THEORY OF ELECTROCHEMICAL ELECTRON TRANSFER

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CERTIFICATE

This is to certify that the thesis bound herewith is an authentic record of research work carried out by the author under my supervision in partial fulfilment of the requirements for the degree of Doctor of Philosophy of Cochin University of Science and Technology, and further that no part thereof has been presented before for any other degree.

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CHAPTER 1

INTRODUCTION

Electron transfer (ET) is clearly one of the most fundamental chemical processes. There are so many different systems - inorganic and organic systems, colloids, metal-liquid electrode interfaces, semiconductor-liquid electrodes, liquid-liquid interfaces and proteins - where ET comes in. This ubiquity and importance have led to a vast amount of research on ET processes and reactions. While a great deal of understanding has been achieved, there remain substantial questions, both experimental and theoretical, whose answers are not at all clear.

Of great interest to the electrochemist is electron transfer across the metal-solution interface. Experimental study of such processes is easy, as one can measure the current as a function of the overpotential. However, the theory of the process needs inputs from different branches - liquid state theory, quantum chemistry and solid state physics. The subject of this dissertation is the development of a theory for the transfer of an electron from an ion which is inside a polar solvent to a metal electrode. The contents of this dissertation are discussed briefly in the following paragraphs.

Chapter 2 is of an introductory nature. It gives a preview of the field of ET. Here, general matters pertaining to the descriptions of various ET systems are considered, namely, the classification of ET processes as outer sphere and inner sphere processes, adiabatic and nonadiabatic ones. The definitions are substantiated with appropriate examples.

Chapter 3 gives an overview of our understanding of ET. It highlights the key role played by ET in chemistry, spanning the boundaries of physical, inorganic, organic, analytical and biological chemistry. The outline of this chapter is clearly depicted by its aims. This chapter gives a historical background regarding the theory of ET and traces categorically the metamorphosis it has undergone in the three decades following the early understanding of ET processes. It discusses in detail the pioneering work in the field due to the two schools of thought, that of Marcus[1] and Levich, Dogonadze and Kuznetsov.[2] These two groups have developed the theory of ET in homogeneous media in several papers and then extended it to the heterogeneous problem. Recent developments in the field of ET constitute considerable progress towards the aim of establishing a reasonably general theoretical account of the commonly encountered ET reaction systems. Hence, in this chapter, we briefly summarize the various approaches advanced by several research groups active in this field and, hopefully, bring up to date the various developments in this fascinating arena of chemistry.

No discussion on ET reactions in solution can be deemed complete without an account of the effect of the dynamics of polar solvent on the reaction rate. Polar solvents often exert a dramatic influence on reactions in solution. Equilibrium aspects of this influence involve differential solvation of reactants compared to the transition state that lead to alteration of the free energy barrier to reaction. Such effects are well known, and often give rise to changes in reaction rates of many orders of magnitude. Less well understood are effects arising from non-equilibrium, dynamical aspects of solvation. During the course of a reaction, charge is rapidly redistributed among reactants. How the reaction couples to its solvent environment depends critically on how fast the solvent can respond to these changes in reactant charge distribution.

In Chapter 4, the influence of solvent dynamical effects on ET reactions are discussed. A hierarchy of models from a continuum model to one incorporating molecular aspects of solvation, combined with computer simulations, discussed in this chapter, gives insight into the underlying dynamics. The focus of this chapter is on the major strides on the theoretical front in understanding the solvent dynamical effects on ET reactions, particularly, those features which we feel are most relevant to the development of our rate theory for the transfer of an electron from an ion in a polar solvent to a metal electrode in contact with it.

Chapter 5 presents the theory that we have developed for ET across the interface between a metal electrode and a solution in contact with it. The process has been the subject of a large number of investigations.

In homogeneous ET processes, the situation can be visualized as follows: The acceptor and donor species are both in solution, in a polar solvent. The donor species has an orbital which accomodates an electron. This electron may be given to an orbital on the acceptor. The energies of these orbitals are shifted due to their interaction with the polar surroundings. The surroundings, in turn, are constantly changing due to thermal movement of the molecules. As a result, the energy of any orbital is randomly changing as a function of time - i.e. it is a stochastic process. ET from the donor orbital to the acceptor orbital occurs when the energies of the two coincide. The time scale for solvent rearrangement is given by τ_L, the time of longitudinal relaxation. If H_{12} is the matrix element for ET, the time scale of ET is $\tau_{ET} = \hbar/|H_{12}|$. If $\tau_{ET} << \tau_L$, then the reaction rate is determined by solvent reorganization and the reaction is termed adiabatic. In the opposite limit of $\tau_{ET} \gg \tau_L$, ET is the rate determining process and the reaction is termed non-adiabatic. Expressions applicable to these two limiting cases have been derived in the literature.

We consider the reaction $A^{2+} \rightarrow A^{3+} + e^-$ occuring at the surface of a metal electrode: The mechanism is similar to the one in homogeneous case. However, the one-electron states in the metal are not affected by the solvent fluctuations. In comparison, the orbital on the ion is strongly affected. Thus the energy of the orbital on the ion is a random function of time. This is caused by the fluctuations of solvent molecules surrounding it. If its energy is below the Fermi level, then there is no transfer of electrons to the metal. Due to thermal movement of solvent molecules, its energy may go above the Fermi level. As soon as it crosses the Fermi level, ET to the metal begins. On the experimental side, there have been several investigations. In fact, the electrochemical exchange of Cobalticinium-Cobaltocene ($Cp_2Co^{+/0}$) at a mercury electrode in various nonaqueous media is believed to be adiabatic.[3] In this connection, it is interesting to ask whether any electrochemical ET, can ever be adiabatic in the conventional meaning of the term which implies that the system remains on a single adiabatic potential energy surface. The question arises because of the existence of a continuum of excited states in the metal, as a result of which the electronic state of the system can change even by a small perturbation, however small. In addition, the density of states for these excitations is rather large. Consequently, many singular effects can arise as a result of time dependent localized perturbations. Sebastian[4] investigated this problem and suggested a bosonization procedure to account for these excitations.

Our approach to the problem is in terms of the effective energy of the orbital |a> on the ion A^{2+}, which we denote by ϵ_a+Q. Here Q represents the part of the energy which fluctuates due to thermal motion of the solvent. Also, due to interaction with the orbitals of the solvent, the orbital |a> is broadened into a resonance of width Δ, which is of the order of 0.01 eV (81 cm^{-1}). As Q fluctuates, the orbital energy ϵ_a+Q can cross the Fermi level, and come into resonance with the unoccupied orbitals of the metal, causing ET from the ion to the electrode. We put this simple picture on a firm mathematical footing by constructing a diffusion-reaction equation describing the process.

The important parameters in the process are the separation between the Fermi level ϵ_F and the orbital energy ϵ_a, i.e., $\epsilon_F - \epsilon_a$, width of the orbital Δ, the time that the ionic orbital's energy would spend above ϵ_F, determined essentially by τ_L, the time of longitudinal relaxation of the solvent, the reorganization energy λ, and of course k_BT where k_B is the Boltzmann constant.

We make use of a new `steady state' approach to the calculation of the rate constant. Using this expression for the rate constant, we analyse the limiting cases, that may arise in different parameter regimes. We also discuss the relationship of this approach to other, time dependent approaches to the definition of a rate constant.

Finally, in Chapter 6, we give a brief summary of the work done.

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CHAPTER 2

ELECTRON TRANSFER REACTIONS: CLASSIFICATION AND EXAMPLES

2.1 Introduction

Electron transfer (ET) has been a subject of intense study, both theoretically and experimentally. This is not surprising, considering the ubiquity and importance of electron transfer processes to chemical reactions occurring on time scales from femtoseconds to seconds, at distance scales from less than 1Å to more than 20Å, in physical, chemical, biological and material systems and in all of the usual subdivisions of the discipline of chemistry. Electron transfer reactions can be classified in different ways as the situation warrants.

2.2 Outer and Inner Sphere ET Reactions

One way to classify ET reactions is as belonging to inner and outer sphere varieties. An outer sphere reaction is defined as one in which there is minimal distortion of the chemical bonds in the reactants during the course of the rate-determining ET step. Subsequent steps, i.e., steps which take place after the completion of the ET, can involve changes in bond geometry and coordination number. However, as the ET is the assumed rate-governing step in the sequence, these later molecular rearragement acts do not figure in the primary measured rate constant. A well known example of a homonuclear outer sphere ET reaction is

$$MnO_4^{-2} + MnO_4^{-} \longrightarrow MnO_4^{-} + MnO_4^{-2}$$

which can be followed by isotope substitution or by NMR line broadening for the central manganese atom. During this process, the coordination spheres remain intact, and the overall process is controlled by ET. An example of an outer sphere heteronuclear ET reaction is

$$[Fe(CN)_6]^{-4} + [IrCl_6]^{-3} \longrightarrow [Fe(CN)_6]^{-3} + [IrCl_6]^{-4}$$

which is accompanied by a net chemical change. Outer sphere reactions, in general, are amenable to theoretical analysis.

On the other hand, a reaction is classified as an inner sphere one, if there is a change in bond character which occurs simultaneously with the ET step. Reactions of this second type present the greatest difficulties in any attempt to formulate a coherent, all-encompassing theory of ET reactions. An example of an inner sphere ET reaction is

$$[(NH_3)_5CoCl]^{+2} + [Cr(H_2O)_6]^{+2} \longrightarrow [Co(H_2O)_6]^{+2} + [ClCr(H_2O)_5]^{+2} + 5\ NH_3$$

The above reaction proceeds by an inner sphere mechanism via an intermediate binuclear complex of the form[1,2] $[(NH_3)_5Co\text{-}Cl\text{-}Cr(H_2O)_5]^{+4}$.

The above distinction between reaction types is somewhat arbitrary. In practice, it is both experimentally, and to a lesser degree, theoretically difficult to place an individual reaction into one or the other category.

2.3 Adiabatic and Nonadiabatic ET Reactions

Often ET reactions are classified as being either `adiabatic' or `nonadiabatic'. As long as the system, in proceeding from the reactant to the product state remains on the lower curve of Fig.1, for any velocity of approach to the top of the energy barrier, the reaction will proceed to completion with unit probability and such a reaction is termed adiabatic. This will be the case only for those systems in which H_{12}, the matrix element for ET, is large enough that in passing through the transition region, there is negligible likelihood that the system can remain in the reactant state. Reaction systems for which there is a relatively high probability that the system jumps from the lower to the upper curve on passage through the transition state region will have smaller number of successful reactive transitions. Such reactions have been termed nonadiabatic. This will be the case where H_{12} is very small. Thus the magnitude of H_{12} determines the degree of adiabatic or nonadiabatic character in the ET reactions.

The distinction between adiabatic and nonadiabatic reactions is quite important. For one thing, the expression for the rate constant depends on the adiabaticity of a reaction. The pre-exponential factor for a nonadiabatic reaction is considerably smaller than that of an adiabatic reaction. However, the problem of the accurate determination of the pre-exponential factors is somewhat difficult experimentally. Thus, the experimental resolution of reactions into clearly adiabatic and nonadiabatic classifications is not absolutely certain.

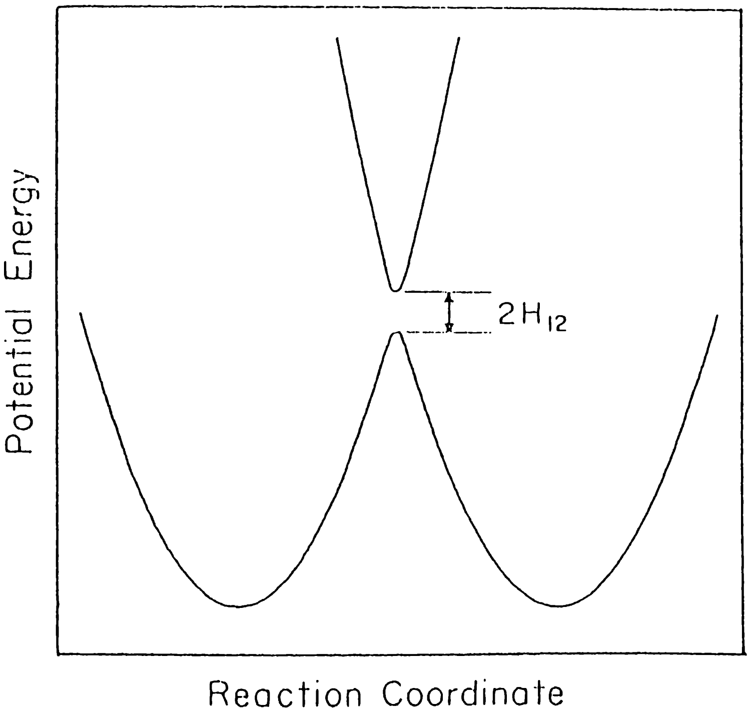

Fig.1 Schematic potential energy-reaction coordinate profile

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CHAPTER 3

HISTORICAL BACKGROUND

3.1 Introduction

An essential aspect of the ET problem is the change in the equilibrium nuclear configuration of an ion or molecule that results from the gain or loss of an electron. In the case of a metal complex in a polar solvent, this involves changes in the metal-ligand and intraligand bond lengths and angles as well as changes in the vibrations and orientations of the surrounding solvent dipoles.

In 1952, Libby[1] and Randles[2] independently made the suggestion that the coupling of ET to these nuclear configuration changes is governed by energy and momentum conservation requirements as dictated by the Franck-Condon principle. According to this principle, internuclear distances and nuclear velocities do not change during an electronic transition: in other words, the ET occurs at essentially constant nuclear configuration and momentum. This requirement is central to the understanding of the classical as well as quantum mechanical ET theories. The classical theories employ the activated-complex formalism in which ET occurs at the intersection of two potential energy surfaces, one for the reactants and the other for the products. The Franck-Condon principle is obeyed since the nuclear configurations and energies of the reactants and products are the same at the intersection.

In the quantum mechanical theories, on the other hand, the intersection of the potential energy surfaces is de-emphasized, nuclear tunneling from the initial to the final state is allowed for, and the ET is treated as a radiationless transition between the reactant and the product states. The fitness of a particular nuclear configuration for ET is related to the square of the overlap of the vibrational wave function of the reactants and products (i.e., to the Franck-Condon factors for the transition).

The early ET theories were nonadiabatic;[1,3-5] that is the rate constant depended explicitly on the electronic transition of the reactants, and the nuclear configuration change was not specfically calculated. These approaches treated the solution as a static dielectric.

Platzman & Franck[6] investigated homogeneous charge transfer reactions within the framework of the so-called radiationless transition theory developed by Lax.[7] These workers described the charge transfer process in solution in terms of the polaron concept, originally developed for polar crystals by Pekar[8] and extended to polar solvents by Davydov.[9] Using essentially the same model, Marcus,[10-13] Hush,[14-16] and the Levich, Dogonadze and Kuznetsov (LDK) group[17-21] have made extensive quantitative calculations for both the outer sphere homogeneous ET process and the corresponding reactions at metal electrodes. In their earlier papers, Marcus and LDK assumed that the metal ion with its inner coordination sphere can be treated as a conducting sphere with all the activation barrier associated with solvent polarization fluctuation. Marcus[10,12,13] developed the model using a classical statistical mechanical description of the solvent, whereas the LDK group developed a quantum statistical mechanical description.[17-21]

Various authors[5-22] including Marcus[11,13] pointed out that the neglect of bond stretching contributions from the inner sphere may be serious, and Marcus[13,23] and Hush[14-16] have taken this into account. The LDK group,[24,25] on the other hand, has omitted the inner sphere contributions on the ground that the vibrational modes of the inner sphere have $\hbar\omega >> kT$, and consequently these bonds require multiple phonon interactions involving far too many phonons to have a reasonable probability of being excited.

Schmidt[26,27] and Schmickler & Vielstich[28,29] have further developed the solvent fluctuation model, the former by presenting a more generalized nonequilibrium statistical mechanical picture and the latter by considering more specifically the effect of the inner coordination sphere.

3.2 Classical Theory of Electron Transfer

The most consistent development of the idea on the role played by nonequilibrium solvent polarization in charge transfer reactions was given by Marcus[30] in 1956 in the framework of a classical description of the solvent for homogeneous outer sphere adiabatic ET reactions. He used the dielectric continuum theory, reworked in order to permit the calculation of the free energy of systems having a nonequilibrium dielectric polarization and computed the polarization function for the activated state by minimizing the free energy subject to the constraint imposed by the Franck-Condon principle. Subsequently, he used a similar treatment in the calculation of ET rates at electrodes and computed exchange currents and transfer coefficients[13].

Using absolute reaction rate theory as a point of departure, Marcus gave the rate constant, k of ET in terms of a free energy of activation $\Delta G^{\neq}$ for the reaction[10,23,31]:

$$k = \kappa Z \exp(-\Delta G^{\neq}/RT), \tag{1}$$

where κ is the transmission coefficient or averaged transition probability for electron transfer and Z is either the collision frequency in a bimolecular reaction or the vibrational frequency in a monomolecular (intramoleclar) reaction. $\Delta G^{\neq}$ is the free energy of activation that is related to λ (described below), to ΔG^{o}, the `standard' free energy of reaction in the prevailing medium, and to the work of bringing the reactants (w^{r}) or products (w^{p}) to the mean separation distance r:[23,32]

$$\Delta G^{\neq} = w^{r} + (\lambda/4)(1 + \Delta G^{o\prime}/\lambda)^{2}, \tag{2}$$

$$\Delta G^{o\prime} = \Delta G^{o} + w^{p} - w^{r}. \tag{3}$$

λ is the total energy of reorganization which is coupled to the ET. It is the energy which would be required to move all the atoms from their equilibrium positions before ET to the equilibrium positions they would have after ET without, however, transferring the electron.

Marcus separated λ into two parts as

$$\lambda = \lambda_{i} + \lambda_{o}, \tag{4}$$

where λ_{i} is the reorganizational energy of the inner shell of atoms and λ_{o} is that of the surrounding solvent molecules. The value of λ_{i} is calculated from the force constants for all molecular vibrations in both the reactant and product, while λ_{o} is determined by the dielectric continuum model of a solvent. λ_{i} and λ_{o} are given by

$$\lambda_i = \Sigma_j \frac{f_j^r f_j^p}{f_j^r + f_j^p} \left(\Delta q_j\right)^2 , \qquad (5)$$

$$\lambda_o = (\Delta e)^2 \left[\frac{1}{2a_1} + \frac{1}{2a_2} - \frac{1}{r} \right] \left[\frac{1}{\varepsilon_{op}} - \frac{1}{\varepsilon_s} \right] , \qquad (6)$$

where f_j^r is the force constant for the jth normal mode in the reactants, f_j^p is that in the products, Δq_j is the change in the equilibrium value of the jth normal coordinate, Δe is the charge transferred from one reactant to the other, a_1 and a_2 are the radii of the two (spherical) reactants, r is the centre-to-centre separation distance, and ε_s and ε_{op} are the static and optical (square of refractive index) dielectric constants of the solvent respectively.

In the derivation of Eqs. 1-6, the vibrations within the reactants were treated as harmonic oscillators, but no such restrictive assumption was made for the solvent outside of the coordination shells. It was assumed that the dielectric polarization outside the coordination shells responded linearly to any change in (real or fictitious) charges, and hence that free energy depended quadratically on charging parameters. Such a treatment allows the individual solvent dipoles to move very anharmonically, as indeed they do in a liquid.

