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CHEMICAL AND ELECTROCHEMICAL
ELECTRON-TRANSFER THEORY[1]

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INTRODUCTION

One of the active areas in reaction kinetics during the post-war years has been that of electron-transfer reactions. These reactions constitute one type of oxidation-reduction process and include both chemical and electrochemical systems. Many rate constants have now been measured (1–8) and they have stimulated a variety of theoretical studies (9–37). The field has been characterized by a strong interplay of theory and experiment, which now includes the testing of theoretically predicted quantitative correlations (34). Because of a certain unique feature of the purely electron-transfer reactions—the absence of bond rupture in the reaction step—these correlations are unusual. They do not have the arbitrary parameters that occur in theoretical studies of most other reactions in chemical kinetics. This review will be limited to purely electron transfer reactions.

A variety of factors have contributed to the growth of this research. The ready availability of isotopes after the war facilitated the extensive study of isotopic exchange reactions. Some of these exchanges proceed via electron-transfer mechanisms and, in this case, form the simplest group of all electron-transfer reactions. Their study permitted a concentration on the major structural feature of the inorganic reactants—the composition and nature of their inner coordination shells (14, 15, 17, 23, 32, 34). The interpretation of the data is free from the added complexity of the effect of relative stability of reactants and products. In a simple electron transfer between two species differing only in their oxidation states there is no difference in stability of products compared with reactants.[3] Then again, but with notable exceptions, many simple electron-transfer reactions are rapid since they do not involve bond rupture. The increasing popularity of electronic instrumentation after the war permitted the study of these fast reactions in electrochemistry, and also in chemistry. Whereas the study of electrochemical reaction mechanisms was once largely confined to hydrogen overvoltage, where the reactions are relatively slow, or to diffusion-controlled processes, many electron-transfer rate constants at electrodes have now been measured and some mechanisms analyzed in detail.

Most of the oxidation-reduction reactions that are of interest here in-

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[1] The survey of literature pertaining to this review was completed on December 15, 1963. Reference is also made to a number of papers appearing in 1964.

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[3] In conformity with common usage (1) an electron-transfer reaction in which the products are chemically indistinguishable from the reactants will be called an electron-exchange reaction.

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volve inorganic reactants. Detailed mechanistic investigations have been made, particularly of homogeneous reactions, primarily with kinetic and isotopic tracer techniques. In turn, the spread of interest in reaction mechanisms from organic to inorganic chemistry has promoted the investigation of electron transfers and of related problems on the stability of inorganic complexes.

Several investigators in this electron-transfer field are physicists (26, 33) —with backgrounds quite different from the chemists, electrochemists, or electroanalytical chemists who dominate it. The problem of electron transfers in solution has much in common with the theory of the "polaron," which is defined as an electron moving in a medium and carrying with it a slightly or extensively polarized atmosphere of the medium. These polarons have been intensively studied, both theoretically (e.g., 38–45) and experimentally, as a quick survey of the entries in *Chemical Abstracts* amply shows. The polaron has been discussed in terms of its role in electron and hole conduction in semiconductors and ionic crystals, in terms of its role in $F-$ and other centers in alkali halides, in liquid ammonia, and in the theory of interactions of an electron with a quantized field (in this case a dielectric polarization field). Some recent theoretical investigations of the polaron include studies on the mechanism of conduction of small and large polarons. These studies take cognizance of the role of vibrations of molecules and of the medium, and may also find application in studies of organic semiconductors and intramolecular electron transfers.

Summary of Recent Developments[4]

Several excellent reviews of experimental studies on chemical and electrochemical electron-transfer reactions have been published recently (1–8). Some of the theoretical work was summarized in these. It is the purpose of the present review to assess the current status of the theoretical studies, their relation to each other and to current experimental research, and to bring up to date the survey of the immediately pertinent experimental investigations. We begin with a brief historical sketch of the recent theoretical contributions.

In 1952, Libby (9) suggested that the rate of electron-exchange reactions was strongly influenced by the Franck-Condon principle: the more similar the inner coordination shells of the donor and acceptor atom, the less difficult would be the electron transfer. The slowness of the $Co(NH_3)_6^{+2} - Co(NH_3)_6^{+3}$ exchange reaction supported this interpretation (46) because of the large difference in the $Co-N$ bond lengths in the two valence states of the cobalt. Independently, in 1952, Randles (10) discussed the mechanism of electron transfers at electrodes in terms of the Franck-Condon principle and of poten-

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[4] In this review, the original arguments have occasionally been slightly recast and simplified, where they were not clear to this reviewer. Some notation also has been modified, to emphasize the relations between the various treatments. For the same reason, more general symbols have sometimes been employed than those used by the authors cited.

tial energy curves. In 1954, R. J. Marcus, Zwolinski & Eyring (12) computed electron tunneling rates from one reactant to the other using estimated barrier heights. Weiss (11) investigated electron tunneling and other aspects about the same time. Much of the subsequent theoretical work has been concerned with assessing the role of the Franck-Condon principle in terms of adiabatic and nonadiabatic mechanisms and with devising a quantitative method for calculating the reaction rate.

The emphasis on differences in bond lengths in the inner coordination shell of a molecule as a reactant and as a product promoted the application of ligand field theory in an attempt to decide, on the basis of number and distribution of d-electrons in transition metal complexes, the magnitude of these differences in bond length (17, 23, 32). An expression was obtained by George & Griffith (23) for the activation energy of electron-exchange reactions in terms of bond force constants and bond length differences, using potential energy curves and neglecting the role of solvation outside the inner coordination shell.

The first calculation of the contribution of the re-orientation of solvent molecules outside the inner coordination shell was given by Marcus in 1956 (16). He used the dielectric continuum theory, reworked in order to permit the calculation of the free energy of systems having a nonequilibrium dielectric polarization (47), 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 calculations of electron transfer rates at electrodes and computed exchange currents and transfer coefficients (18). In 1960, the earlier results were extended to include the contribution from the inner coordination shell. Discussion of the mechanism was in terms of potential energy surfaces and statistical mechanics (30). A series of quantitative correlations between the homogeneous rate constants and between the homogeneous and electrochemical rates were predicted (30, 34). Subsequent work was devoted to seeing how general was the theoretical basis of these correlations (36).

In 1957–1958, Hush (19) discussed electron transfers 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 electron transfers were obtained (32). 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 model and the latter in terms of dielectric continuum theory. (In the earlier quantitative paper of Hush (19), repulsive forces were omitted in the first term and electronic polarization in the second, unfortunately making the numerical results invalid.) The numerical results of the revised treatment may be compared with those obtained by Sutin (1), who examined several potential energy functions to evaluate the force constants and bond lengths appearing in Marcus' formulae. The above treatments of the motions of nuclei in the inner coordination shell of each reactant and in the solvent

are classical. However, Sutin & Wolfsberg (1) have made some calculations of nuclear tunneling effects in the inner coordination shell, and Levich & Dogonadze (26) have made calculations of tunneling in the medium. Any conclusions concerning the contribution of tunneling depended in a sensitive way on the assumed values for the bond force constants and lengths in the former case, properties on which data are now becoming available, and on the assumed polarization frequency in the latter. In the field of polarons there have been a variety of classical and quantum mechanical studies of media having a nonequilibrium dielectric polarization around an electron (e.g., 38, 39). In this work the dielectric polarization vector and its time derivative were expressed in terms of their Fourier components and the sytem was then quantized, which thereby offered a quantum macroscopic description of the motion of the polarized molecules. This method was applied in 1959 by Levich & Dogonadze (22) to the calculation of the rate constants of non-adiabatic electron-transfer reactions in solution. In this paper and in several others (26, 28) the two reactants were assumed to electronically interact very weakly, so that perturbation theory could be applied. In the classical limit to their equations there were marked similarities to the results obtained by Marcus (16), as they pointed out. Their results differed from those of Marcus in one respect since they assumed very weak interaction (cf., non-adiabatic reactions, described later). In 1961, Dogonadze (31) also considered the case of slightly stronger interaction, strong enough to cause an electron transfer probability of about unity at the right nuclear configuration (see below), but not strong enough to badly distort the "potential" energy surfaces. He also used a classical treatment of the nuclei. Rather similar assumptions have been made by Marcus (16) and made in a different way by Hush (32).

Dogonadze, Chizmadzhev and Levich (33, 35) later extended their treatment to electron transfers at electrodes. As before, they assumed that a very weak interaction of the reactants occurred; thus ordinary perturbation theory could be employed. Meanwhile, Dewald (25) had applied Marcus' continuum treatment to semiconductor electrodes; and Gerischer (27) had outlined a formal theory of electrode reactions utilizing Gurney's model (48) for ion-electrode systems and emphasizing the band nature of the electronic energy levels. He made some comparisons with Dewald though he did not calculate the various reorganization energies quantitatively.

The question of possible dielectric saturation effects on the interionic interaction of $Fe^{+2}-Fe^{+3}$ ions was examined by Laidler (20), who also considered, with Sacher (37), effects on the reaction rate due to change in ion size during reaction. Several errors, noted later in this review, did not affect this part of the calculation but unfortunately rendered invalid the calculated rates (20, 37).

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 (15)—and more recently by Halpern (49), Sutin (50) and their co-workers—that in

certain cases electron-transfer reactions occur via bridged intermediates. The bridging groups are sometimes atoms and sometimes groups of atoms; the mechanism is sometimes an atom transfer and sometimes an electron transfer. Again, Dodson & Davidson (51) have pointed out how an apparently simple electron transfer between hydrated ions could involve instead a hydrogen atom transfer between the inner coordination shells of these hydrated ions. There has been some effort, therefore, to study redox reactions between ions with inner coordination shells stable toward such atom transfer; $Fe(phen)_3^{+2} - Fe(phen)_3^{+3}$ for example. In the realm of bridge intermediates Halpern & Orgel (29) 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 (52). Information about these transfers has been derived from spin resonance studies of molecules on which an odd electron has two or more stable sites.

There are a number of novel features in these purely electron-transfer reactions wherein the theoretical work on them differs from most previous work on rate calculations for bond rupture reactions in electrochemical and chemical processes: (i) In the former there is a large separation of charge in the two "resonant" electronic configurations which form the activated complex. This separation requires that the calculation of the free energy of the medium be that of nonequilibrium polarization systems (16, 47, 63, 64). (ii) Although in bond ruptures the reaction coordinate has been assumed to be intuitively obvious, and to involve mainly a linear combination of the distances of the bond being broken and the bond being formed, the reaction coordinate in the purely electron transfer is more complex and has been more elusive. It involves a combination of small changes in bond distances in the inner coordination shell of each reactant, reorientations of solvent molecules outside the shell, changes in distance between the reactants or between the reactant and electrode, and changes in position and bond lengths in the solvent molecules outside of the reactants (16, 30). The many-dimensionality of the system, which could be loosely treated in the bond rupture reaction, now plays a central role and must be considered with more care. (iii) The usually assumed weak electronic interaction in the activated complex of purely electron transfers leads to possible nonadiabatic effects, in contrast with the usual bond rupture reaction which is almost invariably quantum mechanically adiabatic. The problems associated with treating the coupled electronic and nuclear motion causing electron transfer, together with the effect of charge separation and the complexity of reaction coordinate mentioned above, has led to a number of interesting questions in the theoretical literature on this subject. They have also led to a large number of errors.

Before examining the individual theories in detail we consider first a description of electron-transfer reactions in terms of potential energy surfaces (30).

POTENTIAL ENERGY SURFACES AND ELECTRON-TRANSFER PROBABILITIES

In Figure 1 is given a profile of the potential energy surfaces of the reactants (curve R) and of the products (curve P), the dotted lines apply if there was zero interaction of the electronic orbitals of the two reacting species (30). The interaction causes the indicated splitting. The abscissa in Fig. 1 represents any line in many-dimensional configuration space, passing through a stable nuclear[5] configuration (point A) of the reactants and, elsewhere in the space, through one of the products (point B). The R and P surfaces intersect to form a surface S (of one less configurational dimension) indicated by a point in Fig. 1. The corresponding diagram for electrode reactions is slightly more complex (there are many accessible energy levels now) and we shall return to it later. This many-dimensional configuration space involves the positions of all the atoms in the system. Sometimes, however, the coordinates
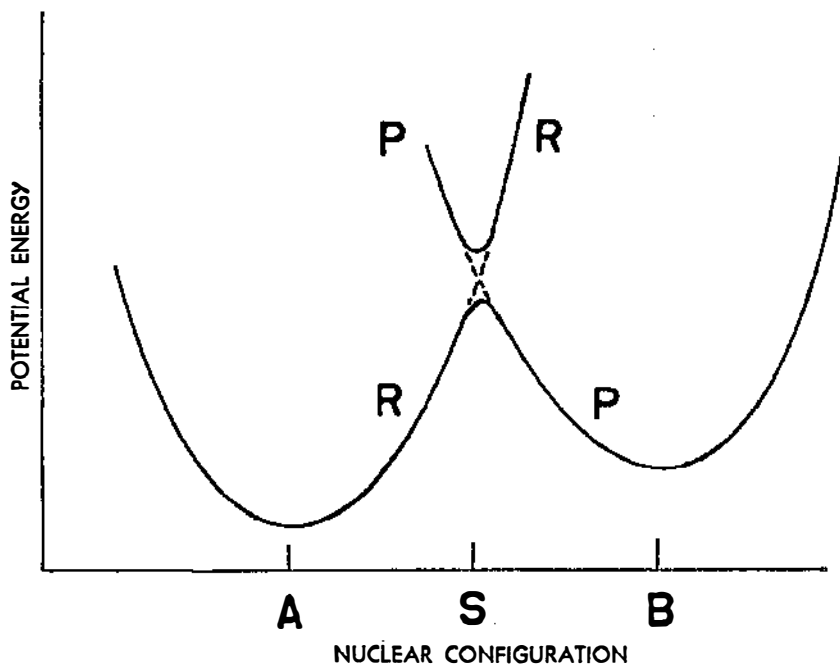

FIG. 1. Profile of potential energy surface of reactants (R) and that of products (P), plotted versus nuclear configuration[5] of all the atoms in the system. - - - =surface for zero electronic interaction of the reacting species. —— =adiabatic surface (The curves are given for a reaction accompanied by an increase in potential energy).

