Electron Transfer in Homogeneous and Heterogeneous Systems

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Abstract: The mechanism of electron transfer in solution and at electrodes is described. A theoretical analysis involving the fluctuations in the chemical bond distances and in the dielectric polarization of the partially oriented solvent molecules about the reactants leads to an expression for the rate constant of these reactions. Relations are obtained between the rate constants of cross reactions k_{12}, self-exchange reactions k_{11}, [e.g., $k_{12} \cong (k_{11}k_{22}K_{12}f_{12})^{1/2}$], and reactions at surfaces (electrodes, both metal and semiconductor type). There are many comparisons between theory and experiment and a survey is given. The effect of standard free energy of reaction and of electrode potential is included, as in the $Co^{+3}(aq)$ anomaly, and the occurrence of chemiluminescence. The discussion is preceded by a brief description of reaction rate theory in general and of atom versus electron transfer mechanisms in particular.

I. Introduction

The rates and mechanism of electron transfer reactions have been extensively studied in solution and, electrochemically, at surfaces. These surface studies have been made primarily with metal electrodes, and in some cases with semiconductor electrodes. In the present survey the extensive relation between theory and experiment in electron transfer reactions is discussed. Most reaction rate studies of electron transfer reactions have involved hydrated or otherwise coordinated inorganic ions. There have also been studies with large organic ions, and some between inorganic

ions and organic ions and with molecules of biological interest. The field has been the subject of many useful reviews, e.g., [1,4,8,10,12,18-23,29,37-45,47].

Before applying any of these concepts and results to problems of sea water it is necessary to identify the species involved, the nature of any surfaces present, the extent of adsorption, and the sequence of steps, if any, constituting the mechanism of the overall reaction. Hopefully this Conference may help define some of these features for various systems.

II. Some General Remarks on Reaction Rates

Typically, for reactions of interest here, one may classify reactions as second order, i.e., those with rates given by

$$-dC_a/dt = k_{rate}C_AC_B \qquad (2.1)$$

for a reaction between A and B, with the C's denoting concentration, or first order

$$-dC_A/dt = k_{rate}C_A \quad . \qquad (2.2)$$

In the case of first order reaction at a surface one would have

$$-dC_A/dt = k_{rate}SC_A \quad , \qquad (2.3)$$

where S is the area of the surface and where the rate per unit area of surface is thereby $k_{rate}C_A$. (Analogously, the rate of a second order reaction at a surface could also be written.) In (2.1)-(2.3) k_{rate} is a constant, the "rate constant." Its units are worth noting: If the units of concentration, time and area are moles cc^{-1}, sec^{-1}, and cm^2, respectively, the units of k_{rate} are cc $mole^{-1}$ sec^{-1} in (2.1), sec^{-1} in (2.2), and cm sec^{-1} in (2.3).

A little computation using kinetic theory shows that if every collision in (2.1) and (2.3) were effective in causing reaction, k_{rate} would equal ca. 10^{14} cc $mole^{-1}$ sec^{-1} and ca 10^4 cm sec^{-1}, respectively. If (2.2) occurred at every vibration of A, the use of a typical vibration frequency shows that k_{rate} of (2.2)

would be ca 10^{13} sec^{-1}. These values for the rate constants in (2.1)-(2.3) thus represent the upper limits. Most observed values will be far below these, because not every collision, nor every vibration in (2.2), leads to reaction.

Activated complex theory will be first considered, since it is the most commonly used approach to reaction rates in general [11]. The reader mainly interested in the comparison of theory and experiment in electron transfer reactions, rather than in the underlying theory, may wish to proceed directly to Sec. V.

III. Activated Complex Theory

The principal theory which has been applied to reaction rates in general has been activated complex theory. A recent review is given in [27].

