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Thermal Electron Transfer Reactions in Polar Solvents

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A quantum mechanical theory of electron transfer reactions is developed using the techniques employed in solid-state and radiationless transition theory. This theory allows one to incorporate the effects of both the long-range polaron modes of the liquid and the short-range specific hydrational modes around the ions. Typical calculations suggest that the resulting temperature dependence of the activation energy may be observed experimentally in some cases.

I. Introduction

The experimental progress in the kinetic studies of ionic oxidation–reduction reactions in polar liquids

$$A^{N+} + B^{M+} \rightleftharpoons A^{(N+1)+} + B^{(M-1)+} \qquad (I.1)$$
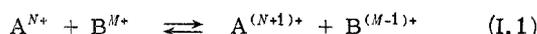
(where A and B are ionic species) has coincided with the development of numerous theories of thermal electron transfer processes.[1-3] From the point of view of the chemist such outer-sphere electron transfer processes in a polar solvent exhibit the following unique features. (a) The chemical reaction does not involve the rupture of chemical bonds. (b) As the chemical process proceeds *via* charge exchange between well-separated ions the pertinent nuclear configurations of the system consists of a huge number (of the order of Avogadro's number) of nuclear coordinates involving the molecules in the first coordination layers and those of all the polar molecules in the bulk. Thus a proper semiclassical or quantum mechanical description of this chemical process has to consider a "supermolecule" consisting of the two ions and the solvent. (c) The interaction inducing the charge transfer process (or in the chemists language the weak electronic interaction in the "activated complex") can result in nonadiabatic chemical reactions, in analogy to unimolecular decomposition processes of some triatomic molecules which involve a change in the electronic state.

An important contribution to the understanding of homogeneous and electrochemical electron transfer processes was provided by the extensive theoretical studies of Marcus,[2,4] which involves the following ingredients. (a) A classical general approach based on absolute reaction rate theory was adopted. (b) The nuclear motion was assumed to be classical. (c) Nonequilibrium dielectric polarization theory was developed to account for the contribution of the rotational (permanent) polarization of the solvent outside the first coordination layer to the reaction coordinate. The bulk was handled as a continuous dielectric medium. (d) The contribution of configurational changes in the first coordination layer to the reaction coordinate was handled classically. (e) All electron transfer reactions were assumed to be adiabatic, although his use of κ allowed for nonadiabatic situations to be considered.

From the point of view of a theoretical chemist outer-sphere electron transfer reactions should be amenable to a fairly complete quantum mechanical description, which should rest on the following general picture. (a) The chemical reaction can be envisaged in terms of a change in the electronic state of the total system which involves the two ions embedded in the polar liquid. (b) The transition between states has to be properly formulated to account for the coupled electronic and nuclear motion of the total system. (c) The total Hamiltonian of the system is partitioned into a zero-order Hamiltonian and a (weak) perturbation term. Within the framework of the Born–Oppenheimer approximation the initial and the final zero-order states of the total system can be conveniently chosen to constitute dense manifolds of vibronic levels, as each of these states involves a superposition of the polar modes of the solvent (which form a continuum analogous to the optical modes of a solid). Provided that the eigenstates of the zero-order Hamiltonian constitute a "reasonable" description of the physical system, the electron transfer reaction can be described in terms of a relaxation process. The zero-order vibronic state corresponding to the initial electronic configu-

ration is nonstationary but is coupled to a continuum of final states, and thus ensuring a reversible decay process.

These general features of the quantum mechanical description of thermal electron transfer processes bear a close resemblance to the theoretical description of a wide class of molecular relaxation processes such as nonradiative intramolecular relaxation processes in large molecules in the statistical limit, radiationless decomposition processes such as predissociation and autoionization in electronically excited states, and unimolecular decomposition processes. Finally and perhaps most important the theoretical description of electron transfer reactions is completely analogous to the study of radiationless process such as thermal ionization of impurity centers and thermal electron capture in semiconductors which were studied by Kubo, Toyozawa, Lax, and others.[5] This theory of multiphonon processes in solids is directly applicable to electron transfer reactions in polar solvents. A major contribution to the quantum mechanical theory of electron transfer processes in solution was provided by Levich[6] and his school[7] which began with the following assumptions. (a) The reaction rate is expressed in terms of the thermally averaged quantum mechanical transition probability between the vibronic levels of the total system. (b) The ions with their first coordination layers are regarded as rigid "metallic" spheres. Configurational changes in the first solvation layer are neglected.[8] (c) The bulk of the solvent is considered as a continuous dielectric. (d) The harmonic approximation was applied for the orientational vibrational polarization modes of the medium. (e) The normal polar modes of the medium are recast in terms of the Fourier components of the total energy of the polarization field, as is common in polaron theory. The equilibrium values of the medium coordinates were recast in terms of the derivatives of the potential energy with respect to these medium coordinates. (f) As common in polaron theory the frequencies of the medium polar modes were approximated by a single frequency. The effect of dispersion was also subsequently studied.[9,10] (g) For a weak electron exchange perturbation the transition probability for electron transfer can be expressed within the framework of first-order time-dependent perturbation theory in terms of Fermi's golden rule. This approach provides the basis for the study of nonadiabatic electron transfer reactions. (h) Adiabatic electron transfer reactions were handled on the basis of a semiclassical treatment in terms of the Landau–Zener theory.

A complete quantum mechanical theory of electron transfer reactions will be of considerable interest because of the following reasons. (a) The quantum mechanical rate expressions do not invoke the classical concept of the activated complex. (b) A general formulation of adiabatic and nonadiabatic chemical reactions should be found without introducing semiclassical theories. (c) The nature of quantum effects on electron transfer reactions, in particular the temperature dependence of the activation energy, can be elucidated.

A partial resolution of these questions was provided by the work of Levich and Dogonadze.[6] Concerning points a and c above it was demonstrated that for nonadiabatic reactions in the low-temperature limit the electron transfer process corresponds to nuclear tunnelling between zero-order states, while in the high-temperature limit the major contribution to the transition probability and to the rate constant originates from the vicinity of the crossing of the potential surfaces. This general feature is common to all nonadiabatic unimolecular and solid-state processes. However the Levich theory cannot reproduce many interesting real life situations as the configurational changes in the first coordination layer were disregarded. Further theoretical work in this field is therefore required. The work of Dogonadze[9] has been in this direction also.

In this paper we pursue the formal analogy between electron transfer reactions and nonradiative relaxation processes in molecular and solid-state physics. The main goals and accomplishments of the present study can be summarized as follows.

(a) The transition probability for electron transfer, which involves a weighted density of states function (i.e., the density of states weighted by different interstate coupling terms for each state), was handled by the mathematical methods previously applied for the Mössbauer effect, multiphonon processes in solids and in large molecules, and the optical line shapes in solids. Indeed, transition probabilities for both radiative and nonradiative processes can be recast in terms of a generalized line shape function, and the nonradiative decay probability can be expressed in terms of the line shape function at zero frequency. The transition probability is expressed in terms of a Fourier transform of a generating function. These technqiues were applied to electron transfer processes and enabled us to handle a system characterized by many vibrational modes, while the original work of Levich and Dogonadze[6] was limited to a quantum mechanical expression for a single-frequency model, and subsequent work utilizes semiclassical approximation for a high-frequency mode.

(b) Numerical techniques based on the steepest descent method and expansion methods of the generating function were introduced to derive general expressions for the electron transfer probability in the high-temperature limit, while in the low-temperature case series expansion of the generating function lead to explicit expressions for the transition probability. Schmidt[11] has also considered these techniques for this application.

(c) The nature of the medium polar modes was reinvestigated. On the basis of polaron theory we were able to derive explicit expressions for the displacement of each normal polar mode, thus providing a slight extension of Levich's continuum model. Configurational changes in the first coordination layer were estimated from experimental spectroscopic and structural data.

(d) We were thus able to derive general quantum mechanical expressions for the nonadiabatic electron transfer transition probability including both the medium modes and the configurational changes in the first coordination layer. Other efforts have recently been made in this area by Dogonadze, Ulstrup, and Kharkats,[12] Schmidt,[13] and Schmickler and Vielstich.[14]

(e) In view of the high frequency of the ligands in the first coordination layer interesting quantum effects on the rate constant are predicted for systems characterized by large local configurational changes.

Let us first recall the general features of the electron transfer problem, where an electron is exchanged between a pair of solvated ions. The initial state of the system consists of a pair of ions ($A^{N+} + B^{M+}$) while the final state involves the A species in its reduced state and the B species in its oxidized state, i.e. ($A^{(N+1)+} + B^{(M-1)+}$). In the present model the two ions interact strongly with their first coordination layers and exert long-range electrostatic interactions on the bulk of the solvent outside the first coordi-
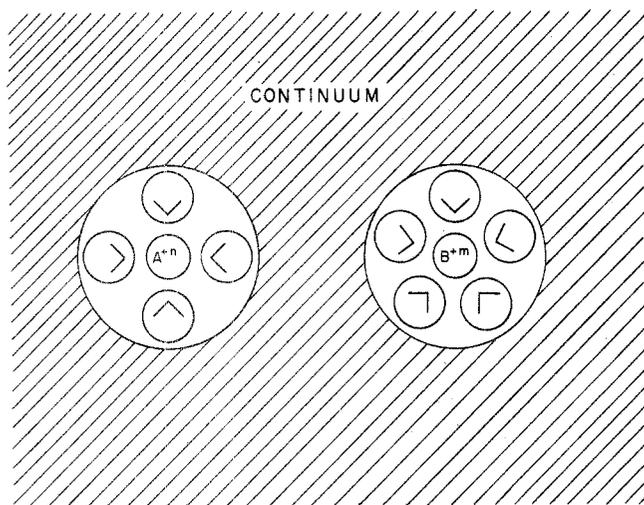
Figure 1. General model of electron transfer reactions. The medium outside the first coordination layer is treated as a continuum. The first solvation sheath is characterized by a totally symmetric vibration.

nation layers (Figure 1). The role of solvent exchange in the first coordination layer is neglected and one considers two supermolecules each consisting of an ion with its first coordination layer embedded in the polar solvent. The long-range interactions between the ionic charge distribution and the solvent outside the first coordination layers bear a close analogy to the problem of the motion of a small polaron in polar crystals.[15]

It is worthwhile to consider the Hamiltonian for this system and the corresponding equation of motion. A reconsideration of this problem is of interest because of the following reasons. (a) The Hamiltonian for the electron transfer problem between the two centers A and B cannot be separated into the simple form $H_A + H_B + V_{AB}$ (where H_A and H_B are the Hamiltonians for the two centers and V_{AB} corresponds to the coupling term) as is the case for energy transfer between atomic or molecular pairs.[16] (b) The Hamiltonian for the electron transfer problem can be conveniently dissected to yield two different zero-order basis sets, corresponding to localization of the electron on center A or on center B, respectively. Either one of these two electronic basis sets is adequate from the formal point of view, and some care must be exerted to avoid overcomplete expansions. (c) These two electronic basis sets are nonorthogonal, and the nonorthogonality problem has to be incorporated in the time-dependent formalism. This problem resembles exchange perturbation theories of intermolecular forces, where elaborate schemes must be employed. Since we are interested in a time-dependent problem we cannot adopt these theories and an alternative approach has to be developed.

The total Hamiltonian for the system can be written as consisting of the following contributions

$$\mathcal{H} = T_E + T_N + H_a + H_b + V_{ab} + V_{ea} + V_{eb} +$$
$$H_s + H_c + V_{int}^s + V_{int}^c \quad (I.2)$$

where the indices a and b refer to the two ionic centers A and B, respectively, e labels a single electron which is being transferred while s and c label the bulk of the solvent and to the first coordination layers. T_e is the kinetic energy of the transferred electron, T_N corresponds to the sum of the nuclear kinetic energy operators for the whole system (con-

taining the contributions of the two ions, T_N^a and T_N^b, the first coordination layers T_N^c, and the solvent T_N^s)

$$T_N = T_N^a + T_N^b + T_N^c + T_N^s \quad (I.3)$$

H_a and H_b correspond to the electronic Hamiltonians (the electronic Hamiltonians contain the relevant electronic kinetic energy contributions) of the bare reduced ions $A^{(N+1)}$ and B^{M+}, respectively, while V_{ea} and V_{eb} correspond to the interaction potential between the electron and these bare reduced ions. V_{ab} is the nuclear repulsion potential between the reduced ions. H_s and H_c represent the electronic Hamiltonians of the solvent and of the first coordination layers, respectively.

Finally V_{int}^s and V_{int}^c are the electrostatic interaction terms of the total ionic and electron charge distribution with the solvent (s) and with the first coordination layers (c), respectively. We have presented this cumbersome notation and definitions as a very recent treatment of this problem failed to include all the pertinent terms (such as V_{int}^s) in the Hamiltonian.

The details of the time-dependent quantum mechanical treatment of the system specified by the Hamiltonian (I.2) are outlined in Appendix A. The electronic states at fixed nuclear configuration, $\mathbf{Q}$, are characterized in terms of the eigenfunctions $\{\Psi_{ai}(\mathbf{r},\mathbf{Q})\}$ for the total system $(A^{N+} + B^{M+})$ and by $\{\Psi_{bj}(\mathbf{r},\mathbf{Q})\}$ for $(A^{(N+1)+} + B^{(M-1)+})$, obtained from eq A.2. The indices i and j refer to all ground and excited electronic states of the systems. The corresponding eigenvalues $E_{ai}(\mathbf{Q})$ and $E_{bi}(\mathbf{Q})$ correspond to the potential energy surfaces of the pairs $(A^{N+} + B^{M+})$ and $(A^{(N+1)+} + B^{(M-1)+})$ in various electronic states, respectively. The time-dependent wave function of the system can be expanded either in terms of a single basis set $\{\Psi_{ai}\}$ or $\{\Psi_{bi}\}$ (e.g., (A.3)) or alternatively in terms of both sets. The physically plausible expansion (A.4) results in a coupled set of equations (eq A.11) for the expansion coefficients. Equation A.11 involves a complicated complete expansion (including continuum states). To simplify the treatment two assumptions are introduced.