[5] Throughout this paper, nuclear motion refers to the motion of the atoms, not to that of their spins, e.g., the nuclear configuration is the totality of translational, rotational and vibrational coordinates of all the molecules.

are conveniently chosen to be bond lengths, bond angles, molecular orientations and positions of the reactants, of the solvent molecules, and of any other species.

In accordance with well-known quantum mechanical deductions, the classical or quasi-classical treatment of the motion of the nuclei in the vicinity of the intersection in Fig. 1 leads to adiabatic and nonadiabatic properties for the electron-transfer process, described qualitatively as follows: when the system passes the intersection with high velocity, there is little time for electron transfer. When the velocity is low there is usually time. In the first case, the system will usually "jump" from the lower R surface to the upper R surface on passing through the intersection region. In the second case, the system will usually remain on the lower solid "adiabatic" surface during this passage.

One may now distinguish in the literature two definitions of "nonadiabatic." One definition used by physicists (and many chemists) is as follows: when the system jumps from one solid "adiabatic" surface to the other on passing through the intersection region (in Figure 1, for example) the process of jumping is called a "nonadiabatic act" (evidently from Figure 1, a jump did not produce a chemical reaction). A second definition, now standard in chemical literature (53) may be stated thusly: when, as a result of nonadiabatic jumps in the intersection region the probability of chemical reaction occurring is small per passage, for the typical velocity distribution, the reaction itself is called a "nonadiabatic chemical reaction." When the probability of a chemical reaction occurring per passage is large (near unity) the reaction is, of course, called "adiabatic." In either case reaction can occur only if a system starting on the lower surface R finally goes over to P on the lower solid "adiabatic" surface.

Expressions for the transition probability due to Landau & Zener (54) and to Coulson & Zalewski (55) are summarized later. Only the former has thus far been applied to nonadiabatic electron-transfer reactions. The frequently-misconstrued role of electron tunneling will also be considered later. The transition probability will be denoted by γ and its nuclear velocity-weighted average by κ.

Analogously to Fig. 1, one may consider the course of electrode reactions in terms of potential energy surfaces. A simplified description, expressed in terms of a mean electronic energy of the electrode, was described in Reference 24. With a view to including nonadiabatic possibilities, as well as to extending the theory to semiconductors, it is better to do as Levich, Dogonadze and Chizmadzhev (33, 35) and as Gerischer (27), have done in different ways; that is, to take into explicit account all electronic levels of the electrode. For this reason, we introduce Fig. 2, below.

For a metal piece of finite size there is a finite spacing between the energy levels, which levels become a continuum when the metal piece becomes infinite (the average number of levels per unit concentration of electrons remains finite). For a metal piece of finite size the analogue of Fig. 1 is, in

the author's view, given in Fig. 2. Each surface is a many-electron energy level of the entire reacting system and is a function of the nuclear coordinates. The different R surfaces differ only in the distribution of these electrons among the "one-electron quantum states" in the metal piece. The different P surfaces differ in a similar way from each other. The unperturbed surfaces are drawn parallel since their energy differences are relatively unaffected by many of the usual changes of nuclear coordinates (those related to bond lengths of the reactant and solvent orientations).

Thus far, no analog of the Landau-Zener (54) or Coulson-Zalewski (55) equations has been published for the case of many nearby potential energy surfaces, at least not in the electrochemical electron-transfer literature, which covers the entire range of low to high transition probabilities. A very special case of the Landau-Zener equation has been used (33, 35) for this system, namely the limiting form for very small transition probabilities (equation 25 with $\bar{v}$ replaced by v).[6] In this limiting case the various final
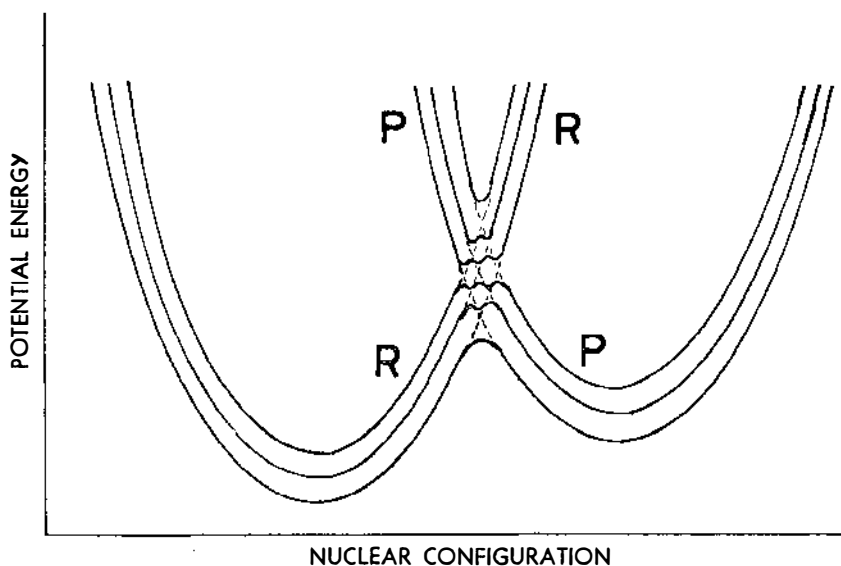

FIG. 2. Same plot as in Fig. 1 but for an electrode reaction. The finite spacing between levels, reflecting the finite size of the electrode, is enormously exaggerated. Only three of the numerous electronic energy levels of this system are indicated. The splitting differs from level to level, and the spacing decreases as the size of the metal increases.

[6] More precisely, a perturbation method was used which in the high temperature limit became equivalent to the weak interaction limit of the Landau-Zener equation, and could in fact be derived from the latter (31). The high temperature limit was the one used most by these authors.

potential energy surfaces P are attained independently (perturbation theory). Hence, for purposes of calculating the transition probability γ from a given R-surface, all R surfaces in Fig. 2 can be ignored except the one under consideration. Dogonadze, Chizmadzhev and Levich (33, 35) and Gerischer (27) have introduced assumptions which, in terms of Fig. 2, correspond to very low electron-transfer probability at the crossing points.

At sufficiently large γ, however, the above perturbation expression for γ must break down. Otherwise, as one can see from Eq. 25, γ could become infinitely large instead of becoming unity, its actual maximum. This error is the usual one in first order perturbation theory: the differential equation associated with the probability of finding the system in the initial state does not correct for the effect of the decrease in this probability during the passage through the intersection region on any subsequent decrease during this passage.

In the case of large γ, we presume, γ will be about unity or perhaps 0.5. Such a case for Fig. 2 will be called an adiabatic electrode reaction, by analogy with the corresponding case for Fig. 1.

For a "weak overlap" *intramolecular* electron transfer reaction viewed under the same approximations, Fig. 1 is applicable, as are the arguments cited earlier. Under certain conditions, an electron transfer occurring via a bridged intermediate can be treated as an intramolecular electron transfer within the intermediate (assuming the population of the intermediates to be an equilibrium one, a calculation of the overall rate constant would then also entail a knowledge of the equilibrium constant for forming these intermediates from the reactants).

COMMON ASSUMPTIONS OF THE TREATMENTS AND SOME DIFFERENCES

Common to the principal treatments (26, 30–33, 56) which calculate reaction rates have been three assumptions: (*i*) The microscopic states or configurations from which the system may undergo reaction (classically or quantum mechanically) are assumed to be in thermal equilibrium with the remaining states. Thus, for example, this assumption appears in the usual equation for absolute reaction rates as well as in the distribution of the polarization oscillators of Levich et al. (*ii*) The interaction of the electronic orbitals of the two reactants (or reactant and electrode) is weak. More precisely, it is assumed to be sufficiently weak that the potential energy surface[7] of the reactants is hardly different from that for zero electronic interaction except for the usual splitting when this surface intersects another potential energy surface, that for which the electronic charge distribution is one which

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[7] Actually, the theory of Levich et al. is a macroscopic theory. The surfaces in their case are those for the free energy of solvation, including ion-ion interaction, and these are plotted versus the Fourier components of a polarization variable. (See later.) The theory of Marcus is statistical mechanical and employs actual potential energy surfaces and actual atomic coordinates. Hush does not use potential energy surfaces. [In an earlier article they were regarded as illusory (19).]

is characteristic of the products. (*iii*) A system having just undergone elec-
tron transfer goes on to form stable configurations of the products (rather
than do anything else, such as recross *S*). For example, in classical calcula-
tions based on the crossing of some surface in phase space, the rate is equated
to the rate of "first passages."

Common to several treatments (26, 30, 31, 33, 56) is the discussion in
terms of potential energy surfaces[7] and the importance of the crossing-point
of the reactants' surface with the products' surface in determining the elec-
tron-transfer probability. In general, these are treatments for which the
quantum mechanical justification is at hand.

Regardless of whether the nuclear motion is treated classically or quan-
tum mechanically the major problem involves calculating the probability of
finding the system in various nuclear[7] configurations (or in various quantum
states of nuclear motion) and calculating the probability of electron transfer
from such configurations or states. Multiplying the two and suitably averag-
ing over all configurations (or states) one then obtains an expression for the
rate constant.

The differences among the treatments range from minor to major. Some
are developed from fundamental considerations, while others are less rigor-
ous. Levich & Dogonadze (26) treat the polarization dynamics macroscopi-
cally but in an elegant fashion. They ignore, for simplicity, dielectric disper-
sion, any changes in the inner coordination shell, and certain other things.
Hush (32) has formulated the problem in such a way so as to calculate from
ion-dipole and ligand field arguments the contribution of the inner coordina-
tion shell. In the statistical mechanical treatment of Marcus (30, 36, 56), a
surface integral in the expression has been expressed in terms of a volume
integral so as to cast some of the difficulties into the evaluation of part of
the Arrhenius frequency factor.

We shall begin with treatments based on a classical description of nuclear
motion. There is evidence in support of a classical treatment and we shall
return later to a brief discussion of the quantum description.

The treatments may be classified, in part, with respect to the effects they
include in their calculation (in whatever language they use) of the probability
of reaching the intersection surface *S*. The probability appears via a free
energy of reorganization term or via some equivalent term. These free energy
terms may have contributions from (*i*) energy (and entropy) changes in the
inner coordination shell due to changes in bond lengths and angles,[8] (*ii*)
changes in ion size due to changes in bond lengths, causing thereby small

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[8] In a number of the cases only an energy of reorganization for contribution (*i*)
was calculated. That is, only the bond lengths which minimize the energy (actually,
the bond energy plus solvation free energy) on *S* are calculated. A large error would
normally be made here by thus omitting any discussion of all the neighboring points
on *S* associated with slightly differe t bond lengths, points through which the system
may pass to reach *P*. This error corresponds to a neglect of a part of the entropy of
the activated complex. It is almost cancelled by the simultaneous omission of the
corresponding entropy term for the stable configurations of the reactants themselves.

changes in the solvation free energy of the medium outside the inner coordination shells, and (iii) for any given size of the ions in the activated complex a change in the vibration-orientation polarization at each point in the medium.

With respect to their inclusion of these effects only, the various quantitative treatments at different stages of their historical development took cognizance of the above three contributions as follows:

Chemical electron-transfer.—Marcus, 1956 (16) (iii); Hush, 1957–58 (19) (i and iii)$^+$; Levich and Dogonadze, 1959–61 (22, 26, 28, 31) (iii); Laidler, 1959 (20) (none); George and Griffiths, 1959 (23) (i, for electron-exchange reactions); Marcus, 1960 (30) (i and iii*); Hush, 1961 (32) (i and iii); Sacher and Laidler, 1963 (37) (i and ii, for electron-exchange reactions); Marcus, 1964 (56) (i, ii,* and iii*); where * = statistical mechanical instead of continuum; $^+$ = neither correctly.

Electrochemical electron-transfer.—Hush, 1957–58 (19) (i and iii)$^+$; Marcus, 1957 (18) (iii); Dogonadze and Chizmadzhev, 1961 (33) (iii); Hush, 1961 (32) (i and iii); Marcus, 1964 (56) (i, ii*, and iii*).

In essentially all treatments absolute values of reaction rate constants have been calculated and extensive comparison with experiment has been made by Hush (32) and by Sutin (1). In the case of Laidler (30, 37) and of Levich and Dogonadze (22, 26, 28, 31) the actual numerical comparison has been largely confined to the electron-exchange between Fe^{+2} and Fe^{+3}. Dogonadze and Chizmadzhev (33) computed the transfer coefficient of an electrode reaction.