In activated complex theory all the relevant coordinates (say N) in the reacting system are considered, including the coordinates of the solvent molecules when the reaction occurs in solution. These coordinates involve the positions of all the molecules, their orientations, and their internal vibrational coordinates, or various combinations of these. For each configuration of these coordinates the system has some potential energy. (The latter is the "Born-Oppenheimer" electronic energy of the system, obtained by solving the Schrödinger equation for each value of the coordinates.)

One can imagine this potential energy to be plotted as a function of all these coordinates in some N-dimensional coordinate space. In activated complex theory it is assumed that some surface (of N-1 dimensions) can be located in this space, such that once the system starting from the reactants' side has crossed it, reaction has occurred. Activated complexes are defined as a set of configurations of the system on this special N-1 dimensional surface. We shall call it an N-1 surface. The rate constant of the reaction equals the probability of finding the system at this N-1 surface, per unit length perpendicular to the surface, multiplied by the velocity of crossing the surface, and integrated over all pos-

sible configurations on the surface and over all velocities of crossing.

In the usual form of activated complex theory one first assumes that an N-1 surface with the property just described actually exists. Secondly, one assumes that the probability of finding the system at the N-1 surface, per unit length normal to the N-1 surface, can be calculated from equilibrium statistical mechanics: A quasi-equilibrium is postulated between reactants and activated complexes moving from the reactants' region to the products' region in this N-dimensional space. Finally, when quantum effects are important for tunneling through the activated complex region one makes some simplifying assumption to permit a calculation of that tunneling.

The net result for an activated complex theory expression for the rate constant k_{rate} is

$$k_{rate} = \varkappa(kT/h)\exp(-\Delta G^{\ddagger}/kT) \quad , \tag{3.1}$$

where k, T, h and $\Delta G^{\ddagger}$ denote Boltzmann's constant, absolute temperature, Planck's constant, and the Gibbs' free energy difference between the activated complex (i.e., the system on the N-1 surface) and the reactants. Tunneling effects, if any, are included in the $\varkappa$ term. Otherwise, $\varkappa$ is usually taken to be unity. Various tests of (3.1) using actual dynamic calculations are available. (A summary is given in [27].)

In bimolecular reactions $\Delta G^{\ddagger}$ depends on the concentration unit used, and these units in turn determine those of k_{rate}. For example, if this unit in $\Delta G^{\ddagger}$ is 1 mole/cc and if the units of kT and of h are ergs/molecule and ergs sec/molecule, the units of k_{rate} prove to be cc/mole/sec, as in Sec. II. In unimolecular reactions $\Delta G^{\ddagger}$ does not depend on concentration units, and the units of k_{rate} are sec^{-1}. In unimolecular reactions at surfaces, if the surface concentration unit of the activated complex in $\Delta G^{\ddagger}$ is 1 mole/cm^2 and if the concentration unit of reactant in solution is 1 mole cc^{-1}, the units of k_{rate} are cm sec^{-1}, as in Sec. II.

Typically, reactions occur as a result of a suitable fluctuation of the coordinates which permits the system to cross the critical set of configurations (the N-1 surface) known as the activated complex. In reactions where chemical bonds are broken or formed these fluctuations in coordinates involve in a major way the increase in distance in the breaking bonds or decrease in distance in any bonds being formed. Sometimes bonds merely rearrange, and the fluctuations then involve simultaneous changes in several bond distances and bond angles. In each case the fluctuations leading to reaction are those from a typical configuration of the reactants to a typical one of the products. We investigate in Sec. IV the type of fluctuations involved in simple electron transfers.

In the activated complex of electron transfer reactions, H. Taube pointed out that the coordination shells of the reactants are either separated ("outer sphere" reactions) or share some atom or group ("inner sphere" reactions), e.g., refs. in [43-45]. In the latter instance the net reaction will involve only an electron transfer if the shared atom is restored to its original owner, or the reaction will involve an atom transfer, if the shared atom is not so restored. We will consider mainly outer sphere electron transfers, though applications of the theory [23,26] have been made to those of the inner sphere type, e.g., [38,49], initially by N. Sutin.