(A) A two electronic level system is considered, including only the lowest states $\Psi_a = \Psi_{a0}$ and $\Psi_b = \Psi_{b0}$ which are characterized by the adiabatic surfaces $E_a(Q)$ and $E_b(Q)$, respectively. This simplifying assumption may be justified as the basis of perturbation arguments as the off-diagonal terms are usually negligibly small (for the case of weak overlap) relative to the electronic excitation energies. This assumption is common in solid-state theory where configuration interaction effects are disregarded.

(B) The contribution of the Born–Oppenheimer operator L, eq A.6, is disregarded. This assumption is fully justified[6] for electron transfer between ordinary ions where $\langle V_{ea} \rangle / \langle L \rangle \sim M/m$. In the case of reduction reactions involving the solvated electron the $\langle L \rangle$ term may be important in view of the strong dependence of the electron wave function on the nuclear coordinates. Thus for a two electronic level system we have the simple expansion $\Psi(r,Q,T) = X_a(Q,t)\Psi_a(r,Q) + X_b(Q,t)\Psi_b(r,Q)$ where the expansion coefficients are obtained from the coupled equations (A.12). At this stage one defines zero-order vibrational wave functions $X_{av}(\mathbf{Q})$ and $X_{bw}(\mathbf{Q})$, satisfying the eigenvalue equations (A.13). The zero-order vibronic states of the two system

$$|av\rangle \equiv \Psi_a X_{av}^0(\mathbf{Q})$$
$$|bw\rangle \equiv \Psi_b X_{bw}^0(\mathbf{Q}) \quad (I.4)$$

are characterized by the energies $E_{av}{}^0$, and $E_{bw}{}^0$, respectively. To obtain the equations of motion and the transition probabilities we have followed the techniques introduced by Holstein[15] in the study of the small polaron (eq A.14 and A.15). Application of second-order perturbation theory to eq A.15 the decay probability W_{av} of a zero-order vibronic level $|av\rangle \equiv \Psi_a X_{av}{}^0$ to the manifold $\{|bw\rangle\} = \{\Psi_b X_{bw}{}^0\}$ results in the familiar Fermi golden rule where the coupling matrix element of

$$V_{av,bw} = (X_{av}{}^0 | \langle \Psi_a | V_{eb} +$$
$$S_{ab}{}^{-1} \langle \Psi_b | V_{eb} | \Psi_a \rangle | \Psi_b \rangle | X_{bw}{}^0) \quad (I.5)$$

the generalized exchange operator and ( ) refers to integration over nuclear coordinates.

$$W_{av} = \frac{2\pi}{\hbar} \sum_w | V_{av,bw} |^2 \delta(E_{av}{}^0 - E_{bw}{}^0) \quad (I.6)$$

The generalized exchange perturbation term $V_{av,bw}$ (I.6) induces transitions between two different vibronic manifolds corresponding to electronic ground states. If we would have incorporated electronically excited states, refraining from accepting assumption A, the exchange operator will act in a dual role. (a) It will induce transitions between different centers, resulting in electron transfer involving electronically excited states. (b) It will force transitions between different electronic states on the same center, in analogy with the role of the nonadiabatic operator which is conventionally allowed for nonradiative relaxation of excited states of molecules and of solvated ions. This is a nice example for the effect of an external field on nonradiative electronic relaxation processes. These externally induced electronic relaxations of excited ionic states can explain the effects of self-quenching of the fluorescence yield of rare earth ions in solution.

Adopting the language of molecular relaxation theory the width, Γ_{av}, of each "initially prepared" zero-order state $|av\rangle$ is related to W_{av} (eq I.5) by

$$\Gamma_{av} = \hbar W_{av} \quad (I.7)$$

The present model (see Figure 1) implies that the zero-order states $|av\rangle$ are metastable. A sufficient validity condition for the irreversible decay of each of these states into the manifold $\{|bw\rangle\}$ is that either the states in the density of the accepting (final) states is exceedingly large, so that the spacing between adjacent levels $\delta E_b = |E_b{}^0 (w + 1) - E_{bw}{}^0|$ is small satisfying the conditions

$$\Gamma_{av} \gg \delta E_b \quad (I.8)$$

whereupon the width Γ_{av} spans a large number of levels. Alternatively one may require that the total width γ_{bv} of each of the accepting states $|bv\rangle$ is large relative to their spacing

$$\delta E_b \ll \gamma_{bv} \quad (I.9)$$

The total width γ_{bv} consists of a nonradiative electron transfer contribution $|bv\rangle \to \{|av\rangle\}$ better than (i.e., the back reaction), Γ_{bv}, and most important, vibrational relaxation in the $\{|bv\rangle\}$ manifold. As we consider here a dense polar liquid coupling to the medium will result in medium induced vibrational relaxation characterized by a width $\bar\gamma_{bv}$ within the manifold $\{|bv\rangle\}$, so that $\gamma_{bv} = \bar\gamma_{bv} + \Gamma_{bv}$. Provided that either of eq I.8 and I.9 (or both) will be satisfied, the manifold $\{|bv\rangle\}$ constitutes an effective continuum for the relaxation process. In a polar liquid we expect that the coupling between the polar modes is always sufficient to

ensure at least effective vibrational relaxation process so that (I.9) is satisfied. In many cases of interest we also believe that the dense dual spacing condition (I.8) for the polar modes holds. We thus conclude that in any case the manifold $\{|bv\rangle\}$ provides an effective dissipative continuum for the electron transfer process.

It is important to notice at this point that the decay probability of an "initial" zero-order state $|av\rangle$ can be expressed by the first-order perturbation expression (II.19) only when it is justified to consider the decay of a single resonance. We thus invoke the basic assumption that the spacing between the resonances $\{|av\rangle\}$ considerably exceeds their widths. Denoting by $\delta E_a = |E_{av} - E_{a(v+1)}|$ the energy spacing between the adjacent order states $|av\rangle$ and $|a(v + 1)\rangle$ we imply that

$$\Gamma_{av} \ll \delta E_a \quad (I.10)$$

We note in passing that condition (I.10) does not violate the irreversibility requirement, as it is sufficient that only relation (I.9) is valid.

Thus, when interference effects between resonances can be disregarded, the decay pattern of each zero-order state is exponential and being characterized by reciprocal decay time (I.5). The applicability of restriction (I.10) will imply that the thermally averaged rate constant will involve a preexponential factor which involves the interstate coupling matrix element $|V_{av,bw}|$. This physical situation is often referred to in chemical kinetics as a nonadiabatic transition.

Up to this point we have been concerned with the decay of an initially prepared isolated resonance, without referring to the "preparation" of the decaying states. Two trivial further assumptions are introduced at this point.

(D) Thermal vibrational excitation (and relaxation) rates in the initial manifold $\{|av\rangle\}$ considerably exceed the nonradiative decay probabilities whereupon

$$\Gamma_{av}/\hbar \ll t_v^{-1} \quad (I.11)$$

where t_v is the vibrational relaxation time.

(E) The width of exact resonance is considerably less that the thermal energy $k_B T$, in the temperature range of interest

$$\Gamma_{av} \ll k_B T \quad (I.12)$$

Thus all the mixed $(|av\rangle + \{|bw\rangle\})$ states in a single resonance are equally thermally populated.

The thermally averaged nonadiabatic electron transfer probability from the initial manifold $|av\rangle$ to the final manifold $\{|bw\rangle\}$ is now

$$W_a = \frac{1}{Z} \sum_v \exp(-\beta E_{av}{}^0) W_{av} \quad (I.13)$$

where

$$Z = \sum_v \exp(-\beta E_{av}{}^0) \quad (I.13a)$$

and

$$\beta = (k_B T)^{-1}$$

In the theory of unimolecular nonadiabatic reactions the "high-pressure" rate constant is identified with W_a, eq II.24. In the present case the zero-order states $\{|av\rangle\}$ and $\{|bw\rangle\}$ which can be obtained from eq A.13 are very complicated. To simplify the problem further we utilize Levich's approach.[6]

(F) We calculate the electron transfer probability at a

fixed relative separation of the ions. This implies neglecting the contribution $T_N{}^a + T_N{}^b$ in eq I.3 and consequently also in eq A.13. The zero-order energies $E_{av}{}^0$ and $E_{bw}{}^0$ are then calculated at a fixed nuclear separation R_{ab} between the two solvated ions. The transition probability (I.5) is a function of R_{ab}, i.e., $W_a \equiv W_a(R_{ab})$. The bimolecular rate constant k is expressed in terms of the volume integral of the probability $f(R_{ab})$ for finding the ions at a distance R_{ab}, whereupon

$$k = \int d^3 R_{ab} f(R_{ab}) W_a(R_{ab}) \qquad (I.14)$$

In the limit of a dilute ionic solution one can approximate each ion with its coordination sphere by a hard-core radius $R = R_i + 2r_s$ (see Figure 2) so that for outer-sphere reactions

$$f(r) = 0 \qquad\qquad r < R$$
$$f(r) = \exp[-\beta u(R)] \qquad r > R \qquad (I.15)$$

with $u(r)$ being the interionic interaction potential

$$u(r) = nme^2/RD_{eff} \qquad (I.16)$$

This concludes an outline of the theory of nonadiabatic outer-sphere electron transfer reactions. This lengthy exposition leads to the original results of Levich. We believe, however, that the present treatment is more systematic than previously attempted. In particular, our expressions are general, being applicable for the interesting case of configurational changes in the first solvation layer.

II. Formal Expressions for the Electron Transfer Probability

In order to evaluate the nonradiative electron transfer probability (I.5) and its thermal average (I.13) we require explicit expressions for the energies $E_a(Q)$ and $E_b(Q)$ which correspond to the adiabatic potential surfaces and the total energies of these states $E_{av}{}^0$ and $E_{bw}{}^0$ (at fixed R_{ab}). To reduce the formal results into a useful and tractable theoretical expression we introduce the following approximations.

(G) The harmonic approximation is invoked for the potential energy surfaces $E_a(Q)$ and $E_b(Q)$. These are multidimensional potentials which are determined by the nuclear coordinates $Q = \{Q_i\}$ of the first coordination layers and of all the solvent molecules outside them are expanded around the equilibrium configurations $Q^{0(a)} \equiv \{Q_i{}^{0(a)}\}$ and $Q^{0(b)} \equiv \{Q_i{}^{0(b)}\}$ in the initial and in the final states.

$$E_a(Q) =$$
$$\frac{1}{2} \sum_{ij} \alpha_{ij}(Q_i - Q_i{}^{0(a)})(Q_j - Q_j{}^{0(a)}) + E(Q^{0(a)}) \quad (II.1)$$

$$E_b(Q) =$$
$$\frac{1}{2} \sum_{ij} \beta_{ij}(Q_i - Q_i{}^{0(b)})(Q_j - Q_j{}^{0(b)}) + E_b(Q^{0(b)}) \quad (II.2)$$

where α_{ij} and β_{ij} are the second derivatives of $E_a(Q)$ and of $E_b(Q)$ with respect to Q_i and Q_j, respectively.

(H) We introduce a further simplifying assumption that the normal modes and their frequencies (corresponding to the two first solvation layers and to the medium) are the same in the two states, except for displacements in the origins of the normal coordinates. This assumption can be relaxed as one can account formally for frequency changes and for the change in the direction of the principal axis of the normal coordinates between the two electronic states. The resulting equations are very cumbersome, and in view
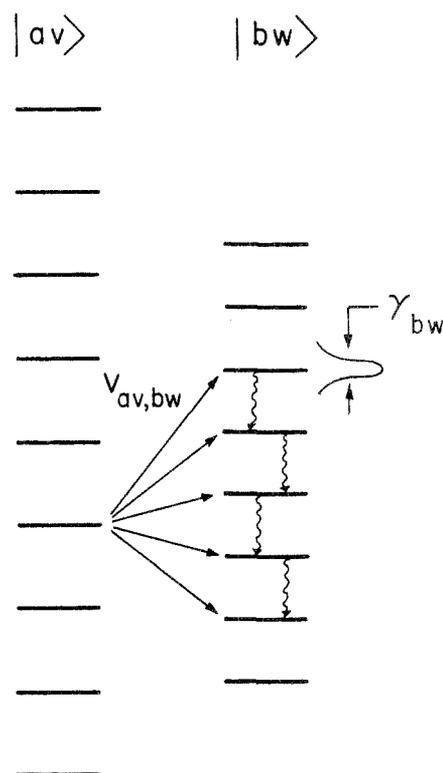
Figure 2. Typical energy level diagram for radiationless transitions or electron transfer reactions. The coupling matrix elements and the width of the accepting states are also indicated.

of our present ignorance of the "molecular" parameters involved we shall use the simple version of the multiphonon relaxation theory which rests on the present approximation.