In another type of comparison with experiment, Marcus (30) has derived equations which predict quantitative correlations among the data. This type of comparison is being investigated by several researchers, including Sutin (57–60), Halpern (61), Taube (62) and their co-workers. We shall later summarize the current status of such comparisons.

We turn now to a review of recent quantitative theoretical contributions.

TREATMENT OF N. S. HUSH

Hush has considered chemical and electrochemical electron transfers in several recent papers (19, 32). We shall consider only the last of these papers (32), for the reason noted earlier.

Hush reasoned that the probability of the electron being on one of the two reactants in the activated complex is intermediate between the values it has in the initial and final states (0 and 1). The probability that the charge density is that of the products was denoted by λ^+. That is, if the reaction is

$$A^{Z_1} + B^{Z_2} \rightarrow B^{Z_1-1} + B^{Z_2+1}$$
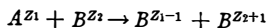
then in the activated complex the mean charge of A is $Z_1 - \lambda^+$ and that of B is $Z_2 + \lambda^+$. The free energy of the system was written as the sum of three parts: (i) the electronic energy of the bare ions, (ii) the intramolecular energy of each inner coordination shell and (iii) the free energy due to interaction of the ions with the medium and with each other (the last being

assumed to be a purely coulombic interaction). Weak overlap was assumed. The mean electronic energy in the activated complex was written as the sum of the electronic energies in the initial and final states, weighted by the factors $1 - \lambda^+$ and λ^+, respectively.

By a thermodynamic argument, Hush then deduced that the free energy of formation of the activated complex from the reactants $\Delta F\ddagger$ is the work required to bring the reactants together, w^r, plus a reorganization term depending on λ^+:

$$\Delta F\ddagger = w^r + ({}^p\Delta^t\mu_{env} - \lambda^{+i}\Delta^f\mu_{env}) + \lambda^+\Delta F^0 \qquad 1.$$

(He used an electrostatic expression for w^r.) In Equation 1 μ_{env} is the environmental free energy, consisting of (*ii*) and (*iii*) above; p denotes a state where the ions are at a typical separation distance occurring in the activated complex but where the system has the charge density of the reactants and is in thermal equilibrium with it; t denotes the transition state; i and f denote the initial and final states (reacting particles far apart). $\Delta F^{0\prime}$ is the "stand ard" free energy of reaction in the prevailing medium.[9]

The main problem now was to evaluate ${}^p\Delta^t\mu_{env}$. There is a contribution from the inner coordination shell and one from the solvation of these complex ions by the medium outside. To calculate the second contribution Hush reasoned as follows:

The free energy of solvation of an isolated ion of radius a (radius of the ion plus inner coordination shell), computed by dielectric continuum theory, is $-q^2(1 - \epsilon_s^{-1})/2a$. Writing this as the sum of two terms

$$\frac{-q^2}{2a}\left(1 - \frac{1}{\epsilon_{op}}\right) - \frac{q^2}{2a}\left(\frac{1}{\epsilon_{op}} - \frac{1}{\epsilon_s}\right) \qquad 2.$$

where ϵ_{op} and ϵ_s are the optical and static dielectric constants, he noted, in effect, that one can imagine the solvation occurring in two steps: (*i*) the ion is immersed in a medium which responds only via electronic polarization, (*ii*) the medium then comes to thermal equilibrium with the ionic charge. Since the free energy change for the first step equals the first term in expression 2, that of the second step must equal the second term. Considering now an isolated ion A having the probability $1 - \lambda^+$ of charge Z_1 and a probability λ^+ of charge $Z_1 - 1$, and solvating it in the above two steps, then noting that the electronic polarization term depends on the charge, the mean value of the first term in expression 2 would be obtained by replacing q^2 by $(1 - \lambda^+) Z_1^2 + \lambda^+(Z_1 - 1)^2$. Letting the nuclei of the medium adjust themselves, now, to a mean charge of $Z_1 - \lambda^+$, Hush said (more rigorously he assumed, since the situations are not entirely analogous) that the free energy change of the second step is given by the second term in Eq. 2 with q equal to this mean charge.

[9] Throughout this review this quantity $\Delta F^{0\prime}$ will appear and the terminology used is that of the reviewer. It is the free energy of the two products, far apart, minus that of the reactants, also far apart, in the prevailing medium. See footnote 4.

He reasoned analogously for the case of two ions of charges Z_1 and Z_2 a distance R apart. The answer ultimately obtained for this dielectric contribution to

$$^p\Delta^t\mu_{env} - \lambda^{+i}\Delta\mu_{env}{}^f$$

was[10]

$$-\left(\frac{1}{2a_1} + \frac{1}{2a_2} - \frac{1}{R}\right)\lambda^+(1-\lambda^+)e^2\left(\frac{1}{\epsilon_{op}} - \frac{1}{\epsilon_s}\right) + \frac{\lambda^+e^2}{R\epsilon_s}(Z_1 - Z_2 - 1) \qquad 3.$$

where a_1 and a_2 are the ionic radii, R the separation distance, and e is the electronic charge. To compute the inner coordination shell energy contribution to $^p\Delta^t\mu_{env} - \lambda^{+i}\Delta^f\mu_{env}$ Hush employed an ion-dipole model for the attractive forces within the inner coordination shell and an inverse power term for the repulsion (a term whose two parameters are assumed to be independent of the valence state of the ion). When the ion is that of a transition metal, and so contains d electrons, a crystal field term is included, varying inversely as the sixth power of the distance and containing the number of d_ϵ and d_γ electrons. To calculate the contribution to μ^t_{env}, the inner coordination shell potential energy function used was that for the products, multiplied by λ^+, plus that for the reactants, multiplied by $1-\lambda^+$, all evaluated at the equilibrium distance for an ion of charge $Z_1-\lambda^+$ in the case of reactant A, and, in the case of B, for an ion of charge $Z_2+\lambda^+$. The contributions to μ^p_{env}, μ^i_{env} and μ^f_{env} were calculated in a straightforward manner.

The resulting expression for $\Delta F\ddagger$ was next minimized with respect to λ^+, and an equation obtained for λ^+ thereby, which could be used to calculate $\Delta F\ddagger$. In computing $\Delta F\ddagger$ for insertion into the activated complex rate equation, the loss in translational entropy in forming the activated complex was not correctly taken into account (the Sackur-Tetrode equation could have been used for example). However, the error introduced into the rate constant was only about a factor of ten (the ratio of kT/h to the collision number in solution, 10^{14} cc mole^{-1} sec^{-1}).

The features of Hush's treatment which are of particular interest, in this reviewer's opinion, are the a priori calculation of the inner coordination shell contribution to the energy barrier, the ligand field effects included thereby, and the interpretation of the quantity λ^+. Assumptions or approximations in Hush's treatment, in addition to the three common to all the treatments, include (i) an adiabatic mechanism (i.e., $\kappa=1$), (ii) a specific model for the inner coordination shell, linear in the charge of the ion and having other specific attributes, (iii) the treatment of the medium as an unsaturated dielectric continuum, (iv) the assumption already noted in the argument leading to Equation 3, (v) neglect of the fact that electron transfers occur over a range of separation distances, (vi) neglect of the detailed mechanics of crossing the intersection surface S, and (vii) the assumption (rather than proof) that the activated complex can be characterized by a single parameter

[10] This result may be deduced by comparing equations 18 and 54 of Reference 32.

λ^+. There are several other approximations including omission of dielectric image effects and of part of the translational contribution to the entropy of formation of the activated complex. The last two appear to be relatively minor (but not negligible) from a numerical viewpoint as do (v) and (vi) which should primarily affect the pre-exponential factor. We shall consider some of the other approximations, including the interpretation of λ^+, when we later compare this treatment with others.

ASPECTS OF CONTINUUM THEORY

The treatment of Levich, Dogonadze and Chizmadzhev (26, 31, 33, 35) and an approximation to the treatment of Marcus (16, 18, 30), make use of dielectric continuum theory for systems whose orientational-vibrational polarization in the medium is not exactly dictated by the charge distribution (38, 39, 47). Hush (32) also makes use of these concepts but in a more intuitive, less formal way. We review briefly the pertinent aspects of this nonequilibrium dielectric continuum formalism. A particular case of this formalism has been actively employed in treatments of polarons as well (e.g., 38, 39).

In these nonequilibrium polarization systems, two quantities characterize the continuum: (i) the field (47) D_c directly due to the permanent charges of the reactants (and of any external fields),[11] (ii) the polarization in the medium $P(r)$, i.e., the net macroscopic dipole moment of the medium per unit volume at the point r. $P(r)$ is due to the orientation of molecules in the medium, the polarized vibrations of chemical bonds of species in the medium, and the polarization of the electrons of those species.

In systems having equilibrium dielectric polarization $P(r)$, the polarization is dictated by the permanent charge distribution. However, the set of configurations (of the oriented and vibrationally polarized particles) occurring in the vicinity of the intersection surface S in Fig. 1 corresponds to a macroscopic polarization dictated neither by the charge distribution of the reactants nor by that of the products but, normally, by some compromise distribution. Particular care must be exerted in calculating the continuum contributions to the free energy of such a system, taking the electronic polarization correctly into account. A method of calculating the free energy of nonequilibrium polarization systems, of which this is one, has been derived and will be considered below (38, 39, 47, 63, 64).

In terms of a continuum picture, there is a free energy associated with the work required to polarize the continuum and with the interaction of this polarization with the permanent charge distribution. An expression for the free energy has been given by Marcus, in the dielectric continuum formalism (47, 63) and also in terms of statistical mechanics (64). When there are

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[11] The distinction between D_c so defined and the dielectric displacement $D (= E + 4\pi P)$, where E is the electric field) does not arise in polaron theory where there are usually no cavities of low dielectric constant. Levich et al. apply polaron theory directly and so do not distinguish between D and D_c. However, cavities are now present, namely those occupied by the ions.

no cavities in the medium this expression reduces to one derived earlier for the polaron theory (38, 39). This second expression was used by Levich and co-workers for electron-transfer reactions, though they did not note this assumption. The error, which leads to a neglect of dielectric image effects due to the cavities occupied by the ions, is not serious, but, also, not negligible. (These image effects were neglected in the application of the more general expression in Refs. (16) and (34) also, but they need not have been.)

Marcus (63) has shown that the continuum expression can be expressed in a form convenient for rapid calculation. The term F has been shown to be equal to the algebraic sum of the free energies of several equilibrium polarization systems (63). ($F = F_0 + F_{1-0}{}^{op} - F_{1-0}$, where the symbols 1 and 0 have been defined elsewhere.) [A statistical mechanical expression for F can be expressed similarly (64).]

When the polarization changes with time, as it always does, there is a kinetic energy difference between the polarized and unpolarized system (38, 39). An expression for this kinetic energy has been derived for ionic crystals (40), based on an analysis of the optical normal modes. As a first approximation, the same macroscopic expression was used for polar liquids (26). In a classical mechanical treatment of the motions of the continuum, this kinetic energy term plays a role of minor importance, affecting only the Arrhenius frequency factor in the expression for the rate constant. In a quantum treatment of these motions, the kinetic energy expression is needed to formulate the Schrödinger equation. (However, in these chemical and electrochemical systems such quantum effects appear to play a comparatively minor role. At very low temperatures the situation should be different, but then the effects might appear first for the inner coordination shell where the vibration frequency is higher than that for molecular reorientation in the medium.)

Levich, Dogonadze and Chizmadzhev employed the kinetic energy expression used in polaron theory for the fluctuating polarization of the medium. For all calculations based on the use of this kinetic energy, quantities closely related to orientation-vibrational polarization and its time derivative, both continuous functions, are usually expressed in terms of their Fourier components (38, 39). In this form the sum of this kinetic energy and the "static" free energy is formally identical with the Hamiltonian for a harmonic oscillator (38). The Fourier components in the one replace the vibration coordinates of the other. The equilibrium value of any Fourier component depends in a simple manner on the permanent charge distribution in the system and differs, therefore, for reactants compared with the products. The analogy to the vibrational coordinate is clear. In this case the equilibrium bond length differs in the initial and final valence states of a reacting species. Some of the pertinent equations concerning these Fourier components follows. They are given in this review for completeness only and could more properly be placed in an appendix.

Dielectric continuum and Fourier components.—A function P_{ir} is defined (26

38, 39) such that $P - P_{ir}$ is independent of the orientation-vibration polarization. (Electronic polarization contributes to both P_{ir} and $P - P_{ir}$.) One may then introduce a Fourier expansion, for example, in standing waves (38)[11a]:

$$P_{ir} = \sqrt{h\nu_0 c/4\pi} \sum_k q_k \frac{k}{k} \chi_k(r),$$

$$\dot{P}_{ir} = \sqrt{h\nu_0^3\pi c} \sum_k p_k \frac{k}{k} \chi_k(r),$$

where ν_0, a characteristic frequency of the oscillators, is assumed to be independent of k;

c is $\left(\dfrac{1}{\epsilon_{op}} - \dfrac{1}{\epsilon_s}\right)$ and $\chi_k(r)$ equals $\sqrt{2/V}\ \cos\ k \cdot r$ for $k_x \leq 0$

and $\sqrt{2/V}\ \sin\ k \cdot r$ for $k_x > 0$, V being the volume of the system. The expansion is made in terms of longitudinal components (i.e., those parallel to k) since the transverse ones do not interact with the charge distribution. The k's in the sum satisfy a periodic boundary condition in the system treated as a cube of length $\sqrt[3]{V}$.

