i' = e_i + m(e_i - e_i^{p}) \qquad (i = 1,2) \quad . \qquad [33]$$

Introducing this result into Eqs. [28] and [30] one obtains

$$\Delta G^{r} = m^2\lambda_0 \qquad [34]$$

and

$$-(2m+1)\lambda_0 = \Delta G_{R}^{0\prime} \quad , \qquad [35]$$

where

$$\lambda_0 = (\Delta e)^2\left(\frac{1}{2a_1} + \frac{1}{2a_2} - \frac{1}{R}\right)\left(\frac{1}{D_{op}} - \frac{1}{D_s}\right) \quad , \qquad [36]$$

and Δe is $e_i^{p} - e_i$, the charge transferred. m is the solution of Eq. [35].

The free energy barrier ΔG^* to reaction consists of the work term w^{r} to bring the reactants together and ΔG^{r}. Further, solving Eq. [35] for m and introducing into Eq. [34] one obtains

$$\Delta G^* = w^{r} + (\lambda_0/4)\left[1 + (\Delta G_{R}^{0\prime}/\lambda_0)\right]^2 \quad . \qquad [37]$$

In the electrode case the electrostatic potential in step 1 is given by Eq. [14], but with the e_2 replaced by the image charge of reactant 1 in the electrode $-e_1$. The image charge ensures that the potential given by Eq. [14] is constant on the surface of the electrode, where $r_1 = r_2$. There is, in addition, another term due to the interaction of ion 1 with the other charges on the electrode and with the surrounding electrolyte. This term is found to cancel, apart from a minor term, in steps 1 and 2 and so will be omitted here for brevity. The derivation continues then as before, where R now denotes the distance from ion 1 to its image, namely twice the distance to the electrode. In computing W_I and W_{II} one computes only the work to charge ion 1. One finds ultimately expressions similar to Eqs. [34]-[37] but now we have

$$-(2m+1)\lambda_0 = -nF(E-E^{0'}) + w^p - w^r \qquad [38]$$

and

$$\lambda_0 = \frac{1}{2}\left(\frac{1}{a_1} - \frac{1}{R}\right)\left(\frac{1}{D_{op}} - \frac{1}{D_s}\right) \quad . \qquad [39]$$

That is, one obtains for this electrode case

$$\Delta G^* = w^r + (\lambda_0/4)[1 + \{-nF(E-E^{0'}) + w^p - w^r\}/\lambda_0]^2 \qquad [40]$$

where F is the Faraday.

This type of simplified derivation of the above results was given earlier in Ref. [12], and has recently been made more readily available in a review [13].

If now one wished to include simultaneously these fluctuations in solvent polarization and those described earlier in reactants' vibrations, one could readily do so: To the right side of Eq. [28] would be added $\frac{1}{2}\sum_i k_i(q_i-q_i^{0r})^2$, and $\frac{1}{2}\sum_i k_i(q_i-q_i^{0p})^2$ would be added to the corresponding expression for ΔG^p. One would then proceed as before, using Eqs. [31]-[32], but now Eq. [31] would contain an extra term $\sum_i k_i(q_i-q_i^{0r})\delta q_i$, and $\delta\Delta G^p$ would contain an analogous extra term. One would find in addition to Eq. [33] the result that

$$q_i^{\ddagger} = q_i^{0r} + m(q_i^{0r}-q_i^{0p}) \quad . \qquad [41]$$

When this $q_i^{\ddagger}$ and the e_i', again given by Eq. [33], are introduced into the expression for ΔG^r, Eq. [34] would again follow, but with λ_0 replaced by $\lambda_0+\lambda_i$, λ_0 being given by Eq. [36] and λ_i by Eq. [13]. Similar remarks apply to the electrode reaction case.