The normal modes of the system in both states are characterized by the frequencies $\{\omega_j\}$ and by the effective masses $\{M_j\}$. It will be convenient to define reduced normal coordinates q_j normalizing the displacements from origin $\{Q_j - Q_j{}^{0(a)}\}$ for one state in terms of the zero energy mean square displacements $\langle Q_j{}^2 \rangle = (\hbar/m_j\omega_j)^{1/2}$ so that

$$q_j = (Q_j - Q_j{}^{0(a)})\left(\frac{M_j\omega_j}{\hbar}\right)^{1/2} \qquad (II.3)$$

Finally the reduced displacements between the origins of the two potential surfaces are given by

$$\Delta_j = \left(\frac{M_j\omega_j}{\hbar}\right)^{1/2}(Q_j{}^{0(a)} - Q_j{}^{0(b)}) \qquad (II.4)$$

The two potential surfaces (see Figure 3) are expressed in the final form

$$E_a(Q) = \frac{1}{2}\sum_j \hbar\omega_j q_j{}^2 \qquad (II.5)$$

$$E_b(Q) = \frac{1}{2}\sum_j \hbar\omega_j(q_j - \Delta_j)^2 + \Delta E = E_a(Q) -$$
$$\sum_j \hbar\omega_j q_j\Delta_j + \frac{1}{2}\sum_j \hbar\omega_j\Delta_j{}^2 + \Delta E \quad (II.6)$$

The energy gap between the minima of the two potential surfaces (see Figure 3) is

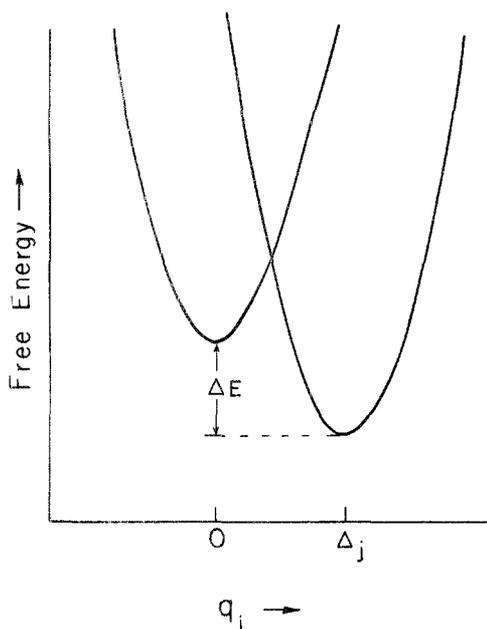$$\Delta E = E_a(Q^{0(a)}) - E_b(Q^{0(b)}) \qquad (II.7)$$

Figure 3. A general diagram for the change in a medium coordinate, q_j, between two states. A quadratic energy dependence is assumed.

The energy term in eq II.6

$$E_M = \frac{1}{2}\sum_j \hbar\omega_j \Delta_j^2 \qquad (II.8)$$

corresponds to the shift of the vertical energy difference between the two potential surfaces at $Q^{0(a)}$ from ΔE. In molecular spectroscopy E_M corresponds to half the Stokes shift.

Finally the quantized energy states $E_{av}{}^0$ and $E_{bw}{}^0$ can be specified in terms of the two sets of vibrational quantum numbers $v \equiv \{v_j\}$ and $w = \{w_j\}$, so that

$$E_{av}{}^0 = \sum_j \left(v_j + \frac{1}{2}\right)\hbar\omega_j + E_a(Q^{0(a)})$$

$$E_{bw}{}^0 = \sum_j \left(\omega_j + \frac{1}{2}\right)\hbar\omega_j + E_b(Q^{0(b)}) \qquad (II.9)$$

The evaluation of the electron transfer transition probability (I.13) is reduced to the calculation of the nonradiative relaxation rates between two harmonic potential surfaces. A further assumption will greatly simplify matters.

(I) The electronic matrix element in (I.6) is weakly dependent on the nuclear coordinates, so that within the "Condon approximation" the interstate coupling matrix element is recast as a product of an electronic matrix element and a vibrational overlap term

$$V_{av,bw} \simeq v(\chi_{av}{}^0 | \chi_{bw}{}^0) \qquad (II.10)$$

where

$$v = \langle\Psi_a| V_{eb} + S_{ab}{}^{-1}\langle\Psi_b|V_{eb}|\Psi_a\rangle |\Psi_b\rangle \qquad (II.11)$$

calculated at $Q^{0(a)}$. This approximation is not valid for nonradiative processes induced by the nuclear momentum operator L, however, for the present case it is perfectly acceptable.

Our problem thus reduces to the calculation of a multiphonon type relaxation rate induced by a coupling b which is independent of changes in nuclear coordinates. The non-

radiative decay probability (I.5) of a single level corresponds to a weighted density of states function where each delta function is the formal expression for the density of states $\rho(E_{av}{}^0) = \Sigma_w \delta(E_{av}{}^0 - E_{bw}{}^0)$ of the manifold $E_{bw}{}^0$ at the energy $E_{av}{}^0$ modified by the vibrational overlap term $(\chi_{av}{}^0/\chi_{bw}{}^0)$. A closed form for (I.5) with (II.10) can be obtained by the Feynman operator techniques and subsequently inserted into (I.13). Alternatively the thermally averaged probability (I.13) can be directly evaluated by the generating functions method. As these techniques have been widely utilized for nonradiative decay processes in solids and molecules we shall just quote the final result.[5,17] The electron transfer probability (I.13) is expressed in terms of a Fourier integral

$$W_a = \frac{|v|^2}{\hbar^2}\int_{-\infty}^{\infty} f(t)\,\exp[-i\Delta E t/\hbar]\,dt \qquad (II.12)$$

where the Fourier transform of the nonradiative decay probability is

$$f(t) = \exp[-G]\,\exp[G_+(t) + G_-(t)] \qquad (II.13)$$

where the auxiliary functions in eq II.13 are

$$G_+(t) = \frac{1}{2}\sum_j \Delta_j^2(\bar{n}_j + 1)\,\exp(i\omega_j t)$$

$$G_-(t) = \frac{1}{2}\sum_j \Delta_j^2 \bar{n}_j\,\exp(-i\omega_j t) \qquad (II.14)$$

$\bar{n}_j$ corresponds to the number of excited vibrations at the frequency in thermal equilibrium

$$\bar{n}_j = [\exp(\beta\hbar\omega_j) - 1]^{-1} \qquad (II.15)$$

Finally the dimensionless quantity

$$G = G_+(0) + G_-(0) = \frac{1}{2}\sum_j \Delta_j^2(2\bar{n}_j + 1) \qquad (II.16)$$

is referred in solid-state physics as the electron–phonon coupling strength. A very rough estimate of G is obtained replacing all the frequencies by an average frequency $\langle\omega\rangle$, which as shown in section III is unjustified for our system. In this case from eq II.11 and II.8 we have

$$G \sim (E_m/\hbar\langle\omega\rangle)\,\coth\,(\beta\hbar\langle\omega\rangle) \qquad (II.17)$$

Two physical situations were distinguished. (a) The weak coupling situation $G < 1$ which is realized at low temperature $(\hbar\langle\omega\rangle \gg k_B T)$ and when $E_M < \hbar\langle\omega\rangle$. (b) The strong coupling limit $G \gg 1$ which is realized at high temperatures $(\hbar\langle\omega\rangle \ll k_B T)$ and/or when $E_M \gg \hbar\langle\omega\rangle$.

Molecular electronic relaxation processes usually correspond to the weak coupling situation, while the corresponding multiphonon processes in solids at high temperatures correspond to the strong coupling limit, which was also applied to Levich[6] for electron transfer processes. We shall now demonstrate that when configurational changes in the first coordination layer are incorporated the electron transfer probability has to be handled in a more complicated manner.

The calculation of the electron transfer probability reduces to the evaluation of the integral (II.12)–(II.16). Integrals of the form

$$I = \int_{-\infty}^{\infty} \exp[-A(t)]\,dt \qquad (II.18)$$

where the integrand is a highly oscillatory function can be approximated by the saddle point method.[17] The saddle point is taken at t_0 where

$$[\partial A(t)/\partial t]_{t_0} = 0 \qquad (\text{II.19})$$

so that the Taylor series expansion

$$A(t) = A(t_0) + \frac{1}{2}(\partial^2 A/\partial t^2)_t (t - t_0) \quad (\text{II.19a})$$

is utilized in (II.19) to yield

$$I \simeq [2\pi/(\partial^2 A/\partial t^2)]_{t_0}{}^{1/2} \exp[-A(t_0')] \qquad (\text{II.20})$$

When the integral (II.12)–(II.16) is handled by this method the saddle point in the complex t plane is obtained from the relation

$$-\Delta E + \sum_i \hbar\omega_i \Delta_i{}^2 (\bar{n}_i + 1) \exp(i\omega_i t) -$$

$$\frac{1}{2}\sum_i \hbar\omega_i \Delta_i{}^2 \bar{n}_i \exp(-i\omega_i t) = 0 \quad (\text{II.21})$$

In the high-temperature case when

$$\hbar\omega_i \ll k_b T \qquad (\text{II.22})$$

for all i, $G \gg 1$ corresponding to the strong coupling situation. Under these conditions one can expand the right-hand side of the saddle point eq II.21 in a power series in t

$$-\Delta E + E_M + i\hbar D^2 t -$$

$$\frac{3}{16}\sum_i \hbar\omega_i{}^3 \Delta_i{}^2 t^2 + \ldots = 0 \quad (\text{II.23})$$

where we have defined

$$D^2 = \frac{1}{2}\sum_i \omega_i{}^2 \Delta_i{}^2 (2\bar{M}_i + 1) \qquad (\text{II.24})$$

and E_M is given by (II.8). Retaining the linear term in t

$$it_0 = -(\Delta E - E_M)/\hbar D^2 \qquad (\text{II.25})$$

whereupon eq II.12 takes the familiar form

$$W = \frac{v^2}{\hbar}\left(\frac{2\pi}{\hbar^2 D^2}\right)^{1/2} \exp\frac{(\Delta E - E_M)^2}{2D^2\hbar^2} \quad (\text{II.26})$$

Equation II.26 has been widely utilized in the electron transfer theory of Levich.[6] It is interesting to note that we can easily obtain a formal relation between this quantum mechanical result and conventional reaction rate theory. The points of intersection of the two harmonic potential hypersurfaces are obtained from the relation $E_a(\mathbf{Q}) = E_b(\mathbf{Q})$. The intersection point of minimum energy, E_A, measured relative to the origin, $E_a(\mathbf{Q}^{0(a)})$, satisfies the relation

$$E_A = (\Delta E - E_M)^2/4E_M \qquad (\text{II.27})$$

Thus eq II.26 can be reduced to the form

$$W = v^2\left(\frac{\pi}{\hbar^2 E_M k_B T^*}\right)^{1/2} \exp[-E_A/k_B T^*] \quad (\text{II.28})$$

where the effective temperature is defined by

$$k_B T^* = \hbar^2 D^2/2E_M \qquad (\text{II.29})$$

In the high-temperature limit (II.22) $T^* \to T$ and the transition probability in the strong coupling limit

$$W = v^2(\pi/\hbar^2 E_M k T)^{1/2} \exp[-\beta E_A] \quad (\text{II.28a})$$

assumes the conventional form of an activated rate equation. This result has been obtained without invoking the concept of the activated complex.

It is important at this point to establish the validity condition for eq II.26, which implies that the term $0(t^2)$ in (II.23) is negligible, so that

$$iD^2 t_0 \gg \frac{3}{16}\hbar\sum_i \omega_i{}^3 \Delta_i{}^2 t_0{}^2 \qquad (\text{II.30})$$

which from eq II.24 and II.25 implies that

$$\hbar[\sum_i \Delta_i{}^2 \omega_i{}^2 (2\bar{n}_i + 1)]^2 \gg |\Delta E - E_M| \sum_i \Delta_i{}^2 \omega_i{}^3$$

$$(\text{II.31})$$

Obviously the validity condition (II.31) is satisfied (for reasonable values of Δ_i) only at high temperature. To demonstrate this point consider single frequency whereupon this condition is simply

$$(2\bar{n} + 1) \gg |\Delta E - E_M|/E_M \qquad (\text{II.27a})$$

and for symmetric electron transfer processes when $\Delta E = 0$ we require that $\bar{n} \gg 1$. In general, for physically realistic model of electron transfer, when the role of the first coordination layer is incorporated relation II.31 does not hold and consequently eq II.26 has to be modified.

III. A Semimolecular Model for Electron Transfer

We adopt a simplified model, which has been popular in the studies of ionic solvation and in classical formulation of electron transfer processes. The first coordination layers of the two ions are treated in terms of a molecular model accounting for the totally symmetric vibrations of the nearest solvent molecules. The contribution of the first coordination layer in the initial $A^{N+} + B^{M+}$ and in the final $A^{(N+1)+} + B^{(M-1)+}$ state to the potential surface is specified in terms of the four equilibrium configurations $r^0(A^{N+})$, $r^0(B^{M+})$, $r^0(A^{(N+1)+})$, and $r^0(B^{(M-1)+})$. These equilibrium configurations are obtained from the ionic radii r_i, so that $r^0 = r_i + r_s$ where r_s is the radius of the solvent molecule. Utilizing the simple model of displaced identical potential surfaces we take the vibrational frequencies of the first coordination layer of the A or of the B ionic species to be equal in both valence states, so that $\omega_A = \omega(A^{N+}) = \omega(A^{(N+1)+})$ and $\omega_B = \omega(B^{M+}) = \omega(B^{(M-1)+})$. The available experimental data (Table I) indicate that this approximation is not too bad.