Throughout, the references will be limited to review articles where possible, because of space limitations and the considerable body of studies available.

IV. Electron Transfer Reactions

In some respects electron transfer reactions are the simplest of all chemical reactions. Simple electron transfers involve no breaking or formation of chemical bonds. Changes do occur in stretching or compressing bonds in the reactants themselves and changes occur in the typical orientations of the solvent molecules around each reactant [23].

Typically, the bond lengths in a reactant are somewhat different when the molecule is in its oxidized form as compared with the case where an electron has been added, and the species is in a reduced form. For example, the Fe-O bonds in an hydrated ferric ion are somewhat shorter, possibly as much as 0.15 Å, than those in a hydrated ferrous ion. Sometimes this bond length change will be large and sometimes, as in MnO_4^- - $MnO_4^=$, quite small. Again, the degree of orientation of the solvent molecules around an ion will depend on the charge of that ion, and so will change when the redox state of the reactant is changed.

To see how the electron transfer occurs, we plot the potential energy of the reactants plus solvent as a function of the N coordinates of the system [23]. One profile of this potential energy surface would appear as the curve labelled R in Fig. 1. If instead an electron (or more than one) has been transferred, we would have products, and the profile might appear as the curve labelled P in Fig. 1. The abscissa in this figure is a "generalized coordinate" involving changes in bond lengths of both reactants and reorientation of solvent molecules in the vicinity of the reactants, such that the system proceeds from a configuration appropriate to reactants (any near the bottom of the well in the R curve) to a configuration appropriate to the products (any near the bottom of the well in the P curve).

When the reactants are far apart the R and P curves merely cross at the intersection (as with the dotted line curves). When the reactants are a small enough distance apart, their electronic interaction perturbs the dotted line curves in Fig. 1 particularly near their point of intersection. At that point the two unperturbed electronic quantum states R and P are degenerate and the degeneracy is broken by the interaction. The new curves are the solid ones, and the energy of the maximum of the lower solid curve is less than that at the intersection by an electronic interaction energy V_{12}, the so-called "resonance energy." The intersection point, con-

tinued into the N-1 dimensions perpendicular to the profile, i.e., perpendicular to the plane of the paper, constitutes the N-1 surface referred to in Sec. III.

When V_{12} is zero, a system on the R curve undergoing thermal fluctuations and passing the crossing point in Fig. 1 as a result, will remain on the R curve and eventually recross the N-1 surface and return to a stable R configuration. No reaction has occurred even though the system crossed the N-1 surface. When V_{12} is no longer zero there is a finite probability that a system starting on the R curve and crossing the N-1 surface as a result of a fluctuation will proceed on the P curve, and the reaction will thereby have occurred. An approximate simple formula is available for calculating this probability that a system which is known to cross the N-1 surface ends up on the P curve. V_{12} and the slopes of the R and P curves at the crossing point are used (Landau-Zener-Stueckelberg formula).

When this electron transfer probability per crossing, κ, is about unity, the reaction is said to proceed adiabatically on the lower surface in Fig. 1. When $\kappa << 1$ the reaction is said to proceed nonadiabatically. If the electronic interaction between the reactants is strong enough in the activated complex, V_{12} will be large and the reaction will be adiabatic, while in the case of a small electronic interaction energy V_{12},, the reaction is nonadiabatic.

One can rephrase some of the above discussion of Fig. 1 in terms of the Franck-Condon principle: In the case of small V_{12} the only place where the system can move from the R curve to the P curve without emitting or absorbing light is at the crossing point. Here, there is no change in the momentum or position when the system "jumps" from the R to the P curve. It thereby obeys the Franck-Condon Principle, a point first discussed by W. F. Libby (Ref. 9 in [23]).