DEDUCTIONS AND APPLICATIONS OF THE THEORY

When a statistical mechanical treatment is undertaken instead of a dielectric continuum one again obtains equations formally similar to Eqs. [10] to [12] and [34] to [41], but with λ_0 having a statistical mechanical value and $\lambda_i+\lambda_0$ replacing λ_i and λ_0 [3]:

$$k_r = \kappa Z \exp(-\Delta G^*/kT) \quad , \tag{42}$$

where in the homogeneous case

$$\Delta G^* = w^r + (\lambda/4)[1+(\Delta G_R^{0\prime}/\lambda)]^2 \quad . \tag{43}$$

$\Delta G_R^{0\prime}$ is given by Eq. [29] and in the electrode case $\Delta G_R^{0\prime}$ is replaced by

$$\Delta G_R^{0\prime} \rightarrow -nF(E-E^{0\prime}) + w^p - w^r \quad , \tag{44}$$

and in both cases λ is the sum of two contributions:

$$\lambda = \lambda_i + \lambda_0 \quad . \tag{45}$$

In these equations κ, Z, w^r and w^p have the same significance as before. $\Delta G^{0\prime}$ is the free energy of reaction for Eq. [4], when the reactants and products are each in unit concentration in the prevailing medium and at the prevailing temperature. $E^{0\prime}$ is the "standard" half-cell potential for Eq. [3] under the same conditions and E is the actual half-cell potential (in the absence of concentration polarization). λ for the electrode case differs from that for the homogeneous case, as before, but in each case contains a vibrational contribution λ_i from the inner coordination shell of the reactant λ_i and a contribution λ_0 from the solvent outside, as in Eq. [45]. λ_i is of the form in Eq. [13] and a dielectric continuum estimate of λ_0 is of the form in Eq. [36] or Eq. [39].

In the lecture on which the present article is based deductions from these various equations were described, together with experimental data regarding them. Since similar material was recently presented elsewhere [14], it will not be reproduced here. Instead, some of the deductions from the theoretical equations are summarized and reference is made to [14] for further details and for most of the experimental references. The references both here and in [14] are intended merely to be representative, rather than complete. Several ones in addition to [14] are also included.

(1) Cross-Reactions and Electron-Exchange Reactions

The following reactions are known as electron exchange reactions and their rates are most frequently measured by use of isotopic tracers.

$$A_1(ox) + A_1(red) \rightarrow A_1(red) + A_1(ox) \qquad [46]$$

$$A_2(ox) + A_2(red) \rightarrow A_2(red) + A_2(ox) \qquad [47]$$

Let their λ's be written as λ_{11} and λ_{22}, and their rate constants as k_{11} and k_{22}. The reaction in Eq. [4] is designated as a cross-reaction with λ written as λ_{12} and rate constant as k_{12}. Because of an additivity property [3] of λ,

$$\lambda_{12} \cong \frac{1}{2}(\lambda_{11} + \lambda_{22}) \quad , \qquad [48]$$

and the form of Eq. [43], one obtains a prediction of k_{12} in terms of k_{11}, k_{22} and K_{12}, the equilibrium constant of Eq. [4], when the κ's for the individual reactions are either near unity or nearly cancel, and when the work terms for the individual reactions are either small or nearly cancel:

$$k_{12} \cong (k_{11}k_{22}K_{12}f_{12})^{1/2} \qquad [49]$$

where

$$f_{12} = (\ell n\ K_{12})^2/4\ \ell n(k_{11}k_{22}/Z^2) \quad . \qquad [50]$$

Sutin, referenced in [14], pioneered the experimental study of these relations between cross-reactions and self-exchange reactions.

(2) Dependence of the slope α of a plot of $\ell n\ k_{12}$ vs $\ell n\ K_{12}$ (Bronsted coefficient) (cf. [14]).

$$\alpha = \frac{1}{2}(1 + \Delta G_R^{0\prime}/\lambda) \quad . \qquad [51]$$

(3) Dependence of the slope α of a plot of ℓn i, where i is the current density for the forward reaction in Eq. [3], vs $-nF(E-E^{0\prime})$ (Tafel slope) [14].

$$\alpha = \frac{1}{2}[1 + \{-nF(E-E^{0\prime}) + w^p - w^r\}/\lambda] \qquad [52]$$

(4) Relations between electrode rates and homogeneous reaction rates [14].

(5) Dependence of $\ell n\ k_r$ on solvent dielectric continuum properties when no specific reactant-solvent interaction exists [15].

(6) Dependence of $\ell n\ k_r$ on changes in equilibrium bond lengths and angles [14].

(7) Dependence of $\ln k_r$ on Δe [16].

(8) Formation of electronically-excited states, and hence chemiluminescence, in highly exothermic reactions, and properties thereof [14].