The `cross-relation' follows from these equations, by noting from Eqs. 3-5 that λ for cross-reaction (λ_{12}),

$$\text{red}_1 + \text{ox}_2 \xrightarrow{k_{12}} \text{ox}_1 + \text{red}_2 , \qquad (7)$$

is approximately the mean of the λ's of the self-exchange reactions λ_{11} and λ_{22}:

$$red_1 + ox_1 \xrightarrow{k_{11}} ox_1 + red_1 \ , \tag{8}$$

$$red_2 + ox_2 \xrightarrow{k_{22}} ox_2 + red_2 \ . \tag{9}$$

From this result one finds when the transmission coefficients κ are approximately unity, and when the self-exchange rate constants k_{ii} are either corrected for the work terms or when the latter approximately cancel, that k_{12} is given by Eq.10:

$$k_{12} = (k_{11}k_{22}K_{12}f_{12})^{1/2}, \tag{10}$$

where K_{12} is the equilibrium constant of reaction 7 in the prevailing medium, i.e., K_{12} is equal to $\exp(-\Delta G^0/kT)$, and f_{12} is a known function of k_{11}, k_{22} and k_{12}:

$$\ln f_{12} = \frac{1}{4} (\ln K_{12})^2/\ln (k_{11}k_{22}/Z^2). \tag{11}$$

In practice, f_{12} is often close to unity. A modification of this equation when the κ's are less than unity has been given.[33]

For electrode reactions involving metals, Marcus assumed that the electronic energy levels of the metal contributing to the reaction are confined to within ±kT of the Fermi level. He then considered the distribution of activated complexes corresponding to radiationless ET to or from various electronic energy levels in the metal to be equivalent to a single activated complex corresponding to the Fermi level. The expressions are similar to Eqs. (1-6), only now Z is replaced by a related quantity which has dimensions of a collision frequency of the ion with unit area of the electrode, r is now twice the distance of the centre of the ion to the electrode surface, $1/2a_2$ is missing from Eq.6 (a_2 tends to infinity), the summation in Eq.5 is over the vibrational coordinates of one ion instead of two, and ΔG^o is replaced by the activation overpotential. When the rate constant for self-exchange in solution, k_{ex} is compared with the rate constant for reaction between one of these ions and an electrode at zero activation overpotential, k_{el}, one finds from Eqs.1-6 and from the equations for the corresponding reactions at an electrode that, approximately,

$$\left[\frac{k_{ex}}{Z_{soln}}\right]^{1/2} \geq \frac{k_{el}}{Z_{el}} \; . \tag{12}$$

Equality exists when the averaged centre-centre distance r of the reactants in the homogeneous reaction is twice that from the centre of the reactant to the electrode. The Marcus treatment also predicts a transfer coefficient of $\beta = 0.5$ for heterogeneous outer sphere ET at relatively low and moderate overpotentials, with deviations from this value at high overpotentials.

From Eq.2 it can be seen that for a series of reactions having the same values of λ and different values of $\Delta G^{o\prime}$ the rate should be a maximum when $-\Delta G^{o\prime} = \lambda$ ("barrierless region") and should decrease if the reaction becomes more exothermic, i.e., $-\Delta G^{o\prime} > \lambda$ ("inverted region"). This is sometimes called the 'energy-gap law', $-\Delta G^{o\prime}$ being the energy gap. Physically, in terms of Fig.2a, this effect of making $\Delta G^{o\prime}$ more negative at constant λ can be seen to correspond to lowering the P surface vertically (or raising the R surface). The intersection of R and P surfaces eventually occurs at the minimum of the R surface and

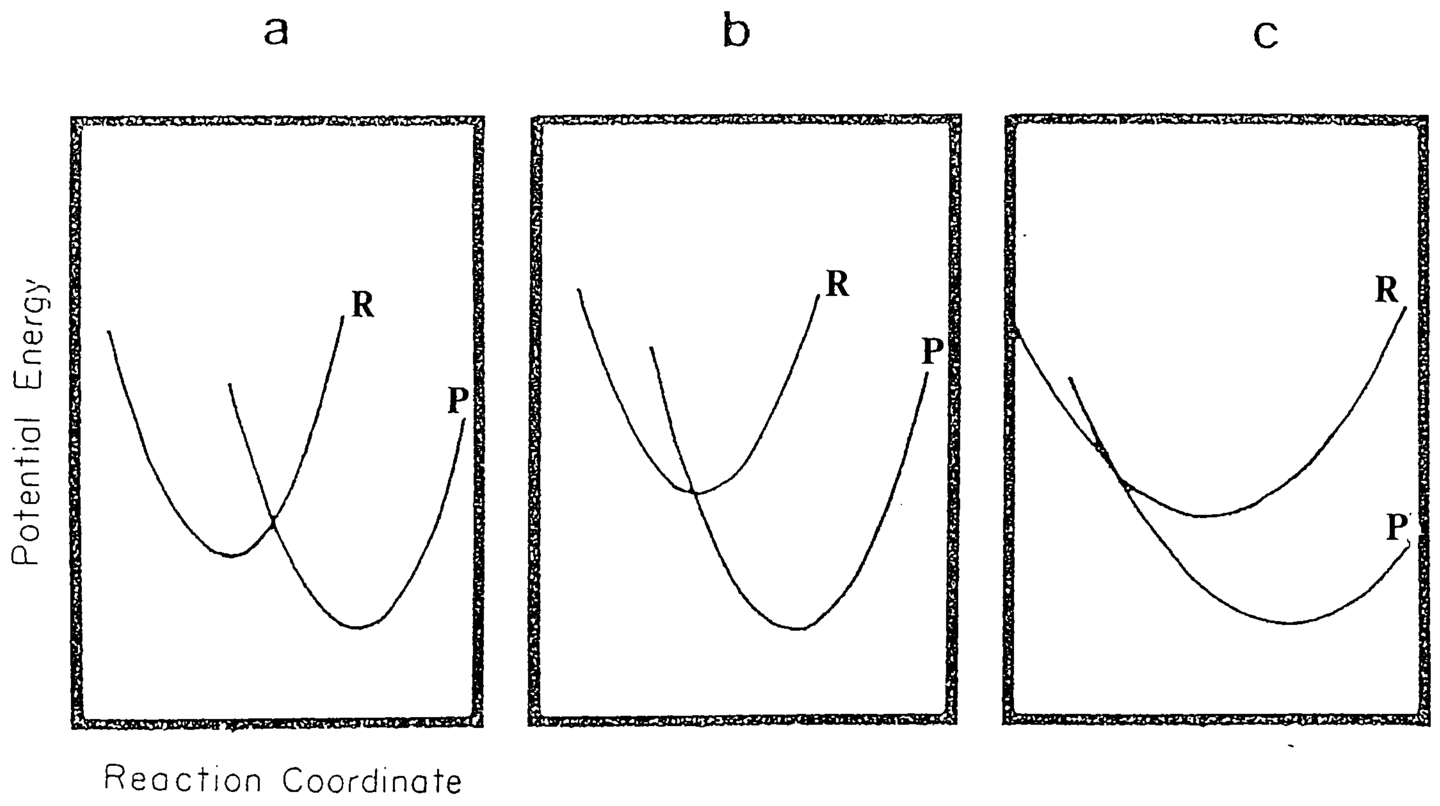

Fig.2 Schematic illustration of the potential energy curves for ET reaction in (a) the normal regime, (b) the barrierless regime, and (c) the inverted regime.

there is no barrier as in Fig.2b. Further lowering raises the point of intersection as in Fig.2c, and hence now raises the barrier, i.e., increases $\Delta G^{\neq}$.

The various assumptions involved in the Marcus treatment impose significant limitations. The estimation of inner sphere contributions by Marcus in the classical limit, considering only symmetric breathing modes, is probably a substantial oversimplification. In recent years, however, efforts by several workers[29,34] to consider the inner sphere quantum mechanically, unfortunately have met with only limited success. Particularly questionable is the separation of the reorganizational contributions into inner and outer solvation sphere values, with one handled in terms of discrete vibrational states and the other with dielectric continuum theory. Sacher and Laidler[22,35] have avoided this arbitrary division into inner and outer solvation contributions by considering changes in the total solvation energy as the radius of the inner coordination sphere changes, but this approach involves continuum concepts.

The collision number in the Marcus treatment of both the homogeneous and heterogeneous electron transfers has been estimated rather crudely. More refined estimates are available for homogeneous case in the literature relating to second order diffusion-controlled reactions (see Ref. 36).

It has been demonstrated[37] that in terms of the free energy of reaction, the theory is strictly applicable only to endothermic reactions in the high-temperature classical limit.

The assumption of negligible resonance stabilization in the activated state limits the Marcus treatment to redox sytems in which the interaction between the reacting ions and the electrode is weak.

In 1960, the earlier results were extended to include the contributions from the inner coordination shell. Discussion of the mechanism was in terms of potential energy surfaces and statistical mechanics.[38] A series of quntitative correlations between the homogeneous and electrochemical rates were predicted.[38,39] Subsequent work was devoted to seeing how general was the theoretical basis of these correlations.[15]

In 1957-1958, Hush[14] discussed ET at electrodes in terms of a charge density parameter and of arguments of a thermodynamic nature. In 1961, numerical results for the rate constants of a number of homogeneous and electrochemical ET were obtained.[40] Both the reorganization of the inner coordination shell and that of the external dielectric were included, the former in terms of an ion-dipole repulsive ligand field theory and the latter in terms of dielectric continuum theory. Hush[14] assumed that the resonance stabilization is sufficient for the transferred electron to become delocalized and distributed between the reacting ions in the homogeneous case or between the reacting ion and the electrode in the heterogeneous case. Hush then considered the fraction of the electron charge transferred to or from the reacting ions or electrode. The Marcus treatment is probably more appropriate for outer sphere ET electrode reactions in which the reacting central ion is separated from the electrode surface by its own inner coordination sphere as well as by a layer of adsorbed solvent molecules on the electrode surface. In instances where the reacting ion is specifically adsorbed, even with its inner coordination sphere intact, the Hush approach may become more appropriate. Under such circumstances, however, a bridge mechanism may need to be considered.

3.3 Quantum Mehanical Treatment of Electron Transfer

In parallel with these developments, Levich[17,21,41] and Dogonadze,[42,43] in 1959, performed the first entirely quantum mechanical calculation for nonadiabatic, homogeneous outer-sphere ET reactions. The first order time-dependent perturbation theory was used to describe the time evolution of the initially prepared zero order states. This represents the first in-depth treatment of non adiabatic ET reactions. Levich, Dogonadze, Kuznetsov and Chizmadzhev[18,19,44,45] later extended their treatment to ET at electrodes. In Ref.18, the totally degenerate Fermi gas model was used to describe the state of the electrons in the electrode and in Ref.19, an integration over the energy spectrum was performed, taking into account of the Fermi distribution of the electrons over a range of energy. Later, this theory was extended to other processes at semiconductors and thin semiconductor films.

Levich, Dogonadze, and Kuznetsov (LDK) considered the reacting ion with its inner coordination sphere as a frozen system, which does not contribute in any way to the activation process. The potential energy of the electron in this frozen system, however, depends on the polarization of the solvent near the ion. Since the molecules of the solvent are in continuous thermal movement, the polarization $\overline{P}$ of the solvent surrounding the ion fluctuates with time until a state of polarization is reached where a radiationless ET can take place between the ion and electrode by tunneling. After the ET, the polarization of the solvent surrounding the ion is the same as the polarization prior to the transfer and then decays as the system reverts to the equilibrium polarization of the final state.

The electrode reduction current is written by LDK in the general form

$$i = e\int dx \int d\varepsilon \; C(x)n(\varepsilon)\rho(\varepsilon)W(\varepsilon,x), \tag{13}$$

where C(x) is the concentration of the reacting ions at a distance x from the electrode surface, $n(\varepsilon)$ is the Fermi distribution function, and $\rho(\varepsilon)$ is the electron density of states in the metal. $W(\varepsilon,x)$ is the transition probability of the system to pass from the initial to the final states. LDK assume that the ET probability is the highest when the reacting ion is at a distance x_o from the electrode surface. The integral over x can then be removed and Eq.13 becomes

$$i = eC(x_o)\int n(\varepsilon)\rho(\varepsilon)W(\varepsilon,x_o)d\varepsilon. \tag{14}$$

According to first order perturbation theory, the transition probability of the system from the initial state i in the mth level to the final state f in the nth level is

$$W_{if} = \frac{2\pi}{\hbar}\sum_{n}\left|\int \psi^{*}_{fn}\, v\, \psi_{im} dv\right|^{2} \delta(E_{im} - E_{fn}), \tag{15}$$

where v is the perturbation parameter, δ is the Dirac delta function, and ψ_{fn} and ψ_{im} are wavefunctions of the final state in the level n and the initial state in the level m, with corresponding energies of E_{fn} and E_{im}. The Franck-Condon principle is assumed to apply to this system. Further, by using the Born-Oppenheimer approximation to separate the electronic and heavy particle wavefunctions and the Condon approximation, which argues the gradual monotonicity of the electronic matrix element, Eq.15 can be written as

$$W_{if} = \left(\frac{2\pi}{\hbar}\right) L^2 \sum_n \left| \int \phi^*_{fn}(q)\phi_{im}(q)\,dR \right|^2 \delta(E_{im} - E_{fn}), \qquad (16)$$

where L is the electronic matrix element given as

$$L^2 = \left| \int \varkappa^*_{fn}(r,R)\, v \varkappa_{im}(r,R)\,dr \right|^2, \qquad (17)$$

where $\varkappa$ is the electronic wavefunction, r is the electron coordinate, R is the inter-reactant coordinate, ϕ is the solvent wavefunction, and q is the solvent normal coordinate. The thermally averaged transition probability W in Eq.14 involving a statistical averaging over all initial states is given as

$$W = \sum_m \rho(\varepsilon_m) W_{im} , \qquad (18)$$

where $\rho(\varepsilon_m)$ is the Gibbs function.

The Hamiltonian of the heavy particle system needed to solve the solvent matrix element in Eq.16 is written by LDK as

$$H = H_s + \varepsilon_{el}(q) \qquad (19)$$

where H_s is the solvent Hamiltonian and $\varepsilon_{el}(q)$ is the energy of the electronic subsystem, which depends on the solvent coordinates. The LDK treatment considers the solvent to be a dielectric continuum, in which thermal fluctuations produce a set of standing polarization waves whose frequency spectrum can be approximated by a single characteristic angular frequency ω_o to be

$\sim 10^{12}$ rad/sec for water, corresponding to the Debye dielectric relaxation frequency. This model yields a Hamiltonian identical with the Landau-Pekar Hamiltonian obtained for polarons in crystals

$$H_s = \sum_k \frac{\hbar\omega_o}{2} \left(q_k^2 - \frac{\partial^2}{\partial q_k^2} \right) \tag{20}$$

where q_k are the dimensionless normal coordinates of the solvent oscillators.

It is further assumed[46] that the change in energy of the electronic subsystem due to changes in the solvent coordinates, is a linear function of the displacement, i.e.,

$$\Delta\varepsilon_{el} = \varepsilon_{el}(q_k) - \varepsilon_{el}(q_k^o) = \sum_k \left(\frac{\partial \varepsilon_{el}}{\partial q_k} \right)_{q_k = q_k^o} (q_k - q_k^o), \tag{21}$$

where q_k^o is the equilibrium solvent coordinate. From equations 20 and 21 the complete Hamiltonian for the heavy particle subsystem can be obtained.

Using harmonic oscillator wavefunctions, the thermally averaged transition probability is then solved to yield

$$W = \frac{2\pi}{\hbar^2} L^2 I_M(z) \exp\left[-\left(\frac{\hbar\omega_o M}{2kT} \right) - z \cosh\left(\frac{\hbar\omega_o}{2kT} \right) \right], \tag{22}$$

where I_M is a Bessel function of Mth order, and

$$M = \frac{(J_f - J_i)}{\hbar\omega_o}, \tag{23}$$

and

$$z = \frac{1}{2}\,\mathrm{cosech}\left(\frac{\hbar\omega_o}{2kT}\right)\sum_k\left[(q_k^o)_i - (q_k^o)_f\right]^2, \tag{24}$$

where J_i and J_f are the equilibrium energies, and $(q_k^o)_i$ and $(q_k^o)_f$ are the equiilibrium solvent coordinates of the initial and final states, respectively.

The general solution can be simplified for two limiting cases. In the high temperature limit, i.e. $kT >> \hbar\omega_o$, equation 22 reduces to

$$W = \left(\frac{\pi}{\hbar E_s}\right)^{1/2} L^2 \exp\left[-\frac{(J_f - J_i + E_s)^2}{4E_s kT}\right] \tag{25}$$

where E_s is the solvent reorganization energy and is given by

$$E_s = \left(\frac{\hbar\omega_o}{2}\right)\sum_k\left[(q_k^o)_i - (q_k^o)_f\right]^2 \tag{26}$$

The physical process involved in the high temperature case is shown in Fig.3a, where the energy-solvent coordinate profile is schematically presented. Here, the energy of the initial system changes due to solvent polarization fluctuations until the solvent configuration attains the coordinate q^*. At this point, a radiationless ET occurs. Subsequently the polarization fluctuation decays to produce the final state in the equilibrium configuration.

On the other hand, in the low temperature limit, i.e., $kT << \hbar\omega_o$, Eq.22 reduces to

$$W = \frac{2\pi(L^2)}{\hbar^2\omega_o\left[(J_f - J_i)/(\hbar\omega_o)\right]!}\left(\frac{E_s}{\hbar\omega_o}\right)^{J_f - J_i/(\hbar\omega_o)} \exp\left[-\frac{E_s}{\hbar\omega_o}\right]\exp\left[-\frac{J_f - J_i}{kT}\right] \tag{27}$$

The physical process involved in this case is shown in Fig.3b. This situation involves a quantum mechanical tunneling transition

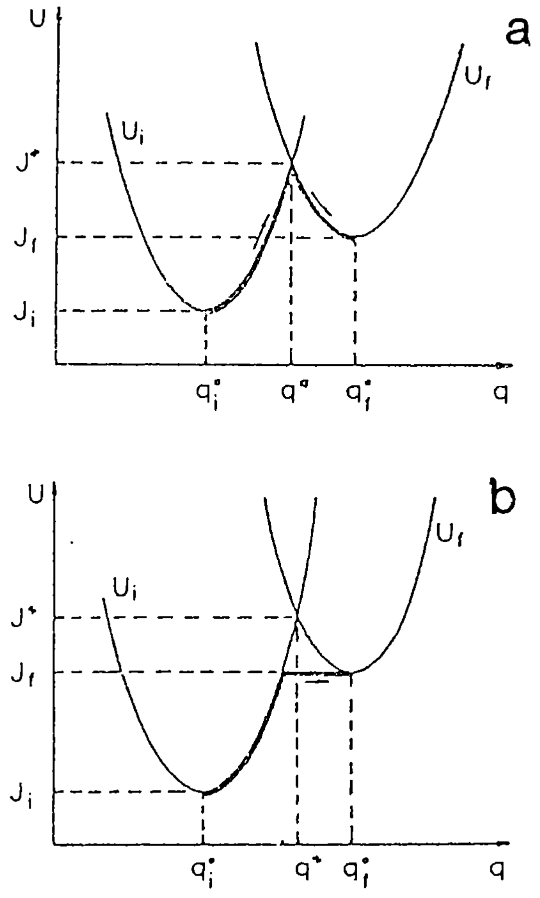

Fig.3 Outer sphere ET according to the LDK model.
(a) High Temperature behaviour ($\hbar\omega_o \ll kT$). (b) Low Temperature behaviour ($\hbar\omega_o \gg kT$). Ordinate: energy of electron; abcissa: generalized solvent polarization coordinate.

from the initial state to the equilibrium configuration of the final state.

Using the transition probability obtained for the high temperature limit in Eq.14 and integrating gives the exchange current density

$$i_o = k\bar{\rho} \left(\frac{\pi}{\hbar^2 kTE_s}\right)^{1/2} L^2 \exp\left[-\frac{E_s}{4kT}\right] \exp\left[\frac{V_{rev}\beta e}{kT}\right] \qquad (28)$$

where $\bar{\rho}$ is an effective density of states, V_{rev} is the reversible electrode potential, and β is the transfer coefficient.