The problem of calculating the rate constant k_{rate} involves the calculation of $\Delta G^{\ddagger}$ in (3.1), which in turn is related to

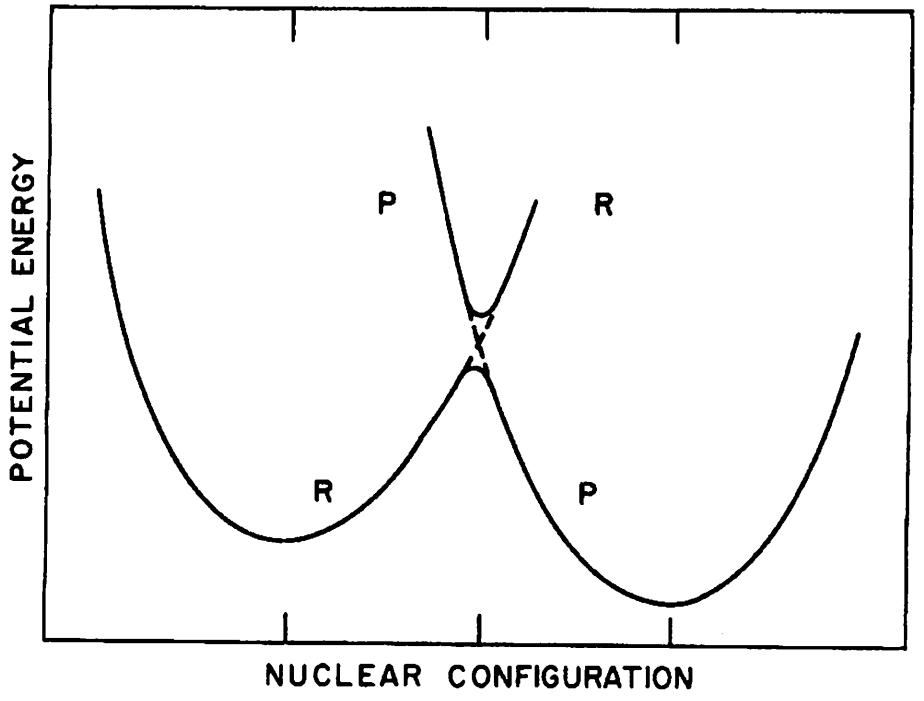

FIG. 1 - Profile of a plot of the potential energy of the system (R) consisting of reactants plus solvent and (P) products plus solvent, as a function of a change in vibrational bond lengths and angles and solvent molecules' orientations [23].

the probability of finding the system as an activated complex, and the calculation of κ. We consider next $\Delta G^{\ddagger}$.

If the potential energy curves R and P were merely quadratic (parabolas), and if one knew the relevant force constants (curvature of the R and P curves), the difference in position of the minima in Fig. 1, and the difference in heights of the minima, the calculation of $\Delta G^{\ddagger}$ would be straightforward; only simple vibrational analysis would be necessary. However, a major problem arises, since the interactions of the solvent molecules with each other and with the reactants are strongly anharmonic. Only in a macroscopic sense can the interaction be approximated by some quadratic approximation, namely, one for the free energy of solvation. Furthermore, this solvation has a peculiarity not considered previously in more conventional reactions, a peculiarity to which we shall turn in a moment. Finally, when the reactants are far apart, a major additional fluctuation is

needed to bring them closer together. Along that coordinate, which is roughly at right angles to the plane of the paper in Fig. 1, the potential energy profile is almost flat at large separation distance rather than being parabolic.

We now consider the major peculiarity of the polarized solvent in these reactions. Typically, for a given charge distribution of the reacting species there is an averaged orientation of the solvent molecules at each point in the solvent, i.e., a dielectric polarization which is a function of position with respect to the reacting ions. Frequently, dielectric continuum theory has been used to calculate this equilibrium position-dependent dielectric polarization and to calculate, approximately, its contribution to the free energy of solvation of ions or of pairs of ions. Standard textbook electrostatics are used. The configurations of the solvent which contribute most are the stabler ones, namely, those corresponding to the configurations near the minimum of the R curve in Fig. 1. Instead, when the reacting species have a different charge distribution, namely the charges of the products, and so when the system is on curve P, the equilibrium dielectric polarization function of the solvent is also different. (Most of the contribution to the latter arise from configurations near the minimum of the P curve.)