Finally we can define reduced displacement coordinates for the first coordination layer

$$q_A = (M_A \omega_A/\hbar)^{1/2}(r(A^{N+}) - r^0(A^{N+}))$$
$$q_B = (M_B \omega_B/\hbar)^{1/2}(r(B^{M+}) - r^0(B^{M+})) \qquad (\text{III.1})$$

and the two displacements

$$\Delta_A = (M_A \omega_A/\hbar)^{1/2}(r^0(A^{(N+1)+}) - r^0(A^{N+}))$$
$$\Delta_B \neq (M_B \omega_B/\hbar)^{1/2}(r^0(B^{(M-1)+}) - r^0(B^{M+})) \qquad (\text{III.2})$$

in terms of the reduced masses M_A and M_B of the ions with the first coordination layer. The contributions of the first coordination layers to the potential energy surfaces (II.5) and (II.6) are

$$f_a(q_A, q_B) = \frac{1}{2}\hbar\omega_A q_A{}^2 + \frac{1}{2}\hbar\omega_B q_B{}^2$$

$$(\text{III.3})$$

$$f_b(q_A, q_B) = f_a(q_A, q_B) - \hbar\omega_A q_A \Delta_A -$$
$$\hbar\omega_B q_B \Delta_B + E_M{}^c$$

TABLE I: Totally Symmetric Vibrations of Coordination Layers and Approximate Radii

Ion	$\hbar\omega$, cm^{-1}	Comments	r, Å^d
$Cr^{3+}-H_2O$	490	Aqueous solution^a and $Cr(H_2O)_6Cl_3$ in crystal^b	0.65
$Cr^{2+}-H_2O$			0.83
$Mn^{2+}-H_2O$	395	Aqueous solution^a and $Mn(H_2O)_6SiF_6$ in crystal^b	
$Fe^{2+}-H_2O$	389	Aqueous solution^a and $Fe(H_2O)_6SiF_6$ in crystal^b	0.83
$Fe^{3+}-H_2O$			0.67
$Ni^{2+}-H_2O$	405	Aqueous solution^a and $Ni(H_2O)_6SiF_6$ in crystal^b	
$Cu^{2+}-H_2O$	440	Aqueous solution^a	
$Hg^{2+}-H_2O$	362	Aqueous solution^a	
$Zn^{2+}-H_2O$	385–400 or 369	$Zn(H_2O)_6$ in crystal^a	
$Ni^{2+}-D_2O$	389	$Ni(D_2O)_6SiF_6$ in crystal^b	
$Co^{2+}-H_2O$			0.83
$Co^{3+}-H_2O$			0.67
$V^{2+}-H_2O$			0.82
$V^{3+}-H_2O$			0.65
$Cr^{2+}-H_2O$			0.83
$Cr^{3+}-H_2O$			0.65
$Eu^{2+}-H_2O$			1.18
$Eu^{3+}-H_2O$			0.99

^{a} Data compiled by D. E. Irish in "Ionic Interactions," Vol. II, S. Petrucci, Ed., Academic Press, New York, 1971. ^{b} I. Nakagawa and T. Shimanovichi, *Spectrochim. Acta*, **20**, 429 (1964). ^{c} R. E. Hester and R. H. Plane, *Inorg. Chem.*, **3**, 513 (1964); 768, 769 (1964). ^{d} Taken from E. Sacher and K. S. Laidler in "Modern Aspects of Electrochemistry," Vol. 3, J. O'M Bockris and B. E. Conway, Ed., Butterworths, Washington, D.C., 1964.

where we defined

$$E_M{}^C = \frac{1}{2}\left(\hbar\omega_A\Delta_A{}^2 + \hbar\omega_B\Delta_B{}^2\right) \quad (III.4)$$

The medium outside the first coordination layers will be handled as a continuum dielectric as originally proposed by Levich[6] who was the first to apply polaron theory to this problem. The vibrational modes of the outer medium are approximated by a single mean vibrational frequency, ω_0, which was estimated from the dielectric loss measurements as $\omega_0 \sim 1$ cm^{-1}. This approach has been common in polaron theory. The polar modes are specified in terms of the set of coordinates $\{Q_\kappa\}$ and reduced masses $\{M_\kappa\}$, which provide the equivalent of lattice optical modes for a polar liquid. The equilibrium configurations of the medium modes are affected by the charge distribution which is different in the initial and in the final state. The equilibrium configurations are $\{Q_\kappa{}^{0(a)}\}$ and $\{Q_\kappa{}^{0(b)}\}$ in the initial and final states. The reduced coordinates and displacements of the outer medium are

$$q_\kappa = (\hbar/M_\kappa\omega_0)^{1/2}(Q_\kappa - Q_\kappa{}^{0(a)}) \quad (III.5)$$

$$\Delta_\kappa = (\hbar/M_\kappa\omega_0)^{1/2}[Q_\kappa{}^{0(a)} - Q_\kappa{}^{0(b)}] \quad (III.6)$$

so that the contribution of the polar modes to the potential surfaces are

$$g_a(Q_\kappa) = \hbar\omega_0\sum_\kappa q_\kappa{}^2 \quad (III.7)$$

$$g_b(Q_\kappa) = \hbar\omega_0\sum_\kappa q_\kappa{}^2 - \hbar\omega_0\sum_\kappa q_\kappa\Delta_\kappa + E_M{}^s \quad (III.8)$$

where the solvent induced Stokes shift is

$$E_M{}^s = \frac{1}{2}\hbar\omega_0\omega\sum_\kappa\Delta_\kappa{}^2 \quad (III.9)$$

Applying polaron theory (see Appendix) we get Levich's result for the contribution of the external medium

$$E_M{}^s =$$
$$\frac{Ce^2}{2}\int\int d^3x\, d^3x'\{[\rho^a(\mathbf{x} - \mathbf{x}_0) - \rho^b(\mathbf{x} - \mathbf{x}_0)] \times$$
$$[\rho^a(\mathbf{x'} - \mathbf{x}_0) - \rho^b(\mathbf{x'} - \mathbf{x}_0)]\}/|\mathbf{x} - \mathbf{x'}| =$$
$$\frac{Ce^2}{8\pi}\int d^3\mathbf{x}(\mathbf{D}^a - \mathbf{D}^b)^2 \quad (III.10)$$

where ρ^a and ρ^b are the charge densities in the initial and in the final state, respectively, while $\mathbf{D}^a$ and $\mathbf{D}^b$ represent the electric displacement vectors in the initial and in the final states, and

$$C = D_0{}^{-1} - D_s{}^{-1} \quad (III.10a)$$

The total potential surfaces for this simplified model take the form

$$E_a(\mathbf{Q}) = f_a(q_A, q_B) + g_a(q_\kappa)$$
$$E_b(\mathbf{Q}) = f_b(q_A, q_B) + g_B(q_\kappa) - \Delta E \quad (III.11)$$

The quantum mechanical treatment of the electron transfer probability is now more complicated than previously considered in view of the appearance of the contributions of the first coordination layers. These local frequencies of the solvent molecules are rather high $\omega_A \sim \omega_B \sim 300$–$400$ cm^{-1} for hydrated ion (see Table I). The high-temperature approximation (II.22) does not hold for the local modes, which under ordinary circumstances at room temperature are "frozen." The frequency of the polar modes is expected to be low $\omega_0 \simeq 1$ cm^{-1} so that for these modes the high-temperature approximation (II.22) is valid. Thus the Levich equation (II.26 or II.28) is valid only for systems where the configurational changes in the first solvation layers are negligible, *i.e.*, $\Delta_A \simeq \Delta_B = 0$. On the other hand, for many outer-sphere electron transfer reactions the theory has to be modified (see also ref 12).

From the foregoing discussion we conclude that for many processes of interest we have to consider the local modes of the first coordination layer $\omega_A \simeq \omega_B \equiv \omega_C$ in the low-temperature approximation while the medium modes have to be handled in the high-temperature limit, *i.e.*, $\bar{n}_\kappa = (\beta\hbar\omega_\kappa)^{-1}$ for all κ. To derive a general expression for the electron transfer probability we separate the local (c) and the medium (s) modes in the vibrational wave function in eq I.4 so that

$$\chi_{av}{}^0 = \chi_{av_c}{}^c(q_A, q_B)\chi_{av_s}{}^s(q_\kappa)$$
$$\chi_{bw}{}^0 = \chi_{bw_c}{}^c(q_Aq_B)\chi_{bws}{}^s(q_\kappa) \quad (III.12)$$

which are characterized by the vibrational energies

$$E_{av}{}^0 = E_{ac} + E_{av} = [(v_A + \tfrac{1}{2}) + (v_B + \tfrac{1}{2})]\hbar\omega_c + \tfrac{1}{2}\sum_\kappa(v_\kappa + \tfrac{1}{2})\hbar\omega_0$$
$$E_{bw}{}^0 = E_{bc} + E_{bw} = [(w_A + \tfrac{1}{2}) + (w_B + \tfrac{1}{2})]\hbar\omega_c + \tfrac{1}{2}\sum_\kappa(w_\kappa + \tfrac{1}{2})\hbar\omega_0 \quad (III.13)$$

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corresponding to an activation energy for this part of the expression E_A' of

$$E_A' \underset{T \to \theta}{=} k_B T^2 \frac{\partial \ln (WT^{1/2})}{\partial T} = (\Delta E - E_M{}^s)^2/4E_M{}^s \quad \text{(IV.9)}$$

For very large z_p, i.e., high temperatures, another limiting expression can be derived. The simplest derivation begins with the basic equation (III.19) and making the strong coupling approximations as in section II but now for the vibrations in the first coordination layer, i.e., we expand the exponentials in (III.19) and obtain

$$F_c(\epsilon) = \int dt \, \exp[-\frac{it}{\hbar}[-(\epsilon + E_c) - \frac{t^2}{2}D_c{}^2]] \quad \text{(IV.10)}$$

where

$$D_c{}^2 = (\Delta_c{}^2/2)^2 \omega_c{}^2 (2n_c + 1) \quad \text{(IV.11)}$$

and

$$E_c = \hbar\omega_c \Delta_c{}^2/2 \quad \text{(IV.12)}$$

This leads to a total rate proportional to

$$\int_0^\infty d\epsilon \, \exp\left[- \frac{(\Delta E - E_m{}^s - \epsilon)^2}{4E_m{}^s k_B T} - \frac{(\epsilon + E_c)^2}{2D_c{}^2 \hbar^2}\right] \quad \text{(IV.13)}$$

This can be integrated to yield

$$(\text{constant}) \exp\left[- \frac{(\Delta E - E_m{}^s)^2}{4E_m{}^s k_B T} - \frac{E_c{}^2}{\Psi E_c k_B T} + \frac{[E_m{}^s E_c - (\Delta E - E_m{}^s)E_c{}^2]^2}{2E_m{}^s E_c (E_m{}^s + E_c)}\right] \quad \text{(IV.14)}$$

which simplifies to

$$(\text{constant}) \exp\left[- \frac{(\Delta E - E_M{}^s - E_c)^2}{4(E_M{}^s + E_c)k_B T}\right] \quad \text{(IV.15)}$$

or

$$E_A' = + \frac{(\Delta E - E_M{}^s - E_c)^2}{4(E_M{}^s + E_c)} \quad \text{(IV.16)}$$

The limiting cases quoted are not useful for most applications as they represent temperature regions not usually studied for typical systems. The low-temperature limit is only applicable if there is only a very slight reorganization of the coordination layer as in the case of strongly bound complexes, e.g., ferro- and ferricyanides, or if extremely low temperatures, way below the medium freezing point. The high-temperature limit is also unlikely in practice since for typical hydration cases it would involve temperatures of 500–1000°.

We can easily evaluate the entire expression, eq IV.3, by a straightforward computer program and extract from it the rates or values of E_A' for typical ranges of the parameters. In Tables III and IV we have tabulated the results for $E_m{}^s = 2$ eV, and for typical values of $\hbar\omega_c$, ΔE, and $\Delta_c{}^2/2$. Typically $\hbar\omega_c$ is about 400 cm^{-1} (see Table I) for hydration of ions and much higher when stable complexes are involved. $\Delta_c{}^2/2$ can be around 10 when major reorganization of hydration layers occurs but is much smaller for strongly bonded complexes.

Before commenting on these results it is useful to present a derivation of a reasonable approximate formula

TABLE II: Activation Energies, E_A' (°K)^a

Temp, T	$\Delta_c{}^2/2 = 5$ $\hbar\omega_c = 400$ cm^{-1}	$\Delta_c{}^2/2 = 5$ $\hbar\omega_c = 600$ cm^{-1}	$\Delta_c{}^2/2 = 15$ $\hbar\omega_c = 400$ cm^{-1}
50	5808.6	5800.7	5825.7
100	5941.1	5852.6	6224.1
150	6115.9	6009.4	6749.6
200	6240.6	6190.0	7123.9
250	6320.3	6342.2	7363.2
300	6371.9	6457.8	7517.1
350	6405.7	6543.2	7619.4
400	6429.7	6606.8	7691.8
450	6446.8	6655.1	7743.3
500	6459.9	6692.0	7780.5
600	6475.2	6743.1	7831.6
1000	6497.3	6825.2	7914.5
∞	6518.8	6878.8	7956.3

^{a} $E_m{}^s = 2$ eV, $\Delta E = 0$.

which is an accurate representation of the computer results.

Expanding eq IV.4 we can rewrite the right-hand side as

$$\exp[-z_p \cosh (\beta\hbar\omega_c/2)] \exp\left[- \frac{(\Delta E - E_M{}^s)^2 \beta}{4E_M{}^s}\right] \times$$

$$\sum_{m=-\infty}^{\infty} \exp(-\alpha m^2) \exp(\gamma m) I_m(z_p) \quad \text{(IV.17)}$$

where

$$\alpha = (\hbar\omega_c)^2/4E_M{}^s k_B T$$

and $\quad$ (IV.18)

$$\gamma = \Delta E \hbar\omega_c/E_M{}^s k_B T$$

For usual hydration parameters $\hbar\omega_c < kT$ and $\hbar\omega_c \ll E_M{}^s$ so that α is small ($\sim 3.9/T$) and $e^{-\alpha m^2} \sim 1$. Using this and the following identity

$$e^{z/2(t+1/t)} = \sum_{m=-\infty}^{\infty} t^m I_m(z) \quad \text{(IV.19)}$$

we can simplify the results to

$$\frac{W}{(V)^2}\left(\frac{\hbar^2 E_M{}^s}{\beta\pi}\right)^{1/2} =$$

$$\exp\left[-z_p \cosh \beta\hbar\omega_c/2 - \cosh\left(\frac{\Delta E}{E_M{}^s}\frac{\hbar\omega_c\beta}{2}\right)\right] \times$$

$$\exp\left[- \frac{\beta}{4E_M{}^s}(\Delta E - E_M{}^s)^2\right] \quad \text{(IV.20)}$$

or

$$= \exp\left[- \frac{\Delta_c{}^2}{2}(\coth x - \operatorname{csch} x \cosh (x\Delta E/E_M{}^s))\right] \times$$

$$\exp[-(\beta/4E_M{}^s)(\Delta E - E_M{}^s)^2] \quad \text{(IV.21)}$$

where $x = \hbar\omega_c/2kT$. This leads to an effective activation energy E_{AA}' of

TABLE III: Activation Energies, $E_A{}'$ (°K)^a

Temp, T	$\Delta_c{}^2/2 = 5$ $\hbar\omega_c = 400$ cm^{-1}	$\Delta_c{}^2/2 = 5$ $\hbar\omega_c = 600$ cm^{-1}	$\Delta_c{}^2/2 = 15$ $\hbar\omega_c = 400$ cm^{-1}	$\Delta_c{}^2/2 = 1.0$ $\hbar\omega_c = 2100$ cm^{-1}	$\Delta_c{}^2/2 = 10$ $\hbar\omega_c = 400$ cm^{-1}
50	5808.6	5800.7	5825.7	5800.0	5817.1
100	5941.1	5852.6	6224.1	5800.0	6082.5
150	6115.9	6009.4	6749.6	5800.1	6432.5
200	6240.6	6190.0	7123.9	5801.0	6682.0
250	6320.3	6342.2	7363.2	5805.2	6841.4
300	6371.9	6457.8	7517.1	5814.9	6944.2
350	6405.7	6543.2	7619.4	5831.3	7012.3
400	6429.7	6606.8	7691.8	5854.8	7060.7
450	6446.8	6655.1	7743.3	5883.5	7094.5
500	6459.9	6692.0	7780.5	5915.9	7119.8
600	6475.2	6743.1	7831.6	5985.7	7153.1
1000	6497.3	6825.2	7914.5	6218.8	7109.2
∞	6518.8	6878.8	7956.3	6554.8	7237.5

^{a} $E_m{}^s = 2$ eV, $\Delta E = 0$.