If the dielectric displacement $D(=E+4\pi P)$ is similarly expanded,

$$D(r) = \sqrt{2\pi h\nu_0/c} \sum_k d_k \frac{k}{k} \chi_k(r),$$

one can express in terms of Fourier components the classical kinetic energy of the polarization plus the solvation free energy due to mutual ion-solvent interactions, obtained from the corresponding expression[11b] in continuous functions. The part which depends on p_k and q_k is

$$\tfrac{1}{2} h\nu_0 \sum_k \left[p_k^2 + q_k^2 - 2q_k d_k\right].$$

According as D refers to the reactants or products so does d_k and, thereby, so does this expression. The equilibrium values of the q_k's are those which minimize $q_k^2 - 2q_k d_k$. They therefore equal d_k. Thereby, the equilibrium values of the q_k's and so of the function $P_{ir}(r)$ depend on the charges on the reactants. The analogy to the harmonic oscillator is apparent.

The terms q_k and $\hbar p_k$ are found to be canonically conjugate and so quantization is readily introduced ($q_k \to q_k$, $\hbar p_k \to i\hbar \partial/\partial q_k$). In the actual system, the total Hamiltonian for the Schrödinger equation and the electronic-nuclear wave function was introduced, rather than just the nuclear Hamiltonian given above, which refers to a system of specified electronic configuration (that of reactants or that of products).

It should be noted that, consistent to some extent with the neglect of

[11a] Levich & Dogonadze (26) used an expansion in traveling waves instead, but introduced a second transformation later in the paper, which made the final expansion the same as Pekar's.

[11b] Cf the last three terms of Equation 10.1, Ref. 38, for the part depending on P_{ir}.

dielectric image effects, the Fourier expansion made was one in terms of plane waves. If one wishes P_{ir} to vanish inside each ionic cavity, the use of many components of very small k would be required. The assumption of a frequency ν_0 independent of k would then be still more questionable. On the other hand, expansion in the appropriate complete set of functions which vanish inside the cavities and satisfy the appropriate differential equation would be more complicated. In fact, a reformulation of the entire Hamiltonian so as to include dielectric image effects might then be desirable. In virtue of the other approximations (neglect of dielectric dispersion, for example) such refinements are perhaps unwarranted at this time.

TREATMENT OF LEVICH, DOGONADZE AND CHIZMADZHEV

In a series of very interesting papers these authors have treated chemical and electrochemical electron transfers, both classically and quantum mechanically (22, 26, 28, 33, 35). The medium outside the inner coordination shell of each reactant was treated as a dielectric continuum and the reactions considered were those involving no changes in equilibrium bond lengths and angles in the inner coordination shell. The overlap of the electronic orbitals of the two reactants was assumed to be so weak that perturbation theory could be used to calculate the transfer rate in chemical and electrochemical electron transfers, by a nonadiabatic method. (The high temperature-limiting form of their formula contained a weak-interaction form of the Landau-Zener equation given by Equation 25, *post.*) The idea that perturbation theory is inadequate to describe chemical electron transfers was discussed by Dogonadze (31), whose results are described in a later section. The case where perturbation theory is inapplicable to electrode processes has not yet been discussed by them. The Hamiltonian for the motion of the polarization was employed. Profiles of the R and P surfaces, plotted as a function of the Fourier components were given and the importance of the intersection region was recognized (26, 33). In this region the electronic wave function is sensitive to nuclear configuration. A Schrödinger equation, written in a form which takes cognizance of this sensitivity, was used in the one-electron approximation; the nuclear part of the Hamiltonian was described by Fourier components. In the approximate solution of the equation the separation distance of the reactants was held fixed. Actually, one should consider the entire Hamiltonian (including the R-kinetic energy). Otherwise, an error results.[12] However, appreciable simplification was achieved. The formal expression for the rate was based on the quantum treatment of the polarization modes (and the additional assumptions contained therein and already described). Because of the observed high activation energy for electron transfer, the classi-

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[12] One can show from Eq. 17 below that this step, together with the subsequent use of Equation 6, is equivalent to the neglect of the contribution of R to the "reaction coordinate," i.e., to the coordinate leading to the crossing of S. The other extreme is that made in simple collision theory, where the reaction coordinate is R itself. (In that case S is a surface on which R is a constant, equal to the collision diameter.)

cal limit is the one of current interest, as pointed out by Levich & Dogonadze (26).

For homogeneous reactions their expression for w_{12}, the probability of electron transfer at a separation distance R between the reactants, can be written with a notational change as (26):

$$(\kappa \ll 1) \qquad w_{12} = \sqrt{\frac{\pi}{kT\lambda_0}} \frac{\epsilon_{12}^2}{\hbar} e^{-(I_\beta - I_\alpha + \lambda_0)^2/4\lambda_0 kT} \qquad\qquad 4.$$

where $\hbar$ is $h/2\pi$ and[13]

$$\lambda_0 = \frac{(\Delta e)^2}{2} \left(\frac{1}{2a_1} + \frac{1}{2a_2} - \frac{1}{R} \right) \left(\frac{1}{\epsilon_{op}} - \frac{1}{\epsilon_s} \right) \qquad\qquad 5.$$

where a_1 is the radius of ion 1, Δe is the charge transferred, and $2\epsilon_{12}$ is the splitting term at the intersection of the R and P surfaces. I_α is the value of the solvation free energy plus electronic energy of the reactants for the equilibrium solvation of the reactants at the separation distance R. I_β is the corresponding term for the products. In terms of a notation used later, $I_\beta - I_\alpha$ is $\Delta F_R^{0\prime}$ the "standard free energy of reaction at the separation distance R."[14]

It was then argued that the rate constant k_{12} is related to w_{12} according to Eq. 6 (26).

$$k_{12} = \int_0^\infty w_{12} e^{-w^r/kT} 4\pi R^2 dR \qquad\qquad 6.$$

where w^r denotes here $Z_1 Z_2 e^2/\epsilon_s R$, the work required to bring the two reactants together (infinite dilution assumed). In Eq. 6, w_{12} and w^r were replaced by their values at $\overline{R}$, the R for which the integrand has a maximum. The remainder of the expression was replaced by $4\pi \overline{R}^2 \delta R$, because of the Gaussian-like nature of the integrand (26a, 28), δR being some narrow width. In a later paper (28) an approximate estimate of ϵ_{12} was also made to evaluate the various parameters.

For electrochemical electron transfers, an expression was obtained (33) for the probability of transfer of an electron from an ion A^{+2} to energy level of the electrode.

$$A^{+2} + M \rightarrow A^{+3} + M(e) \qquad\qquad 7.$$

[13] Instead of Eq. 5, the value of λ_0 of Levich et al. was normally given in terms of dielectric displacements. They calculated the latter for the $Fe^{+2}-Fe^{+3}$ reaction. The same method easily extends to nonequal radii, thereby yielding Equation 5.

[14] This quantity, rather than $\Delta F^{0\prime}$ itself, is the important quantity affecting the reorganization free energy at the separation distance R (21), since $\Delta F^{0\prime}$ is the free energy of reaction when the reactants are infinitely far apart. $\Delta F_R^{0\prime}$ appears, though sometimes in a hidden way, in the first four quantitative treatments described in this review. $\Delta F_R^{0\prime}$ equals $\Delta F^{0\prime} + w^p - w^r$ where the w's are the actual work terms, often approximated by an electrostatic calculation at infinite dilution, as in Reference 26.

It can be rewritten as in Eq. 8 for a given separation distance R between the ion and the electrode.

$$(\kappa \ll 1) \qquad w_{2f} = \sqrt{\frac{\pi}{kT\lambda_0}} \frac{\epsilon_{2f}^2}{\hbar} \, \varepsilon^{-[I_f - I_2 + \lambda_0]^2 / 4\lambda_0 kT} \qquad \qquad 8.$$

where $2\epsilon_{2f}$ is the splitting term for the R and P levels involved. I_f and I_2 are the term values appearing in an approximate one-electron Schrödinger equation for the equilibrium initial and final states. As in Eq. 4, they are each the sum of the free energy of solvation and of the electronic energy of the system in the two states. In terms of the number of energy levels in the electrode per unit energy, ρ_f, and of the probability of finding a level of energy E_f occupied, $n(E_f)$, (Fermi-Dirac distribution function) the rate constant for transfer from ion 2 to the electrode was (35):

$$(\kappa \ll 1) \qquad k_{es} = \int_{R=0}^{\infty} \frac{c_2(R)}{c_2(\infty)} dR \int w_{2f}(R)[1 - n(E_f)]\rho_f dE_f \qquad 9.$$

where $c_2(\infty)$ is the concentration for ion 2 at any point outside the electrical double layer.

The rate constant for the reverse reaction, k_{se}, for electron transfer from the electrode to ion 3 was (35):

$$(\kappa \ll 1) \qquad k_{se} = \int_{R=0}^{\infty} \frac{c_3(R)}{c_3(\infty)} dR \int w_{f2}(R) n(E_f) \rho_f dE_f \qquad 10.$$

where w_{f2} equalled (by a thermodynamic argument) $w_{2f} \exp(I_f - I_2)/kT$. Denoting by R_0 the position of the outer Helmholtz plane, the R-integrals were replaced by $c_2(R_0)\delta R/c_2(\infty)$ and $c_3(R_0)\delta R/c_3(\infty)$, respectively, where δR is an effective range of the R's contributing to the integrals.

Noting that w_{f2} increased rapidly with E_f in the vicinity of the Fermi level while $n(E_f)$ decreased rapidly (and conversely for w_{2f} and $[1 - n(E_f)]$ in Eq. 9) the integrands have sharp maxima in the vicinity of the Fermi level and were evaluated by noting their δ-like character there. The resulting expression for the rate of transfer of an electron from ion 2 into the electrode was (33b):[15,16]

[15] The exponent has been recast in this review, with the introduction of the symbols w^r and w^p, for example, so as to emphasize the similarity to other equations, chemical and electrochemical. In the electrostatic approximation of the authors, w^r and w^p equalled $Z_2 e\Delta\phi$ and $Z_3 e\Delta\phi$, respectively, where $\Delta\phi$ is the potential in the outer Helmholtz plane minus that in the bulk of the solution. Although the equation was derived by the authors for reaction 7, it also applies to any one-electron transfer.

In Reference 35 a Gaussian method was used instead of the δ-method to integrate Eq. 9 over E_f, obtaining thereby a slightly different numerical constant.

[16] (a) With the change of notation mentioned in Footnote 9 it becomes clear that $e(E - E_0')$ plays the same role in the electrode reaction that $\Delta F_o'$ does in the homogeneous reaction. (b) In Eq. 11 and 12, ρ_f is proportional to V, the volume of the electrode, but an "improper" eigenfunction ϕ_f appearing in the expression for ϵ_{2f} is normalized to V and so is inversely proportional to $\sqrt{V}$. Hence $\rho_f \epsilon_{2f}^2$ is independent of V.

$$(\kappa \ll 1) \qquad k_{ee} = \sqrt{\frac{\pi kT}{\lambda_0}} \, \rho_f \frac{\epsilon_{2f}^2}{\hbar} \, e^{-w^r/kT} \delta R \, \exp \left\{ \frac{-[w^p - w^r - e(E+E_0') + \lambda_0]^2}{4\lambda_0/kT} \right\} \qquad 11$$

$$(\kappa \ll 1) \qquad k_{ee} = \sqrt{\frac{\pi kT}{\lambda_0}} \, \rho_f \frac{\epsilon_{2f}^2}{\hbar} \, e^{-w^p/kT} \delta R \, \exp \left\{ \frac{-[w^r - w^p - e(E-E_0') + \lambda_0]^2}{4\lambda_0 kT} \right\} \qquad 12.$$

where E is the metal-solution potential difference, E_0' being the corresponding term when $c_2(\infty) = c_3(\infty)$ and when there is electrochemical equilibrium (the formal potential); w^r and w^p are the work terms in reaction 7 to bring ions 2 and 3, respectively, from any point in the bulk of the solution to the outer Helmholtz plane. $E-E_0'$ was subdivided into the activation overpotential, $\eta(=E-E_e)$ and a concentration term, $E_e - E_0'[= kT \ln c_2(R_\infty)/c_3(R_\infty)]$, where E_e is the equilibrium metal-solution potential difference for the bulk concentrations $c_2(R_\infty)$ and $c_3(R_\infty)$.

Levich, Dogonadze and Chizmadzhev (33, 35) have also discussed the application of these considerations to semiconductors and to metallized semiconductors. In this case it is useful to replace $w^p - w^r - e(E - E_0')$ by the quantity which it, in effect, originally replaced, namely the free energy of reaction when the ions are each at the outer Helmholtz plane. This free energy change was expressed in terms of the change in solvation free energy of the ion, in terms of the changes in electronic energy of the ion and electrode, and in terms of the potential at the Helmholtz plane. In the case of semiconductors, electron transfer with valence and conduction bands are both possible (25, 27, 33) and are computed separately. In computing the above free energy difference cognizance was taken of the fact that the bands were bent near the semiconductor electrode surface.