In the case of a system located at the intersection in Fig. 1 (the N-1 surface), neither of these polarization functions is appropriate, since the configurations which occur at the intersection are quite different from those which occur at either minimum in Fig. 1. To calculate the polarization function appropriate to the intersection region, it was therefore useful to derive an expression for the free energy of the entire system as a function of fluctuations in the solvent dielectric polarization (Ref. 16 in [23]). To do this, a reversible path was found for producing this nonequilibrium polarization (Ref. 47 in [23]).

The value of the polarization function occurring at the intersection was then found by minimizing this free energy of formation of the activated complex, subject to the condition that the system was at the intersection. This condition was imposed by showing that it was equivalent to one in which an R system and a P system, which had R charges and P charges, respectively, had the same dielectric polarization function and the same total free energy.

The contribution of the vibrations of the reactants to $\Delta G^{\ddagger}$ was included in a straightforward way [23,24], as was the free energy change arising from the formation of a collision pair. (The latter proves to be $-kT\,\ell n\, Zh/kT$, where Z is a collision frequency.) One obtains Eq. (4.1) for bimolecular reactions in solution or for a unimolecular reaction at a surface. (A minor factor ρ is omitted; $\rho \cong 1$.)

$$k_{rate} = \varkappa Z \exp(-\Delta G^{\ddagger}/kT) \tag{4.1}$$

$\varkappa$ is an electron tunneling probability factor; Z is about 10^{14} cc $mole^{-1}$ sec^{-1} for bimolecular reactions and about 10^{4} cm sec^{-1} for surface reactions; ΔG^{*} is the contribution to $\Delta G^{\ddagger}$ arising from the solvent polarization and vibrational contributions described above and from the work w^{r} required to bring the reactants together. This work may arise from both ionic and nonpolar interactions between the reactants. One finds [23,24]

$$\Delta G^{*} = w^{r} + \frac{\lambda}{4} + \frac{\Delta G^{o\prime}(R)}{2} + \frac{\Delta G^{o\prime}(R)^{2}}{4\lambda}\,, \tag{4.2}$$

where R is the most probable separation distance of the reactants in the activated complex; λ is a reorganization property which depends on the polar properties of the solvent and on the differences in equilibrium bond lengths (and angles) of the R and P systems. Expressions are given in the Appendix of this paper. $\Delta G^{o\prime}(R)$ is given by

$$\Delta G^{o\prime}(R) = \Delta G^{o\prime} + w^{p} - w^{r}\,, \tag{4.3}$$

where $\Delta G^{o\prime}$ is the "standard" Gibbs free energy of reaction in the prevailing medium, i.e., it is the free energy of

reaction for unit concentrations of reactants and products at the prevailing temperature and pressure and in the prevailing solvent environment; w^p is the work required to bring the products together to the separation distance R. $\Delta G^{o\prime}(R)$ is seen from (4.3) to be the Gibbs free energy of reaction at a distance of separation R between the reactants.

The quantity λ in (4.2) has a very useful additivity property: In the cross-reaction

$$A_1(ox) + A_2(red) \rightarrow A_1(red) + A_2(ox) \qquad (4.4)$$

and in the self-exchange reactions

$$A_1(ox) + A_1(red) \rightarrow A_1(red) + A_1(ox) \qquad (4.5)$$

$$A_2(ox) + A_2(red) \rightarrow A_2(red) + A_2(ox) \ , \qquad (4.6)$$

with λ written as λ_{12}, λ_{11}, and λ_{22}, respectively, we have [22,24]

$$\lambda_{12} \cong \tfrac{1}{2}(\lambda_{11} + \lambda_{22}) \ , \qquad (4.7)$$

a relation with far reaching consequences, as we shall see. (Rates of self-exchange reactions (4.5) and (4.6) have been measured by isotopic tracer techniques, and by broadening of electron spin resonance and nuclear magnetic resonance absorption lines.)