TABLE IV: Activation Energies, $E_A{}'$ (kcal/mol)^a

Temp (T), °K	$\Delta E = 0$ Numerical result^b	$\Delta E = 0$ Approximate formula^c	$\Delta E = 1$ eV Numerical result^b	$\Delta E = 1$ eV Approximate formula^c	$\Delta E = -1$ eV Numerical result^b	$\Delta E = -1$ eV Approximate formula^c
50	11.546	11.547	2.9566	2.9636		26.02
100	11.810	11.818	3.2302	3.2483	26.28	26.31
150	12.157	12.168	3.4757	3.4880	26.53	26.55
200	12.405	12.416	3.6389	3.6402	26.70	26.70
250	12.564	12.573	3.7414	3.7334	26.80	26.79
300	12.666	12.674	3.8068	3.7923	26.87	26.85
350	12.733	12.742	3.8508	3.8311	26.91	26.89
400	12.781	12.788	3.8810	3.8577	26.94	26.92
450	12.958	12.822	3.9030	3.8767	26.90	26.94
500	12.841	12.846	3.9176	3.8906	26.98	26.95
600	12.871	12.879	3.9398	3.9093	27.00	26.97
1000	12.915	12.929	3.9764	3.9375	27.04	27.00
∞	12.958^d	12.958^e	3.9933^d	3.9496^e	27.05^d	27.01^e

^{a} $E_m{}^s = 2$ eV, $\Delta_c{}^2/2 = 5$, $\hbar\omega_c = 400$ cm^{-1}. ^{b} From eq IV.3. ^{c} From eq IV.20. ^{d} Asymptotic limit from eq IV.16. ^{e} Asymptotic limit from eq IV.23.

$$E_{AA}{}' = \frac{(\Delta E - E_M{}^s)^2}{4E_M{}^s} + \left(\frac{\Delta_c{}^2}{2}\right)\left(\frac{\hbar\omega_c}{2}\right) \operatorname{csch} x \times$$

$$\left[- \operatorname{csch} x + \cosh\left(\frac{\Delta E}{E_M{}^s}x\right) \coth x - \right.$$

$$\left. \frac{\Delta E}{E_m{}^s} \sinh\left(\Delta E x/E_M{}^s\right) \right] \quad \text{(IV.22)}$$

This approximate formula goes to the proper low-temperature limit but has a small error at high temperatures. Its high-temperature limit is

$$E_{AA}{}'(T \longrightarrow \infty) = \frac{E_M{}^s + E_c}{4} - \frac{\Delta E}{2} +$$

$$\frac{(\Delta E)^2}{4E_M{}^s}\left(1 - \frac{E_c}{E_M{}^s}\right) \quad \text{(IV.23)}$$

vs. the exact result of eq IV.16 which can be written as

$$E_A{}'(T \longrightarrow \infty) = \frac{E_M{}^s + E_c}{4} - \frac{\Delta E}{2} + \frac{(\Delta E)^2}{4(E_M{}^s + E_c)} \quad \text{(IV.24)}$$

In both cases $E_c = (\Delta_c{}^2/2)\hbar\omega_c$ represents the shift in the zero-point energy of the primary solution layers. The two results are correct through the first order of $(E_c/E_M{}^s)$ and since this is usually small (<0.25) the error involved in using is also small, i.e.

$$\sim \left[(\Delta E)^2/4E_M{}^s\right](E_c/E_M{}^s)^2 \quad \text{(IV.25)}$$

The results of this approximate formula are also tabulated in Table IV for comparison.

In Figure 4 we also plot the activation energies determined from the exact formula for various values of $\Delta_c{}^2/2$ and $\hbar\omega_c$ for $\Delta E = 0$ and $E_M{}^s = 2$ eV.

In order to evaluate these expressions for actual ions we need to evaluate $E_M{}^s$ (eq III.10). This can be given in terms of D_i the initial electric displacement and D_f the final dis-
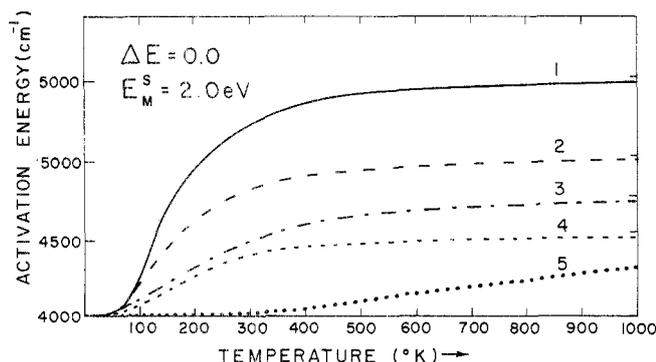
Figure 4. Typical results for the change in the effective activation energy with temperature for various values of the parameters. The parameters are curve 1, $\hbar\omega_c$ 400 cm^{-1}, $\Delta_c^2/2$ 15; curve 2, $\hbar\omega_c$ 400 cm^{-1}, $\Delta_c^2/2$ 10; curve 3, $\hbar\omega_c$ 600 cm^{-1}, $\Delta_c^2/2$ 5; curve 4, $\hbar\omega_c$ 400 cm^{-1}, $\Delta_c^2/2$ 5; curve 5, $\hbar\omega_c$ 2100 cm^{-1}, $\Delta_c^2/2$ 1. The horizontal lines to the right represent the asymptotic limits of these curves.

placement. If we initially have an ion with charge $+m$ on center A and an ion with charge $+n$ on center B with sizes a_m and b_n leading to ions of charges $m + 1$ with size a_{m+1}, and charges $n - 1$ with size b_{n-1}, on centers A and B, respectively, and if we further adopt Marcus' method of evaluating the terms using the concepts of metallized ions we have

$$D_i = D_{ma} + D_{mb}$$
$$D_f = D_{(m+1)a} + D_{(m-1)b} \qquad \text{(IV.26)}$$

where, for example

$$D_{ma} = \begin{cases} 0 & r < a_m \\ me\vec{r}/r^3 & r > a_m \end{cases}$$

$$D_{(m+1)a} = \begin{cases} 0 & r < a_{m+1} \\ (m + 1)e\vec{r}/r^3 & R > a_{m+1} \end{cases}$$

and

$$D_{mb} = \begin{cases} 0 & |\vec{r} - \vec{r}_{ab}| < b_m \\ me(\vec{r} - \vec{r}_{ab})e/|\vec{r} - \vec{r}_{ab}|^3 & |\vec{r} - \vec{r}_{ab}| > b_m \end{cases} \qquad \text{(IV.27)}$$

It is important to note that because we consider separately the first coordination layer all ionic radii refer to those of hydrated ions.

Since $a_m > a_{m+1}$ and $b_n < b_{n-1}$ we have

$$E_M{}^s = Ce^2\left[\frac{(m + 1)^2}{2a_{m+1}} + \frac{n^2}{2b_n} - \frac{n^2 - 1}{2b_{n-1}} - \frac{m(m + 1)}{2a_m} - \frac{1}{R}\right] \qquad \text{(IV.28)}$$

For an isotopic exchange reaction $m = n - 1$, thus $b_n = a_{m+1}$ and $b_{n-1} = a_m$ so that the results reduce to

$$E_M{}^s = Ce^2\left[\frac{n^2}{a_n} - \frac{n^2 - 1}{a_{n-1}} - \frac{1}{R}\right] \qquad \text{(IV.29)}$$

When $a_n = a_{n-1} = r_a$ we obtain the simplified formula often quoted

$$E_M{}^s = Ce^2\left[\frac{1}{r_a} - \frac{1}{R}\right] \qquad \text{(IV.30)}$$

Our approximate formula (eq IV.21) is predicated on the magnitude of α being small. To justify this we must consider the available experimental parameters which determine the important quantities. In this work we will consider only the totally symmetric vibration of the hydration layer, although in principle all modes could be considered. The difficulties in using the other modes is that there is no simple way to estimate the shift in these coordinates between various oxidation states of an ion. These shifts are probably smaller than the radial mode whose change we can relate to the size of the ion. In Table I we list the experimental results for the totally symmetric mode for the hydration layer as determined by the Raman spectrum of aqueous solutions or crystals containing hydrated ions. The other quantity needed is the radius of the ions in the various oxidation states. In our discussion we will use those values quoted in Table I.

Since many redox couples have similar vibrational energies we shall concentrate on but one typical reaction, namely, the Fe^{2+}–Fe^{3+} system assuming that it proceeds *via* a direct outer-sphere mechanism. We will assume that $\hbar\omega_c = 389$ cm^{-1} in both oxidation states. From the definition

$$\Delta_c = \left(\frac{M_c\omega_c}{\hbar}\right)^{1/2}\Delta R = 2.2 \qquad \text{(IV.31)}$$

since M_c is the appropriate reduced mass $\mu = (18)(1.66 \times 10^{-24}) = 2.98 \times 10^{-23}$ g and $\Delta r = 0.16$ Å. Thus $E_M{}^C = (\hbar\omega_c\Delta_c^2/2)2 = 0.117$ eV $\times 2 = 0.233$ eV

$$z_p = 2.42 \operatorname{csch} x \qquad \text{(IV.32)}$$

and $x = (1.4388)(389)/2T = 280/T$. The factor of 2 is required since two ions are involved. The other quantity needed in our calculation is $E_M{}^s$, the medium reorganization energy. Since we consider the first coordination layer separately, this quantity can only include effects of the medium beyond the primary solvation layer. The size of our ions are therefore the ionic radius plus the thickness of the solvation layer which we take to be 2.76 Å. Thus the ferrous ion has an effective size for the continuum medium contributions of $a_2 = 3.59$ Å and the ferric ion $a_3 = 3.43$ Å. Using the formula derived for $E_M{}^s$

$$E_M{}^s = Ce^2\left(\frac{9}{a_3} - \frac{8}{a_2} - \frac{1}{R}\right) \qquad \text{(IV.33)}$$

and substituting the values appropriate to the Fe^{3+}–Fe^{2+} couple we get

$$E_M{}^s = \left(3.13 - \frac{7.94}{R_{ab}}\right)\text{eV} \qquad \text{(IV.34)}$$

where R_{ab} is in Å. For a transition region of $R \sim 7$ Å we get $E_m = 2.0$ eV or less.

We now have all of the factors to investigate the approximate formula derived earlier. For the Fe^{2+}–Fe^{3+} couple we obtain

$$\alpha = x(\hbar w_c/E_M{}^s)/4 = \left(\frac{280}{T}\right)\left(\frac{0.0482}{4}\right) = \frac{3.87}{T} \qquad \text{(IV.35)}$$

Thus at ordinary temperatures, α is quite small. If it is small enough our approximate formulas will be reasonable.

We have already seen that there is a good agreement between the approximate and the exact formulation for such a range of α.

We can give further evidence by comparing the formula for $\Delta E = 0$, $i.e.$,

$$\sum_{m=-\infty}^{\infty} e^{-\alpha m^2} I_m(z_p) = G(\alpha, z_p) \exp(z_p) \quad (IV.36)$$

where for small α we expect $G(\alpha) \sim 1$. In Table V we list the function calculated or typical values of the parameters. From these results we can see that the error involved is only a few per cent, certainly an acceptable approximation in a rate calculation. For a specific estimate of the error we can consider the $Fe^{2+}-Fe^{3+}$ couple at room temperature ($300°K$) where we find $x = 0.93$, $z_p = 2.02$, and $\alpha = 0.0113$ corresponding to $G(\alpha, z_p)$ of about 0.98. At lower temperatures or larger $\hbar\omega_c$, it is even closer to one.

V. Evaluation of the Rate Constant

The rate constant can be written (I.14)

$$k = \int_R^{\infty} d^3 R_{ab} \exp[-\beta U(R_{ab})] W_a(R_{ab})$$

where $U(R_{ab})$ is defined in eq I.15 and R is the distance of closet approach of the ions.

We can either substitute the numerical values for $W_a(R_{ab})$ or use the approximate formula from (IV.21). Using the latter course of action we have

$$k = \frac{4\pi}{\hbar} \left(\frac{\pi}{4E_M^s k_B T} \right)^{1/2} \int_R^{\infty} \exp\left[-\frac{\Delta_c^2}{2}(\coth x - \right.$$

$$\left. \text{csch } x \cosh (x\Delta E/E_M^s) \right] \exp[-(\beta/4E_M^s)(\Delta E -$$

$$E_M^s)^2] |v'R_{ab})|^2 \exp[-\beta U(R_{ab})] R_{ab}^2 dR_{ab} \quad (V.1)$$

where specifically

$$U_{ab} = mne^2/R_{ab}D_{eff} \quad (V.2)$$

for the ions involved using an effective dielectric constant D_{eff}.