The description of the solvent polarization waves and the consideration of only a single effective frequency ω_o in the early papers of the LDK group$^{18-21}$ are at best only a coarse approximation. Even within this simple model, Schmickler and Vielstich^{28} have questioned the appropriateness of using a value for ω_o corresponding to the Debye dielectric frequency and have pointed out that ω_o probably changes appreciably in the vicinity of the ions.

However Dogonadze et al$^{24,47-49}$ have made a sustained effort to refine the solvent model and have taken into account both local contributions (single dipoles performing orientational vibrations at a limiting frequency ω_o) and nonlocal contributions (interactions of polarization at different points in space) to the potential energy of the solvent. The latter effect is considered in terms of space correlation functions of the dipole moments of solvent molecules. The Hamiltonian obtained from this model accounts for dispersion effects in both frequency and momentum space and has the general form

$$H_s = \sum_{ik} \frac{\hbar\omega_i(k)}{2} \left[q_k^2 - \frac{\partial^2}{\partial q_k^2}\right] \qquad (29)$$

where $\omega_i(k)$ is complex and has a spectrum of values depending on the correlation functions. Vorotyntsev et al[50,51] have solved for the transition probability for an ET process, using the Hamiltonian given in Eq.29, without taking into consideration any contribution from the inner cordination sphere.

The LDK treatment does not include any contribution from the inner solvent sphere. Schmickler and Vielstich,[28] Kestner et al,[34] Hale,[52] and Bockris et al[53,54] have pointed out the importance of taking such effects into account. This has been done in Marcus's treatment.[11,23] Dogonadze[24] and Vorotyntsev et al,[55-57] however, advocate the view that the degrees of freedom for which $\hbar\omega >> kT$ take part only in the transfer process in a quantum mechanical sense (tunneling) and their effects are manifested in only the pre-exponential factor, whereas degrees of freedom with $\hbar\omega << kT$ take part in the activation process. Since most of the stretching frquencies in the inner solvent sphere have $\hbar\omega >> kT$, they do not contribute to the activation process according to these authors. Dogonadze and Kuznetsov[56] have considered the effect of inner sphere degrees of freedom with $\hbar\omega \cong kT$ and have shown that the transition probability W_{if} is decreased by a factor that depends on the frequencies and normal coordinates of the inner coordination sphere modes.

3.4 Other Developments

A semi-classical formalism, in which the classical expressions for the intramolecular configuration change were corrected for nuclear tunneling effects was introduced by Sutin in 1962.[40]

Dewald[59] applied Marcus' continuum treatment to semiconductor electrodes. Gerischer[60] developed the theory of nonadiabatic electrochemical ET reactions at semiconductors. This approach was a statistical one. It takes into account that, owing to the thermal fluctuations in the solvent, there is a statistical distribution of the electronic states, corresponding to the oxidized and the reduced forms of the reactants. Gamow's formula was used to calculate the probability of electron tunneling. For an entirely classical system, this approach enables the correct value of the activation energy to be calculated but not the pre-exponential factor, since the Gamow formula is applicable only for the description of the tunneling through the time-independent potential barriers.

The question of possible dielectric saturation effects on the interionic interaction of Fe^{+2}-Fe^{+3} ions was examined by Laidler,[61] who also considered, with Sacher,[35] effects on the reaction rate due to change in ion size during the reaction.

During the course of these theoretical investigations, a number of stimulating qualitative proposals of a more chemical nature were made. One of the major developments was the demonstration by Taube & Myers[62] and later by Halpern,[63] Sutin[33] and their co-workers that in certain cases, ET reactions occur via bridged intermediates. Halpern & Orgel[64] investigated theoretically, the electronic aspects of transfer of an electron from one part of the intermediate to the other and discussed the role of conjugated bridging groups.

Intramolecular electron transfers have been discussed by McConnell.[65] Information about these transfers has been derived from spin resonance studies of molecules on which an odd electron has two or more stable sites.

In the 1970s various quantum mechanical aspects of the ET problem were treated in detail[24,34,56,66-71] and *ab initio* molecular orbital calculations of exchange rates were initiated.[72,73] Major advances in the application of the radiationless transition formalism to the ET processes were made, culminating in an elegant treatment in which the electron donor, electron acceptor, and the surrounding solvent were treated as a "supermolecule".[74] Much of the theoretical work of this period was directed towards explaining the distance and temperature dependence of the ET processes in biological systems.[75-79]

At the same time, a growing body of experimental evidence[80-83] indicated the need for revisions to the classical and quantum mechanical treatment of highly exothermic reactions. Although there has been much discussion of this problem and progress has been made,[67,68,83-85] many questions still remain. Despite the shortcomings of the theories in the highly exothermic region, there is general agreement concerning the treatment of thermoneutral and moderately exothermic ET reactions.

The study of the influence of dynamical effects on ET reactions has been the mainstay of most theoretical and experimental investigations on ET in the eighties. We discuss the developments in this direction in the next chapter.

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CHAPTER 4

THE ROLE OF SOLVENT DYNAMICS IN ELECTRON TRANSFER

4.1 Introduction

Most fundamental research activities concerned with electrochemical[1] as well as homogeneous electron transfer (ET) processes[2,3] have emphasized the importance of reactant structure and intermolecular (or reactant-electrode) interactions to the observed kinetics. Recently, however, the role of the solvent medium has come under increasing scrutiny. Besides the well-known influence of the solvent on the barrier height and reaction thermodynamics, a number of recent theoretical[4-12] and experimental studies[13-20] have presented evidence pointing to the additional importance of solvent *dynamics* to the nuclear barrier-crossing frequency, ν_n. The latter studies have encompassed examinations of solvent-dependent exchange kinetics in both electrochemical[13,14d,15,16] and homogeneous-phase environments.[14,15,17,18] The central concept of solvent `friction' whereby the collective solvent motion necessary to surmount the activation barrier slows the rate below that expected from transition state theory (TST) has spawned a myriad of theoretical treatments that attempt to describe the effect of solvent dynamics. The ensuing interplay with experiment has considered chemical systems ranging from highly activated thermal reactions to ultrafast photoinduced processes where the solvation dynamics alone determines the reaction time scale.

In this chapter, we review the theoretical, experimental, and computer simulation studies of the dynamical solvent effects on ET reactions. Several reviews that have appeared recently provide a current status report on this area.[20-24] The focus of this chapter is rather different, with emphasis on major strides on the theoretical front in understanding the solvent dynamical effects on ET reactions, particularly, those features which we feel are most relevant to the development of our rate theory for the transfer of an electron from an ion in a polar solvent to a metal electrode in contact with it.

4.2 Theory of Electron Transfer

4.2.1 The Reaction Coordinate

Any theoretical treatment of a chemical reaction, identifies what is known as the reaction coordinate. In usual chemical reactions, it is rather easy to identify the reaction coordinate. On a simplistic level, it is some bondlength or bond angle, while a more detailed theory would identify it with a coordinate, specifying the state of the system along the minimum energy path on the potential energy hypersurface connecting the reactant configuration with the product one, which measures the progress of the reaction.

In an electron transfer reaction, occuring in a liquid, what may be identified with the reaction co-ordinate? This has been investigated by Calef and Wolynes[7a] and others. For the electron transfer, assuming that the donor and acceptor are held fixed at a given distance from one another, one may write the appropriate Hamiltonian as

$$H = (\epsilon_a + Q_a)n_a + (\epsilon_b + Q_b)n_b + V\,(c_a^+ c_b + c_b^+ c_a) + H_{solv} \qquad (1)$$

The above Hamiltonian is written in the second quantized notation. $|a\rangle$ is an orbital on the donor and $|b\rangle$ is an orbital on the acceptor, invloved in the electron transfer. ϵ_a and ϵ_b are their energies. $c_a(c_b)$ and $c_a^+(c_b^+)$ are the corresponding annihilation and creation operators and n_a and n_b the occupation number operators. V is the hoppping matrix element, responsible for the transfer of the electron. In the above, Q_a and Q_b are the shifts in the energies of the two orbitals $|a\rangle$ and $|b\rangle$ caused by the polarization of the solvent. Explicitly one may write them as $Q_i = -\int \bar{D}_i(\bar{r}).\bar{P}(\bar{r})d\bar{r}$, where $\bar{D}_i(\bar{r})$ would be the "bare" electric induction field around the reactant complex, if the electron was in the ith orbital (i = a or b) and $\bar{P}(\bar{r})$ is the polarization vector of the solvent, at $\bar{r}$. The above Hamiltonian is equivalent to the one considered by Calef and Wolynes. The difference in the shifts of the two orbital is

$$Q = Q_a - Q_b \qquad (2)$$

$$= \int [\bar{D}_b(\bar{r}) - \bar{D}_a(\bar{r})].\bar{P}(\bar{r})d\bar{r}. \qquad (3)$$

The electric fields in the above are long ranged, as a consequence of which the motion of many molecules in the neighbourhood of the donor and acceptor would be important in determining the value of Q. As the moleclues would be executing thermal motion, the value of Q would fluctuate randomly. Thus, one can have the crossings of the effective energies of the two orbitals, which are $(\epsilon_a + Q_a)$ and $(\epsilon_b + Q_b)$. The electron transfer, can occur without violating the Franck-Condon principle whenever these crossings happen. That is, for the ET to occur, the polarization state of the solvent must be such that

$$\epsilon_a + Q_a - (\epsilon_b + Q_b) = 0$$

$$\text{i.e., } \epsilon_a - \epsilon_b + Q = 0 \qquad (4)$$

Thus Q has to attain the critical value $Q_c = \epsilon_b - \epsilon_a$. Therefore a very plausible candidate for reaction coordinate is Q. This has been argued by Calef and Wolynes in considerable detail.

4.2.2 The Activation Energy

In order for the reaction to occur, Q should take the critical value Q_c. Clearly, there are a large number of polarizations, $\bar{P}(\bar{r})$ consistent with

$$\int [\bar{D}_b(\bar{r}) - \bar{D}_a(\bar{r})].\bar{P}(\bar{r})d\bar{r} = Q_c. \qquad (5)$$

The probability of attainment of this may be calculated using a free energy functional. This functional, which we will denote by $\mathcal{F}$, is the amount of thermodynamic work required to create a given state of polarization. The probability of attainment of polarization is then $e^{-\beta\mathcal{F}[\bar{P}(\bar{r})]}$, where $\beta = 1/k_BT$, k_B being the Boltzmann constant.

4.2.2.1 The Continuum Model

As the solvents of interest are all polar, their molecules have permanent dipoles. So the dynamics of attainment of the critical configuration is closely related to the subject of dielectric relaxation, which is determined by the frequency dependent dielectric constant, $\varepsilon(\bar{r},\bar{r}',\omega)$ for the system. In the continuum approach, one usually takes

$$\varepsilon(\bar{r},\bar{r}',\omega) = \varepsilon(\omega)\delta(\bar{r}-\bar{r}')$$

with $\varepsilon(\omega)$ having the Debye form

$$\varepsilon(\omega) = \varepsilon_{\infty} + \frac{\varepsilon_{0} - \varepsilon_{\infty}}{1 - j\omega\tau_{D}}$$

where ε_0 is the static dielectric constant, ε_∞ the limiting, high frequency dielectric constant, and τ_D the Debye relaxation time.

Assuming the solvent to be dielectric continuum, the free energy functional may be taken to be the Marcus functional[25]

$$\mathcal{F}[\bar{P}(\bar{r})] = \frac{1}{2}\,\frac{4\pi\varepsilon_{0}}{\varepsilon_{\infty}(\varepsilon_{0} - \varepsilon_{\infty})}\int P^{2}(\bar{r})\,d\bar{r} - \int \bar{P}(\bar{r}).\bar{D}(\bar{r})\,d\bar{r} \qquad (6)$$

where $\bar{D}(\bar{r})$ is the external electric field existing at $\bar{r}$. With such a free energy functional having quadratic dependence on $\bar{P}(\bar{r})$, it is easy to find that the dynamics of Q takes place on a potential that has a quadratic dependence on Q, in both the initial and final states. Further, in these two cases the parabolas have equal curvature. This is proved in a straightforward manner in the following. This fact is quite well known, though we have not been able to find the following proof in the published literature.

If the electron is in |a>, then the free energy functional is given by

$$\mathcal{F}_{a}[\bar{P}(\bar{r})] = \epsilon_{a} + \frac{1}{2\alpha}\int P^{2}(\bar{r})\,d\bar{r} - \int \bar{P}(\bar{r}).\bar{D}_{a}(\bar{r})\,d\bar{r} \qquad (7)$$

$$= \epsilon_{a} + \frac{1}{2\alpha}\int (\bar{P} - \bar{D}_{a}\alpha)^{2}\,d\bar{r} - \frac{\alpha}{2}\int D_{a}^{2}(\bar{r})\,d\bar{r} \qquad (8)$$

where

$$\alpha^{-1} = 4\pi\varepsilon_{0}\varepsilon_{\infty}/(\varepsilon_{0} - \varepsilon_{\infty}).$$

As our interest is in Q, which is our reaction coordinate, we would like to write the above as $\mathcal{F}_a = V_a(Q)$ + other terms, where other terms account for motions perpendicular to the reaction coordinate. $V_a(Q)$ is the minimum of $\mathcal{F}_a$, for that particular value of Q, and may hence be defined by

$$V_a(Q) = \min \mathcal{F}_a[\bar{P}(\bar{r})],$$

subject to $\int P(\bar{r}).\Delta\bar{D}(\bar{r})\, d\bar{r} = Q$, where $\Delta\bar{D}(\bar{r}) = D_b(\bar{r}) - D_a(\bar{r})$.

Now let $\bar{P}'(\bar{r}) = \bar{P}(\bar{r}) - \alpha\, \bar{D}_a(\bar{r})$. (9)

Then, we can write

$$\mathcal{F}_a = \epsilon_a - \frac{\alpha}{2}\int D_a^2(\bar{r})d\bar{r} + \frac{1}{2\alpha}\int \bar{P}'^2(\bar{r})d\bar{r} \qquad (10)$$

The condition, $\int \bar{P}(\bar{r}).\Delta D(\bar{r})\, d\bar{r} = Q$, may now be expressed as

$$\int dr\, (\bar{P}'(\bar{r}) + \alpha\bar{D}_a(\bar{r})).\Delta\bar{D}(\bar{r}) = Q. \qquad (11)$$

Let $S_a = \alpha\int \bar{D}_a(\bar{r}).\Delta\bar{D}(\bar{r})\, d\bar{r}$ (12)

Then the condition becomes $\int dr\, \bar{P}'(\bar{r}).\Delta\bar{D}(\bar{r}) = Q - S_a$. (13)

$\mathcal{F}_a$ in Eq.(10) has to be minimized with the condition given by Eq.(13). Minimization of an integral subject to constraints is a problem dealt with by the calculus of variations; a Lagrange multiplier of the constraint to be evoked here (here, Eq.(13)) is combined with the function to be minimized, viz.

$$\frac{1}{2\alpha}\int \bar{P}'^2(\bar{r})d\bar{r} - m\left[\int d\bar{r}\, \bar{P}'(\bar{r}).\Delta\bar{D}(\bar{r}) - (Q - S_a)\right]$$

has to be minimized, where m is the Lagrange multiplier.

Extremisation of this gives

$$\bar{P}'(\bar{r}) = \alpha m\, \Delta\bar{D}(\bar{r}). \qquad (14)$$

m may be determined by using Eq.(14) in Eq.(13), which gives

$$m = (Q - S_a)/\left[\int d\bar{r}\ \Delta D^2(\bar{r})\ \alpha\right] \qquad (15)$$

Therefore $\bar{P}'(\bar{r})$ is given by

$$\bar{P}'(\bar{r}) = \frac{(Q - S_a)}{\int d\bar{r}\ \Delta\bar{D}^{\ 2}(\bar{r})}\ \Delta D(\bar{r}). \qquad (16)$$

This expression for $\bar{P}'(\bar{r})$ may be used to obtain $V_a(Q)$, the potential energy when the electron is in $|a\rangle$ as

$$V_a(Q) = \epsilon_a - \frac{\alpha}{2}\int D_a^2\ d\bar{r} + \frac{1}{2\alpha}\ \frac{(Q - S_a)^2}{\int d\bar{r}\ \Delta D^2} \qquad (17)$$

Now we define reorganization energy by

$$\lambda = \frac{\alpha}{2}\int d\bar{r}\ (\Delta D)^2. \qquad (18)$$

Then, one obtains

$$V_a(Q) = \epsilon_a - \frac{\alpha}{2}\int D_a^2\ d\bar{r} + \frac{(Q - S_a)^2}{4\lambda}. \qquad (19)$$

Similarly, if the electron is in $|b\rangle$, the corresponding potential energy is $V_b(Q)$:

$$V_b(Q) = \epsilon_b - \frac{\alpha}{2}\int D_b^2\ d\bar{r} + \frac{(Q - S_b)^2}{4\lambda}. \qquad (20)$$

Now, we can find the point of intersection of the two potential energy curves, $V_a(Q)$ and $V_b(Q)$. Defining $\tilde{Q} = Q - S_a$, and taking the shifting of the free energy axis such that the minimum of $V_a(Q)$ has the value 0, we may write

$$V_a(\tilde{Q}) = \tilde{Q}^2/4\lambda, \qquad (21)$$

$$V_b(\tilde{Q}) = \epsilon_b - \epsilon_a - \frac{\alpha}{2}\int (D_b^2 - D_a^2)\ d\bar{r} + \frac{[\tilde{Q} - (S_b - S_a)]^2}{4\lambda}. \qquad (22)$$

$$S_b - S_a = \alpha\int(\bar{D}_b - \bar{D}_a).\Delta\bar{D}\; d\bar{r}. \tag{23}$$

$$= \alpha\int \Delta D^2\; d\bar{r}, \tag{24}$$

$$= 2\lambda. \tag{25}$$

Thus

$$V_b(Q) = \epsilon_b - \epsilon_a - \frac{\alpha}{2}\int(D_b^2 - D_a^2)\; dr + \frac{(\tilde{Q} - 2\lambda)^2}{4\lambda}. \tag{26}$$

The first three terms on the right hand side of the above equation stand for the free energy change ΔG involved in the transfer of the electron from the orbital |a> to |b>. Hence

$$V_b(Q) = \Delta G + \frac{(\tilde{Q} - 2\lambda)^2}{4\lambda}. \tag{27}$$

Equating the expressions (21) and (27) for $V_a(Q)$ and $V_b(Q)$, we get the point of intersection to obey

$$\tilde{Q}^{\neq 2}/4\lambda = \Delta G + (\tilde{Q}^{\neq} - 2\lambda)^2/4\lambda. \tag{28}$$

Then $\Delta G - \tilde{Q}^{\neq} + \lambda = 0.$ (29)

In other words,

$$\tilde{Q}^{\neq} = \Delta G + \lambda. \tag{30}$$

The energy at this point is

$$\Delta G^{\neq} = (\Delta G + \lambda)^2/4\lambda, \tag{31}$$

which is the activation energy, so that going from a to b (see Fig.4) needs this amount of activation energy.