The additivity relation (4.7) can be given a simple physical interpretation, arising from the fact that solvent's and coordination shell reorganizations in (4.4) occur around an A ion and a B ion in (4.4) and around two A ions in (4.5) and two B ions in (4.6).

The preceding remarks, up to and including (4.1), apply both to reactions at metal electrodes as well as to homogeneous reactions, Z now denoting the collision frequency with unit area of the surface

$$A(ox) + ne(M) \rightarrow A(red) + M \ , \qquad (4.8)$$

where M denotes the electrode and n is the number of electrons transferred. Now, reaction occurs upon suitable close

approach of A to M, plus a suitable fluctuation in bond lengths (angles) of A and in the dielectric polarization of the solvent near A and M.

One difference which does exist is that when the surface is a metal electrode there are numerous electronic states present, corresponding to different distributions of the electrons in the metal. Thereby, there is not merely one R curve and one P curve in Fig. 1, but numerous curves, one for each different electronic state (cf. Fig. 2 of [23]). This modification presents no major difficulty, since most of the transfers are to and from the Fermi energy level in the metal (the level below which the metal's electron states are largely occupied by electrons and above which they are largely unoccupied) [4,18,23,24]. With this modification Eq. (4.1) is still applicable but now ΔG^* is given by [23]

$$\Delta G^* = w^r + \frac{\lambda_e}{4} + \frac{\Delta G_e^{o\prime}(R)}{2} + \frac{\Delta G_e^{o\prime 2}(R)}{4\lambda_e} , \qquad (4.9)$$

where

$$\Delta G_e^{o\prime}(R) = \Delta G_e^{o\prime} + w_e^p - w_e^r \qquad (4.10)$$

and

$$\Delta G_e^{o\prime} = -nF(E-E^{o\prime}) \qquad (4.11)$$

In these equations w_e^r is the work required to bring the reactant from the bulk of the solution to a position R from the electrode, R being the most probable separation distance in the activated complex (it is also weighted in accordance with the distance-dependent electron transfer probability, as in the homogeneous reaction case); w_e^p is the corresponding property for the product; E is the electrode potential; E_o' is the value the latter would have under equilibrium conditions if the reactant and product concentrations were equal (E_o' is thereby the "standard potential," but for the prevailing medium); λ_e is a reorganization parameter (Appendix), which is approximately related to the λ_{11} of reaction (4.5) by

$$\lambda_e \geq \frac{1}{2}\lambda_{11} \quad , \tag{4.12}$$

where the equality applies when the distance between reactant and electrode is one-half that between the two reactants in (4.5), and the inequality applies when, because of an extra adsorbed solvent layer in the electrode case, R_e is larger than R/2. Eq. (4.12) has a simple physical interpretation: there is only one A in (4.8) but two in (4.5). We note, too, that $-ne(E-E_o')$ has replaced $\Delta G_o'$ as the driving force for the reaction.

V. Predictions from the Theoretical Relations

A number of theoretical predictions result from these equations [22]. They can be tested experimentally and are listed below.

(1) One immediate consequence of (4.1)-(4.7) is the cross-relation (5.1), which obtains when the work terms either cancel or can be neglected

$$k_{12} \cong (k_{11}k_{22}K_{12}f_{12})^{1/2}, \tag{5.1}$$

where

$$f_{12} = (\ln K_{12})^2/4 \ln(k_{11}k_{22}/Z^2) \quad . \tag{5.2}$$

Here, k_{12}, k_{11} and k_{22} are the rate constants of (4.4)-(4.6), K_{12} is the equilibrium constant of (4.4) (in that $-kT \ln K_{12}$ equals $\Delta G^{o\prime}$); f_{12} arises from the $\Delta G^{o\prime 2}/4\lambda$ term in (4.2). The relation (5.1) has also been used to predict and interpret k_{12}'s or k_{11}'s or in some cases K_{12}, depending on which of the quantities in (4.8) have been measured experimentally. Sometimes the self-exchange rate constants k_{11} and k_{22} may not be known, and then (5.1) has found use in calculating relative values of k_{12} for various A_e's, for a series in which k_{22} is approximately constant.