If we restrict our attention to the $Fe^{2+}-Fe^{3+}$ couple where $\Delta E = 0$ and

$$E_M^s = (9/Q_3 - 8/Q_2 - 1/R_{ab})(c\beta e^2/4) \quad (V.3)$$

the formulas simplify greatly to yield

$$k = \frac{4\pi}{\hbar} \left(\frac{\pi}{4E_M^s k_B T} \right)^{1/2} \exp\left[-\frac{\Delta_c^2}{2}(\coth x - \right.$$

$$\left. \text{csch } x \right] \int_R^{\infty} e^{-\beta U(R_{ab}) - E_M^s/4kT} |v(R_{ab})|^2 R_{ab}^2 dR_{ab} \quad (V.4)$$

In any case, to proceed further we need to evaluate the matrix element v. As has been pointed out in section II, this matrix is simply

$$v(R_{ab}) = \frac{1}{D_{eff}} \left\langle a \left| \frac{e^2}{\vec{r}_a - \vec{R}_{ab}} \right| b \right\rangle \quad (V.5)$$

For the moment we shall consider v as a parameter although the value will be related to the orbital exponent of the d orbitals as

$$v(R_{ab}) = 2e^2\gamma \exp(-\gamma R_{ab})/D_{eff} \quad (V.6)$$

TABLE V: Value of $G(\alpha, z_p)$ (Eq IV.36) for Typical Values of the Parameters

α	z_p	$G(\alpha, z_p)$
0.000	All values	1.0000
0.010	1.0	0.9902
	2.0	0.9807
	3.0	0.9714
	4.0	0.9624
	5.0	0.9537
0.020	1.0	0.9808
	2.0	0.9626
	3.0	0.9454
	4.0	0.9290
	5.0	0.9135
0.030	1.0	0.9717
	2.0	0.9456
	3.0	0.9215
	4.0	0.8991
	5.0	0.8782
0.040	1.0	0.9629
	2.0	0.9296
	3.0	0.8994
	4.0	0.8720
	5.0	0.8469
0.050	1.0	0.9544
	2.0	0.9144
	3.0	0.8790
	4.0	0.8473
	5.0	0.8188

We now consider only the R_{ab} dependent factors in the integral in eq V.4, $i.e.$, for $Fe^{2+}|Fe^{3+}$

$$\int_R^{\infty} \exp(6\beta e^2/R_{ab}D_{eff}) \exp[C\beta e^2/\Psi R_{ab}] \times$$

$$\exp[-2\gamma R_{ab}] R_{ab}^2 dR_{ab} \quad (V.7)$$

and assuming that D_{eff} is only weakly dependent on R_{ab}. Following Levich we shall approximate this integral by its value at the distance where the expontial is a minimum, $i.e.$, at the value of R_{ab} called R_m, such that

$$-\frac{\beta e^2}{R_{ab}} \left[\frac{6}{D_{eff}} - \frac{C}{4} \right] - 2\gamma R_{ab} \quad (V.8)$$

is a minimum. If this number is less than R, R_m is taken to be R. The value of R_m is found by setting the derivative of (V.8) equal to zero

$$R_m = \left[\frac{e^2}{2\gamma k_B T} \left(\frac{6}{D_{eff}} - \frac{C}{4} \right) \right]^{1/2} \quad (V.9)$$

for reasonable values of γ ($i.e.$, 1–5 $Å^{-1}$) and $20 < D_{eff} < 40$, R_m is real but small, less than 5 Å. As a reasonable estimate regardless of D_{eff}, we shall use $R = R_m$. The meaning of this is important. The rate constant increases with decreasing R and thus it is dominated by the interaction at the distance of closest approach. This is in contrast to the work of Levich[6] who used an extremely unphysical value for γ, namely, about $(6/D_{eff})$ $Å^{-1}$, taking D_{eff} about 45. Although we expect γ to be modified from its value in a free atom, there is no theoretical justification for dividing it by

D_{eff}. Using $R = R_m$ we now obtain

$$k = \frac{4\pi}{\hbar} \left(\frac{\pi}{4E_M^3 kT}\right)^{1/2} \exp\left[-\frac{\Delta_c^2}{2}(\coth x - \right.$$

$$\left. \operatorname{csch} x)\right] x v^2(R_{ab}) \exp\left[-\left(\frac{9}{a_3} - \frac{8}{a_2} - \frac{1}{R}\right) \times \right.$$

$$\left(\frac{C\beta e^2}{4}\right)\Big] \exp[-6e^2\beta/RD_{\text{eff}}] x (R^3/3) \quad \text{(V.10)}$$

or

$$k = A \exp(-V/kT) \quad \text{(V.11)}$$

where

$$A = \frac{4\pi}{E}\left(\frac{\pi}{4E_M^s k_B T}\right)^{1/2}\left(\frac{R^3}{3}\right) v^2(R_{ab}) \quad \text{(V.12)}$$

and

$$V = \frac{k_B T \Delta_c^2}{2}(\coth x - \operatorname{csch} x) + \left(\frac{9}{a_3} + \frac{8}{a_2}\right) \times$$

$$\left(\frac{Ce^2}{4}\right) + \frac{e^2}{R}\left(\frac{6}{D_{\text{eff}}} - \frac{C}{4}\right) = \frac{k_B T \Delta_c^2}{2}(\coth x -$$

$$\operatorname{csch} x) + \frac{E_M^s}{4} + \frac{6e^2}{RD_{\text{eff}}} \quad \text{(V.13)}$$

As a check this expression goes to the proper high-temperature limit of

$$U(T \to \infty) = \frac{E_c}{4} + \frac{E_M^s}{4} + \frac{6e^2}{RD_{\text{eff}}} \quad \text{(V.14)}$$

For the general case of $\Delta E \neq 0$ we can derive an equivalent expression if $R_m = R$. It is the same as (V.11) except that V becomes more complicated than in eq V.13, namely

$$V = \frac{k_B T \Delta_c^2}{2}[\coth x - \operatorname{csch} x \cosh(x\Delta E/E_M^s)] +$$

$$(\Delta E - E_M^s)^2/4E_M^s + U(R) \quad \text{(V.15)}$$

However at the temperatures involved in most experiments there will be a temperature-dependent contribution from the first coordination layer. For moderate temperatures we can expand the results about $x = 0$. It is more important to concentrate our attention on the activation energy E_A and not on V itself since

$$E_A = k_B T^2 \frac{\partial \ln k}{\partial T} = E_A' + k_B T^2 \frac{\partial \ln A}{\partial T} +$$

$$k_B T^2 \frac{\partial}{\partial T}(\beta V) \quad \text{(V.16)}$$

where E_A' is the numerical results derived in the last section or the approximate form E_{AA} (eq IV.24). We shall use the approximate form here in which case

$$E_A(T) = E_{AA}\frac{kT}{2} - kT^2 \frac{mne^2}{R}\frac{\partial}{\partial T}\left(\frac{1}{kTD_{\text{eff}}}\right) \quad \text{(V.17)}$$

$$= E_{AA}' + U(R) - \frac{kT}{2} + \frac{Tmne^2}{RD_{\text{eff}}}\left(\frac{\partial D_{\text{eff}}}{\partial T}\right)$$

$$\text{(V.18)}$$

An approximate result can be obtained for moderate temperatures by expanding E_{AA}' about $x = 0$

$$E_{AA}(T) = \frac{(\Delta E - E_M^s)^2}{4E_M^s} + \frac{E_c}{2}\left(\frac{1}{2} - \frac{y^2}{2}\right) +$$

$$\frac{E_c x^2}{2}\left(-\frac{1}{8} + \frac{y^2}{4} - \frac{y^4}{8}\right) + \ldots \quad \text{(V.19)}$$

where $y = \Delta E/E_M^s$. Thus

$$E_A(T) = E_A(T \to \infty) - \frac{E_c x^2}{16}(1 - 2y^2 + y^4) +$$

$$\frac{Tmne^2}{RD_{\text{eff}}^2}\left(\frac{\partial D_{\text{eff}}}{\partial T}\right) \quad \hbar\omega_c \ll kT \quad \text{(V.20)}$$

At low temperatures the activation energy is known exactly from IV.9 so we can find

$$E_A(T) = E_A(T \to \infty) + \frac{(\Delta E - E^s)^2}{4E_M^s} -$$

$$\frac{(\Delta E - E_M^s - E_c)^2}{4(E_M^s + E_c)} + \frac{Tmne^2}{RD_{\text{eff}}^2}\left(\frac{\partial D_{\text{eff}}}{\partial T}\right)$$

$$\hbar\omega_c \gg kT \quad \text{(V.21)}$$

if $\Delta E = 0$ the results simplify to

$$E_A(T) = E_A(T \to \infty) - \frac{E_c}{16}\left(\frac{\hbar\omega_c}{2kT}\right)^2 +$$

$$\frac{mne^2}{RD_{\text{eff}}^2}\left(\frac{\partial D_{\text{eff}}}{\partial T}\right) \quad \hbar\omega_c \ll kT$$

$$= E_A(T \to \infty) - E_c - \left[\frac{1}{4} - (2kT/\hbar\omega_c)\right] +$$

$$\frac{mne^2}{RD_{\text{eff}}^2}T\left(\frac{\partial D_{\text{eff}}}{\partial T}\right) \quad \hbar\omega_c \gg kT \quad \text{(V.22)}$$

As an example of the magnitudes of these quantities we will consider the $Fe^{2+}|Fe^{3+}$ couple. In this case $E_c = 0.23$ eV = 5.30 kcal/mol and thus at room temperature the activation energy differs from its asymptotic limit by about 0.30 kcal/mol, at low temperatures ($\sim 100°K$) it differs by $E_c/4$ or about 1.3 kcal/mol. For typical examples see Figure 4.

It is important to realize that these high- and low-temperature limits are accessible to experimental verification. There is another low-temperature limit discussed by Levich[6] corresponding to the low temperature relative to the polaron modes but such effects can only be observed at extremely low temperatures, probably below 10°K. In both cases the activation energy decreases due to the increased importance of tunneling at the lower temperatures.

For the $Fe^{2+}|Fe^{3+}$ couple the preexponential factor is (in cgs units)

$$3.16 \times 10^{18} v^2 \quad \text{(V.23)}$$

If we use the best single Slater orbital exponent to represent the 3d wave function we should use 4.7 Å^{-1} as calculated by Watson and quoted by Slater[21] we obtain

$$v = 0.61 \times 10^{-24}/D_{\text{eff}} \quad \text{(V.24)}$$

which leads to an extremely low value of A. The value of v is extremely sensitive to the orbital exponent. Unfortunately, we do not know the exact value to use in this system since the integral depends on the tails of the wave functions and these are greatly affected by all sorts of medium effects: orthogonality, screening, etc. As a reference, in the accurate evaluation of exciton states, Katz, et al.,[22] found that these integrals in the range of 7–8 Å were about 1 cm^{-1} for organic crystals. If we adopt such a value we find

$$v = 2 \times 10^{-16} \text{ ergs} \qquad (V.25)$$

or $A = 1.25 \times 10^{-14} \text{ cm}^3/\text{sec molecule}$ or $0.75 \times 10^{+7} \text{ sec}^{-1} \text{ mol}^{-1}$.

Working backward that value of v corresponds to about $\gamma = 0.9 \text{ Å}^{-1}$ if $D_{\text{eff}} \sim 10$. This value is not unreasonable as in a very accurate nonrelativistic SCF calculation on iron, Clementi has one small 3d exponent of 1.45 Å^{-1}, however, its coefficient is only 0.15 in the 3d orbital wave function. Until better ways are found to estimate this matrix element, our value of 1 cm^{-1} is a reasonable estimate. The actual activation energy for this couple at room temperature is $E_A = E_A(T \to \infty) - 0.30 \text{ kcal/mol}$ where $E_A(T \to \infty) = (12.87 + 285/D_{\text{eff}}) \text{ kcal/mol}$, neglecting $(\partial D_{\text{eff}}/\partial T)$.[23] These values are slightly larger than those of Levich due to our improved treatment of $E_M{}^s$ and the contribution of the first coordination layer.

The effects calculated for the $Fe^{2+}|Fe^{3+}$ couple are small. However, in many systems these effects could be much larger. Stynes and Ibers[24] from X-ray studies of cobalt-amine complexes obtain a charge in radius of 0.178 Å based on the Co(II)–N and Co(IV)–N distances. This leads to $\Delta_c{}^2/2 = 7.9$ which along with an A_{1g} vibration of 495 cm^{-1}[25] leads to a somewhat larger effect. The activation would be expected to change by about 6.3% in going from 200 to 350°K. Much larger temperature dependences should be observed in more complicated cobalt ligands [Co([14]dieneN$_4$)(CH$_2$)$_2$].[26] In that case the Co–O distance can change by 0.54 Å along one axis. This can lead to huge $\Delta_c{}^2/2$ values of about 58. Using a reasonable guess for the vibrational frequency of 300 cm^{-1} one expects the activation energy to vary by 17.3% from 200 to 350°K and even 3.1% from 300 to 350°K (using the approximate algebraic expression).