For completeness, we note that at the other extreme the low temperature limit of the quantum expression obtained for a homogeneous electron transfer reaction is given by Eq. 13 (26).

$$w_{12} = \frac{2\pi}{\hbar} \frac{\epsilon_{12}^2 e^{-\lambda_0/h\nu_0}}{[(I_\beta - I_\alpha)/h\nu_0]! h\nu_0} \cdot (\lambda_0/h\nu_0)^{(I_\beta - I_\alpha)/h\nu_0} e^{-(I_\beta - I_\alpha)/kT} \qquad 13.$$

where ν_0 is the frequency associated with the polarization motion.

In this limit transitions occur from those lowest possible quantum states of the reactants from which reaction is energetically possible. It would appear, from a physical point of view, that Eq. 13 was designed for a reaction for which $I_\beta - I_\alpha$ is positive. For the reverse process they found: $w_{21} = w_{12} \exp(I_\beta - I_\alpha)/kT$. The low temperature limit, Eq. 13, was also based on perturbation theory and so presumably is appropriate at low temperatures if the splitting is small.

For an electron-exchange reaction $I_\beta - I_\alpha$ vanishes and the above expression simplifies $(0 != 1)$. The reaction rate in this low temperature limit would have a negligible temperature coefficient and proceed at a low rate. The equation for the w_{12} of an electron-exchange reaction covering the entire temperature range has also been given [cf. Equation 43 in (26b)].

In addition to the assumptions common to all treatments, the classical

version of Levich, Dogonadze and Chizmadzhev's assumes (*i*) a dielectrically unsaturated continuum, (*ii*) no dispersion of frequencies of the motion of the continuum, (*iii*) neglect of dielectric image effects, (*iv*) approximate treatment of the relative motion of the reactants, (*v*) absence of a damping term in the macroscopic equation of polarization in these liquids, (*vi*) neglect of changes of bond length within the inner coordination shell, and (*vii*) nonadiabaticity and the assumptions involved in the weak interaction limit of the Landau-Zener equation.

TREATMENT OF DOGONADZE

In addition to the method described above, Dogonadze (31) has also considered the possibility that $\kappa \cong 1$. He has also derived an expression for the nonadiabaticity effect using the method of Zener (54). The remaining assumptions are identical with those summarized earlier for the Levich, Dogonadze and Chizmadzhev treatment (*i* to *vi*). He obtained Equation 14 for the electron-transfer probability at the separation distance R, for the case of an adiabatic electron-exchange reaction.

$$(\kappa = 1) \qquad w_{12} = \nu_0 e^{-\lambda_0/4kT} \qquad \qquad 14.$$

where λ_0 given by Eq. 5 with $a_1 = a_2$.

For completeness and for later comparison we note that Eq. 14 can easily be generalized to adiabatic electron-transfer reactions:

$$(\kappa = 1) \qquad w_{12} = \nu_0 e^{-(I_\beta - I_\alpha + \lambda_0)^2/4\lambda_0 kT} \qquad \qquad 15.$$

The rate constant k_{12} is again given by Eq. 6.

TREATMENT OF R. A. MARCUS

Marcus used nonequilibrium dielectric polarization theory (47) to calculate the free energy of activation for a system with rigid inner coordination shells (16). These results for homogeneous electron transfers were extended to electrochemical ones (18) and led eventually to prediction of correlations among the data (30, 34).

A clearer insight into the actual mechanism of the electron transfer itself was afforded (24, 30) by the introduction of the potential energy surface described in Fig. 1. The treatment for homogeneous systems was extended so as to include changes in bond length in the inner coordination shell (30). The entire system was treated in terms of statistical mechanics (30). An "equivalent equilibrium distribution," described in more detail below, was introduced to facilitate the calculation. In one of the last steps of derivation the statistical mechanically derived contribution of the medium to the free energy of activation was replaced by its dielectric continuum equivalent.

The predicted correlations have received some experimental support (34, 57–62). The recent work of Marcus (56) has been concerned primarily with generalizing the statistical mechanical treatment so as to place the correlations on a relatively broad theoretical basis. We summarize below this latest extension.

Making the three assumptions common to all treatments described earlier and the assumption of classical motion of the nuclei the resulting equation for the rate constant was given by Eq. 16 when κ is unity (56).

$$k_{\text{rate}} = \frac{kT}{h} e^{-(F^{\neq}-F^r)/kT} \qquad \qquad 16.$$

where $F^{\neq}$ is the configurational free energy of a system constrained to exist on the intersection surface, and F^r is that of the reactants. Eq. 16 was first derived for chemical reactions by Eyring (65) using a special form of the kinetic energy term ($p^2/2\mu$+terms independent of p, where μ is a constant and p is the momentum conjugate to the reaction coordinate). It holds for the general kinetic energy expression as well (56).

When the reaction is homogeneous and bimolecular in an isotropic medium, integration over a number of coordinates may be performed because of symmetry considerations. The resulting expression is given below in a form which includes the presence of κ, the velocity-weighted average of the transition probability, γ, described later. Typically, however, a value of $\kappa \cong 1$ was assumed (i.e., adiabatic reaction).

$$k_{\text{rate}} = \sqrt{8\pi kT} \int_S (\kappa \overline{R^2}/\sqrt{m^*}) e^{-U/kT} dS/Q \qquad 17.$$

where U is the potential energy for any configuration in the reacting system, dS is the area element of the surface S to be crossed, R is the distance between the mass centers of the two reactants, m^* is the reduced mass for motion normal to the surface S, and Q is the configurational partition function of the reactants. Because of the integrations already performed in obtaining Eq. 17, several coordinates in the equation are fixed.[17] Both R and m^* vary on S, and a precise expression for m^* can be given in terms of the properties of S. (For a collision diameter R, incidentally, Z, the collision frequency of uncharged species would be $R^2\sqrt{8\pi kT/\mu}$ for a reduced mass μ.)

The equation for a heterogeneous reaction at an interface, derived on the same assumptions as Eq. 17 is:

$$k_{\text{rate}} = \sqrt{kT/2\pi} \int_S \kappa e^{-U/kT}(1/\sqrt{m^*})dS/Q \qquad 18.$$

In obtaining Eq. 18, certain integrations have already been performed, and so several coordinates in Eq. 18 are fixed[18] (the collision frequency Z_{el} with unit area of the electrode is, incidentally, $\sqrt{kT/2\pi\mu}$ for a reduced mass μ).

In Eq. 18, κ is again the velocity-weighted average of γ, but properly weighted in accordance with the distribution of filled and unfilled states in the electrode. For very weak overlap, $1-\gamma$ would be given by Eq. 23 (post) if one used the Landau-Zener approximation.

[17] In the numerator the fixed coordinates are five in number: the center of mass of one reactant and the orientation of the line of centers of the two reactants. In Q six are held fixed: the coordinates of the two centers of mass of two reactants.

[18] In the numerator the two coordinates of the center of mass of the reactant parallel to the electrode surface are held fixed. In Q, the center of mass of the reactant is fixed.

For intramolecular electron transfers k_{rate} is now given by Eq. 18 (but now with the center of mass of the reactant held fixed in the numerator), with κ given by the value for a homogeneous reaction.

A comparatively general expression was used for the potential energy of the entire system and introduced into Eq. 17 and 18. It was based on a "particle description" for molecular interaction (66). This description minimizes the assumptions by treating each of the two reactants and the entire medium outside it as individual "particles" having rather general properties. It emphasizes the functional dependence of the potential energy on the electronic charge distribution of the reactants (surface R) and on that of the products (surface P).

To simplify the calculation of the surface integral appearing in Eq.17 and 18 (more precisely of an approximate form of this integral) the $(n-1)$-dimensional surface integral was expressed in terms of an n-dimensional volume integral and a one-dimensional partition function. The volume integral had a Boltzmann distribution of configurations of the nuclei, centered on the intersection surface S (the "equivalent equilibrium distribution" of Ref. 30). The partition function described the motion away from S in the latter distribution. The advantage of the volume integral was the absence of the constraint present in the surface integral.

A number of previous (16, 30) limitations were removed (56): the ion-dipole treatment of polar media (30) was replaced by a much more general one (64, 66). The assumption of dielectric unsaturation of the medium outside the inner coordination shells was replaced by the milder one of partial dielectric saturation (i.e., linear polarization response to the change of charge distribution on going from reactants to products, rather than on going from uncharged species to charged reactants or products) (63, 64).

The effect of the expansion or shrinkage of the inner coordination shell on the medium's contribution to the solvation free energy, noted by Sacher & Laidler (37), was included in the above statistical mechanical treatment. As in all treatments thus far, however, correlations between fluctuations of bond lengths about their mean values in the activated state and configurational fluctuations outside the inner coordination shell were neglected[18a]. The fact that electron transfer could arise from a range of separation distances, mentioned by Levich & Dogonadze (26) and by Laidler (20), was also included (such a range automatically occurs in the surface integral of Eq. 17 and 18 and carries over to the volume integrals).

In the case of the inner coordination shell the harmonic approximation was used for the intramolecular vibrations. Instead, the procedure in the previous paper (30) could have been followed; namely that of using the general intramolecular potential energy for this coordination shell. Later, to attain the predicted correlations, an approximation milder than the harmonic approximation might have been introduced. The present procedure was used partly in the interests of simplicity and partly because calculations

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[18a] This assumption has now been removed in (56).

by Sutin (1) have indicated that over the usual bond length changes, the harmonic approximation sufficed. To obtain the desired functional form for the predicted correlations, it was then shown that only a minor error in the rate constant was introduced when every force constant in the reactant K^r and the corresponding one in the product K^p were replaced by a reduced force constant $2K^rK^p/(K^r+K^p)$. Introduction of these various quantities into the expression for the rate constant for homogeneous electron transfers had the form given by Eq. 19 (56).

$$k_{\text{rate}} = \kappa\rho Z e^{-\Delta F^*/kT} \qquad\qquad 19.$$

where[19]

$$\Delta F^* = \frac{w^r + w^p}{2} + \frac{\lambda}{4} + \frac{\Delta F^0}{2} + \frac{(\Delta F^{0'} + w^p - w^r)^2}{4\lambda} \qquad 20.$$

and where Z is approximately the number of collisions occurring between two neutral species in unit volume of solution in unit time at the mean separation distance in the activated complex.[20] The symbol ρ is the ratio of the root mean square fluctuations in separation distance in the activated complex to the root mean square fluctuations of a coordinate for motion away from the intersection surface in the volume integral mentioned earlier and should have a value of the order of unity.

In Eq. 20, w^r is the work required to bring the reactants to their mean separation distance R, and $-w^p$ is the work required to separate the products from R to infinity. It can include polar (e.g., electrostatic) and nonpolar contributions. $\Delta F^{0'}$ is the "standard free energy of reaction" for this elementary step in the prevailing medium (so $\Delta F^{0'}+w^p-w^r$ is the "standard free energy of reaction at the separation distance R" in this medium).[14] The term λ is the sum of an "inner" contribution λ_i (from changes in coordinates in each inner coordination shell) and an "outer contribution" λ_0 (from the medium outside). It was shown that λ is essentially an additive function of the two redox reagents.[21] That is, it could be written as the sum of two other terms, one of which depended only on the properties of one reaction species in its initial (reactant) and final (product) equilibrium states, and the other of which depended only on the initial and final equilibrium properties of the second reactant.

For the electrochemical reaction rate an expression analogous to Eq. 19 can be derived in the following way: As Dogonadze, Chizmadzhev, Levich

[19] The formal similarity of the exponents in Equations 4–6 and 19–20 becomes clearer when ΔF^* is rewritten as $w^r+(\Delta F_R^{0'}+\lambda)^2/4\lambda$ and $I_\beta-I_\alpha$ as $\Delta F_R^{0'}$. It may be noted, however, that both λ and the w's are more general in Eq. 19. Similar formal similarity of the exponents occurs in Eq. 11, and 19 plus 21.

[20] The detailed expression for Z is given in Reference 56.

[21] (a) However, the proof of the approximate additivity of the R-dependent part of λ was given by resorting to dielectric continuum theory, a limitation which probably can be removed. (b) The proof of equality of the R-dependent parts of λ_0 and $\lambda_0^{el}/2$ was given similarly.

(33, 35) and Gerischer (27) have emphasized, the contribution to electron transfer for each initial electronic level of the system is calculated. Since one of the reactants is an electrode there are many such levels occupied with appreciable probability. Each electronic level of the system as a whole corresponds to a different distribution of the electrons among the energy levels of the electrode. There is no need to introduce any very specific model of the electrode for our immediate purposes and no need to introduce an approximation of "one-electron levels."

In the case of a metal electrode most of the occupied electronic levels of the system as a whole, which contribute to the rate, lie within kT of each other (compare with Fermi-Dirac distribution among one-electron levels). Since the probability of electron transfer for a given electronic level of the reactants varies very little over an energy range of the order of kT, it can be expressed in a manner relative to its mean value and the latter can be extracted from the integral. Integration over the distribution of electronic levels of the system is then easily performed. In the case of a nonadiabatic electron transfer, the κ in Eq. 19 thereby becomes that for the Fermi level.