(2) A second consequence, and actually a corollary of (1) has been the dependence of $-kT \ln k_{rate}$ on $\Delta G^{o\prime}$ for a series of reactions of similar λ_{12}. The slope decreases to zero at larger $-\Delta G^{o\prime}$ and increases to unity at larger $+\Delta G^{o\prime}$, in the range $|\Delta G^{o\prime}| < \lambda$. It is 0.5 when $|\Delta G^{o\prime}| \ll \lambda$.

(3) Similarly, if in an electrode reaction the electrode potential E is systematically varied, the slope α of the plot of $-kT\,\ell n\, k_{rate}$ vs. $-neE$ is 0.5 when $|ne(E-E_o^{o'})/\lambda|$ is small. α approaches zero when $-ne(E-E^{o'})$ becomes quite negative, and it approaches unity when $-ne(E-E^{o'})$ becomes quite positive, in the range $|ne(E-E^{o'})|/\lambda < 1$.

(4) One consequence of (4.1)-(4.12) is a relation between the rate constant of an self-exchange reaction k_{11} and that for the electrode redox reaction (4.8) k_e at $E = E^{o'}$.

$$k_e/Z_e \cong (k_{11}/Z)^{1/2} \quad , \tag{5.3}$$

when the work terms can be neglected and when the condition regarding the R's ($R_e \approx \frac{1}{2} R_{11}$) is fulfilled. Here, Z_e is the collision frequency per unit area of the electrode surface, and Z is the collision frequency for (4.5).

(5) From (4.1)-(4.12) it also follows that when a series of homogeneous reactions (4.4) are studied, varying A but keeping B fixed, and when the rates are compared with those of a series of electrode reactions (4.8) at a given E but varying E_o', one expects

$$k_{12}/k_e \cong \text{constant} \quad , \tag{5.4}$$

provided both series are in the range of ΔG^* vs. $\Delta G^{o'}$ [ΔG^* vs. $-ne(E-E_o')$ in (4.8)] slopes of 1/2, and provided work terms either cancel or are negligible.

(6) From the dependence of λ_{12}, λ_{11} and λ_e on the properties of the system (Appendix), one expects that (i) λ_{12}, λ_{11} and λ_e should increase with increasing difference in equilibrium bond lengths (bond angles) of corresponding bonds in A_{ox} and A_{red}, other things being equal; thereby k_{rate} decreases; (ii) when the dielectric reorganization can be treated by a dielectric continuum approximation and when specific solvent effects are absent each λ increases linearly with $(1/D_{op})-(1/D_s)$, where D_s is the usual dielectric constant of the medium, and D_{op} is the square of the refractive index (the "optical dielectric constant"); the

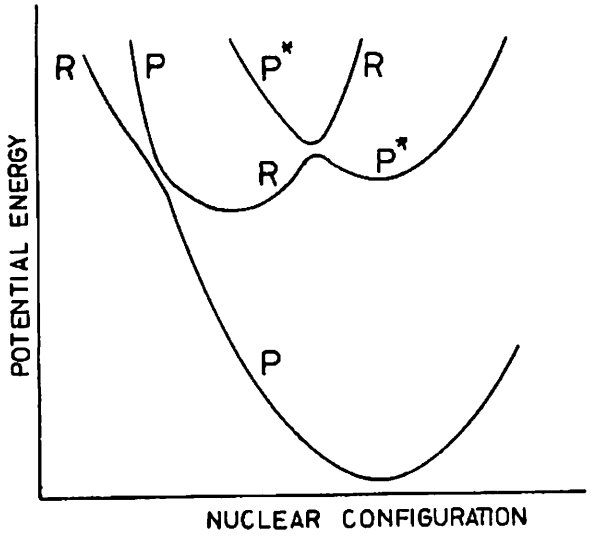

FIG. 2 - Plot similar to Fig. 1 but for a reaction so exothermic that an electronically-excited state of the products also becomes accessible [25].