(9) Contributions to the entropy of activation of reactions [17].

(10) Electrolyte affects in electrode reactions [18] and in homogeneous reactions [17].

More recently, evidence regarding the dependence of Tafel slope in electrode reactions on $E-E^{0\prime}$ may be found in [19] and on chemiluminescence in [20]. (For further theoretical studies on references related to highly exothermic reactions, such as those involving chemiluminescence, see [14].) A nice example of a test of Eq. [43] is given in [21]. An application of the present electron transfer theory to electron transfer reactions with negative activation energy [22] is found in [23]. Other interesting developments in electron transfer theory include the study of reactions at semiconductor electrodes [24-26].

COMMENTS ON SEVERAL DEVELOPMENTS SINCE 1957

Elsewhere in this volume ONR Technical Report No. 12 (1957) is reproduced. It contains the formulation of this electron transfer theory for electrode reactions. That Report was concerned with the dielectric continuum contribution to the free energy barrier, a contribution for which a simplified derivation was given in an earlier section of the present paper. The derivation in ONR Technical Report No. 12 is given in terms of vector-fields, vectors associated with the dielectric polarization, with the electric field due to the charges themselves, and with the total electric field due to the charges and the polarization. In the simplified derivation given in a previous section the electrostatic quantities are not expressed in terms of vector-fields but rather in terms of scalar-fields associated with potentials and charges, though fields of a restricted kind, namely of the functional form given by Eq. [14]. A more general derivation is given in terms of scalar-fields in [3], and vector-fields in ONR Technical Report No. 12. No assumption is made initially, for example, that the reactant(s) is(are) spherical.

One generalization of the dielectric continuum result in Eqs. [36] and [39] for λ_0 is to include the fact that there is a dispersion of frequencies characterizing the dielectric response [27,28]. The correction in the λ_0 value amounts to 18% [28].

One point of interest regarding derivation in [9,10] terms of vector-fields (viz. electric vectors) versus one in terms of scalar fields (viz. charge densities and electrostatic potentials) in [3] is the following: In the vector-field derivation in ONR Technical Report No. 12 [10] and in its predecessor [9] the transcription of the final vector-field equations for the electrostatic free energy into scalar-field quantities was needed and was made. This transcription is avoided by using instead scalar-field expressions throughout.

Two of the generalizations in Ref. [3] are to use statistical mechanics instead of dielectric continuum theory and to treat the inner shell contribution to the fluctuations in coordinates. (This second generalization was given also in Ref. [29].) The generalizations led to similar predictions as those given earlier in the present paper, but without the simple dielectric equations [36] and [39] for λ_0 and hence without the simple predictions of solvent effects for reactants which do not specifically interact with the solvent. A statistical mechanical expression for λ_0 was given instead, [3], one whose evaluation must await further application of the statistical mechanics of polar liquids. When a dielectric continuum estimate was made of this contribution one obtains the result for λ_0 given in Eq. [36] for homogeneous reactions and Eq. [39] for electrode reactions. When the inner contribution is included, the same final equations obtained, but with λ_0 replaced by $\lambda_0+\lambda_i$, as in Eq. [45].

In the statistical mechanical treatment it was recognized [3,29] that when the q in Fig. 1 in the vicinity of $q^{\ddagger}$ is primarily a solvent orientational or solvent vibrational coordinate the free energy change given by Eq. [43] is actually the free energy of a fluctuation of coordinates to values centered on the intersection hypersurface rather than being confined to it. This effect introduces a minor correction factor ρ [3] in the pre-exponential factor in Eq. [42]; ρ is of the order of unity.

Among other developments since 1957 has been the recognition of the various consequences of the theoretical equations, listed earlier. The relation given by Eq. [49] was first given essentially in 1960 [29], applied to experimental data in 1963 [30], and given a more general derivation in 1965 [3]. The dependence of Tafel coefficient on $E-E^{0'}$ was not confirmed until 1975 [19], and use was made of Mohilner's treatment [18] of electrolyte effects to calculate the work terms w^r and w^p. The solvent effect was tested in 1970 [15] and the effect of Δe in Eq. [39] in 1969 [16]. A comparison between some rates of electrode reactions and the electronic structure of the reacting species, aimed at correlating qualitatively with charges of equilibrium bond lengths is given in

Ref. [14]. Applications of the cross-relation Eq. [49] to biological systems have also been made and referenced in [14].