4.2.2.2 Molecular Models

Most investigations of `static' solvent effect have made use of the continuum model for the liquid. However, in reality,

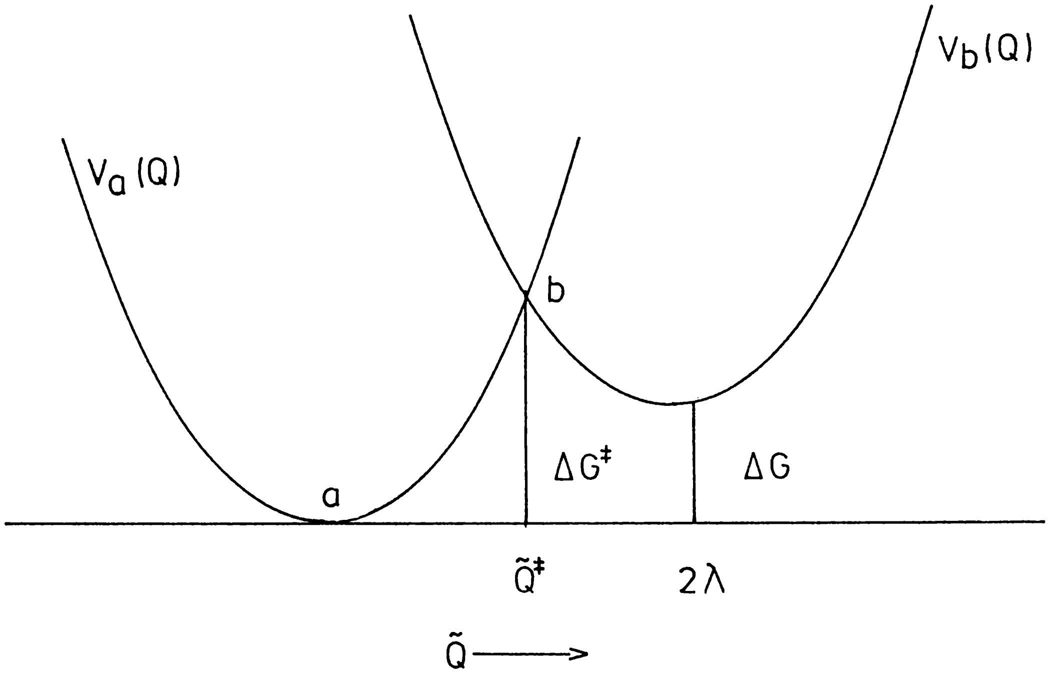

Fig.4 Free energies for the states a and b (electron on ion a) and b(electron on ion b) as a function of the reaction coordinate Q.

the solvent molecules surrounding the reactants will be ordered to some degree. This leads to significant deviations from the predictions of the continuum model. Even the simplest molecular theory needs such data as the form of the potentials between solvent molecules and between the solute and solvent as well as a method to calculate the structure of the fluid.

To date, the most successful of the molecular theories is the dynamical mean spherical approximation (MSA) model proposed by Wolynes[26] and extended by Rips et al[27] and Nichols and Calef.[28] In this theory, it is assumed that the molecular nature of the surroundings of a solute in a real solvent is roughly the same as that surrounding a hard-sphere ion or dipole in a hard-sphere dipolar liquid. Wolynes[26] demonstrated that linearized equilibrium theories of solvation[29,30] can be straightforwardly extended to treat dynamic situation by what amounts to the replacement of ε_o by $\varepsilon(\omega)$. In this approach, use of the full $\varepsilon(\omega,\overline{k})$ is actually avoided. Instead, effects of solvent molecularity are incorporated into the dynamics via the equilibrium solvation structure predicted by the linear model. The static structure in the idealized hard-sphere model is solved for in the closed form within the MSA model.[31] The influence of this structure on the dynamics is analysed in an approximate, semiempirical way with the solute-solvent size ratio and the experimental $\varepsilon(\omega)$ of the solvent under consideration used as input. Such a model accounts semiquantitatively for many of the features of the experimental data.[17,32] The solvation times predicted by this theory are uniformly greater than the continuum τ_L prediction.

Recently, the "Interaction Site Method" (ISM)[33] has become quite popular, wherein the intermolecular potentials are constructed from "sites", usually associated with the atoms in the molecule.

Chandra and Bagchi[34] have proposed a molecular theory of collective orientational relaxation of dipolar molecules in a dense liquid. Their work is based on a generalized, Smoluchowski equation (GSE) that includes the effects of intermolecular interactions through a mean-field force term. The effects of translational motion of the liquid molecules on the orientational relaxation is also included self-consistently in the GSE. They find that for a dipolar liquid of spherical molecules, the correlation function is biexponential. They also find that the wave-vector-dependent relaxation times depend strongly on the microscopic nature of the dense liquid. At intermediate wave vectors, the tranlational diffusion greatly accelerates the rate of orientational relaxation. Thus their study indicates that one must pay proper attention to the microscopic structure of the liquid while treating the translational effects.

4.2.3 Solvent Dynamics

The rate of attainment of the critical configuration must clearly depend on the ease with which molecules can move about, around the reactant complex. Just the way the statics has been examined in terms of continuum theory, it is possible to examine the dynamics too in the continuum approximation.

4.2.3.1 Continuum Models

With this model, it is possible to show that the transverse component of polarization could relax (rearrange) exponentially with a time constant τ_D while the longitudinal one with $\tau_L = \tau_D\varepsilon_\infty/\varepsilon_0$. τ_L is referrred to as time of longitudinal relaxation. Usually, τ_D, the Debye time is often associated with the time of re-orientation of a dipole in a liquid. τ_L arises in here, because of the collective nature of the relaxation. τ_L is much larger than τ_D. This happens because as the polarization relaxes, it is effective in partially screening the charges, causing the relaxation to be more efficient.

The homogeneous continuum model of solvation dynamics ignores, among other things, the details of solute-solvent interactions and the spatial and orientational order that are present in a dense dipolar liquid. Recently, Bagchi et al[35] and Castner[36] proposed an inhomogeneous dielectric continuum model to rectify some of these shortcomings. Two models that invoked a distance dependent dielectric constant, $\varepsilon(\bar{r})$, were studied. In the first model, $\varepsilon(\bar{r})$ was allowed to vary continuously as a function of distance $(\bar{r})$ from the polar solute molecule. The main effect of the dielectric inhomogeneity was to introduce relaxation times lower than τ_L and to make the decay non-exponential. In the second model,[36] a discrete shell representation of the position-dependent dielectric function was assumed. The advantage of this model is that it can be solved analytically for ionic solvation, although not for the dipolar case. For both the above models, the deviation of the average relaxation time from that predicted in a homogeneous continuum model increases as the dielectric constant and the length parameter, which specifies the rapidity of approach to the bulk dielectric value, increase. The simple continuum model result is recovered in the limit of very large solute-solvent size ratio. The merit of these inhomogeneous dielectric models is that they provide a simple and intuitive picture of solvation dynamics and at the same time incorporate some aspects of solute-solvent interactions.

4.2.3.2 Molecular Models

Molecular treatments would give a lower value for relaxation time. For going beyond the continuum model, several approaches have been proposed.

Tembe et al[37] and Newton[38] included molecular information by inclusion of a solvent shell complex around the reactants, and embedding this solvated reactant complex in a dielectric continuum. Calef and Wolynes,[7b] in an interesting paper, investigated the dynamics of charge transfer process with special emphasis on the molecular nature of the solvent. A detailed calculation of one-dimensional reaction free energy surface was made by using density functional theory of inhomogeneous liquid. The most important conclusion was that a continuum approximation can dramatically overestimate the reaction barrier. They found that the molecular theory prefactors are significantly lower than those calculated completely within a continuum model.

In addition to the original calculations of Calef & Wolynes,[7b,39] there have been recent calculations by Loring and Mukamel[40] and Wolynes.[26] The picture that emerges from all three calculations show three important points. First, the polarization is relaxing with different rates depending on the distance from the ion. The polarization relaxes more slowly near the ion than far away. Second, the relaxation is not given by a single exponential at any distance. Third, the non-exponential relaxation rate is occuring on a time scale between τ_D and τ_L. The results of Wolynes[26] suggest an explanation for the recent experiments.[41,42]

Recently, Bagchi, Chandra, and Fleming[43] have presented a molecular theory of the dynamical solvent effects on an outer sphere adiabatic ET reaction. This theory includes the microscopic descriptions of the structure and the dynamics of the solvent. They have argued that the usage of continuum model description to account for the dynamical solvent effects can be seriously flawed because the continuum model includes only the long wavelength relaxation processes whereas in ET, the intermediate wavelengths are quite important. Also, they have included, the effects of the translational modes of the solvent in the dynamics of electron transfer. They show that these translational modes can have a significant effect on the dynamics of ET; especially, they can significantly enhance the rate over that given by the rotational modes alone. An interesting prediction of this study is that the long time rate constant of an adiabatic barrierless ET reaction is equal to the average solvation rate of the newly formed charge transfer state.

4.2.4 The dynamics of Charge Transfer

The rate of charge transfer, as has been pointed out earlier, is determined by the dynamics of Q. In general, one expects Q to obey a Generalized Langevin Equation (GLE).[44,45] In the limit where solvent motion is overdamped, one may write down a Smoluchowski equation for it. We have seen that if the system is initially in the state a, the dynamics of Q is on the potential energy curve $V_a(Q)$ (Eq. 21). We now write the Smoluchowski equation using the following two facts:

(1) As t ⟶ ∞, the equation should have the solution $\exp(-V_a/kT)$.

(2) Q is a linear combination of polarization of the system (see Eq.3, defining Q). Any non-equilibrium polarization would decay exponentially with a rate constant $1/\tau_L$.[11]

Therefore, the equation is

$$\frac{\partial P(Q,t)}{\partial t} = D\,\frac{\partial^2 P}{\partial Q^2} + D\beta\,\frac{\partial}{\partial Q}\left[\left(\frac{\partial V_a}{\partial Q}\right)P\right] \qquad (32)$$

with the `diffusion coefficient' D equal to $2\lambda kT/\tau_L$.

It is easily seen that the above equation satisfies the two conditions. This equation is analogous to that of Sumi and Marcus,[11] who write the same kind of equation in terms of their variable X, which is proportional to our Q, or to that of Calef and Wolynes. Using such an equation, one can calculate the rate of crossing of the barrier. The deailed expressions are given in Calef and Wolynes. Calef and Wolynes have also considered the inertial effects.

Marcus and Sumi,[11] consider the effect of an intramolecular vibrational coordinate on the rate of the reaction. They analyse the diffusion-reaction equation, (in our notation)

$$\frac{\partial P}{\partial t} = D\,\frac{\partial^2 P}{\partial Q^2} + \frac{D}{kT}\,\frac{\partial}{\partial Q}\left[P\,\frac{\partial V}{\partial Q}\right] - k(Q)P \qquad (33)$$

where k(Q) is a Q dependent sink term, accounting for the fact that electron transfer may occur at certain values of Q. The rate is calculated from a time dependent procedure. They point out that the rate may be defined in different ways. Two definitions that they suggest are

$$\tau_a = \int_0^\infty dt\ P_e(t) \tag{34}$$

where $P_e(t)$ is the population remaining on the excited state surface at a time t after excitation and

$$\tau_b = \left\{\int_0^\infty dt\ tP_e(t)\right\} / \int_0^\infty dt\ P_e(t) \tag{35}$$

An interesting result of their work is that, as the inner sphere reorganizational energy increases, the rate constant assumes a power law dependence on τ_L such that it is proportional to $\tau_L^{-\alpha}$ where α is a fraction between 0 and 1.

Recently, Zhu and Rasaiah[46] have extended the results of Sumi and Marcus to the study of the dynamics of reversible ET reactions in Debye solvents by employing two coupled diffusion-reaction equations with the rate constants depending on the reaction coordinate. Their solutions reduce to those of Sumi and Marcus when the reverse reaction is ignored. They have compared their solutions with numerical solutions to the diffusion-reaction equations. They have also suggested a method for extending their results to non-Debye solvents.

Recently, Fonseca,[47] using the stochastic Liouville equation in a way similar to that introduced by Zusman[4,5] and used recently by Rips and Jortner[9] in their treatments of the ET reactive process in Debye solvents, has derived a general theoretical expression for the time evolution of the reactant's population, and therefore for the rate constant for an outer sphere ET reaction that can be applied to any solvent whose relaxation behaviour can be mimicked by a multiple-time exponential decay, i.e., non-Debye solvents. The theory is based on the common assumptions in the theoretical treatments of outer sphere ET reactions, i.e., the reactive potential is represented as two harmonic wells (one corresponds to the reactant's region and the other to the products); the ET occurs at a single point on the reactive potential surface and the solvent motion is overdamped. When the relaxation of the solvent can be described by a single-time exponential decay this theoretical treatment reduces to that used by Zusman or Rips and Jortner. The results of the theory are in excellent agreement with the results provided by a numerical simulation study in the limit where solvent relaxation is the rate limiting step.

4.3 Experimental Investigations

Experimental evidence for dynamical solvent effects on ET has come from several sources. Gennett et al[15] studied the kinetics of ET reactions involving metallocene complxes by varying both solvent and reactant properties. The experimental studies were interpreted with the statistical theories[3,4,6,7,37,48] of outer sphere ET eactions, and good agreement with theory was claimed. Subsequently, several studies[14c,16,18] have found dependence of ET rate on solvent polarization relaxation. McManis et al[18] found that for self-exchange reactions in metallocene complxes in associated/highly polar solvents, the observed reaction rate was faster than the rate of solvation as measured in time-dependent Stokes shift experiments. In early electrochemical studies of the heterogeneous oxidation of phenothiazine and 1,4-phenylenediamine, Opallo et al.[13] noted a correlation between k_{ET} and the longitudinal relaxation time of the solvents studied. For both compounds there was a distinct difference between the k_{ET}-τ_L correlations observed in hydrogen bonding versus non-hydrogen bonding solvents. In another early study, McGuire and McLendon[49] measured the ET quenching of ruthenium compounds by methylviologen in glassy glycerol matrices. Temperature-dependent quenching data were interpreted in terms of ET rates that varied with the solvent longitudinal relaxation time as $k_{ET} \propto \tau_L^{-0.6}$. Rips and Jortner[50] later quantitatively explained this fractional dependence on τ_L within the context of their theory of adiabatic ET and the non-Debye dielectric response of glycerol. In both these cases there does not seem to be a close relation between k_{ET} and τ_L.

A number of workers have also observed a simple correlation between the rates of photoinduced intramolecular ET and solvation times. Kosower and co-workers[51] and Su and Simon[52] have observed that $k_{ET} \sim \tau_L^{-1} \sim \langle\tau_{OBS}\rangle^{-1}$ for a variety of so-called "twisted intramolecular charge transfer" (TICT) reactions in alcohol solvents. Here $\langle\tau_{OBS}\rangle$ is the average observed solvation time. Barbara and co-workers[53] have observed analogous behaviour for bianthryl in polar aprotic solvents, except that in this case $k_{ET} \sim \langle\tau_{OBS}\rangle^{-1}$ but $\langle\tau_{OBS}\rangle^{-1} < \tau_L^{-1}$. Recently, they[54] have explored dynamic solvent effects on an ET reaction in the inverted regime of the Marcus theory. They have studied the nonradiative charge separation of betaine-30 using ultrafast spectroscopy. They have reported that the ET of the betaines offers an exciting opportunity to test the dramatic predictions of recent theoretical models that simutaneously include solvation and vibration dynamical degrees of freedom, such as the Jortner and Bixon[55] approach that treats the relevant vibrational degrees of freedom in the quantum limit, and the Sumi and Marcus[11] approach that treats the vibrational modes classically. They have shown that the kinetic behaviour of betaine-30 in slowly relaxing solvents can be accounted for by a hybrid of the Jortner/Bixon and Sumi/Marcus theories.

Michele-Beyerle and co-workers[56] compared the temperature dependence of TICT formation of two model compounds in the solvents, propionitrile and propylene glycol. They observed that the relative ET rates in these two solvents behaved as would be expected based on the adibatic-nonadiabatic theory of Rips and Jortner.[9] They were able to quantitatively model the observed temperature dependence by assuming that propionitrile and propylene glycol corresponded, respectively, to the theoretical nonadiabatic and solvent-controlled adiabatic regimes.

Not all data on TICT processes point to a simple relation between k_{ET} and solvent dynamics. The careful study of the TICT dynamics of dimethylaminobenzonitrile (DMABN) in alcohol solvents performed by Su and Simon[57] provides a good counterexample. These authors observed ET rates in DMABN that appeared to be correlated with, but much faster than, $<\tau_{OBS}>^{-1}$. Su and Simon interpreted this behaviour as indicating involvement of intramolecular vibrational dynamics within the framework of Sumi-Marcus theory. It is worth pointing with respect to the above studies that in some cases attainment of the TICT state requires large amplitude motion of the solute. This motion may involve (viscous) aspects of solvent-reaction coupling of a sort not considered in present theories.

Fawcett and co-workers[58] have analysed the dynamic solvent effects on the rate constants of both homogeneous and heterogeneous ET reactions on the basis of current models which consider the role of dynamic relaxation processes in determining the magnitude of the pre-exponential factor. They have described a statistical method for separating the effects of the solvent longitudinal relaxation time, τ_L from those of the solvent permittivity parameter, γ and applied it to 15 sets of experimental data for which results are available in at least four solvents. The degree to which the explained variation in the logarithm of the rate constant could be attributed to either of these effects varied all the way from 0 to 100% depending on the degree of reaction adiabaticity and the relative sizes of the inner and outer sphere components of the Gibbs energy of activation. They have analysed further, data for the limiting cases in which there is no τ_L dependence in the pre-exponentila factor or in which the pre-exponential factor is proportional to τ_L^{-1} to obtain the size-distance parameter and the components of the pre-exponential factor relevant to the encounter pre-equilibrium model. They have discussed these parameters with respect to current developments in ET theory.

Some of the most thorough studies of dynamical solvent effects on ET are the intermolecular electron-exchange measurements of Weaver and co-workers.[17] These researchers have measured self-exchange rates for couples such as $Co(cp)_2^{0/+}$ (cp is cyclopentadienyl) using both electrode half-reaction measurements as well as nuclear magnetic resonance (NMR) linewidth measurements of the homogeneous reactions. In polar aprotic solvents, the prefactor of the electron-exchange rates were observed to correlate reasonably well with τ_L^{-1} as a function of solvent. These authors are careful to point out that, in studies performed in different solvents, it is important to account for any solvent dependent changes in the free-energy barrier $\Delta G^{\neq}$ before looking for dynamical solvent effects. As mentioned earlier, dynamical effcts manifest themselves in the prefactor and can be confused or obscured by equilibrium solvation effects if changes in $\Delta G^{\neq}$ are ignored. Weaver and co-workers[17] also noted that there was some deviation between the effective solvation time scale inferred from the ET rates and the solvent longitudinal relaxation times. They also observed that k_{ET} was much greater in alcohols than would be expected based on τ_L (or $<\tau_{OBS}>$). Using the frequency-dependent friction approach of Hynes,[8] McManis and Weaver[18] found that inclusion of a relatively small amplitude rapid component in the dielectric response leads to a large enhancement in the frequency factor in excess of that expected for a single Debye response. The effect is particularly marked in alcohol solvents and accounts for a substantial fraction of the enhanced rates observed in these solvents. It is clear that great care must be exercised in relating the dielectric response of a solvent to the frequency factor of an ET reaction.

Most of the reactions studied earlier were either known to[15,16] or believed to[13,14] involve small or negligible inner shell barriers so that the overall activation energy was dominated by the outer shell component.In a recent study, Nielson and Weaver[19] have investigated the solvent dependent electrochemical kinetics of two cobalt clathrochelate couples, $Co(dmg)_3(BX)_2^{+/0}$, where X = fluorine or n-butyl, with the objective of ascertaining whether, and to what extent, overdamped solvent relaxation controls the barrier-crossing frequency for these reactions which involve substantial inner shell barriers. They have measured standard rate constants using phase-selective ac voltammetry at gold and mercury electrodes in six solvents: actonitrile, acetone, methylene chloride, benzonitrile, nitrobenzene and propylene carbonate. Although not without ambiguity, their results are in qualitative accord with the expectations of the Sumi-Marcus theory that solvent dynamics can provide a substantial contribution to nuclear barrier crossing frequency even for such reactions featuring significant inner shell barriers. These results therefore add to the growing body of evidence indicating that solvent friction can play a significant role in determining the kinetics of outer sphere ET processes at electrodes as well as in homogeneous solution.

4.4 Computer Simulation Studies

Recently, Warshel and Chu[59] have considered the importance of tunneling corrections. Theorists have also been able to carry out simulations of the liquids that take account of tunneling, using path integral Monte Carlo methods. McCammon and his coworkers[60] have studied the quantum paths involved in the rearrangement of the inner sphere in an ET reaction. Recently, Chandler and others[61] have studied the solvent nuclear tunneling effect on the aqueous ferrous-ferric ET reaction through computer simulation. They used the path integral Monte Carlo techniques to evaluate the role of quantum dynamics in the more distant solvent molecules. They have concluded that the motions of the hydrogen atoms in the solvent can be dominated by tunneling. Measured isotope effects on the rates agree with this result.