For these metal electrodes one obtains Eq. 19, but with the ΔF^* given below and with Z being approximately equal to the number of collisions of an uncharged species with unit area of the electrode in unit time,[19,20] one obtains

$$\Delta F^* = \frac{w^r + w^p}{2} + \frac{\lambda^{el}}{4} + \frac{ne(E - E_o')}{2} + \frac{(neE - neE_o' + w^p - w^r)^2}{4\lambda^{el}} \qquad 21.$$

where E_o' is the formal electrode potential and E is the observed potential (as defined earlier); w^r is the work required to bring the reactant to the electrode to the mean separation distance and $-w^p$ is the work to remove the product. (As in Eq. 20, they can contain polar and non-polar terms. In the statistical mechanical derivation, no specific assumption restricting the calculation to an electrostatic work term was made.) The term λ^{el} is the sum of two terms, an inner λ_i^{el} and an outer λ_o^{el} contribution. The former is one half that found for the corresponding homogeneous electron-exchange reaction involving the same two valence states of this electrochemically active ion. The latter (λ_o^{el}) has one half the value for this homogeneous electron-exchange reaction when the mean separation distance between the two reactants, R, is twice that between the reactant and the electrode.

The λ_i appearing in the above equations can be written as a scalar product, in terms of the intramolecular coordinates q_i of the inner coordination shell of one reactant in the electrode case and of the two reactants in the homogeneous one. It is given in Eq. 22.

$$\lambda_i = \Delta q^T \cdot K \cdot \Delta q / 2 \qquad 22.$$

where Δq is a column matrix whose elements are differences in equilibrium values of q_i, $q_i^p - q_i^r$, and whose transpose is Δq^T; K is the matrix whose elements are the reduced force constants. For homogeneous electron transfers λ_i is the sum of two terms, one for each reactant. When the off-diagonal force

constants appearing in Eq. 22 are neglected it reduces to an expression, $\Sigma_s k_s (\Delta q_s)^2/2$, cited in an earlier paper (34).

When a dielectric continuum expression is used to determine λ_o its value for a homogeneous reaction is given by Eq. 5 (and its value for the electrode reaction is one-half that) if one assumes dielectric unsaturation, infinite dilution, no dielectric image effects, spherical reactants, and no difference in sizes of an ion in its initial and final state (16, 30, 34). It is given by somewhat more complicated expressions when any of these approximations are removed (56). For example, it depends somewhat on the ion atmosphere. However, for the correlations described later none of these approximations is necessary, since it is the functional form of λ for the homogeneous and electrochemical reactions which is the essential feature.

Other than the three common assumptions and a classical treatment of the nuclei, the principal assumptions on which Eq. 19 to Eq. 22 are based are (i) partial dielectric unsaturation approximation outside the inner co-ordination shells, (ii) harmonic forces in the inner coordination shell, and (iii) negligible correlation of fluctuations of coordinates inside and outside this shell in the activated complex.[18a] Some of the difficult problems were shown to affect the pre-exponential factor, e.g., κ and the evaluation of the two terms appearing in ρ. Other problems were cast into a form in which they could be considered separately, e.g., the evaluation of λ_o, of λ_i (either a priori or using data derived from vibrational spectra and X-ray diffraction), and the evaluation of w^r and w^p.

NONADIABATIC PROCESSES

When the nuclear motion for travelling from one many dimensional potential energy surface to another is representable by a one-dimensional Cartesian motion, and when certain other assumptions mentioned below are introduced, one obtains the Landau-Zener equation (54) for a probability P of a nonadiabatic jump per passage of the system through the intersection region, e.g., from one solid (adiabatic) curve in Fig. 1 to the other one.

$$P = \exp\left\{-\frac{2\pi\epsilon_{12}^2}{\hbar v \, |s_1 - s_2|}\right\} \qquad\qquad 23.$$

$2\epsilon_{12}$ is the splitting in Fig. 1 at the intersection, v is the velocity with which the system passes the intersection point and s_1 and s_2 are the slopes of the two (unperturbed) curves at that point (in the derivation of Eq. 23 these curves were approximated by straight lines in the vicinity of the inter-section).

This formula and those of Coulson & Zalewski (55) below, apply to processes in which nonadiabatic jumps from one potential energy surface to the other may occur, processes such as excitation transfer, predissociation, electron transfer, internal conversion, etc. Whenever the nonadiabatic jump occurs, none of these processes can occur, as one may see from Fig. 1. Hence,

the reaction probability per passage through the intersection region of the two potential energy curves, γ, equals $1 - P$.

The value for γ is high at low velocities and low at high velocities. When an equilibrium distribution function of velocities is assumed, the velocity weighted average of γ, κ, is obtained by averaging with respect to the velocity-weighted Boltzmann distribution $Av \exp(-mv^2/2kT)dv$ (for a Cartesian coordinate), where A is a normalizing factor and m is the reduced mass for this one-dimensional motion. One finds (in the second case by expanding the exponential in Eq. 23 and retaining only the leading term):

Adiabatic: $\kappa \cong 1$ (when γ is high)   24.

Nonadiabatic: $\kappa \cong \dfrac{2\pi\epsilon_{12}^2}{\hbar\bar{v}\,|\,s_1 - s_2\,|}$ (when $\langle\gamma\rangle \ll 1$)   25.

where $\bar{v}$ is the ordinary one-dimensional velocity, averaged with respect to the non-velocity weighted Boltzmann distribution, $A' \exp(-mv^2/2kT)dv$, namely $\sqrt{2kT/\pi m}$.

Coulson & Zalewski (55) have recently described[22] the assumptions leading to the Landau-Zener Eq. 23 and have developed alternative expressions. These approximations in the Landau-Zener equation include: (i) quasi-classical treatment of the nuclear motion of the atoms, (ii) retention of only quadratic terms in an expansion of the phase difference for initial and final wave functions in the vicinity of the crossing-point, and (iii) assumption that the above phase difference, $(\int_{a1}^u p_1 du - \int_{a2}^u p_2 du)/\hbar$, varies rapidly in Δu,

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[22] To obtain Eqs. 23, 27 and others, Coulson and Zalewski considered, in terms of Fig. 1, a system in a discrete nuclear (vibrational) state on surface R going over into a continuum of nuclear states on surface P. They also considered a system in any given initial state in a continuum of nuclear states on surface R going over into a continuum of states on P, but in a less general way. If one writes the formula for the discrete-continuum case as $P = \exp(-2x)$ then Eqs. 23, 30 and 39 of Ref. 55 indicate that the formula for the continuum-continuum case is $P = \exp[-2x/(1+x)]$, where P is now the probability of remaining in the original state of the continuum on surface R.

Two interesting features warrant further analysis: (i) for large x the second equation tends to $1/e^2$ rather than to the intuitively expected adiabatic limit of zero. (ii) The second equation is not the limit of the first when the vibrational spacing is made very small (x is independent of spacing at least in the cases of interest here, see below). Perhaps there is a lower vibrational spacing limit beyond which the $\exp(-2x)$ formula is inapplicable, or perhaps the $\exp[-2x/(1+x)]$ expression is in error. The lower limit of vibrational spacing was not given, it appears, but differences in the two formulae are evident early in their derivations (cf. the two Eqs. 13b and the three Eqs. 13c of Ref. 55). The value of x is, incidentally, $\pi\epsilon_{12}^2/\hbar v|s_1 - s_2|$ and

$$\left|\int_{-\infty}^{\infty}\epsilon_{12}(u)du\right|^2 \bigg/ \hbar^2 v^2$$

in Eqs. 23 and 27 of this review.

Predissociation (a "discrete" to the continuum transition) has also been considered by Harris, (81) who uses an experimentally-based choice of initial states, and discusses the choice of Coulson and Zalewski.

the effective range of ϵ_{12} along the one-dimensional coordinate (the coordinate u involves motion away from S).

Assumption (i) did not lead to a serious limitation for the Landau-Zener equation, but assumption (ii) led to an upper limit for the effective range Δu, and assumption (iii) led to a lower limit, as one can see. The conditions for validity of the Landau-Zener equation were found to be (55):

$$3\sqrt[4]{E/m} \ll \Delta u \ll 3 \text{ Å} \qquad\qquad 26.$$

where E is the kinetic energy of the system along this coordinate, at the crossing point, in electron volts; m is the effective mass for the motion along this coordinate (atomic weight units). The term $3\sqrt[4]{E/m}$ is of the order of 0.6 Å in electron-transfer reactions in solution or at electrodes.

One limiting alternative to the Landau-Zener equation was obtained by replacing assumption (iii) by its converse. This alternative corresponded to very high kinetic energies at the crossing-point, of the order of one electron volt or more, and so not of interest to the electron-transfer reactions considered here (cf. Eq. 50 of Ref. 55).

Another limiting alternative to the Landau-Zener equation was valid if $\Delta u \ll \lambda/2\pi$, where λ is the wavelength for the one-dimensional motion, computed at the crossing point. This limiting case was designed for low velocities. The probability of a nonadiabatic jump P from a one "adiabatic" curve to another (e.g., from one solid curve in Fig. 1 to the other) was given by Eq. 27.

$$P = \exp\left\{\frac{-2}{\hbar^2 v^2}\left|\int_{-\infty}^{\infty}\epsilon_{12}(u)du\right|^2\right\} \qquad\qquad 27.$$

The limits of validity of Eq. 27 were:

$$0.05\sqrt[3]{F^2/m} \ll E \ll 0.2/m(\Delta u)^2 \qquad\qquad 28.$$

where E is the kinetic energy at the crossing-point (in electron volts), F is typical slope of the potential energy curve at the crossing point in units of 10^{-4} dynes, and Δu is now in units of 0.1Å.

In order to determine which of the one-dimensional formulae is the most useful for the electron-transfer reactions of interest here, and to then apply that formula, considerable knowledge about the one-dimensional motion is needed (no many-dimensional calculation of γ, based on all coordinates rather than just the polarization ones, has been given).

The one-dimensional treatment presumes that a coordinate system may be found in which the equation of motion is separable into one for a coordinate for motion away from the intersection surface S and into one for all other motions; i.e., it presumes that a partial differential equation, namely the Schrödinger equation—or in classical mechanics the Hamilton-Jacobi equation—can be so separated into two ordinary differential equations. Normally, such a separation will not be feasible, although conditions for the separation have been derived (67–69).

If one assumes that such a separation is made, at least in some approxi-

mate sense, the one-dimensional motion will, in general, be a complicated one, containing a number of contributions: relative motion of the two reactants, change of orientation-vibration polarization, and change of bond coordinates in the inner coordination shells. In the treatment of Levich, Dogonadze and Chizmadzhev the motion was assumed (tacitly in part) to be of the second type only. Because of the quadratic nature of the Schrödinger equation for the Fourier components of the polarization, rotation of coordinates in this component space then permitted Dogonadze (31) to achieve separability. He then made assumptions of the type embodied in the Landau-Zener expression.

A detailed analysis of the one-dimensional motion for electron transfers in these liquid media is needed but has not been made yet. If it were a vibration, either of the polarization or in the inner coordination shell, ϵ_{12} would vary relatively little with the one-dimensional motion and so Δu would be relatively large, perhaps consistent with the conditions in Eq. 26, therefore. If, on the other hand, the motion was found to be largely a relative motion of the two reactants, Δu would be less. Using uncertain electron tunneling calculations to estimate the dependence of ϵ_{12} on the separation distance, Δu would roughly be of the order of 0.3 to 1Å for this case and so perhaps consistent with Eq. 26. A more detailed analysis in this nonabiatic realm is evidently desirable. If the nonadiabaticity proves to be relatively small (i.e., if γ is between 0.1 and 1, say) all such considerations may be ignored in calculations of the reaction rate.

Role of Electron Tunneling

Electron tunneling calculations have often appeared in the electron-transfer literature (11, 12, 20, 37, 70),[23] but their relation to the solution of the Schrödinger equation for the electronic and nuclear motion was not discussed, apparently. As a consequence a misunderstanding has often arisen concerning the relation between nonadiabatic transfers, electron tunneling and nuclear tunneling, as occurred recently in a review article (70).

Nonadiabatic transitions should be treated by solving the Schrödinger equation for electronic-nuclear motion, regardless of whether the transitions involve excitation transfer, internal conversion, predissociation or, as in the present case, electron transfer. The discussion thereby involves potential energy surfaces of the type given in Fig. 1.

In electron tunneling calculations a barrier for electron tunneling is estimated in some way (it is not the barrier in Fig. 1, of course) and all nuclei are held fixed. A tunneling formula is then used to compute a tunneling probability, p. This p is usually (and erroneously) used as a "transmission coefficient" in the Eyring rate equation. The question arises as to where this calculated p can be made to fit into a method based on the solution of the complete Schrödinger equation for electronic-nuclear motion. A fitting can

[23] Dr. John Bockris kindly sent the writer a portion of his forthcoming volume of *Modern Aspects of Electrochemistry*.

be performed as follows: If ν_e is the number of times the electron in its orbit "strikes" the above barrier per second (ν_e is the classical frequency of electronic motion, about 10^{16} sec^{-1}), then the final electronic configuration is formed from the first $p\nu_e$ times a second. Consider now, instead, the solution of the time-dependent Schrödinger equation for electronic motion at any fixed nuclear configuration on the intersection surface S ("exact resonance"). A system with a nonstationary state electronic wave function initially having the R electronic configuration forms a system in the P electronic configuration $\epsilon_{12}/\pi\hbar$ times a second (71). Equating these two frequencies it follows that $\epsilon_{12}/\pi\hbar$ equals $p\nu_e$ (in the approximation of electron tunneling calculations).