Eq. [49] has been widely tested (referenced in [14]) and has been very useful in correlating a large body of data. The main anomaly observed thus far in this equation is for reactions of $Co^{+3}(aq)$ ion. This ion undergoes an extensive electronic rearrangement in forming $Co^{+2}(aq)$ and a possible explanation for the anomaly is given in [14].

Quantum effects on the vibrational or solvent motion have also been treated [7,8,13,31b]. At sufficiently low temperatures the system does not use the energy ΔU^{*} in Fig. 1 to go from the R curve to the P curve. Instead it can "tunnel" through the barrier there. This tunneling, in many-dimensional q-space, has been treated by means of Fermi's Golden Rule for radiationless transitions and Franck-Condon factors [7,8,13,31b]. At high temperatures the expression for the free energy barrier reduces to the classical one given earlier in this paper. An analogous formalism has been used to treat [31] biological electron transfers [32] at very low temperatures.

In the quantum treatment [7,8,13] a treatment of the vibrations of the reactants is relatively straightforward, but the solvent vibrations are treated as though they are vibrations of a solid and hence undamped. In the liquid there is a strong damping. (This approximation was not made in the classical statistical mechanical treatment [3].) A modification for the damping on the quantum mechanical result has been described [33].

Again, when curve P in Fig. 1 crosses curve R on the left hand side, so that the slopes of both curves are both negative at the crossing point, the transition from R to P curve can only occur nonadiabatically and quantum treatments involving the Franck-Condon factors and related closely to the just mentioned quantum formalism [7,8,13], have been used, referenced in [14]. Such treatment are needed for highly exothermic reactions: When ΔU in Fig. 1 is sufficiently negative the crossing will indeed be such that the R and P curves have the same slopes at the crossing point.

Finally, there are reactions of the redox or electrochemical type where bonds are actually broken and formed during the reaction. Here, the description of the potential energy surfaces given in Fig. 1 is suggestive though not adequate. Other models have been used, the bond energy-bond order model [34] for example [35,36], and an analog to Eqs. [43], [40] and [50] has been obtained [36] but with

$$\Delta G^* = w^r + (\lambda/4) + (\Delta G_R^{0\prime}/2) + (\Delta G_R^{0\prime}/2y)\ln\cosh y \quad [53]$$

and

$$f_{12} = (K_{12})^{(\ln\cosh y)/y} \quad [54]$$

where

$$y = (2\gamma\Delta G_R^{0\prime}/\lambda) = (\ln K_{12})\gamma/\ln(k_{11}k_{22}/Z^2)\ , \quad \gamma = \ln 2\ . \quad [55]$$

(The case of the hydrogen discharge reaction, Eq. [1], will be treated in a forthcoming publication [1] using a combination of nonequilibrium polarization, BEBO, and Franck-Condon overlap methods to treat different aspects of the overall problem.) Whereas the slope of a Bronsted plot (homogeneous reaction) or Tafel plot (electrode reaction) was given by Eqs. [51] and [52], they are given [36] in a BEBO model by Eq. [56] when the work terms can be neglected.

$$\alpha = \frac{1}{2}(1 + \tanh y) \quad [56]$$

where y is given by Eq. [55]. In the electrode case the $2\Delta G_R^{0\prime}/\lambda$ is replaced by $2\{-nF(E-E^{0\prime}) + w^p - w^r\}/\lambda$.

The theory of electron transfer reactions in solution and at electrodes continues to be in an active and developing state. An estimate has been made for the κ in Eq. [42] for the ferrous-ferric electron exchange reaction [37]. Calculations are desirable, using increasingly accurate theories of electronic structure, for κ's of this and other reactions including those of $Co^{+3}(aq)$ for which extensive electronic rearrangement occurs. Such calculations will also permit more insight into orientational effects [38] in electron transfer reactions. Again, developments can be expected in statistical mechanical evaluation of the term obtained for fluctuations in orientations of solvent molecules, needed to reach the intersection region of Fig. 1. There have been numerous enlightening interactions between theory and experiment, and we can continue to look forward to this fruitful interplay in the future.

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