4.5 Conclusion

In this chapter, we have summarized the modern theoretical methods, computer simulations and recent developments on the experimental side that are available to help understand the solvent dynamical effects on ET reactions. This is still a vigorous and growing field with growth in two distinct directions. First, more realistic models of the solvent structure are possible due to both theoretical advances and advances in computer technology. Second, sophisticated model systems are yielding insight into the fundamental behaviour of the charge transfer, especially in regimes where our simple ideas on the separation of time scales are not valid. Connecting these two approaches should provide means of understanding and predicting solvent effects on ET reactions.

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CHAPTER 5

ELECTROCHEMICAL ELECTRON TRANSFER: A DIFFUSION-REACTION EQUATION APPROACH

5.1 Introduction

The theory of electron transfer (ET) from a metal electrode to an ion, surrounded by a polar solvent has been the subject of several theoretical investigations.[1-11] These investigations take their cue from the work on homogeneous ET reactions. The theory of homogeneous ET was developed mainly by Marcus[1,2] and Levich, Dogonadze and Kuznetsov (LDK).[3-5] Marcus investigated the adiabatic limit of the process using a continuum description of the solvent polarization. He was concerned with the calculation of activation energy. Subsequently, LDK presented a theory of nonadiabatic ET reactions in which the electronic process rather than the polarization relaxation of the solvent controls the rate of the reaction. Certain aspects of the problem have been explored by Bockris et al.[6] Recent investigations attempt to include the microscopic models for liquids. It has been shown that the pre-exponential factor in the Arrhenius rate expression depends on τ_L, the time of longitudinal relaxation of the solvent polarization.[12]

5.2 Survey of Existing Theories

The dynamics of ECET has been the focus of interest of several recent theoretical investigations. Schmickler[8] has suggested a theory for adiabatic ET reactions at metal electrodes.

His approach is similar to that of the Levich and Dogonadze[13] theory for nonadiabatic reactions. Schmickler's Hamiltonian is an extension of the Newns-Anderson Hamiltonian[14] to the electrochemical context. It has a continuum of one electron states of the metal coupled to an ionic orbital, which in turn is coupled to the solvent. The harmonic oscillators are treated classically. The sum of the electronic and potential energy of the harmonic oscillators is looked at and for certain values of the parameters, it is a double well type. Schmickler calculates the height of the barrier to be overcome in going from one minimum to the other and writes the rate as $A\exp-\{\text{barrier height}/k_BT\}$. An explicit expression for the barrier height is obtained in terms of the parameters occuring in the Hamiltonian. The pre-exponential factor, A is not derived explicitly, but plausible forms for it are suggested.

Sebastian and Ananthapadmanabhan[10] have investigated the dynamics of adiabatic ET reactions at metal electrodes using the Hamiltonian suggested by Schmickler.[8] They show that in the adiabatic limit the problem reduces to that of the dynamics of a single variable, Q(t), the change in the energy of the ionic orbital caused by its interaction with the solvent. This variable is defined as the reaction coordinate for the problem. They show that in certain limits, this variable obeys a stochastic integral equation. In certain cases, this equation can be solved by converting it into a stochastic differential equation, and thus the rate of ET can be obtained from this. Thus, they obtain an explicit expression for Schmickler's pre-exponential factor A. The expression contains certain correction factors to the one suggested by Schmickler.

Electrochemical electron transfer has been analysed by Morgan and Wolynes.[9] They consider the dynamics to take place on a continuum of potential energy surfaces. The electronic states are grouped into two and labeled as α_I and α_e: those in which the electron is on the ion and those in which it has been transferred to the electrode. They write a master-Smoluchowski equation for $\rho_i(x,t)$, where i = I or e, the probability that the system may be found in the state I (electron on the ion) or e (electron on the electrode). This equation is simplified to obtain a Smoluchowski equation with a sink, which they have solved approximately to obtain the expression for the rate constant. Subsequent sections contain more details about this work.

Recently, Sebastian[11] has investigated the role of electronic excitations of metal in ECET. Most treatments in the literature have not been able to account for the infinity of potential energy surfaces. Sebastian considers the Hamiltonian investigated by him earlier.[10] He suggests an approach in which the electron-hole excitations are treated as bosons. Using this, he derives an expression for the rate, which accounts for both the solvent dynamics and electron-hole excitations. His analysis amounts to a solution of the problem of calculating the electronic transmission coefficient $\varkappa$, for a continuum of crossing diabatic surfaces.

5.3 General Remarks and Outline

In this chapter, we develop a simple diffusion-reaction equation approach to the problem of electrochemical electron transfer (ECET). As has already been pointed out earlier, the dynamics of ECET, has been analysed by Schmickler,[8] Morgan & Wolynes,[9] Sebastian & Ananthapadmanabhan[10] and Sebastian.[11] References 8 and 10 consider only the adiabatic limit, while Ref.11 starts from the adiabatic limit and accounts for nonadiabaticity due to the continuum of levels in the metal by a bosonization procedure. The approach of these papers have been further developed by Gorodyskii *et al.*[15] Morgan and Wolynes[9] do not account for electronic excitations in the metal, arising in the dynamics. They have written down and analysed a master-Smoluchowski equation, to obtain the rate of ECET.

In this chapter, we give a simple description for the process. In comparison with the approach of Morgan and Wolynes, the physical picture is clearer and it leads, naturally to the diffusion-reaction equation. This diffusion-reaction equation is then analysed in an exact fashion, to obtain the rate.

5.4 Our Approach

The goal of the present study is to investigate the problem of electrochemical electron transfer using a diffusion-reaction equation approach. We consider the case where *electron transfer is the rate determining step, rather than diffusion from the bulk*. We treat the reaction dynamics in the framework of a Smoluchowski equation. In such an approach, one encounters two problems. They are:

(1) Defining the rate constant. One can adopt several different, reasonable definitions.[16,17,18] Sumi and Marcus[16] in their theory of low-barrier ET reaction, defined two kinds of average survival

times, the first one being the customary "mean first passage time" defined by $\tau_a = \int_0^\infty P_e(t)dt$, where $P_e(t)$ is the survival probability. They introduced an average survival time τ_b of the second kind by $\tau_b = \int_0^\infty tP_e(t)dt/\int_0^\infty P_e(t)dt$, which detects the information contained by $P_e(t)$ in a time regime later than does τ_a. Bagchi[17] studied barrierless electronic relaxation in solution and found that the traditional definition of rate constant in terms of a steady flux across the reactive region was not applicable. Since the relaxation in the absence of a high activation barrier may depend strongly on the initial conditions, there may be strong dependence on the wavelength of the exciting light. Hence he introduced two different rate constants. The first one is the average rate constant, k_I, defined through

$$k_I^{-1} = \int_0^\infty P_e(t)dt,$$

where $P_e(t)$ is the population remaining on the excited state surface at a time t after the excitation. This rate constant is identical to τ_a^{-1} defined earlier. The second is the long time rate constant k_L, defined through the behaviour of the long time limit of $P_e(t)$,

$$k_L = -\lim_{t\to\infty} \frac{\partial}{\partial t} \ln P_e(t).$$

For an exponential decay, when $P_e(t) \sim e^{-kt}$, all the three rate constants, k_I (τ_a^{-1}), k_L and τ_b^{-1} are identical and equal to k. However, in general, decay of $P_e(t)$ is multi-exponential and the rate constants have different values.

(2) To calculate the above rate constants, one has to solve a partial differential equation, which in general, is difficult.

Our approach overcomes these two problems in a natural fashion. We imagine reactants being fed into the system (this is the actual situation for the electrochemical problem) so that a steady, time independent state shall be attained. The time independent state is governed by an ordinary differential equation and can be found easily. The rate constant can also be determined by the analysis of the steady state.

We consider an ion in solution, in the vicinity of an electrode. We take it to be at a fixed distance from the surface of the electrode. It has an orbital $|a\rangle$, which contains one electron that may be given to the electrode. For convenience we denote it as A^{2+} Let the energy of the orbital, when the ion is in vacuum (negative of the energy required to remove an electron) be ε_a^0. In the solvent, the energy required to remove an electron has an additional contribution, as the electron can interact with the polarization of the solvent. Let us denote by $\bar{D}_a(\bar{r})$, the bare electric field around the ion A^{2+}. Then, due to interaction with the solvent, the energy of the system is shifted by

$$-\int \bar{D}_a(\bar{r}).\bar{P}(\bar{r})d\bar{r},$$

where $\bar{P}(\bar{r})$ is the polarization vector at position $\bar{r}$ so that the energy of the system may be written as

$$\varepsilon_a^0 - \int \bar{D}_a(\bar{r})\bar{P}(\bar{r})d\bar{r} + E_{solv},$$

where E_{solv} is the energy of the solvent. If the electron is removed from the orbital, so that the ion is now A^{3+} then the energy of the system would be

$$-\int \bar{D}_b(\bar{r}).\bar{P}(\bar{r})d\bar{r} + E_{solv}.$$

Here $\bar{D}_b(\bar{r})$ is the bare electric field due to A^{3+} ion. Therefore, the energy of the orbital may be taken to be

$$\varepsilon_a^o - \int [\bar{D}_a(\bar{r})-\bar{D}_b(\bar{r})].\bar{P}(\bar{r})d\bar{r} .$$

We now put

$$\Delta\bar{D} = [\bar{D}_b(\bar{r})-\bar{D}_a(\bar{r})],$$

so that the energy of the orbital is

$$\varepsilon_a^o + \int \Delta\bar{D}(\bar{r}).\bar{P}(\bar{r})d\bar{r}.$$

This is for arbitrary polarization $\bar{P}(\bar{r})$ of the solvent. The energy of the orbital, when the solvent has the polarization $\bar{P}_a(\bar{r})$, which is the equilibrium polarization of the solvent for A^{2+}, is then given by

$$\varepsilon_a = \varepsilon_a^o + \int \Delta\bar{D}(\bar{r}) .\bar{P}_a(\bar{r})d\bar{r}.$$

Hence the energy of the ionic orbital for arbitrary polarization of the solvent is given by

$$\varepsilon_a + \int \Delta\bar{D}(\bar{r}) .\Delta\bar{P}(\bar{r})d\bar{r} \qquad (1)$$

where $\Delta\bar{P} = \bar{P}(\bar{r}) - \bar{P}_a(\bar{r})$. We write this as $\varepsilon_a + Q$, where

$$Q = \int\Delta\bar{D}(\bar{r}) .\Delta\bar{P}(\bar{r})d\bar{r}. \qquad (2)$$

The energy of the orbital when the ion is in solution is thus the sum of a constant (ε_a) and a randomly fluctuating quantity, Q ($=\int\Delta\bar{D}(\bar{r}) .\Delta\bar{P}(\bar{r})d\bar{r}$). As the average value of $\Delta\bar{P}(\bar{r}) = 0$, it is clear that $<Q> = 0$. The metal has all the orbitals having energy upto ε_F occupied (see Fig.5). We assume $\varepsilon_a < \varepsilon_F$ and the orbital $|a>$ on the ion A^{2+} to be occupied initially. The orbital $|a>$ interacts with the states of the metal, leading to a broadening of its energy by an amount Δ. However, as its energy is less than ε_F, resonance transfer of the electron to the metal is impossible. But as time passes, the value of Q changes randomly and the orbital energy, $\varepsilon_a + Q$ can cross the Fermi level. When this happens, there is the possibility of resonance electron transfer, producing A^{3+}at a rate Δ. This would continue as long as $\varepsilon_a + Q >$

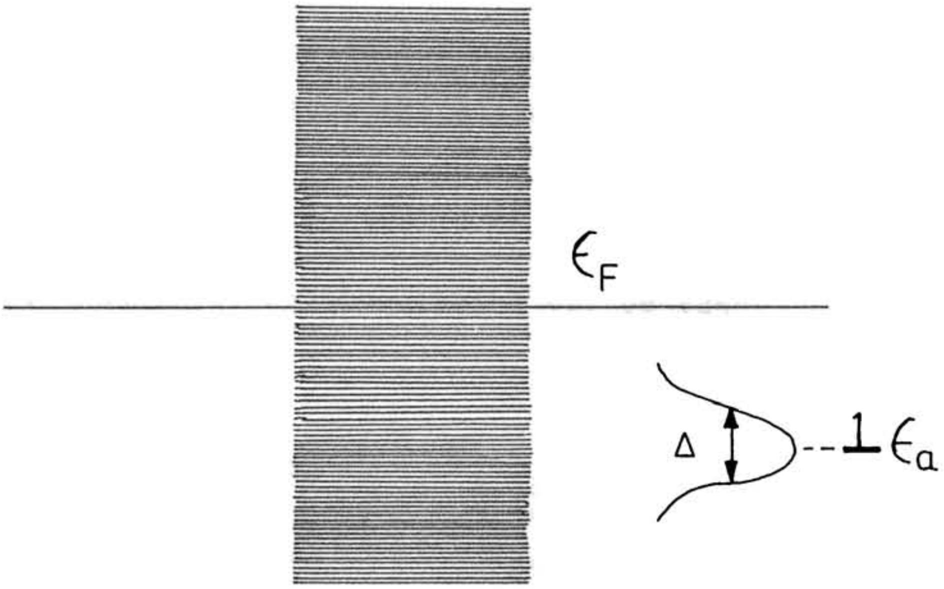

Fig.5 Energy of orbitals in the metal and on the A^{2+} ion. ϵ_a is the energy of orbital on the ion. Δ is the broadening caused by interaction with the metal.

ϵ_F, but would start in the reverse direction when the $\epsilon_a + Q$ falls below ϵ_F. Therefore, the dynamics of Q (or crossing of Fermi level by the effective orbital energy) plays an important role in ECET.

In the following, we put this picture of the process on a firm mathematical footing. In the following section, we analyse the electronic problem rigorously, bringing out the conditions under which the above picture of the process may be applied, while in sec.5.7, we give and analyse the diffusion-reaction equation.

5.5 Dynamics of the shift Q

From chapter 3, we know that Q may be taken to obey a Fokker Planck equation,

$$\frac{\partial P}{\partial t} = D \frac{\partial^2 P}{\partial Q^2} + \frac{D}{kT} \frac{\partial}{\partial Q}\left[P \frac{\partial V_a}{\partial Q}\right], \tag{3}$$

As in the case of homogeneous ET, $V_a(Q)$ may be obtained by minimising the free energy functional,

$$\mathcal{F}_a[\bar{P}(\bar{r})] = \epsilon_a^0 - \int \bar{P}(\bar{r}).\bar{D}_a(\bar{r})d\bar{r} + \frac{1}{2\alpha}\int P^2(\bar{r})d\bar{r} \tag{4}$$

The equilibrium polarization corresponding to A^{2+} is given by

$$\frac{\delta[\mathcal{F}_a(\bar{P}(\bar{r}))]}{\delta \bar{P}(\bar{r})} = 0. \tag{5}$$

This gives

$$\bar{P}(\bar{r}) = \alpha \bar{D}_a(\bar{r}). \tag{6}$$

The potential on which the dynamics of Q takes place may be obatined by minimising $\mathcal{F}_a[P(\bar{r})]$, subject to the constraint,

$$Q = \int \Delta\bar{D}(\bar{r}) \,.\Delta\bar{P}(\bar{r}) d\bar{r}. \quad (7)$$

This can be done as in Chap.4, to obtain

$$V_a(Q) = \frac{Q^2}{4\lambda} + \epsilon_a - \frac{\alpha}{2} \int D_a^2(\bar{r}) \, d\bar{r} \quad (8)$$

Shifting the free energy axis such that minimum of $V_a(Q)$ has the value 0, we may write,

$$V_a(Q) = Q^2/4\lambda. \quad (9)$$

In the above equation, the average of Q at time t, given by $\langle Q(t)\rangle = \int P(Q,t)QdQ$, satisfies $d\langle Q(t)\rangle/dt = -\langle Q(t)\rangle/\tau_L$, with a relaxation time τ_L for the coordinate Q given by $\tau_L = k_BT/D$. Therefore, τ_L^{-1} determines the rate with which P(Q,t) approaches thermal equilibrium distribution function determined by the potential V(Q). Because of the reaction, P(Q,t) at any time t can differ from the equilibrium distribution function.

In the following, we first introduce the problem in the elctrochemical context and show that Δ determines the rate of ET.

5.6 Dynamics of Electron Transfer

We consider A^{2+} in a polar solvent, kept in the vicinity of the surface of a metallic electrode. It has an occupied orbital $|a\rangle$ in it, which may give one electron to the electrode. This orbital interacts with the orbitals of the metal, as a result of which it is broadened into a resonance of small width. We assume the metal to be described by a one-electron Hamiltonian, the one electron eigen states of this Hamiltonian being denoted as $|k\rangle$. The energy of this orbital is ϵ_k. The metal has all the orbitals having energy less than the Fermi energy ϵ_F filled. As seen earlier, solvent fluctuations will change the energy of the orbital $|a\rangle$ in a time-dependent fashion by Q(t) and we denote it by $\epsilon_a(t) = \epsilon_a + Q(t)$.

The physical picture that we have of the ET is the following: The orbitals $|k\rangle$ of the metal are in constant interaction with the orbital $|a\rangle$ of the ion. Hopping from the ion to the metal can be caused by the hopping matrix elements V_{ka}. However, if the electron transfer is to take place to the orbital $|k\rangle$, $|k\rangle$ must initially be empty (i.e. $\epsilon_k > \epsilon_F$) and further $\epsilon_a(t) = \epsilon_k$, so that the ET to the electrode will happen when the ionic orbital, during its wandering in the energy space goes into the region above ϵ_F. However, as soon as it wanders into the region below ϵ_F, ET to the electrode would stop and it would now go in the reverse direction. This simple physical picture can be made quantitative by analysing the following Hamiltonian:

$$H_e(t) = \sum_{\sigma} \left\{ \epsilon_a(t) n_{a\sigma} + H_s + V \right\} \tag{10}$$

σ stands for spin. In this, the metal is described by a one electron Hamiltonian, H_s. Its one elctron eigen functions obey

$$H_s|k\rangle = f_k|k\rangle \tag{11}$$

The functions $|k\rangle$ form a continuum and are taken to be normalized according to $\langle k|k'\rangle = \delta(k-k')$. Note also that k stands for a collection of indices, as many as is required for specifying the states. V is the term in the Hamiltonian causing the electron transfer. We take it to be such that it causes only electron transfer, and does not mix metal eigen functions. i.e., $\langle k|V|k'\rangle = 0$, and $\langle a|V|a\rangle = 0$, but $\langle k|V|a\rangle \neq 0$. We denote $\langle k|V|a\rangle$ by $V(k,a)$ and $\langle a|V|k\rangle$ by $V(a,k)$. $n_{a\sigma} = C_{a\sigma}^{+}C_{a\sigma}$, where $C_{a\sigma}$ ($C_{a\sigma}^{+}$) is the annihilation (creation) operator for $|a\sigma\rangle$, and $n_{a\sigma}$ is the corresponding occupation number operator.

We assume that at the time $t = 0$, we start with the metal in a state with ionic orbital $|a\uparrow\rangle$ having one electron and the metal having all orbitals with $\epsilon_k < \epsilon_F$ filled. As our Hamiltonian has no spin flipping term, we can consider the dynamics of up and down spin electrons separately. So we do not specify the spin index anymore. We take the initial state to be $|I\rangle = |k_1,\ldots k_F,a\rangle$ which is a Slater determinant of all states with $\epsilon_k < \epsilon_F$ and the orbital $|a\rangle$.