VI. Discussion

We were able to derive quantum mechanical expressions for nonadiabatic electron transfer reactions where the role of configurational changes in the first coordination layer was incorporated in the theory. The probability for the electron transfer process was recast in terms of a generalized line shape function including the contribution of both the high-frequency modes of the first coordination layers and the low frequencies of the external medium resulting in manageable expressions. The present formulation provides an extension of the classical approach of Marcus and Hush to include the role of the first coordination layer, and of the early quantum mechanical theory of Levich and Dogonadze[6,11] who disregarded these effects. Recent efforts by Dogonadze[9,10,12] and others[11,13,14] have also begun to include these contributions but in a less formal way. It is gratifying that the conventional simple-minded concepts of the ionic solvation and of the structure of the solvated electron, separating the role of the first solvation layer and the polarizable medium outside it, can be incorporated into a quantum mechanical rate theory for outer-sphere electron transfer. The present treatment is analogous to electron relaxation in a large supermolecule. The pertinent information for the relevant displacements and frequencies in the first coordination layer is obtained from structural and spectroscopic data, while the other medium is represented as a continuum dielectric. Thus this approximation in Levich's approach which was recently criticized by Bockris[27] can be relaxed. It is important to note (see Appendix B) that the treatment of the outer medium in terms of polaron

theory does not imply treating its interaction with a loosely bound electron (*i.e.*, the transferred electron) as suggested by Bockris.[27] Rather, polaron theory is applied to account for the response of the polar medium to the influence of the charge distribution of the ionic species in the initial and the final states, thus accounting properly for the configurational charges in the external medium. The present treatment rests on the relation between the bimolecular rate constant and the nonradiative electron transfer probability which are related in terms of an integral of an approximate distribution fraction. Thus relative ionic motion is disregarded. Schmidt[28] in his early work had attempted to account for the role of relative ionic motion on electron transfer processes. Unfortunately, Schmidt's early formulation of the electron transfer problem is open to some serious criticism.[29] The Hamiltonian employed by him (eq 7 ref 28a) is inappropriate as it omits some crucial terms which involve the ion–solvent interaction. It is desirable to write the Hamiltonian in the Schrödinger representation as was done by us before proceeding to second quantization formation. In his formal treatment Schmidt disregards the reverse reactions in the derivation of eq 12 of ref 28a which is inconsistent with the general formalism. Finally, in the Fourier transform of the autocorrelation function[28a] Schmidt assumes that the coefficients are time independent, which is not valid in general. In addition, there are some other technical details in Schmidt's work[28] regarding commutation relations which were not properly handled. Thus we believe that Schmidt's results[28] cannot be considered as a valid extension of the Levich's theory. We assert that the role of ionic diffusion is still open. It should be noted, however, that the approximation of electron transfer between stationary ions is consistent with the adiabatic approximation and as thus it is not expected that ionic diffusion will result in appreciable corrections for the rate constant for these activated processes.

The final form of our rate expressions are summarized by eq V.1, V.4, and V.10. It is important to note that the quantum mechanical expression utilizing a continuum model outside the first coordination layer yields free energy contributions for the external solvent bulk. We did not attempt to follow conventional chemical treatments separating the free energy and the enthalpy of activation but rather defined the activation energy *via* eq IV.9 and V.16. The activation energy at room temperature includes a 10–20% temperature-dependent corrections due to quantum effects of the first coordination layer in systems where $h\omega_c \sim 400 \text{ cm}^{-1}$. The outer medium can always be handled classically, as in view of its low characteristic frequency, extremely low and physically inaccessible temperatures will be required to study quantum effects originating from the effect of these modes.

The preexponential factor for the nonadiabatic rate constant exhibits a strong dependence on the scaling parameter of the electronic wave function. Its value depends on the behavior of the electronic wave functions at large distances, which is very poorly given even by the best available Hartree–Fock approximations. Similar problems were encountered in theoretical studies on electron mobility and triplet exciton band structure in molecular crystals in which the excess electron and the triplet exciton band structures are determined by intramolecular electron exchange or electron transfer matrix elements. The choice of $v \sim 1 \text{ cm}^{-1}$ is reasonable as much lower values suggested by the Hartree–Fock calculations for Fe^{2+} will result in an un-

physically low value for the electron transfer probability. Under these circumstances condition III.22 will be satisfied and outer-sphere electron transfer reactions will be always nonadiabatic and exceedingly slow. Adiabatic electron transfer processes as advocated by Marcus require that $V_{av,bw} > k_B T$ so that interference effects are crucial.

Nonadiabatic processes will occur when interference effects are negligible. The usual semiclassical description of a nonadiabatic transition is provided by implying that the splitting of the zero-order potential surfaces at the intersection point is "small." Levich and Dogonadze[6,19] have provided a complete semiclassical criterion for the applicability of the nonadiabatic limit. To the best of our knowledge a complete quantum mechanical formulation of the adiabatic case has not yet been provided. In this context, Mies and Krauss[30] have provided a simplified model (equal resonance spacings and widths) which exhibits the transition from the adiabatic to the nonadiabatic case. This formalism is not applicable for the present problem as the resonance widths cannot be taken as constant, but rapidly increasing toward the intersection of the potential surfaces. Our nonadiabatic theory incorporating quantum effects of the first coordination layer results in a transmission coefficient of $\kappa \sim 10^{-4}$, when the temperature coefficient of the dielectric constant is neglected.[23] Similarly by the same calculations many other outer-sphere electron transfer reactions would exhibit transmission coefficients of 10^{-3} to 10^{-4} and we would have to concur with Levich[6] that these processes correspond to nonadiabatic reactions. This nonadiabatic pattern in ionic solution is similar to many nonradiative processes in solids such as thermal ionizations and thermal electron capture which are adequately described in terms of second-order perturbation theory and where comparison with experiment provides a legitimate basis for the validity of the nonadiabatic limit. The relevent parameters for thermal electron transfer in solution and for thermal electron capture or ionization in solids are quite similar, so we believe that nonadiabatic outer-sphere electron transfer processes in polar solvents are encountered in real life.

Appendix, A. Quantum Mechanical Manipulation

In this appendix we provide the details of the quantum mechanical treatment of the wave function of the Hamiltonian (II.1) Let us first rewrite the Hamiltonian (I.2) in two alternative forms

$$
\begin{aligned}
\mathcal{H} &= H_{ea} + V_{eb} + T_n \\
&= H_{eb} + V_{eb} + T_n
\end{aligned} \tag{A.1}
$$

where

$$
\begin{aligned}
H_{ea} &= T_e + V_{ea} + H_a + H_b + V_{ab} + \\
&\quad H_s + H_c + V_{int}^s + V_{int}^c \\
H_{eb} &= T_e + V_{eb} + H_a + H_b + V_{ab} + \\
&\quad H_s + H_c + V_{int}^s + V_{int}^c
\end{aligned} \tag{A.1a}
$$

Following the conventional treatment applied for the separation of electronic and nuclear motion one can define two sets of electronic wave functions at fixed nuclear configurations.

$$
\begin{aligned}
H_{ea}\Psi_{ai}(\mathbf{r}, \mathbf{Q}) &= \epsilon_{ai}(\mathbf{Q})\Psi_{ai}(\mathbf{r}, \mathbf{Q}) \\
H_{eb}\Psi_{bj}(\mathbf{r}, \mathbf{Q}) &= \epsilon_{bj}(\mathbf{Q})\Psi_{bj}(\mathbf{r}, \mathbf{Q})
\end{aligned} \tag{A.2}
$$

where $\mathbf{r}$ and $\mathbf{Q}$ refer to all the electronic coordinates and to all the nuclear coordinates of the system, respectively. The complete orthonormal set $\{\Psi_{ai}\}$ represent all the electronic states of the total system with the excess electron localized on center A [*i.e.*, the ground and excited states of the pair $(A^{N+} + B^{M+})$]. Each of these electronic states is characterized by the nuclear potential energy surface $\epsilon_{ai}(\mathbf{Q})$. Similarly the set $\{\Psi_{bj}\}$ characterized by the nuclear potential surfaces $\epsilon_{bj}(\mathbf{Q})$ describes the ground and the excited electronic states of the pair $(A^{(N+1)+} + B^{(M-1)+})$. From the mathematical point of view either of these two basis sets is adequate for the expansion of the total time-dependent wave function $\bar{\Psi}(r, Qvt)$ of the system

$$
\bar{\Psi}(\mathbf{r}, \mathbf{Q}, t) = 2\sum_i \chi_{ai}(\mathbf{Q}, t)\Psi_{ai} = 2\sum_j \chi_{bj}(\mathbf{Q}, t)\Psi_{bj} \tag{A.3}
$$

where $2\chi_{ai}$ and $2\chi_{bj}$ are expansion coefficients. However, such an expansion is inadequate from the practical point of view as a large number of basis functions of type ai (including continuum states) will be required to describe the system with the extra electron on center b. One should follow chemical intuition by setting

$$
\bar{\Psi}(\mathbf{r}, \mathbf{Q}, t) = \sum_\alpha \chi_\alpha(\mathbf{Q}, t)\Psi_\alpha \tag{A.4}
$$

where the index α spans both ai and bj. The time-dependent Schrödinger equation for the total system yields a coupled set of equations for the expansion coefficients χ_α

$$
\sum_\alpha S\beta_\alpha \left[T_N + \epsilon_\alpha(\mathbf{Q}) - i\hbar\frac{\partial}{\partial t} \right] \chi_\alpha(\mathbf{Q}, t) =
$$
$$
-\sum_\alpha \langle \Psi_\beta | U_{e\alpha} | \Psi_\alpha \rangle \chi_\alpha(\mathbf{Q}, t) \sum_\alpha \langle \Psi_\beta | L | \Psi_\alpha \rangle \chi_\alpha(\mathbf{Q}, t) \tag{A.5}
$$

where $\langle \rangle$ refers to integration over electronic coordinates. L is the Born–Oppenheimer breakdown operator

$$
L\Psi_\alpha = 2\frac{\partial\Psi\alpha}{\partial\mathbf{Q}}\frac{\partial}{\partial\mathbf{Q}} + \frac{\partial^2\Psi\alpha}{\partial\mathbf{Q}^2} \tag{A.6}
$$

The electrostatic interaction is defined by

$$
U_{e\alpha} = U_{eb} \text{ for } \alpha \in ai; \ U_{ea} \text{ for } \alpha \in bj \tag{A.7}
$$

δ is the electronic overlap matrix

$$
\delta_{\alpha B} = \langle \Psi_\alpha | \Psi_B \rangle =
$$
$$
\begin{cases}
\delta_{\alpha\beta}; \ \alpha, \ \beta \in ai \text{ or } \alpha, \ \beta \in bj \\
S_{\alpha\beta}; \ \alpha \in ai, \ \beta \in bj \text{ or } \alpha \in bj, \ \beta \in ai
\end{cases} \tag{A.8}
$$

Defining the inverse S^{-1} of the overlap matrix

$$
\sum_\alpha S_{\gamma\alpha}^{-1} S_{\alpha\beta} = S_{\alpha\beta} \tag{A.9}
$$

eq A.7 can be recast in the form

$$\left[T_N + \epsilon_\gamma{}^{(Q)} - i\hbar \frac{\partial}{\partial t} \right] \chi_\gamma =$$

$$- \sum_\alpha \sum_\beta S_{\gamma\beta}{}^{-1} [\langle \Psi_\beta | U_{e\alpha} | \Psi_\alpha \rangle + \langle \Psi_\beta | L | \Psi_\alpha \rangle] \chi_\alpha \quad (A.10)$$

Regrouping the diagonal matrix elements from the right-hand side of eq A.10 we get

$$\left[T_N + \epsilon_\gamma{}^{(Q)} + \langle \Psi_\gamma | U_{e\gamma} | \Psi_\gamma \rangle + \sum_\beta S_{\gamma\beta}{}^{-1} \langle \Psi_B | U_{eB} + \right.$$

$$\left. L | \Psi_\gamma \rangle - i\hbar \frac{\partial}{\partial t} \right] \chi_\gamma = - \left[\sum_{\substack{\alpha \\ \alpha \neq \gamma}} \langle \Psi_\gamma | U_{e\alpha} + L | \Psi_\alpha \rangle + \right.$$

$$\left. \sum_{\substack{\alpha \neq \gamma}} \sum_{\beta \neq \gamma} S_{\gamma\beta}{}^{-1} \langle \Psi_\beta | V_{e\alpha} + L | \Psi_\alpha \rangle \right] \chi_\alpha \quad (A.11)$$

This coupled set of equations for the nuclear motion is general. For the sake of simplicity and relevance let us assume that Ψ_γ corresponds to one of the two ground state electronic wave functions $\Psi_{a0} \equiv \Psi_a$ or $\Psi_{b0} \equiv \Psi_b$. The first sum of the right-hand-side of eq 13 then involves direct coupling between the ground state γ with the ground electronic state on the other site and with excited electronic states on both sites. The second sum involves an overlap correction to the coupling between the lowest zero-order electronic states on the two sites and overlap exchange contributions of excited states. Restricting the treatment to a two electronic level system Ψ_a and Ψ_b, and neglecting the contribution of the nonadiabatic operator L eq A.11 now reduces to the following pair of equations

$$\left[T_N + \epsilon_a(Q) + \langle \Psi_a | U_{eb} | \Psi_a \rangle + S_{ab}{}^{-1} \langle \Psi_b | V_{eb} | \Psi_a \rangle - \right.$$

$$\left. i\hbar \frac{\partial}{\partial t} \right] \chi_a = [\langle \Psi_a | U_{eb} | \Psi_b \rangle + S_{ab}{}^{-1} \langle \Psi_b | U_{eb} | \Psi_b \rangle] \chi_b$$

$$(A.12a)$$

[same as (A.12a) with b in place of a and vice versa]$\chi_b =$ [same as (A.12a) with b in place of a and vice versa]χ_a (A.12b)

Following conventional procedures and neglecting the terms on the right-hand side eq A.12 one obtains the eigenvalue equations for the (zero order) vibrational wave functions $\chi_{av}{}^{0(Q)}$ and $\chi_{bw}{}^{0(Q)}$ of the two electronic states

$$[T_N + \epsilon_a(Q) + \langle \Psi_a | U_{eb} | \Psi_a \rangle +$$

$$S_{ab}{}^{-1} \langle \Psi_b | U_{eb} | \Psi_a \rangle - E_{av}{}^0] \chi_{av}{}^0 = 0$$

[same as above with b in place of a and a in place of b]$\chi_{bw}{}^0 = 0$ (A.13)

The energies $E_{av}{}^0$ and $E_{bw}{}^0$ represent the zero-order vibronic states $\Psi_a \chi_{av}{}^0$ and $\Psi_b \chi_{bw}{}^0$ corresponding to the ground electronic states of the systems $(A^{N+} + B^{M+})$ and $(A^{(N+1)+} + B^{(M-1)+})$, respectively. Again, each of the sets $\{\chi_{av}{}^0\}$ and $\{\chi_{bw}{}^0\}$ completely spans the nuclear space.