Hence, an electron tunneling calculation actually serves as a crude method for evaluating ϵ_{12}, an ϵ_{12} which can be introduced into the Landau-Zener equation (although it is better to evaluate ϵ_{12} directly). Sometimes the computed ϵ_{12} will be large and the system will remain on the lower solid ("adiabatic") surface in Fig. 1 on passing through the intersection region. Thus, the mere use of an electron tunneling calculation (here to evaluate ϵ_{12}) does not imply, as is occasionally presumed in the literature (37, 70), that one is assuming the chemical reaction to be a nonadiabatic one. Such calculations are more properly regarded as the way for evaluating ϵ_{12}. The error of simply regarding p as a "transmission coefficient" can amount, incidentally, to a factor of the order of 10^3 in the rate constant (16).

An instructive interpretation of the Landau-Zener formula in terms of the mean time required to change the electronic configuration compared with that to pass through the intersection region has been given by Kauzmann (Ref. 71, pp. 539–41).

COMPARISON OF THE TREATMENTS

The individual assumptions of the various quantitative treatments have been summarized above. The treatments are based on closely related ideas about the qualitative nature of the free energy barriers for electron transfers. They differ in their generality, accuracy, interpretation and application.

There are similarities and differences with regard to adiabaticity. The treatment of Hush (19, 32) is adiabatic. That of Levich, Dogonadze and Chizmadzhev (26, 28, 33, 35) is nonadiabatic, while the paper by Dogonadze (31) uses the Landau-Zener (54) equation to bridge the gap for homogeneous reactions. That of Marcus (56) leaves the decision for the final step where for κ one might use an assumed adiabatic value ($\kappa = 1$) or a calculated value (the former is usually used in the absence of any evidence to the contrary).

There are similarities and differences in the calculation of the reorganization free energy and of other aspects. Hush (32) used a specific model for the inner coordination shell and a continuum model for the medium. His numerical comparison with the data was of particular interest, though the fine details present in the more rigorous derivations were simply absent. These details affected the Arrhenius frequency factor principally. Any specific molecular model of the coordination shell itself, Hush's (32) or Sutin's (1)

for example, can be tested directly as more information on force constants and bond lengths become available. The latter data can also be fed directly into Eq. 22 of the Marcus treatment, thereby avoiding the use of any specific molecular model. On the other hand, Levich and co-workers have employed a more idealized model for the system than Hush's, a nondispersive continuum containing reactants which undergo no changes in inner coordination shell properties, and developed it in a more rigorous and elegant manner. Two limitations, aside from those imposed by the original model, are (i) the tacit neglect of the fact that the coordinate normal to the intersection surface is not a pure polarization mode (the separation distance of the reactants also contributes) and (ii) the neglect of dielectric image effects.

As mentioned earlier, some of the difficult problems have been recast in the classical statistical mechanical treatment of Marcus (30, 56) so as to appear in various terms in the final rate expression. The latter is based, therefore, on relatively few assumptions. Should absolute rates rather than data correlations be an immediate aim, specific assumptions can then be introduced. In fact, we may use this circumstance to illustrate more clearly the relation of the various treatments (72). For example, Hush's equation (32) in the harmonic approximation can be obtained if one introduces in Marcus' Eq. 19, the following; (i) Hush's ion-dipole model for the inner coordination shell, (ii) a dielectrically unsaturated continuum model for the medium outside, with dielectric image effects neglected, (iii) spherical reactants, (iv) an electrostatic calculation of the work terms, (v) $\kappa = 1$, and (vi) neglect of a number of factors omitted by Hush, factors appearing in the Arrhenius frequency factor and which include some partition functions and a term for the loss of translational entropy on forming the activated complex.

Eqs. 4, 6, and 11 of Levich, Dogonadze and Chizmadzhev (26, 33) would be obtained if, instead, one introduced in Eq. 19 the following; (i) no changes in equilibrium coordinates in the inner coordination shell, (ii) Fourier component treatment of the medium, treated as a dielectrically unsaturated continuum with dielectric image effects neglected, (iii) a polarization motion for the reaction coordinate (i.e., no contribution of the separation distance to this coordinate), (iv) spherical reactants, (v) electrostatic calculation of the work terms and (vi) Landau-Zener equation for nonadiabatic reactions. If (vi) were replaced by the adiabatic assumption of $\kappa = 1$, then Eqs. 6 and 14 of Dogonadze (and Eq. 15) would be obtained instead.

The treatments of Hush, of Dogonadze, and (in its classical limit) that of Levich, Dogonadze and Chizmadzhev can therefore be regarded as rather different particular cases of a more general formulation.

The quantum aspect of the nonadiabatic treatment of Levich and co-workers is of interest. The high temperature, classical limit shows the usual exponential dependence of the rate on $1/T$. At the low temperature limit the rate depends but slightly on T, for the calculated rate is then entirely due to nuclear tunneling. Before any quantitative application is made to any data (should they become available at sufficiently low temperatures where quantum effects would be large), a modification of the Levich-Dogonadze treat-

ment (26) would appear to be desirable, even aside from the limitation due to the contribution of the separation distance to the reaction coordinate mentioned earlier. At least one additional vibration frequency should be introduced. Much of the free energy barrier in the continuum model is due to orientation polarization, a motion of low frequency (and so also of relatively thick barriers). Hence, quantum effects due to it alone might be relatively small. Larger quantum effects would probably arise from the vibrational polarization of the medium and from the inner coordination shell motions. Levich and co-workers have already noted the calculational difficulties of including additional frequencies in their nonadiabatic treatment, however.

Turning next to the validity of Hush's interpretation of the parameter λ^+ (Marcus' $-m$), it may have been noted that Hush introduces a viewpoint apparently different from that which might be deduced from the other treatments. We explore this difference further. Hush assumes that λ^+ describes the actual charge distribution of the reactants in the activated complex, and uses an ionic charge model for both inner coordination shell and medium to compute the energy. Yet, on the intersection surface S—and this is the "activated complex" in the other treatments (30, 31)—the charge density has only a minor effect on the energy. The maximum change it can produce is $2\epsilon_{12}$, the splitting term in Fig. 1. This term is negligible, by assumption of all the treatments, Hush's included.

Although the charge distribution is unimportant on S, the Boltzmann distribution of configurations of the atoms on S is important. Here, then, we have an alternative interpretation of λ^+. One can show that λ^+ characterizes the "equivalent equilibrium distribution" of Marcus' treatment (for it equals $-m$, and m has the latter property). Because of the "equivalence" it therefore characterizes the Boltzmann distribution on S. We conclude, therefore, that Hush's intuitive interpretation of λ^+ is not correct but that it may be replaced by the alternative interpretation given above. (Hush has intuitively used, in fact, a particular type of equivalent equilibrium distribution, one which is expressible in terms of a charge density parameter, being based on an electrostatic calculation inside the coordination shell and outside.)

One might perhaps call λ^+ a "virtual charge density" for the reactants, as Sutin has suggested to the writer, or a "virtual" probability distribution for the initial and final electronic configurations of the reacting species. It describes the electronic distribution of the reacting species to which the nuclear coordinates of the entire system adjust in the activated complex. It need not describe their actual electronic distribution there, however.

SEVERAL OTHER TREATMENTS

The treatments of R. J. Marcus, Zwolinski and Eyring (12, 13) and the treatments of Laidler (20) and of Laidler and Sacher (37, 70) are summarized and discussed below.

R. J. Marcus, Zwolinski and Eyring.—These authors estimated an electron-tunneling factor p, as mentioned earlier. In their first paper they wrote the rate constant as a product of this p-factor (regarded as a "transmission coefficient") and an Eyring rate expression involving the sum of two terms in the free energy of activation: the coulombic repulsion (w^r) and a free energy of reorganization. They assumed for simplicity that the free energy of reorganization was independent of the nature of the reactants and selected a value empirically which best fitted the data. In their second paper the error of using p as a transmission coefficient was recognized and a more acceptable (but still inaccurate) procedure was used: $\tau p \nu_e$ was regarded as the transmission coefficient, τ being the collision time for the ions, perhaps of the order of 10^{-18} sec.

This paper represented one of the interesting first steps toward quantitative calculation of the rate constant, though it is clear in retrospect that the reorganization free energy is the principal factor responsible for the large differences of electron-exchange rates of different systems rather than being a constant. They estimated from the data upon which the analyses is based an empirical mean reorganization free energy. The major task of the four treatments, described in detail earlier, has been to calculate this free energy of reorganization a priori.

Laidler and Sacher.—In his first paper on electron-exchange reactions Laidler (20) wrote the rate as a product of three terms: a diffusion-controlled rate constant, the electron tunneling factor p, and a coulombic repulsion term, $\exp(-w^r/kT)$. w^r was calculated by electrostatic methods and was based on a rough estimate of dielectric saturation effects.

The rate expression was criticized on several grounds. (*i*) One cannot use a hybrid-diffusion controlled-activation controlled-rate expression given by a simple product of the two terms. One must solve the diffusion equation instead and one then finds that for the reaction considered, $Fe^{+2} - Fe^{+3}$ exchange, no diffusion term should have appeared; the reaction was much too slow (81). (*ii*) There was no free energy of reorganization term in this expression, so the reaction mechanism postulated was actually impossible (81), and (*iii*) (by prior criticism) (16) it was incorrect to use p as a transmission coefficient.

Laidler and Sacher subsequently modified the above expression to take cognizance of two criticisms that were made (*i* and *ii*): p was once more regarded as a transmission coefficient (as in the first paper of R. J. Marcus, Zwolinski and Eyring) but the remaining two factors were replaced by an Eyring rate expression in which the free energy of activation was taken to be the sum of three terms: (*i*) w^r, calculated as before, (*ii*) an energy of reorganization in the inner coordination shell and (*iii*) a change in free energy of solvation due to a change in ion size. In addition, electron-transfer reactions were classified into three groups (a) those for which the splitting term ϵ_{12} is large ("adiabatic"), (b) those for which ϵ_{12} is small and (c) those for which the mechanism is one of electron tunneling ("nonadiabatic").

Although this new paper no longer had the diffusion error nor the absence of a reorganization term, there remained several errors: (i) p was still regarded as a transmission coefficient, which it is not, for reasons discussed in the electron-tunneling section, (ii) the major contribution to the free energy of reorganization of the medium outside the inner coordination shell was still neglected, and (iii) the third class of reactions above should be omitted as a separate class, for reasons discussed in the electron-tunneling section.

The neglected contribution to the free energy of reorganization of the medium is included in each of the four treatments described in detail in this review and, we conclude with several final remarks to show explicitly what was neglected in the papers of Laidler and of Laidler and Sacher.

We have seen from the detailed discussion in the review that the contributions to the total free energy barrier include (i) the work required to bring the reactants together w^r, (ii) the free energy of reorganization term at the separation distance R permitting the system to reach S, and (iii) any nonadiabaticity factor, κ. When an activated complex is formed there are several contributions to the free energy of reorganization, (i) those from changes in bond lengths and angles in the inner coordination shell, (ii) those from the change in solvation free energy due to the resulting change in ion size, small though it may be, and finally (iii) those on which the nonequilibrium polarization section was based: for these given bond lengths, bond angles and ion size, there are fluctuations in the vibration-orientation polarization of the medium at any point outside the coordination shell, and the most favorable value of this polarization depends (in the $Fe^{+2}-Fe^{+3}$ case, for example) on whether the ion has a charge of $+2$, $+3$ or (on the average in the activated complex) $+2.5$. The third contribution to the free energy of reorganization, then, is that which is associated with this particular change of polarization of the medium on forming the activated complex. This is the one neglected by Sacher and Laidler. Because of the electronic polarization problem one cannot use ordinary electrostatics to calculate it. One can either use the intuitive approach of Hush or the more formal approach of Levich or of Marcus. The latter (34) is the most general.

COMPARISON WITH EXPERIMENT

In comparisons made with experiments the principal application of the treatment of Levich and co-workers has been in the computation of the electrochemical transfer coefficient and in the calculation of the electron-exchange rate for the ferrous-ferric reaction.[24] In the former case it was shown that a value of 0.5 would be expected for metallic electrodes (when any necessary corrections for the work terms are made) and that a quite

[24] In Refs. 26 and 28, the exponent in Eq. 6 (i.e., Eq. 4 plus 6) was interpreted as the activation energy. However, the latter is always defined operationally as a slope, $-k\partial \ln k_{rate}/\partial(1/T)$. One then finds that only part of the exponent serves as the activation energy, and part of it serves as an activation entropy, which thereby appears in the value of the Arrhenius frequency factor.

different value would be expected, typically, for semiconductors (because of the effect of the large energy gap on the equivalent of the free energy change). One may correctly object to the calculation of the Fe^{+2}–Fe^{+3} rate since the inner coordination contribution has been ignored. For this system, the contribution is large (1, 32, 73b).

The principal application of Hush's treatment has been in the calculation of the rate constants of a wide variety of electron-exchange reactions (32). The agreement is encouraging. An independent test of some assumptions made for properties of the inner coordination shell can be made when extensive data on force constants and bond lengths in the inner coordination shell become available. In such cases, incidentally, one can directly substitute the latter data into theoretical equations (34, 56) for the rate constants themselves, when such equations are based on a general potential energy expression, rather than on a specific model for the inner coordination shell.