The energy of the orbital $|a\rangle$, ϵ_a is changing with time, and hence is denoted by $\epsilon_a(t)$. The problem is to calculate $\langle n_a(t)\rangle$, the occupation number of this orbital at the time t, given that the state was $|I\rangle$ at the time $t = 0$.

As $H_e(t)$ is a one electron Hamiltonian, the evolution in time until t would lead to a Slater determinant of the orthonormal set

$$\left\{U(t,0)|k_1\rangle,\ U(t,0)|k_2\rangle\ ..\qquad U(t,0)|a\rangle\right\}$$

where $U(t,0)$ is the time development operator, obeying the equation

$$i\frac{\partial\ U(t,0)}{\partial t} = H_e(t)\ U(t,0); \qquad U(0) = 1 \qquad (12)$$

(Note that we have put $\hbar = 1$). With the above function, occupation number of |a> at the time t is

$$\langle n_a(t)\rangle = \int_{\epsilon_k<\epsilon_F} dk \left|\langle a|U(t,0)|k\rangle\right|^2 + \left|\langle a|U(t.0)|a\rangle\right|^2 \tag{13}$$

The calculation of the matrix element, U(t,0) is more convenient, if we switch over to the interaction picture. We define

$$\tilde{U}(t,0) = U_o{}^{+}U(t,0)U_o \tag{14}$$

where

$$U_o = \exp\left\{-i\int_0^t H_o(t_1)dt_1\right\} \tag{15}$$

with

$$H_o(t) = H_s + \epsilon_a(t)n_a. \tag{16}$$

Clearly

$$\left|\langle a|\tilde{U}(t,0)|k\rangle\right| = \left|\langle a|U(t,0)|k\rangle\right| \tag{17}$$

$\tilde{U}(t,0)$ obeys

$$i\frac{\partial \tilde{U}(t,0)}{\partial t} = \tilde{V}(t,0)\tilde{U}(t,0) \tag{18}$$

with

$$\tilde{V}(t) = U_o{}^{+}V\ U. \tag{19}$$

Taking the matrix elements of the Eq.(18) and introducing the resolution of identity $|a\rangle\langle a| + \int dk\ |k\rangle\langle k|$, between $\tilde{V}(t)$ and $\tilde{U}(t,0)$ in Eq.(18) and using the fact that $\langle a|V|a\rangle$ and $\langle k|V|k'\rangle = 0$, leads to

$$i\frac{\partial}{\partial t}\ \tilde{U}(a,k,t) = \int dk_1 \tilde{V}(a,k_1,t)\ \tilde{U}(k_1,k,t), \tag{20}$$

$$i \frac{\partial}{\partial t} \tilde{U}(k_1,k,t) = \tilde{V}(k_1,a,t)\, \tilde{U}(a,k,t), \qquad (21)$$

where

$$\tilde{U}(a,k,t) = \langle a|\tilde{U}(t,0)|k\rangle, \quad \tilde{V}(a,k,t) = \langle a|\tilde{V}(t)|k\rangle, \text{ etc.}$$

Integrating eq.(21) from 0 to t gives

$$\tilde{U}(k_1,k,t) = \delta(k_1-k) - i\int_0^t \tilde{V}(k_1,a,t_1)\, \tilde{U}(a,k,t_1)dt_1. \qquad (22)$$

Use of eq.(22) in eq.(20) gives

$$i \frac{\partial}{\partial t} \tilde{U}(a,k,t) = \tilde{V}(a,k,t) - i\int dk_1 \tilde{V}(a,k_1,t)\int_0^t dt_1 \tilde{V}(k_1,a,t_1)\tilde{U}(a,k,t_1).$$

(23)

The matrix elements of $\tilde{V}(t)$ can be easily found. Thus

$$\tilde{V}(k_1,a,t_1) = \langle k_1|\tilde{V}(t_1)|a\rangle$$

$$= \langle k|V|a\rangle \exp i\int_0^t dt_1 \{\epsilon_k - \epsilon_a(t_1)\} \qquad (24)$$

$$\therefore i \frac{\partial}{\partial t} \tilde{U}(a,k,t) = \langle a|V|k\rangle \exp i\left[\int_0^t \big(\epsilon_a(t_1) - \epsilon_k\big) dt_1\right]$$

$$- i\int_0^t dt_1 \int dk_1 \langle a|V|k_1\rangle\langle k_1|V|a\rangle \exp{-i}\left[\int_{t_1}^t \big(\epsilon_{k_1} - \epsilon_a(t_1)\big) dt_1\right]\tilde{U}(a,k,t_1).$$

(25)

Now we define

$$\Delta(\epsilon) = 2\pi\int dk_1 \left|\langle a|V|k\rangle\right|^2 \delta(\epsilon-\epsilon_k). \tag{26}$$

Then the above equation becomes

$$i\frac{\partial \tilde{U}(a,k,t)}{\partial t} = \langle a|V|k\rangle \exp i\left[\int_0^t \left(\epsilon_a(t_1) - \epsilon_k\right)dt_1\right]$$

$$-i\int_0^t dt_1 \int_{-\infty}^{+\infty} d\epsilon \frac{\Delta\epsilon)}{\pi} \exp -i\left[\int_{t_1}^{t}\left(\epsilon_k - \epsilon_a(t_1)\right)dt_1\right]\tilde{U}(a,k,t_1)$$

$$\tag{27}$$

Now, if $\Delta(\epsilon)$ may be taken to be independent of ϵ, and the bandwidth of the states to be very large, then

$$\int_{-\infty}^{+\infty}\Delta(\epsilon)\exp-\{i\epsilon(t-t_1)\}\ d\epsilon \simeq 2\pi\Delta\delta(t-t_1)$$

so that the Eq.(27) becomes

$$i\frac{\partial \tilde{U}(a,k,t)}{\partial t} = \langle a|V|k\rangle \exp i\left[\int_0^t \left(\epsilon_a(t_1) - \epsilon_k\right)dt_1\right] - i\frac{\Delta}{2}\tilde{U}(a,k,t). \tag{28}$$

In a simlar fashion, as $\langle a|V|a\rangle = 0$,

$$i\frac{\partial}{\partial t}\tilde{U}(a,a,t) = -i\frac{\Delta}{2}\tilde{V}(a,a,t) \tag{29}$$

Equations (28) and (29) may be solved, subject to the conditions

$$\tilde{U}(a,k,0) = 0,$$

$$\tilde{U}(a,a,0) = 1. \tag{30}$$

The solutions, when substituted into the expression for $<n_a(t)>$, given in Eq.(13) gives

$$<n_a(t)> = (2\pi)^{-1}\Delta\ e^{-t\Delta}\int_{-\infty}^{\epsilon_F} d\epsilon \left| \int_0^t dt_1\ \exp\left[\frac{\Delta}{2}\ t_1 - i\left\{\epsilon t_1 + \int_{t_1}^{t} dt' \epsilon_a(t')\right\}\right] \right|^2 + e^{-t\Delta}. \tag{31}$$

This is similar to analogous expression, due to Brako and Newns[19] who consider ion neutralization scattering from surfaces. In their case, $\epsilon_a(t)$ was a deterministic function, while in our case, it is a random function. One would now like to calculate the rate of ET. For this, we find the derivative of $<n_a(t)>$ from Eq.(31) as

$$\frac{d<n_a(t)>}{dt} = -\Delta<n_a(t)> + \pi^{-1}\Delta \int_{-\infty}^{\epsilon_F} d\epsilon \times \int_0^t dt_1\ \exp[-\frac{\Delta}{2}(t-t_1)]\ \cos\left[\epsilon(t_1-t) - \int_t^{t_1} dt' \epsilon_a(t')\right]. \tag{32}$$

This equation may be reduced to a simple differential equation, in the following limiting cases:

(1). $\epsilon_a(t)$ varies slowly during the time Δ^{-1}. The second term in Eq.(32) is

$$I(t) = \Delta\pi^{-1}\mathrm{Re}\int_{-\infty}^{\epsilon_F} d\epsilon \int_0^t dt_1 \exp\left[(\frac{\Delta}{2} + i\epsilon)(t_1-t) - i\int_t^{t_1} dt'\epsilon_a(t')\right]. \qquad (33)$$

Re denotes that we have to take real part of whatever that follows The important contribution to the above integral is from $t_1 \simeq t$, so that we approximate

$$\int_t^{t_1} dt'\epsilon_a(t') \simeq \epsilon_a(t)(t_1-t).$$

Further, in $\int_0^t dt_1$, one can replace the lower limit by $-\infty$, without significantly altering the value of I(t). Thus

$$I(t) \simeq \Delta\pi^{-1}\mathrm{Re}\int_{-\infty}^{\epsilon_F} d\epsilon \int_{-\infty}^{t} dt_1 \ \exp(\frac{\Delta}{2} + i\epsilon - i\epsilon_a(t)(t_1-t)$$

$$\simeq \Delta\pi^{-1}\mathrm{Re}\int_{-\infty}^{\epsilon_F} d\epsilon \ (\frac{\Delta}{2} + i\epsilon - i\epsilon_a(t))^{-1}$$

$$\simeq \Delta\pi^{-1}\int_{-\infty}^{\epsilon_F} d\epsilon \ (\Delta/2)[(\Delta/2)^2 + (\epsilon - \epsilon_a(t))^2]^{-1}$$

$$\simeq \Delta \ n_a(\epsilon_a(t)) \qquad (34)$$

where $n_a(\epsilon_a(t))$ would be the occupation number of orbital $|a\rangle$, provided its energy was kept constant at $\epsilon_a(t)$. Using Eq.(34), we get Eq.32 to be

$$\frac{d}{dt}\langle n_a(t)\rangle = -\Delta\left\{\langle n_a(t)\rangle - n_a(\epsilon_a(t))\right\} \qquad (35)$$

If Δ is small, $n_a(\epsilon_a(t)) = \theta(\epsilon_F - \epsilon_a(t))$. Then

$$\frac{d\langle n_a(t)\rangle}{dt} = -\Delta\left\{\langle n_a(t)\rangle - \theta(\epsilon_F - \epsilon_a(t))\right\} \tag{36}$$

For large values of Δ, one obtains

$$\frac{d\langle n_a(t)\rangle}{dt} = -\Delta[\langle n_a(t)\rangle - 1/2]. \tag{37}$$

This particular limit corresponds to the sudden or adiabatic limit of electron transfer, when the ET is instantaneously occuring upon crossing of the Fermi energy level.

(2). $\epsilon_a(t)$ varies considerably during the time Δ^{-1} and Δ is small. Given this constraint, we can write

$$\int_{t_1}^{t} dt_2\, \epsilon_a(t_2) \simeq \bar{\epsilon}_a(t,t_1)(t-t_1)$$

where $\bar{\epsilon}_a(t,t_1)$ is the average energy of the orbital $|a\rangle$ during the time interval (t_1,t). It is quite straightforward to see that $\langle n_a(t)\rangle$ obeys the same differential equation (36) as in the earlier case for small values of Δ, the only difference being that we have $\bar{\epsilon}_a$ instead of ϵ_a. $\bar{\epsilon}_a$ may be thought of as an average energy.

Therefore, it is clear that $\langle n_a(t)\rangle$ obeys an equation of the form

$$\frac{d\langle n_a(t)\rangle}{dt} = -\Delta\left\{\langle n_a(t)\rangle - \langle n_a\rangle^{eq}\right\} \tag{38}$$

and hence Δ may be identified with the rate of transfer.

Now one has to worry about spin. If one extends the above line of argument, one is tempted to conclude that an equation like (38) is valid for each spin and hence the rate of ET would be 2Δ. However, if one includes electron-electron repulsions in the description, this conclusion would change. If U denotes the coulombic repulsion integral between two up and down spin electrons in |a>, then, if one electron of up spin has been put in |a>, the effective energy of down spin orbital would be $\epsilon_a + U$, (U being typically 2-10 eV) so that the second electron has to be transferred to an orbital of much higher energy. Therfore, we take the rate to be given by Δ itself.

5.7 Diffusion-Reaction Equation

5.7.1 Background

We have seen earlier that the Fokker-Planck equation for the probability, P(Q,t) that the shift has a value Q at the time t to be

$$\frac{\partial P(Q,t)}{\partial t} = \frac{2kT\lambda}{\tau_L} \frac{\partial^2 P(Q,t)}{\partial Q^2} + \frac{\partial}{\partial Q} \frac{Q}{\tau_L} P(Q,t) \tag{39}$$

If $\epsilon_a + Q(t)$ moves above the Fermi energy ϵ_F of the metal, then an electron may be transferred to the electrode. As mentioned earlier, we assume that if $\epsilon_a + Q(t) > \epsilon_F$, then the electron is transferred at the same rate Δ, irrespective of what the energy of the orbital is. This actually implies that we are considering a metal of a fairly large bandwidth and further that we assume the rate of electron transfer to be independent of the energy of the orbital, as long as it is above the Fermi level. Therefore, the probability P(Q,t) is now given by the equation

$$\frac{\partial P(Q,t)}{\partial t} = \frac{2kT\lambda}{\tau_L}\,\frac{\partial^2 P(Q,t)}{\partial Q^2} + \frac{\partial}{\partial Q}\,\frac{Q}{\tau_L}P(Q,t) - k(Q)P(Q,t) \qquad (40)$$

Note that the above equation has a sink term, $k(Q) = \theta(Q-Q_F)\Delta$, which is a constant if $Q > Q_F$ and zero otherwise. This physically means that the ET to the electrode takes place only in those regions of the potential energy curve for which $Q > Q_F$ (see Fig.6). $Q_F = \epsilon_F - \epsilon_a$ is that particular value of Q, at which the energy of the orbital is equal to the Fermi energy ϵ_F. Thus the activation process for the ECET consists in going over from $Q = 0$ to $Q = Q_F$. P(Q,t) *is now the probability that the shift has a value* Q*, at the time t, and that the electron has not been transferred to the electrode.* For the above diffusion-reaction equation, if k(Q) is nonzero, in principle, there is no time independent state. The time dependent decay of P(Q,t) is, in general, multi-exponential. Therefore one has the problem of defining/identifying the rate constant. For this, different approaches are available in the literature[16,17] as discussed in Sec.5.4. We, however, adopt an approach that is motivated by the actual physical problem.

5.7.2 The Steady-State Approach

As has been already mentioned, we adopt a steady state approach to the calculation of the rate constant. We make our procedure clear with a simple example.

Generally, the kinetic study of a given first order reaction, say, $A \longrightarrow B$ involves measuring the decrease of the concentration of the reactant, A with time. Writing down the rate expression as

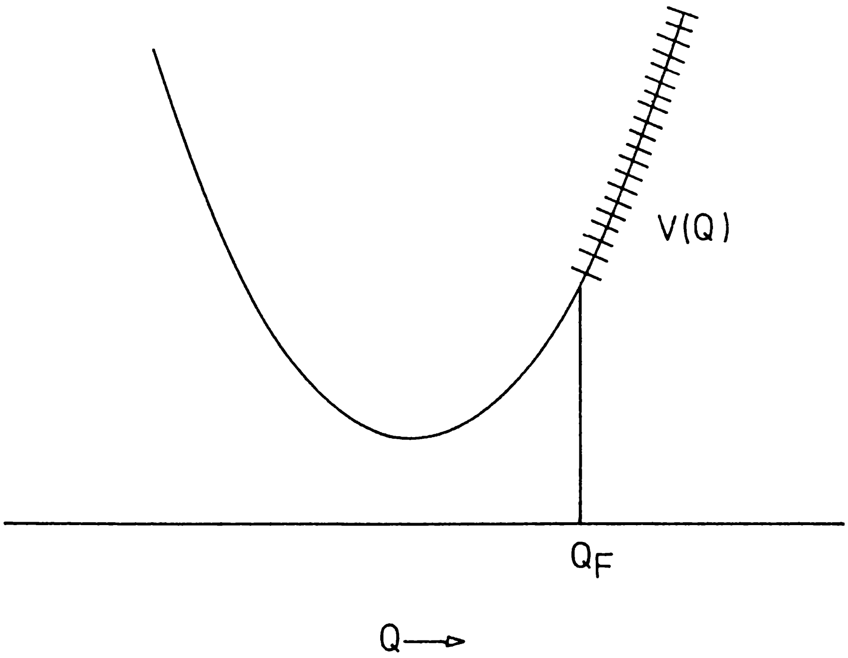

Fig.6 Free energy for the initial state (A^{2+} ion near the electrode) as a function of the reaction coordinate Q. The reaction occurs in the hatched portion at a rate Δ.

$$\frac{d[A]}{dt} = -k_A[A], \tag{41}$$

the usual procedure for evaluation of the rate constant would involve actually solving the equation (30) to obtain ln A = $-k_A t$ + constant, and making a plot of ln A against t to obtain the slope k_A. Another procedure for determining k_A would be the following:

We imagine that the reactant is being fed into the system at a constant rate k_f. The equation describing the system is then

$$\frac{d[A]}{dt} = - k_A[A] + k_f , \tag{42}$$

where k_f is the rate at which the reactant is being fed into the system. The system would eventually attain a steady state, when

$$\frac{d[A]}{dt} = -k_A[A] + k_f = 0.$$

If one then determines the concentration of A in the steady state and the rate at which the reactant is being fed in, one can determine the rate constant from these two, as

$$k_A = k_f/[A].$$

In the following, we adopt the same kind of approach for the evaluation of the rate of electrochemical electron transfer.

In a previous study, Morgan and Wolynes[9] have formulated a rate theory for electron transfer from an ion in solution to an electrode. They consider the dynamics to be on a continuum of potential energy surfaces. Starting from a master equation, they arrive at an effective Smoluchowski equation for the probability density. This has been solved approximately, to find the rate constant, using the method of Doi,[20] which however, fails to account for the deviation of the population $P(Q,t)$ from the equilibrium one. In the present study, we present an approach which can account for the deviation of the population from the equilibrium one. In the electrochemical discharge, there is a supply of the ion from the solution so that a steady state is attained. Therefore we modify the Eq.40, by including in it a source term, which corresponds to reactant being supplied at a rate $k_r(t)P_e(Q)$, where $P_e(Q)$ is the equilibrium probability distribution function appropriate to the bulk so that eventually a time independent state would be attained. *This feeding has to be done in such a fashion that the reaction is not rate limited by this process.* Thus we take $k_r(t)$ to satisfy the condition,

$$k_r(t) = \int_{-\infty}^{+\infty} dQ\ P(Q,t)\ k(Q) \tag{43}$$

i.e., the feeding is just at the rate at which the reactant is consumed. Thus, we now have the equation

$$\frac{\partial P(Q,t)}{\partial t} = \frac{2kT\lambda}{\tau_L} \frac{\partial^2 P(Q,t)}{\partial Q^2} + \frac{\partial}{\partial Q} \frac{Q}{\tau_L} P(Q,t) - k(Q)P(Q,t) + k_r(t)P_e(Q). \tag{44}$$

As t ⟶ ∞, a steady, time independent state shall be attained. The value of $k_r(t)$ in this limit is the rate of the reaction. The distribution, $P(Q,t)$ in this limit shall be denoted by $P_s(Q)$. As it is time independent, the $\frac{\partial P(Q,t)}{\partial t}$ term above may be removed and one obtains

$$\frac{2kT\lambda}{\tau_L}\;\frac{d^2P_s(Q)}{dQ^2} + \frac{d}{dQ}\;\frac{Q\,P_s(Q)}{\tau_L} - k(Q)P_s(Q) + k_rP_e(Q) = 0. \tag{45}$$

We use k_r to denote $k_r(\infty)$ which obviously would be time independent. In terms of the dimensionless variable, $z = Q/(2kT\lambda)^{1/2}$, the above diffusion-reaction equation becomes

$$\mathcal{L}\, P_s(z) - \nu\,\theta(z - z_F)P_s(z) + \varkappa_r P_e(z) = 0 \tag{46}$$

where $\mathcal{L}P = d^2P/dz^2 + d(zP)/dz$, $\nu = \tau_L\Delta$, $\varkappa_r = k_r\tau_L$, and $z_F = Q_F/(2\lambda kT)^{1/2}$. We have made use of the expression, $k(Q) = \Delta\,\theta(Q-Q_F)$. $P_e(z)$ is the equilibrium probability population that would exist in the bulk. $P_e(z)$ would obey the Fokker-Planck equation

$$\frac{d^2P}{dz^2} + \frac{d(zP)}{dz} = 0,$$

which does not contain any source or sink. On solving this, one gets $P_e(z) = (2\pi)^{-1/2}\; e^{-z^2/2}$, where we have taken the normalization to be $\int_{-\infty}^{+\infty} dz\; P_e(z) = 1$.