The general nuclear functions $\chi_a(Q)$ and $\chi_{bw}(Q)$ can be expanded in the complete zero-order basis sets

$$\chi_a(Q, t) = \sum_v C_{av}(t) \chi_{av}{}^0(Q) \exp\left[-\frac{i}{\hbar} E_{av}{}^0 t \right]$$

$$\chi_b(Q, t) = \sum_w C_{bw}(t) \chi_{bw}{}^0(Q) \exp\left[-\frac{i}{\hbar} E_{bw}{}^0 t \right] \quad (A.14)$$

Utilizing eq A.14 we are immediately led to the equations of motion for the expansion coefficients

$$i\hbar \frac{\partial C_{av}}{\partial t} = - \sum_w C_{bw}(t) V_{av,bw} \exp\left[-\frac{i}{\hbar} (\epsilon_{bw}{}^0 - \epsilon_{av}{}^0) t \right]$$

$$(A.15)$$

$$i\hbar \frac{\partial C_{bw}}{\partial t} = - \sum_v C_{av} V_{bw,av} \exp\left[-\frac{i}{\hbar} (E_{av}{}^0 - E_{bw}{}^0) t \right]$$

resulting in the conventional expressions for the transition probability in second order.

Appendix B. Origin Displacements for the Polar Medium by Model Polaron Theory

The nuclear Hamiltonians for the initial and final states

$$\mathcal{H}^a = T_N{}^c + T_N{}^s + f_a(Q_A, Q_B) + g_a(Q_{\mathcal{K}})$$

$$(B.1)$$

$$\mathcal{H}^b = T_N{}^c + T_N{}^s + f_b(Q_A, Q_B) + g_b(Q_{\mathcal{K}})$$

which will be separated into the contributions of the first coordination lever and the medium outside it

$$\mathcal{H}^{a,b} = H_c{}^{a,b} + H_s{}^{a,b} \quad (B.2)$$

where the continuum Hamiltonian is

$$H_s{}^i = T_N{}^s + g_i(Q_{\mathcal{K}}) \quad i \equiv a, b \quad (B.3)$$

The Hamiltonian (B.3) can be handled by using the formal results of polaron theory as suggested by Levich. We shall apply the formalism of Frohlich and Allcock for the strong coupled polaron to drive the reduced displacements Δ_κ and show how our result reduces to that of Levich. The physical situation is essentially as follows: in the initial state of the continuum at $\mathbf{x}$ is polarized by a charge distribution $(\mathbf{x} - \mathbf{x}_0)$, where $\mathbf{x}_0$ is an arbitrary origin, while in the final state b the change distribution is $\rho^b(\mathbf{x} - \mathbf{x}_0)$. The polar modes can be represented in terms of the Fourier components of the polarization field, the coordinate and conjugate momentum of the V component being q_V and P_{ea}, respectively. The formulation of the Hamiltonian is equivalent to the Hartree approach for the strongly coupled polaron except that the change distributions $\rho^i(\mathbf{x} - \mathbf{x}_0)$ $(i = a,b)$ are static. The strongly coupled polaron Hamiltonian is

$$H_s{}^i = \sum_v (p_v{}^2 + q_v{}^2) + \sum_v [i(\alpha_v{}^{i*} - \alpha_v{}^i) p_v - $$

$$(\alpha_v{}^{i*} + \alpha_v{}^i) q_v] \quad (B.4)$$

where the linear coupling coefficients are

$$\alpha_v{}^i = \left(\frac{4\pi \delta_p}{S} \right)^{1/2} (1/v) \int d^3x \exp(i\mathbf{v} \cdot \mathbf{x}) \rho(\mathbf{x} - \mathbf{x}_0)$$

$$(B.5)$$

here the polaron coupling constant is

$$\delta_p = \frac{e^2}{C\hbar} \left(\frac{m}{2\hbar \omega_0} \right) \quad (B.6)$$

while S is the reduced volume, Ω

$$S = (2m\omega_0/\hbar)^{3/2} \Omega \quad (B.7)$$

and the polaron coupling term is

$$C = (D_0{}^{-1} - D_s{}^{-1}) \quad (B.8)$$

As $\alpha_v{}^* = a_{-v}$ and $\alpha_{-v}{}^* = \alpha_v$ one can define new field coordinates for $v > 0$

$$q_{1v} = (1/\sqrt{2})(q_v + q_{-v})$$

$$q_{2v} = (1/\sqrt{2})(p_v - p_{-v}) \tag{B.9}$$

$$p_{1v} = (1/\sqrt{2})(p_v + p_{-v})$$

$$p_{2v} = (1/\sqrt{2})(q_v - q_{-v})$$

The Hamiltonian (A.4) takes the form

$$H_s{}^i = \sum_v (q_{1v}{}^2 + q_{2v}{}^2 + p_{1v}{}^2 + p_{2v}{}^2) -$$

$$\sum_{v>0} [\sqrt{2}(\alpha_v{}^i + \alpha_v{}^i)q_{1v} + \sqrt{2}(\alpha_v{}^i - \alpha_v{}^i)q_{2v}] \tag{B.10}$$

Comparing (A.8) with a general harmonic Hamiltonian we notice that the displacements of the origins of the normal polar modes induced by the static charge distribution ρ^i (relative to the unperturbed medium) are

$$\Delta_{1v}{}^i = (1/\sqrt{2})(\alpha_{-v}{}^i + \alpha_v{}^i)$$

$$\Delta_{2v}{}^i = (1/\sqrt{2})(\alpha_v{}^i - \alpha_v{}^i) \tag{B.11}$$

which from eq A.5 are

$$\Delta_{1v}{}^i = \left(\frac{4\pi\delta p}{S}\right)^{1/2}\frac{1}{V}\int d^3\mathbf{x} \cos(\mathbf{v}\cdot\mathbf{x})\rho^i(\mathbf{x} - \mathbf{x}_0) \tag{B.12}$$

$$\Delta_{2v}{}^i = \left(\frac{4\pi\delta p}{S}\right)^{1/2}\frac{1}{V}\int d^3\mathbf{x} \sin(\mathbf{v}\cdot\mathbf{x})\rho^i(\mathbf{x} - \mathbf{x}_0)$$

both of these displacements are real.

The relative displacements between the two states a and b $\Delta_{\mathfrak{K}} = \Delta^a - \Delta^b$ are from (B.11)

$$\Delta_{\mathfrak{K}} = \Delta_{1v}, \Delta_{2v} \tag{B.13}$$

$$\Delta_{1v} = \Delta_{1v}{}^a - \Delta_{1v}{}^b$$

$$\Delta_{2v} = \Delta_{2v}{}^a - \Delta_{2v}{}^b \tag{B.14}$$

The relevant energy parameter $E_M{}^S$ (eq II.8) is now

$$E_M{}^S = \frac{1}{2}\hbar w_0 \sum_v [(\Delta_{1v}{}^a - \Delta_{1v}{}^b)^2 + (\Delta_{2v}{}^a - \Delta_{2v}{}^b)^2] \tag{B.15}$$

Utilizing eq A.10 we get

$$E_M{}^s = \frac{\hbar w_0}{2}\left(\frac{4\pi\delta p}{S}\right)\left\{\sum_v\frac{1}{v^2}\int d^3\mathbf{x} \cos(\mathbf{v}\cdot\mathbf{x})[\rho^a(x - x_0) - \rho_1{}^b(x - x_0)]^2 + \sum\frac{1}{v^2}[d^3x \sin(\mathbf{v}\cdot\mathbf{x})[\rho^a(x - x_0)\rho^b(\mathbf{x} - \mathbf{x}_0)]^2\right.$$

Performing the relevant integrations in (A.14) and using

$$\frac{1}{S}\Sigma = \frac{1}{(2\pi)^3}\int d^3\mathbf{x}$$

we get

$$E_M{}^S = \frac{Ce^2}{2}\iint d^3x\, d^3x\, (\{[\rho^a(x - x_0) + \rho^b(x - x_0)][\rho^a(x' - x_0) + \rho^b(x' - x_0)]\}/|x - x'|)$$

$$= \frac{Ce^2}{2}\iint d^3x\, d^3x'\{[\rho^a(x)\rho^a(x') + \rho^b(x)\rho^b(x') + 2\rho^a(x)\rho^b(x')]/|x - x'|\} \tag{B.16}$$

This is our final result. Equation B.15 can be recast in terms of the displacement vectors $\mathbf{D}^a$ and $\mathbf{D}^b$ in the initial and final states. It is easy to show that

$$J = \iint d^3\chi\, d^3\chi'\, \frac{\rho^i(x - x_0)\rho^j(x' - x_0)}{|x - x'|} = \frac{1}{4\pi}\int \mathbf{D}^i\mathbf{D}^j\, d^3x \tag{B.17}$$

so that we get Levich's result

$$E_M{}^S = \frac{Ce^2}{8\pi}\int(\mathbf{D}^a - \mathbf{D}^b)^2\, d^3\mathbf{x}$$

We have exposed the derivation of the $E_M{}^S$ term in considerable detail to demonstrate that the application of polaron theory to the present problem does not involve the conventional picture of one loosely bound electron (i.e., the transferred electron) with the polar liquid, but rather the energy, changes accompanying the response of the medium to the different static charge distributions in the initial and in the final states. Our final expression is, of course, equivalent to the results of many other researchers.

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Unimolecular Reactions and Energy Partitioning. Three- and Four-Centered Elimination Reactions of Chemically Activated 1,1,2-Trichloroethane-d_0, -d_1, and -d_2

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The unimolecular three- and four-centered hydrogen chloride elimination reactions of chemically activated 1,1,2-trichloroethane-*1-d*, formed by the combination of CH_2Cl and $CDCl_2$ radicals, have been studied. Two other isomers, 1,1,2-trichloroethane-d_0 and -$2,2$-d_2, also were studied to confirm reaction mechanisms and to establish intermolecular isotope effects. Partitioning of vibrational energy to the dichlorolefin was characterized by observing the cis–trans unimolecular isomerization rate of 1,2-dichloroethene. Approximately 81% of the total available energy was retained as internal energy of the olefin from the $\alpha\alpha$ process; both the average energy and the energy distribution are consistent with statistical partitioning of the *excess* energy. The results are less definitive for the $\beta\alpha$ elimination reaction, but substantially less of the available energy was released to the olefin. The energy release data are consistent with the different *potential* energy changes for the two channels. Fitting the magnitude of the various experimental rate constants to RRKM calculations using optimized four- and three-centered transition-state models gave E_0 values of 59, 57, and 60 kcal mol^{-1} for the $\beta\alpha$, $\alpha\beta$, and $\alpha\alpha$ processes, respectively, of the d_0 isomer. In addition to trichloroethane, chemically activated 1,2-dichloroethane and 1,1,2,2-tetrachlorethane also were generated and the half-quenching pressures were as follows: 1,1,2-trichloroethane-d_0, -d_1, and -d_2, 17, 11, and 8.0 Torr, respectively; 1,2-dichloroethane, 18 Torr; 1,1,2,2-tetrachlorethane, 10 Torr.

Introduction

The four-centered HX elimination reactions of halogenated alkanes are well characterized with respect to thermally and chemically activated unimolecular rate constants.[1] Generalized models[2-4] of the transition state match the experimental rate data including inter- and intramolecular isotope effects. Three-centered ($\alpha\alpha$) elimination (followed by rapid rearrangement of the carbene to an olefin) competes with four-centered ($\beta\alpha$) elimination if two halogens are located on the same carbon.[5-7] We previously used the intramolecular competition between HF and DF elimination from CD_3CHF_2 to characterize the transition state model for $\alpha\alpha$ elimination.[6] In the current work the elimination reactions of chemically activated 1,1,2-trichloroethane-d_0, -*1-d*, and -$2,2$-d_2 are reported. An advantage of the 1,1,2-trichloroethane system is that the energy released to the dichloro olefins can be deduced from the cis–trans isomerization rates, if the elimination reactions give nonequilibrium cis:trans ratios of 1,2-dichloroethene.

The energy release pattern for a unimolecular reaction depends upon the excess energy, $\langle E \rangle - E_0$, and the characteristics of the potential energy surface on the product side of the barrier. Since RRKM theory appears to be ade-

quate for describing the rate constants for HX elimination,[1-4,6-8] we will assume, subject to testing, that the energy distribution of the microcanonical ensemble of systems attaining the transition-state configuration is statistical. In contrast to this statistical distribution of the excess energy, the potential energy (*i.e.*, the threshold energy for the reverse reaction) will be released according to the characteristics of the potential surface and associated dynamics of motion in a manner analogous to direct bimolecular exchange reactions.[9] Thus energy partitioning data supplement conventional rate data for unimolecular reactions and give some information about the potential surface on the product side of the barrier. The potential energy changes associated with the $\alpha\alpha$ and $\beta\alpha$ elimination reactions differ. The four-centered process releases ~30 kcal mol^{-1} of excess energy plus ~50 kcal mol^{-1} of potential energy after crossing the barrier configuration. The three-centered process releases about the same excess energy since the threshold energies, E_0, are similar, but virtually no potential energy is released in passing from the HCl elimination barrier to the carbene (*i.e.* the activation energy for addition of :CClCH₂Cl to HCl is not known, but must be small). However, a large intramolecular energy release accompanies the rearrangement of the carbene to the dichloroethene. Since