The principal application of the writer's treatment, in comparisons with experiment, has been via predicted correlations among the experimental data. Application has also been made to the calculation of the rate constants (1, 73). The correlations expected on the basis of Eqs. 19, 20 and 21, if κ and ρ are unity (or, less strongly, are either constant in a series, or have a geometric mean property, etc., depending on the correlation) are given below (30, 34).

(a) The rate constant of a homogeneous "cross-reaction," k_{12}, is related to that of the two electron-exchange reactions, k_{11} and k_{22}, and to the equilibrium constant K_{12} in the prevailing medium by Eq. 30, when the work terms are small (or cancel).

$$Ox_1 + Red_2 \overset{k_{12}}{\rightleftharpoons} Red_1 + Ox_2 \qquad 29.$$

$$k_{12} = \sqrt{k_{11}k_{22}K_{12}f} \qquad 30.$$

where

$$\ln f = (\ln K_{12})^2/4 \ln (k_{11}k_{22}/Z^2) \qquad 31.$$

(b) The electrochemical transfer coefficient at metal electrodes is 0.5 for small activation overpotentials (i.e., if $|nF\eta| < |\Delta F_0^*|$, where ΔF_0^* is the free energy of activation for the exchange current), when the work terms are negligible.

(c) When a substituent in the coordination shell of a reactant is remote from the central metal atom and is varied in a series, a plot of the free energy of activation ΔF^* versus the "standard" free energy of reaction in the prevailing medium $\Delta F^{o'}$ will have a slope of 0.5, if $\Delta F^{o'}$ is not too large (i.e., if $|\Delta F^{o'}|$ is less than the intercept of the plot at $\Delta F^{o'} = 0$). When the work terms are small or cancel this relation would be a special case of Eq. 30, but this smallness or cancellation is not needed for its fufillment. The slope of the ΔF^* versus $\Delta F^{o'}$ plot has been termed the chemical transfer coefficient (34), by analogy with the electrochemical terminology.

(d) When a series of reactants is oxidized (reduced) by two different reagents the ratio of the two rate constants is the same for all members of the

series in the region of chemical transfer coefficients equal to 0.5 (i.e., in the region where $|\Delta F^\circ| < (\Delta F^*)_{\Delta F^\circ = 0}$ in each case).

(e) When the series of reactants in (d) is oxidized (reduced) electrochemically at a given metal-solution potential difference the ratio of the electrochemical rate constant to either of the chemical rate constants in (d) is the same for all members of the series, in the region where the chemical and (work-corrected) electrochemical transfer coefficient is 0.5.

(f) The rate constant of a (chemical) electron-exchange reaction, k_{ex}, is related to the electrochemical rate constant at zero activation overpotential, k_{el}, for this redox system, according to Eq. 32 when the work terms are negligible.

$$\sqrt{k_{ex}/Z_{soln}} \cong k_{el}/Z_{el} \qquad\qquad 32.$$

where Z_{soln} and Z_{el} are collision frequencies, namely about 10^{11} cc mole^{-1} sec^{-1} and 10^4 cm sec^{-1} (56).

When the work terms are not negligible, or do not cancel in the comparison, the deductions which depend on this condition refer to rate constants, to K_{12} and to an electrochemical transfer coefficient corrected for these terms (19).

There is a growing body of experiments, principally by Sutin (57–60), Halpern (61), Taube (62), and their co-workers in the chemical reaction field, by Vlcek (74) and a number of other contributors in the electrochemical field [cf survey in (5, 6, 34)], with which the above deductions may be compared.

Sutin and co-workers (58, 60) have described data for about a dozen reactions which may be used to test deduction (a). In some cases the electron-exchange rates are not yet known, so ratios of rate constants were compared to permit cancellation of the unknown constants. A value was then assigned on the basis of one reaction to see if that for the others could be predicted. In some other cases, only upper or lower limits for the constants were known. In every case but two the results were in good agreement with Eq. 30, or in the case of the upper or lower limits, consistent with it. The exceptions were the $Co^{+3} - Fe^{+2}$ and $Co^{+3} - Fe(phen)_3^{+2}$ reactions (58, 60) the calculated rates being too high by a factor of 10^5. When one reactant had inorganic ligands and the other had highly organic ones, there was a consistent effect which suggested a work term for bringing these two species together, in excess of the mean work for bringing two inorganic ones and two organic ones together, of about 2 kcal mole^{-1} (60).

Endicott & Taube (62) have obtained results consistent with (a) for a few reactions involving the $Ru(NH_3)_6^{+2,+3}$ system. However, in reactions involving a cobalt system, $Co(NH_3)_6^{+2,+3}$, the exchange rate constant predicted from Eq. 30 was too high by a factor of at least 10^6 for one case and by a factor of at least 100 for the second. Although an error of a factor of 100 might be due to errors in the harmonic approximation (the Co–N bond has a very dif-

ferent length in the two valence states), a discrepancy of 10^6 could not be due
to such a source. One possible explanation of this large discrepancy (and that
in the Co^{+3} reactions mentioned earlier) might invoke the participation of
excited electronic states for at least one of the reactions or of the influence of
spin selection rules for one of them (58).

A substantial number of electrochemical transfer coefficient have been
measured, usually at high salt concentration to minimize the work terms.
With a few exceptions they are close to 0.5, as noted in a recent survey (34),
in agreement with deduction (b).

Sutin and co-workers (60) have studied four series of reactions to investigate
the dependence of ΔF^* on $\Delta F^{o'}$: $Fe(phen)_3^{+3}+Fe^{+2}$, $Ce(IV)+Fe(phen)_3^{+2}$,
$Mn(III)+Fe(phen)_3^{+2}$, and $Co(III)+Fe(phen)_3^{+2}$. In the first three reac-
tion series the f correction factors in Eq. 31 were uninfluential and the chem-
ical transfer coefficient was close to 0.5, in agreement with deduction (b).
In the fourth case the f factor was considerably different from unity and the
slope was only 0.27. However, the appropriate plot, namely $\Delta F^*+0.5$
$RT \ln f$ versus $\Delta F^{o'}$, had the predicted slope, in agreement with deduction
(c) (the slopes for these plots were 0.56, 0.48, 0.49 and 0.51 in the four reac-
tion series, and the predicted one is 0.50).

Several series of studies bear on deductions (d) and (e). Halpern and
co-workers (61) have studied the reduction of a series of reactants
$Co(NH_3)_5 X(III)$ of varying X. They used Cr^{+2}, Eu^{+2}, V^{+2} and $Cr(dipy)_3^{+2}$.
Endicott and Taube (62) have made similar studies using $Ru(NH_3)_6^{+2}$.
Finally, Vlcek (74) has studied the electrochemical reduction of the series
at a dropping mercury electrode. Of these reagents, Cr^{+2} is known to react
via an inner sphere activated complex. $Ru(NH_3)_6^{+2}$ has a stable coordination
shell and should react via an outer sphere complex, as Endicott and Taube
point out. The theoretical equation applies only to outer sphere activated
complexes, and so not to Cr^{+2}. The results obtained for Cr^{+2} were consider-
ably different from the remaining ones, being considerably more sensitive
to the nature of X.

The chemical results for V^{+2}, $Cr(dipy)_3^{+2}$, $Ru(NH_3)_6^{+2}$ and the electro-
chemical results all fell substantially on the same plot, consistent thereby
with a supposition that all reactions proceed via an outer sphere mechanism
(but, a few points for V^{+2} were scattered). The comparison between
$Ru(NH_3)_6^{+2}$ and the electrochemical data support deduction (e). If one pre-
sumes that both V^{+2} and $Cr(dipy)_3^{+2}$ proceed via an outer sphere mechanism,
their mutual agreement and the agreement with the $Ru(NH_3)_6^{+2}$ data sup-
port deduction (d). In the case of Eu^{+2}, where there were some differences,
it has been suggested that the reaction occurs via an inner sphere mecha-
nism (61). The electron-exchange rate in the $Eu^{+2}-Eu^{+3}$ in aqueous HCl
systems becomes negligible, incidentally, when the chloride concentration
becomes negligible (75) (unlike the $Fe^{+2}-Fe^{+3}$ exchange) and could con-
ceivably reflect an inner sphere mechanism.

Rate constants of homogeneous exchange reactions and of electrode reactions have been summarized recently. In a recent test of (f) for a variety of systems care was taken to compare rates measured in the same electrolyte medium (34). The agreement with deduction (f) was encouraging. The least favorable agreement occurred for the case of the system having the most high charged reactants, $Fe(CN)_6^{-3,4}$ where the two sides of Eq. 32 differed by a factor of 100. The discrepancy could be due to the presence of work terms which could not be ignored, to the long extrapolation of some isotopic exchange data from one electrolyte concentration to the medium used in the electrochemical experiments, or to the presence of specific effects.

Entropies of activation for electron transfer reactions are of considerable interest. A number of trends have been found, and these have been reviewed by Sutin (1) and Halpern (2). No major developments on this subect appear to have occurred since then, however.

Finally, no attempt has been made in this review to discuss the experimental data in the closely related field of $3d$ electron and hole conduction in the transition metal oxides and in related semiconductors (76, 77). The activation energy observed for such conduction provides evidence for local electron transfers between adjacent sites, (76, 77) and the results have been interpreted in chemical terms (76). Further correlation of these studies with those in homogeneous and electrochemical electron transfers would of course be desirable.

On the whole, the agreement between theory and experiment in chemical and electrochemical electron transfer reactions may be considered encouraging.

Relation of Data to Several Theoretical Problems.—There are a variety of theoretical questions which could be explored and several where further elegance and precision of treatment would be desirable. The possibility of testing such refinements experimentally is uncertain at present. Suitable data would permit some tests.

The work of Levich and co-workers describes quantum effects and the treatments of the other investigators could be placed on a quantum basis. However, there are no data in the field of homogeneous and electrochemical electron transfers which clearly show the presence of quantum effects[25] due to the nuclear motion, other than measurements of relative rates in water and in heavy water (in that case, unfortunately, there are several possible

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[25] Nevertheless, when the bond length changes required in the reorganization are so small that they became comparable with zero-point fluctuations in bond lengths, any accurate calculation of this reorganization free energy would have to be a quantum one. The reorganization free energy for small bond length changes is small, however. It may be noted that the rate constants of electron-exchange reactions vary by 16 orders of magnitude or more (e.g., 1, 34). Quantum effects of a factor of 10 or so would play only a relatively minor role, considering the various errors in absolute calculations. They would also be expected to largely cancel in their effect on the predicted correlations.

explanations). Low temperature measurements of the rates are needed, and these are experimentally impractical in aqueous systems (for measurements in ice see Ref. 78). In other solvents, an alcohol for example, measurements at lower temperatures can be made (79), but precautions are needed in the interpretation because of ion pairing, etc.

There are essentially no data which unambigously provide information about adiabatic versus nonadiabatic electron transfers in these media. The main source of such information would be the magnitudes of the Arrhenius frequency factors in the rate constants of homogeneous and electrochemical reactions. There are a number of other factors influencing these frequency factors and corrections for these must be made first. For example, unless the work terms are small they can cause large entropies of activation, and so affect the frequency factors. If the homogeneous reaction is not an electron-exchange the standard entropy of reaction ΔS^o will not be zero and this will also normally contribute to the entropy of activation (typically, but not always, $\Delta S^o/2$) If the electrochemical reaction is not proceeding at zero activation overpotential, i.e., if the rate constant is not that corresponding to the electrochemical exchange current, a similar remark would apply to it.

In summary, to obtain fairly direct information about the nonadiabaticity or adiabaticity it is desirable; (i) to study electron-exchange reactions or exchange currents, at least until there is experimental support in the homogeneous case for the predicted contribution of ΔS^o, and (ii) to study systems where the work terms are small.

In the case of the $MnO_4^{-1} - MnO_4^{-2}$ reaction the ionic charges and, hence, the coulombic repulsion are relatively small. The experimental frequency factor (80) in that case is close to the value of Z. This value is the expected one when the reaction is adiabatic. In the case of electrochemical exchange currents at high salt concentrations the values of the Arrhenius frequency factor $10^3 - 10^5$ cm sec^{-1} are close to the value of Z_{el} ($\sim 10^4$ cm sec^{-1}). In both cases, however, specific salt effects remain so these results should be interpreted with some reserve. Further experimental measurements on slightly charged systems would be desirable.

Among the theoretical refinements which can be made, many of these would amount to obtaining better expressions for the Arrhenius frequency factors or, in terms of the writer's theory, be equivalent ot the evaluation of some of the terms appearing there (κ and ρ in particular). However, the measurements do not distinguish between a κ-contribution to the frequency factor and some of the others (there is reason to believe, incidentally, that ρ will be close to unity).

Ultimately, with the testing of correlations and estimation of the work terms, one may be able to interpret more reliably the significance to be ascribed to any deviations of Arrhenius factors from any picture based on $\kappa \cong \rho \cong 1$. The correlations should also serve to isolate the exceptional cases, where major differences in the mechanism seem to be operative, and several examples apparently of this type, all involving cobalt ions, have been cited. Further theoretical work could then profitably include such cases also.

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