From Eq.46, it is evident that $P_s(z)$ obeys a second order differential equation and that its second derivative with respect to time has a finite discontinuity. This implies that its first derivative with respect to time is continuous as well as trhe function $P_s(z)$ itself across the boundary, $z = z_F$.

5.8 Results and Discussion

5.8.1 Rate Constant Expression

In this section, we discuss the solution of equation (46).

(a). Region I, where $z < z_F$

In this region, Eq (46) becomes

$$\left[\frac{d^2}{dz^2} + \frac{d}{dz} z\right] P_s(z) = -(2\pi)^{-1/2} \varkappa_r \, e^{-z^2/2} \qquad (47)$$

Ths solution must be such that $P_s(z) \longrightarrow 0$ as $z \longrightarrow -\infty$. The homogeneous equation, $\left[\frac{d^2}{dz^2} + \frac{d}{dz} z\right] P_s(z) = 0$ has the solution, A $e^{-z^2/2}$ while the particular solution (p.s.) is

$$\text{p.s.} = -(2\pi)^{-1/2} \varkappa_r \, e^{-z^2/2} \int_0^z dz_1 \, e^{z_1^2/4} \, D_{-1}(-z_1) \qquad (48)$$

where

$$D_{-1}(-z) = (\pi/2)^{1/2} \, e^{-z^2/4} \, e^{z^2/2} \, \mathrm{Erfc}(-z/\sqrt{2}). \qquad (49)$$

We use the symbol, $D_\nu(z)$ to denote parabolic cylinder function[21] (see Appendix A for definition and some important properties of parabolic cylinder functions). Hence we write the solution as

$$[P_s(z)]_{z<z_F} = A \, e^{-z^2/2} - (2\pi)^{-1/2} \varkappa_r \, e^{-z^2/2} \int_0^z dz_1 \, e^{z_1^2/4} \, D_{-1}(-z_1), \qquad (50)$$

(b). Region II, where $z > z_F$

Equation (46) now reads

$$\left[\frac{d^2}{dz^2} + \frac{d}{dz} z - \nu\right] P_s = -(2\pi)^{-1/2} \varkappa_r \, e^{-z^2/2} \qquad (51)$$

Here, $P_s(z) \longrightarrow 0$ as $z \longrightarrow +\infty$. Therefore we take

$$[P_s(z)]_{z>z_F} = B\ e^{-z^2/4}\ D_{-\nu}(z) + (2\pi)^{-1/2}\ \nu^{-1}\ \varkappa_r\ e^{-z^2/2} \qquad (52)$$

The first term is the solution of homogeneous equation, while the second is the particular solution.

There are now three unknowns in our solution, viz., A,B and $\varkappa_r$. See Eqs.(50) and (52). $\varkappa_r$ and rate are related by $k_r = \varkappa_r/\tau_L$. Now one can make use of the three conditions that are available, namely, that P_s and its derivatives are both continuous at $z = z_F$, the boundary of regions I and II and that we supply reactants exactly at the rate at which they are consumed, so that we have $\int_{-\infty}^{+\infty} P(Q,t)\ dQ = 1$ at all t. By using these three conditions, A, B and $\varkappa_r$ are uniquely determined and so we arrive at an expression for the rate constant. The reader who is not interested in the details of obtaining A, B, $\varkappa_r$ can go to Eq.(69) for the rate constant.

Continuity of the function at $z = z_F$ implies that the constants A and B in the Eqs.(50) and (52) are related by

$$A = (2\pi)^{-1/2}\ \varkappa_r \int_0^{z_F} dz\ e^{z^2/4}\ D_{-1}(-z) + B\ e^{z_F^2/4} D_{-\nu}(z_F) + (2\pi)^{-1/2} \nu^{-1} \varkappa_r . \qquad (53)$$

The fact that the first derivative of the function $P_s(z)$ is also continuous across $z = z_F$ yields

$$B\left[\frac{d}{dz}\, e^{z^2/4}\, D_{-\nu}(z)\right]_{z=z_F} = -(2\pi)^{-1/2}\varkappa_r\left[\frac{d}{dz}\int_0^z dz_1\, e^{z_1^2/4}\, D_{-1}(-z_1)\right]_{z=z_F}. \tag{54}$$

After simple manipulations (Refer Appendix A for details), we obtain $\varkappa_r = \alpha B$, (55)

where α is given by

$$(2\pi)^{-1/2}\nu^{-1}\alpha = \frac{D_{-\nu-1}(z_F)}{D_{-1}(-z_F)}\ . \tag{56}$$

We shall make use of this equation later. Now substituting for $\varkappa_r$ as αB in Eq.(53) we get

$$A = \left[(2\pi)^{-1/2}\nu^{-1}\alpha + e^{z_F^2/4}\, D_{-\nu}(z_F) + (2\pi)^{-1/2}\alpha\int_0^{z_F} dz\, e^{z^2/4}\, D_{-1}(-Z)\right]B. \tag{57}$$

Making use of Eqs (56) and (57) in Eq.(50) for $[P_s(z)]_{z<z_F}$,

$$[P_s(z)]_{z<z_F} = B\, e^{-z^2/2}\left[(2\pi)^{-1/2}\nu^{-1}\alpha + e^{z_F^2/4} D_{-\nu}(z_F) + (2\pi)^{-1/2}\alpha\, \times\right.$$
$$\left\{\int_0^{z_F} dz\, e^{z^2/4}\, D_{-1}(-z) - \int_0^z dz_1\, e^{z_1^2/4}\, D_{-1}(-z_1)\right\}. \tag{58}$$

Now

$$\int_0^{z_F} dz\, e^{z^2/4}\, D_{-1}(-z) - \int_0^z dz_1\, e^{z_1^2/4}\, D_{-1}(-z_1) = \int_z^{z_F} dz_1\, e^{z_1^2/4}\, D_{-1}(-z_1).$$

∴ Eq.(58) can be simplified as

$$[P_s(z)]_{z<z_F} = B\, e^{-z^2/2}\left[e^{z_F^2/4}\, D_{-\nu}(z_F) + (2\pi)^{-1/2}\nu^{-1}\alpha + (2\pi)^{-1/2}\alpha\, \times\right.$$

$$\int_z^{z_F} dz_1 \; e^{z_1^{\,2}/4} \; D_{-1}(-z_1)\Bigg]. \tag{59}$$

Putting $\varkappa_r = \alpha B$ and making use of the result (56) in Eq.(52), the expression for $[P_s(z)]_{z>z_F}$ becomes

$$[P_s(z)]_{z>z_F} = B\left[D_{-\nu}(z)e^{-z^2/4} + (2\pi)^{-1/2}\,\nu^{-1}\alpha\; e^{-z^2/2}\right]. \tag{60}$$

Remembering that we supply reactants exactly at the rate at which they are consumed, we have $\int_{-\infty}^{+\infty} P(Q,t)\; dQ = 1$ at all t.

Therefore $$\int_{-\infty}^{+\infty} P_s(z)\; dz = 1. \tag{61}$$

ie., $$\int_{-\infty}^{z_F} dz\; [P_s(z)]_{z<z_F} + \int_{z_F} dz\; [P_s(z)]_{z>z_F} = 1. \tag{62}$$

$$\int_{-\infty}^{z_F} dz\; [P_s(z)]_{z<z_F} = B\left\{e^{z_F^2/4}\; D_{-\nu}(z_F) + (2\pi)^{-1/2}\nu^{-1}\alpha\right\}\int_{-\infty}^{z_F} dz\; e^{-z^2/2}$$

$$+ \; B\;(2\pi)^{-1/2}\alpha\int_{-\infty}^{z_F} dz\; e^{-z^2/2}\int_z^{z_F} dz_1\; e^{z_1^2/4}\; D_{-1}(-z_1).$$

Defining $G(z_F)$ as

$$G(z_F) = \int_{-\infty}^{z_F} dz\; \exp(-z^2/2)\int_z^{z_F} dz_1\; \exp(z_1^2/4)\; D_{-1}(-z_1), \tag{63}$$

the above expression simplifies as

$$\int_{-\infty}^{z_F} dz\; [P_s(z)]_{z<z_F} = B\left\{e^{z_F^{\,2}/4}\; D_{-\nu}(z_F) + (2\pi)^{-1/2}\nu^{-1}\alpha\right\}\int_{-\infty}^{z_F} dz\; e^{-z^2/2}$$

$$+ B(2\pi)^{-1/2}\alpha\, G(z_F). \tag{64}$$

$$\int_{z_F}^{\infty} dz\ [P_s(z)]_{z>z_F} = B\left[\int_{z_F}^{\infty} dz\ e^{-z^2/4}\ D_{-\nu}(z) + (2\pi)^{-1/2}\alpha\nu^{-1}\int_{z_F}^{\infty} dz\ e^{-z^2/2} \right] \tag{65}$$

The above expression reduces to

$$\int_{z_F}^{\infty} dz\ [P_s(z)]_{z>z_F} = B\left[e^{-z_F^2/4}\ D_{-\nu-1}(z_F) + (2\pi)^{-1/2}\ \alpha\nu^{-1}\int_{z_F}^{\infty} dz\ e^{-z^2/2}\right]. \tag{66}$$

(Refer Appendix A for details of arriving at the above expression).

Substituting Eqs.(64) and (66) in Eq.(62), we get

$$B\left[(2\pi)^{-1/2}\ \nu^{-1}\alpha\int_{-\infty}^{+\infty} dz\ e^{-z^2/2} + e^{z_F^2/4}\ D_{-\nu}(z_F)\int_{-\infty}^{z_F} dz\ e^{-z^2/2} + (2\pi)^{-1/2}\alpha G(z_F) + e^{-z_F^2/4}\ D_{-\nu-1}(z_F)\right] = 1. \tag{67}$$

Making use of the fact that $\int_{-\infty}^{+\infty} dz\ e^{-z^2/2} = (2\pi)^{1/2}$, we arrive at the following expression for B:

$$B = \left[\alpha\nu^{-1} + D_{-\nu}(z_F)D_{-1}(-z_F) + (2\pi)^{-1/2}\alpha G(z_F) + D_0(z_F)D_{-\nu-1}(z_F)\right]^{-1} \tag{68}$$

(Refer Appendix A for further details of obtaining the above equation).

Since $\varkappa_r = \alpha B$, $k_r = \varkappa_r \tau_L^{-1}$ and $\Delta = \nu \tau_L^{-1}$, after substituting for α the expression for k_r reads as follows:

$$k_r = \frac{\Delta}{\left[1 + (2\pi)^{-1/2} \nu\, G(z_F) + (2\pi)^{-1/2} [D_0(z_F)\, D_{-1}(-z_F) + D_{-1}^2(-z_F) \times D_{-\nu}(z_F)/D_{-\nu-1}(z_F))] \right]} . \tag{69}$$

For ready reference we give definitions of z_F, ν and $G(z_F)$ once more.

$z_F = (\epsilon_F - \epsilon_a)/(2\lambda kT)^{1/2}$, $\nu = \tau_L \Delta$ and

$$G(z_F) = \int_{-\infty}^{z_F} dz\, \exp(-z^2/2) \int_{z}^{z_F} dz_1\, \exp(z_1^2/4)\, D_{-1}(-z_1),$$

5.8.2 Analysis of the limiting cases

The above rate expression can be analysed in different limits, as below.

Case 1. $z_F >> 1$

In this limit, $\operatorname{erf} z_F \simeq 1 - \pi^{-1/2} z_F^{-1} e^{-z_F^2} + O(1/z_F^3)$

$$D_{-\nu}(z_F) \simeq z^{-\nu} e^{-z_F^2/4} [1 + O(1/z_F^2)] \text{ and}$$

$$D_{-1}(-z_F) \simeq (\pi/2)^{1/2} e^{z_F^2/4} [2 - (\pi/2)^{-1/2} z_F^{-1} e^{-z_F^2/2} + O(1/z_F^3)].$$

$G(z_F) \simeq 2\pi\, z_F^{-1} e^{z_F^2/2} + O(1/z_F^2)$. (See Appendix B for details).

In this limit, the orbital $|a\rangle$ has its average energy much below

ϵ_F and is in resonance with occupied orbitals of the metal. Crossing of ϵ_F by $\epsilon_a + Q$ is a rather infrequent event and so rate of ET to the electrode is low.

The rate expression (69) becomes

$$k_r = \frac{\dfrac{\Delta\, e^{-z_F^2/2}}{(2\pi)^{1/2} z_F}}{1 + \nu / z_F^2} \, . \tag{70}$$

In the limit $\nu/z_F^2 >> 1$, this becomes

$$k_r = \frac{(\epsilon_F - \epsilon_a)\, e^{-(\epsilon_F - \epsilon_a)^2/4\lambda kT}}{(2\pi)^{1/2}\, \tau_L (2\lambda kT)^{1/2}}$$

As $\nu/z_F^2 = \dfrac{\Delta\tau_L (2\lambda kT)}{(\epsilon_F - \epsilon_a)^2}$, this limit corresponds to

$$\tau_L \Delta >> \frac{(\epsilon_F - \epsilon_a)^2}{2\lambda kT} >> 1.$$

So even though crossing the Fermi level in the upward direction is infrequent, the orbital remains there for a sufficiently long time that an electron is almost surely transferred. Hence the rate is limited by the rate of crossing and is independent of Δ. Notethat this can happen for even small values of Δ. The value of τ_L can vary from 0.12 ps (Acetonitrile) to 8.8 ps (hexamethylphophoramide). In order that $\Delta\tau_L \simeq 5$, this means that Δ should be in the range from ~ 750 cm^{-1} in acetonitrile to ~ 20

cm^{-1} in hexamethyl phosphoramide. For water, Δ should be $\simeq$ 80 cm^{-1}. Weaver *et al*[22] have investigated the electrochemical exchange of cobalticinium-cobaltocene ($Cp_2Co^{+/0}$) at a mercury electrode in 9 organic solvents. The solvents used had τ_L values ranging from 0.2 ps to 6 ps. They report a proportionality between the pre-exponential factor and τ_L^{-1} for the solvents considered by them, except for actonitrile. In the case of $Ru(NH_3)_6^{2+/3+}$ couple in water, Iwasita *et al*[23] report that the exchange current density is independent of the nature of the metal for six metals - i.e., independent of Δ, indicating that the reaction is adiabatic.

Note also that the concept of adiabaticity itself, as used above is somewhat different from that in the case of homogeneous ET. In homogenous ET, one regards the reaction as adiabatic if it remains on the adiabatic potential energy surface (PES) and does not cross over from it to another. On the other hand, in the above, the reaction is adiabatic if an electron is transferred from A^{2+} to the metal, once the orbital has crossed the Fermi level. The rate of crossing may be very small, but still an electron could be transferred with probability one, provided solvent relaxation is slow enough that the orbital's energy remains above ϵ_F. This however, does not mean that the system is on the same PES. As there is a continuum of surfaces available, it would have traversed through many of them.

In the conventional nonadiabatic limit $\Delta\tau_L/z_F^2 << 1$, solvent relaxation is fast compared to electron hopping. Electron hopping is now rate determining. Eq.(70) becomes

$$k_r = \frac{\Delta}{\left[(2\pi)^{1/2}\,\frac{(\epsilon_F - \epsilon_a)}{(2\lambda kT)^{1/2}}\right]}\; e^{-(\epsilon_F - \epsilon_a)^2/4\lambda kT}$$

This result is identical to the results of Ulstrup, Levich, Morgan and Wolynes.[5,9,24]

Case 2. z_F is negative and $|z_F| >> 1$.
In this limit, erf $z_F \simeq -1 + \pi^{-1/2}|z_F|^{-1}e^{-z_F^2} - O(1/|z_F|^3)$,

$D_{-1}(-z_F) \simeq \pi^{-1/2}|z_F|^{-1}e^{-z_F^2/4}$, and

$G(z_F) \simeq e^{-|z_F|^2/2}/|z_F|^3$. (See Appendix B)
Then

$$k_r = \frac{\Delta}{1 + \dfrac{e^{-|z_F|^2/2}\,[2|z_F|^2 + \nu]}{(2\pi)^{1/2}|z_F|^3}} \qquad (71)$$

As $\epsilon_a >> \epsilon_F$, the electron can easily jump from A^{2+} to the unoccupied orbitals of the metal. So rate is not strongly influenced by solvent dynamics and is obviously proportional to Δ.
Case 3. $z_F \longrightarrow 0$. In this limit,
$D_{-\nu}(z_F)/D_{-\nu-1}(z_F) \simeq 2^{-1/2}\nu\ [q + 2^{1/2}z_F\{(\nu q^2/2) - 1\}]$
where

$$q = \frac{\Gamma(\nu/2)}{\Gamma[(1+\nu)/2]},$$

$D_{-1}(-z_F) \simeq (\pi/2)^{1/2} + z_F$ and

$G(z_F) \simeq 2^{-1/2}\pi\,[2^{-1/2}z_F + \pi^{-1/2}\ln 2]$. (See Appendix B)

With these limiting forms, the rate expression (69) becomes

$$k_r = \frac{\Delta}{1 + 2^{-1}[1 + \nu(\ln 2 + \pi^{-1/2}q)] + (2\pi)^{-1/2}z_F[1 + \nu\{(\pi/2) - 1 + (\nu q^2/2)\}]} \quad \ldots(72)$$

In this case, because of the closeness of the level ϵ_a to ϵ_F, frequent crossings of the Fermi level are likely and hence the rate of ET is determined mainly by Δ. The above expression for the rate constant which is proportinal to Δ has corrections from solvent dynamics.

5.8.3 Rate Constant - Overpotential Relationship

The relationship between the Fermi energy, ϵ_F and the overpotential η can be expressed as $\epsilon_F = \epsilon_F^o - \eta$, where ϵ_F^o is the Fermi energy when there exists an equilibrium between the electrode and the solution. By changing the overpotential, the energy gap between the levels, ϵ_F and ϵ_a could be varied so that it may be possible for an electrode system to change from nearly adiabatic transfer in one potential range to nearly diabatic transfer in another range. In terms of the rate expressions presented here, it can be seen that crossover from predominantly adiabtic ET ($\nu/z_F^2 >> 1$) regime to a predominantly nonadiabatic one ($\nu/z_F^2 << 1$) is possible by increasing z_F. In other words, a change in the overpotential,η is likely to effect this transition.

5.8.4 Comparison with Earlier Studies

Our expressions (71) and (72) in the cases where z_F is negative or $z_F \longrightarrow 0$ are different from those of Morgan and Wolynes.[9] This is not at all surprising. Our approach takes deviation of P(Q,t) from its equilibrium value in the vicinity of the electrode exactly. In comparison, the method of Doi,[20] which has been adopted by Morgan and Wolynes does not do this. In the limit where $z_F = (\varepsilon_F - \varepsilon_a)/(2\lambda kT)^{1/2} >> 1$, the Fermi level is much above ε_a and electron transfer to the metal is rather an infrequent event. Therefore deviation of the population P(Q,t) from equilibrium is rather negligible and hence our results are in agreement with those of Morgan and Wolynes in this limit.

An interesting aspect of our study is that our rate constant for electrochemical electron transfer, k_r turns out to be the same as the average rate constant, k_I of Bagchi[18] *et al* (or τ_a^{-1} of Sumi and Marcus[16]) as shown below.

Bagchi *et al*[18] and Sumi and Marcus[16] have analysed the diffusion-reaction equations. They consider time dependent solutions of the diffusion-reaction equation and define different kinds of rate constants. One can think of adopting the same kind of approach to defining rate constants. In this approach one considers Eq.(40), with the initial condition

$$P(Q,0) = P_e(Q) \tag{73}$$

and find the time dependent solution P(Q,t). Physically, this means that one does not supply the reactant from the bulk, as was done in our approach, as a result of which

$$P(Q,t) \longrightarrow 0 \text{ as } t \longrightarrow \infty. \qquad (74)$$

Using this P(Q,t), so found, we can now define the rate by any of the following:

$$k_I^{-1} = \int_0^\infty dt\ P_{sur}(t), \qquad (75)$$

where $P_{sur}(t)$ is the survival probability of the reactant at the time t, defined by

$$P_{sur}(t) = \int_{-\infty}^{+\infty} dQ\ P(Q,t). \qquad (76)$$

The long time rate constant k_L, is defined through the behaviour of the long time limit of $P_s(t)$,

$$k_L = -\lim_{t \to \infty} \frac{\partial}{\partial t} \ln P_s(t). \qquad (77)$$

Interestingly, we show below that our k, obtained by the steady-state approach is just the k_I defined in the time dependent approach. This is fairly easy to prove. For this we consider the Laplace transform of P(Q,t), defined by

$$\mathcal{P}(Q,s) = \int_0^\infty dt\ e^{-st}\ P(Q,t). \qquad (78)$$

Clearly,

$$k_I^{-1} = \int_{-\infty}^{+\infty} dQ\ \mathcal{P}(Q,0) \qquad (79)$$

Now, the equation obeyed by $\mathcal{P}(Q,s)$ may be found by performing the Laplace transform of the equation (40), when we obtain

$$s\mathcal{P}(Q,s) - \frac{2kT\lambda}{\tau_L}\frac{d^2\mathcal{P}(Q,s)}{dQ^2} - \frac{1}{\tau_L}\frac{d\,Q\mathcal{P}(Q,s)}{dQ} + k(Q)\mathcal{P}(Q,s) = P_e(Q). \tag{80}$$

So $\mathcal{P}(Q,0)$ obeys

$$-\frac{2kT\lambda}{\tau_L}\frac{d^2\mathcal{P}(Q,0)}{dQ^2} - \frac{1}{\tau_L}\frac{d\,Q\mathcal{P}(Q,0)}{dQ} + k(Q)\mathcal{P}(Q,0) = P_e(Q). \tag{81}$$

Comparing this with our equation (40), we find that

$$\mathcal{P}(Q,0) = P_s(Q)/k_r. \tag{82}$$

As our definition of $P_s(Q)$ is such that

$$\int_{-\infty}^{+\infty} P_s(Q)dQ = 1,$$

We find

$$k_I^{-1} = \int_{-\infty}^{+\infty}\mathcal{P}(Q,0) = 1/k_r. \tag{83}$$

Hence our $k_r = k_I$, defined as per Eq.(79).

This interesting result also suggests that one can make use of a time dependent approach, to calculate k_I, which has been calculated using the time dependent approach by Bagchi *et al.* All that is needed is to solve an ordinary second-order differential equation, which can be easily done, numerically, for any arbitrary V(Q)!

Appendix A

Parabolic Cylinder Functions

The parabolic cylinder functions are solutions of the differential equation,

$$\frac{d^2y}{dx^2} + (ax^2 + bx + c)y = 0, \tag{A.1}$$

which, by a simple change of variable, reduces to the form

$$\frac{d^2y}{dx^2} + (\nu + \frac{1}{2} - \frac{1}{4} z^2)y = 0. \tag{A.2}$$

Following Ref.21, the solutions of this equation are denoted by $D_\nu(z)$. It is usual to take the values of $D_\nu(0)$ and $D_\nu'(0)$ to be

$$D_\nu(0) = \frac{\Gamma(1/2)2^{\nu/2}}{\Gamma\big((1-\nu)/2\big)} , \qquad D_\nu'(0) = \frac{\Gamma(-1/2)2^{(\nu-1)/2}}{\Gamma(-\nu/2)} . \tag{A.3}$$

Also

$$D_0(z) = \exp(-z^2/4); \tag{A.4}$$

$$D_{-n-1}(z) = (\pi/2)^{1/2} \frac{(-1)^n}{n!} e^{-z^2/4} \frac{d^n}{dz^n} \left[e^{z^2/2} \operatorname{erfc}(z/\sqrt{2})\right], \qquad n = 0,1,2,\ldots, \tag{A.5}$$

where

$$\operatorname{erfc}(z) = 1 - \operatorname{erf}(z) = 1 - \frac{2}{\sqrt{\pi}} \int_0^x dt\ e^{-t^2} .$$

$$\frac{d}{dz}\left[e^{z^2/4}\ D_{-\nu}(z)\right] = -\nu e^{z^2/4}\ D_{-\nu-1}(z). \tag{A.6}$$

Usage of this identity reduces Eq.(54) to Eq.(55).

We make use of the identity,

$$\int dz\ e^{-z^2/4}\ D_{-\nu}(z) = -e^{-z^2/4}\ D_{-\nu-1}(z) \tag{A.7}$$

and simplify Eq.(65) to Eq.(66).

$$\int_{-\infty}^{z_F} dz\ e^{-z^2/2} = (\pi/2)^{1/2}\ \mathrm{erfc}(-z_F/\sqrt{2}).$$

$$\therefore\ e^{z_F^2/4}\int_{-\infty}^{z_F} dz\ e^{-z^2/2} = (\pi/2)^{1/2}\ e^{z_F^2/4}\ \mathrm{erfc}(-z_F/\sqrt{2})$$

Putting n = 0 in the identity (A.5) reduces the right hand side of the above equation to $D_{-1}(-z_F)$. Thus

$$D_{-\nu}(z_F)e^{z_F^2/4}\int_{-\infty}^{z_F} dz\ e^{-z^2/2} = D_{-\nu}(z_F)D_{-1}(-z_F) \tag{A.8}$$

Usage of (A.4) and (A.8) leads to the simplification of Eq.(67) to Eq.(68).

$D_{-\nu}(z)$ has the asymptotic form,

$$D_{-\nu}(z_F) \simeq z^{-\nu}\ e^{-z_F^2/4}\ [1 + O(1/z_F^2)]. \tag{A.9}$$

We make use of this expression in the analysis of our rate expression in the limit $z_F \longrightarrow \infty$. Also, the expression for $D_{-1}(-z_F)$ obtained by putting n = 0 in the identity (A.5), reduces to various limiting forms as $z_F \longrightarrow +\infty$ or $-\infty$ in accordance with the asymptotic forms for $\mathrm{erf} z_F$ in these limits.

For $z_F \longrightarrow 0$, expanding $D_{-\nu}(z_F)$ as a Taylor series,

$$D_{-\nu}(z_F) \simeq D_{-\nu}(0) + z_F\, D_{-\nu}'(0) \qquad (A.10)$$

Making use of (A.3) to obtain the values of $D_{-\nu}(0)$ and $D_{-\nu}'(0)$, we arrive at the following expression for $D_{-\nu}(z_F)$:

$$D_{-\nu}(z_F) \simeq \frac{\Gamma(1/2)\ 2^{-\nu/2}}{\Gamma\big((1+\nu)/2\big)} + z_F\, \frac{\Gamma(-1/2)\ 2^{-(1+\nu)/2}}{\Gamma(\nu/2)}. \qquad (A.11)$$

Since $\Gamma(1/2) = \sqrt{\pi}$ and $\Gamma(-1/2) = -2\sqrt{\pi}$,

$$D_{-\nu}(z_F) \simeq \sqrt{\pi}\ 2^{-\nu/2}\Big[\ 1/\Gamma\big((1+\nu)/2\big)\ -\ \sqrt{2} z_F/\Gamma(\nu/2)\Big] \qquad (A.12)$$

Similarly

$$D_{-\nu-1}(z_F) \simeq \sqrt{\pi}\ 2^{-(1+\nu)/2}\Big[\ 1/\Gamma\big(1+(\nu/2)\big)\ -\ \sqrt{2} z_F/\Gamma\big((1+\nu)/2\big)\Big]. \qquad (A.13)$$

Using the identity, $\Gamma(1+\nu/2) = \nu/2\ \Gamma(\nu/2)$, we obtain

$$D_{-\nu}(z_F)/D_{-\nu-1}(z_F) \simeq 2^{-1/2}\nu\ \frac{\Gamma(\nu/2)\ -\ 2^{1/2} z_F\ \Gamma\big((1+\nu)/2\big)}{\Gamma\big((1+\nu)/2\big)\ -\ 2^{-1/2} z_F\ \nu\ \Gamma(\nu/2)} \qquad (A.14)$$

We make use of the identity, $1/(a + bz) \simeq 1/a - bz/a^2$ and simplify the denominator in the above expression so that (A.14) becomes $D_{-\nu}(z_F)/D_{-\nu-1}(z_F) = 2^{-1/2}\ \nu\ [q + 2^{1/2}\ z_F\ \{(\nu q^2/2) - 1\}]$, where q =

$\Gamma(\nu/2)/\Gamma((1+\nu)/2)$. This is the expression used in the analysis of the rate expression in the limit $z_F \longrightarrow 0$. Putting $\nu = 1$ in (A.10) yields the expression, $D_{-1}(-z_F) \simeq (\pi/2)^{1/2} + z_F$ which we have made use of in our analysis.

Appendix B

Evaluation of $G(z_F)$

In this appendix, we arrive at the various limiting forms of $G(z_F)$ used in the derivations. $G(z_F)$ is defined as

$$G(z_F) = \int_{-\infty}^{z_F} dz\ \exp(-z^2/2) \int_{z}^{z_F} dz_1\ \exp(z_1^2/4)\ D_{-1}(-z_1). \tag{B.1}$$

Case 1. $z_F \longrightarrow \infty$.

(B.1) can be written as

$$G(z_F) = (\pi/2)^{1/2} \int_{-\infty}^{z_F} dz\ e^{-z^2/2} \int_{z}^{z_F} dz_1\ e^{z_1^2/2}\ \mathrm{erfc}(-z_1/\surd 2). \tag{B.2}$$

Making use of the identity,

$$\int_0^{\infty} ds\ e^{-x^2 s^2 - ys} = (\pi)^{1/2}\ (2x)^{-1} \exp(y^2/4x^2)\ \mathrm{erfc}(y/2x),$$

(B.2) can be written as

$$G(z_F) = (2)^{-1/2} \int_{-\infty}^{z_F} dz\ e^{-z^2/2} \int_{z}^{z_F} dz_1 \int_0^{\infty} ds\ e^{-(s^2/4) + (z_1 s/\surd 2)}. \tag{B.3}$$

Putting $(s/\surd 2) = s$,

$$G(z_F) = \int_{-\infty}^{z_F} dz\ e^{-z^2/2} \int_0^{\infty} ds\ e^{-s^2/2} \int_{z}^{z_F} dz_1\ e^{z_1 s}. \tag{B.4}$$

Let $z_F - z = y$. Then

$$G(z_F) = \int_0^\infty dy\; e^{-(z_F-y)^2/2} \int_0^\infty ds\; e^{-s^2/2} \int_{z_F-y}^{z_F} dz_1\; e^{z_1 s}. \tag{B.5}$$

$$= e^{-z_F^2/2} \int_0^\infty dy\; e^{-(y^2/2)\;+\;z_F y} \int_0^\infty ds\; e^{-s^2/2} \int_0^\infty dy_1\; e^{(z_F-y_1)s}.$$

$$= e^{-z_F^2/2} \int_0^\infty dy\; e^{-(y^2/2)\;+\;z_F y} \int_0^\infty ds\; e^{-(s^2/2)\;+\;z_F s} \int_0^\infty dy_1\; e^{-y_1 s}.$$

$$G(z_F) = e^{-z_F^2/2} \int_0^\infty ds\; \frac{e^{-(s^2/2)\;+\;z_F s}}{s} \int_0^\infty dy\; (1 - e^{-ys})\; \bar{e}^{(y^2/2)\;+\;z_F y}. \tag{B.6}$$

The role of $(1-e^{-ys})$ is very significant in the region where both y and $s \simeq 0$, because then $(1-e^{-ys}) \simeq 0$. So the integral, in the limit of large z_F may be written as

$$G(z_F) \simeq e^{-z_F^2/2} \int_0^\infty dy\; e^{-(y^2/2)\;+\;z_F y} \int_0^\infty ds\; \frac{e^{-(s^2/2)\;+\;z_F s}}{s}\;.$$

$$\simeq e^{-z_F^2/2}[2\pi\; z_F^{-1}\; e^{z_F^2}\;] + O(1/z_F^2).$$

$$\simeq 2\pi\; z_F^{-1}\; e^{z_F^2/2} + O(1/z_F^2). \tag{B.7}$$

Case 2. $z_F \longrightarrow -\infty$.

In this case, the maximum contribution to the integral in (B.6) comes from the vicinity of $s \simeq 0$ and $y \simeq 0$. Then s^2 and y^2 may be neglected. Hence $G(z_F)$ may be written as

$$G(z_F) \simeq e^{-|z_F|^2/2} \int_0^\infty ds\ s^{-1}\ e^{-|z_F|s} \int_0^\infty dy\ (1 - e^{-ys})\ e^{-|z_F|y}.$$

$$\simeq e^{-|z_F|^2/2} \int_0^\infty ds\ s^{-1}\ e^{-|z_F|s} \Big[|z_F|^{-1} - (|z_F| + s)^{-1}\Big].$$

$$\simeq e^{-|z_F|^2/2}\ |z_F|^{-1} \int_0^\infty ds\ e^{-|z_F|s}\ (|z_F| + s)^{-1}.$$

$$\simeq |z_F|^{-3}\ e^{-|z_F|^2/2} + 0(1/|z_F|^2). \qquad \text{(B.8)}$$

Case 3. $z_F \longrightarrow 0$.

We shall write $G(z_F)$ as defined in (B.1) in yet another way:

$$G(z_F) = \int_{-\infty}^{z_F} dz\ e^{-z^2/2} \int_{-\infty}^{z_F} dz_1\ e^{z_1^2/4}\ D_{-1}(-z_1)\theta(z_1-z). \qquad \text{(B.9)}$$

$$= \int_{-\infty}^{z_F} dz_1\ e^{z_1^2/4}\ D_{-1}(-z_1) \int_{-\infty}^{z_F} dz\ e^{-z^2/2}\ \theta(z_1-z).$$

$$= \int_{-\infty}^{z_F} dz_1\ e^{z_1^2/4}\ D_{-1}(-z_1) \int_{-\infty}^{z_1} dz\ e^{-z^2/2}\ .$$

Defining $y = -z/\sqrt{2}$,

$$\int_{-\infty}^{z_1} dz\ e^{-z^2/2} = (\pi/2)^{1/2}\ \mathrm{erfc}(-z_1/\sqrt{2}),$$

Then

$$G(z_F) = (\pi/2)^{1/2} \int_{-\infty}^{z_F} dz_1 \; e^{z_1^2/4} \; D_{-1}(-z_1) \; \mathrm{erfc}(-z_1/\sqrt{2}). \qquad (B.10)$$

Since $D_{-1}(-z) = (\pi/2)^{1/2} \; e^{z^2/4} \; \mathrm{erfc}(-z/\sqrt{2})$,
(B.10) becomes

$$G(z_F) = \frac{\pi}{2} \int_{-\infty}^{z_F} dz_1 \; e^{z_1^2/2} \; \mathrm{erfc}(-z_1/\sqrt{2}).$$

Let $y = -z_1/\sqrt{2}$.

$$\therefore G(z_F) = (\pi/\sqrt{2}) \int_{-z_F/\sqrt{2}} dy \; e^{y^2} \mathrm{erfc}^2 y.$$

$$= (\pi/\sqrt{2}) \left[\int_{-z_F/\sqrt{2}}^{0} dy \; e^{y^2} \mathrm{erfc}^2 y + \int_{0}^{\infty} dy \; e^{y^2} \mathrm{erfc}^2 y \right].$$

$\int_{0}^{\infty} dy \; e^{y^2} \mathrm{erfc}^2 y = (\pi)^{-1/2} \ln 2.$ (See Ref.9 for details.)

When $z_F \longrightarrow 0$, $\mathrm{erfc}\; y \simeq 1 - 2(\pi)^{-1/2} y \; e^{-y^2}$.

$$\therefore \int_{-z_F/\sqrt{2}}^{0} dy \; e^{y^2} \mathrm{erfc}^2 y \simeq \int_{-z_F/\sqrt{2}}^{0} dy \; e^{y^2} [1 - 2\pi^{-1/2} y e^{-y^2}]^2 .$$

$$\simeq z_F/\sqrt{2} + 0(1/z_F^{\,2}).$$

$$\therefore G(z_F) = 2^{-1/2} \pi \, [2^{-1/2} z_F + \pi^{-1/2} \ln 2 + O(1/z_F{}^2)]. \qquad (B.11)$$

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CHAPTER 6

CONCLUSION

Of late, there have been several experimental[1,2] and theoretical studies[3-7] on electrochemical electron transfer reactions. The theoretical studies are extensions of the theory of homogeneous electron transfer reactions. Quite recently, there have also been investigations into the role of solvent dynamics in determining the rate of the reaction.

We have adopted a diffusion-reaction equation approach to the problem. The central quantity in our study is Q, the shift of the energy of the ionic orbital, due to the fluctuations in solvent polarization. Electron transfer starts from A^{2+} to the metal as soon as the value of Q increases to such a value that the energy of the orbital on A^{2+} crosses the Fermi level. Taking the dynamics of Q to be overdamped and to be describable by an appropriate Fokker-Planck equation, one can take the reaction into account by introducing a sink term into the equation (Eq.(40) in Chap.5). This has only one time independent solution, viz. $P(Q,t) = 0$. All other solutions are time dependent, and hence difficult to find. One also has the problem of defining a rate constant from such time dependent solutions, as the decrease of $P(Q,t)$ with time is usually exponential only in limiting situations. Following the physical situations in the electrochemical case, we solve both the above problems, by introducing a source term into the diffusion-reaction equation, to obtain Eq.(44) of Chap.5. This equation has a time independent solution - a steady - state -

the analysis of which allows us to find the rate constant.

Using this rate constant, we have analysed the different parameter regimes. If $\frac{(\epsilon_F - \epsilon_a)^2}{2\lambda kT} \gg 1$, the crossing of the Fermi level is level is relatively infrequent. When $\frac{2\lambda kT}{(\epsilon_F - \epsilon_a)^2} \Delta\tau_L \ll 1$, the orbital spends only a small amount of time above the Fermi level. Then the rate would be proportional to Δ, the width of the orbital, due to its interaction with the metal. In this situation, the prefactor in the rate expression has no dependence on τ_L. On the other hand, if $\frac{2\lambda kT}{(\epsilon_F - \epsilon_a)^2} \Delta\tau_L \gg 1$, the orbital spends sufficiently long time above ϵ_F, that the electron transfer would take place with certainty. In such a situation, Δ is not important for the rate. The prefactor for the rate would be proportional to τ_L^{-1}. This is the adiabatic limit and experiments of Iwasita *et al*[1] and those of Weaver[2] must be in this regime.

We have also analysed the other limiting cases, $\epsilon_a > \epsilon_F$ and $\epsilon_a \simeq \epsilon_F$, and found the prefactor to be proportional to Δ in both the cases. As ϵ_F can be varied experimentally, by changing the overpotential, it should be possible to observe this changeover of prefactor from Δ independence to proportionality to Δ in experiments.

We now mention an interesting offshoot of our work. We have also compared our approach to the calculation of rate constant to earlier time dependent approaches to the calculation of rate constants. We have shown that our rate constant is identical to k_I as defined by Bagchi *et al*. This implies that to find the rate constant k_I, it is not necessary to solve the time dependent modified Smoluchowski equation, but one can obtain k_I by solving (perhaps numerically) a time independent equation, which is clearly much easier.

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