dependence of λ on this difference reflects the fact that only fluctuations in orientation and vibrational polarization of the solvent occur along the abscissa in Fig. 1; the electronic polarization has a value dictated by the local field; (iii) each λ increases with the square of the charge transferred, ne.

(7) Since κ in Eq. (4.1) is closer to unity the greater the probability of an electron transfer, when the system is in the vicinity of the intersection region in Fig. 1, a weak electronic interaction between the two reactants leads to a small k_{rate}.

(8) In the case of highly exothermic reactions, as in Fig. 2, the electron transfer may occur to form an electronically excited state of the system (P^* in Fig. 2). The electronically excited product can then emit light, either directly or after a sequence of reactions, and one thereby has an electron transfer chemiluminescent reaction [25,8].

(9) An apparent possibility, evident from (4.2), is that ΔG^* will first decrease with increasingly negative $\Delta G^{o\prime}$ and then, when $-\Delta G^{o\prime}(R) > \lambda$, increase as $\Delta G^{o\prime}$ is made

still more negative. The same effect is evident by displacing the P curve in Fig. 2 increasingly downward, and following the position of the "intersection" point of the R and P curves.

However, tunneling of the nuclei from an R to a P curve (instead of passing to a P curve at the "intersection") might reduce the extent of this upturn in ΔG^* when $-\Delta G^{o\prime}(R) > \lambda$ [6,14,46]. Quantum effects related to nuclear tunneling were first discussed by Levich and Dogonadze, refs. in [4,18].

(10) From the definition of the activation energy E_a of a reaction as the slope of a $-k \ln k_{rate}$ versus $1/T$ plot,

$$E_a = - k \partial \ln k_{rate}/\partial (1/T) \quad , \tag{5.5}$$

and the pre-exponential factor A as

$$k_{rate} = A \exp(-E_a/kT) \quad , \tag{5.6}$$

use of Eq. (4.1) and neglect of the minor temperature dependence of $\varkappa Z$ yields

$$A = Z\varkappa \exp(\Delta S^*/k) \quad , \tag{5.7}$$

where

$$\Delta S^* = - \partial \Delta G^*/\partial T \quad . \tag{5.8}$$

ΔS^* is the entropy of formation of the activated complex (apart from the portion included in $k \ln Zh/kT$). Its main contribution comes from $\partial w^r/\partial T$, $\partial w^p/\partial T$, and $\Delta S^{o\prime}$, the entropy of reaction ($= - \partial \Delta G^{o\prime}/\partial T$). When $\Delta S^{o\prime}$ is very negative or very positive, it tends to make ΔS^* very negative or very positive, respectively [28]. When there is extensive coulombic repulsion between the reactants, the contribution to ΔS^* (via the dw/dT terms) is a very negative one. The pre-exponential factor A in (5.6) is small (e.g., $\ll 10^{14}$ cc mole^{-1} sec^{-1} for bimolecular homogeneous reactions or $\ll 10^4$ cm sec^{-1} for first order surface reactions) when $\varkappa \ll 1$ or when ΔS^* is very negative.

VI. Tests of the Theoretical Equations

Most of the tests have been of Eq. (5.1). These tests include comparison of k_{12}(calc) and k_{12}(expt) of reactions involving metal ion hexacyanide and octacyanide complexes, hexaquo and hexammine ones, complexes with EDTA and related compounds, phenanthroline and related complexes, reactions of tri-p-anisylamine with various ferrocenes, reactions of various ferrocenes with various ferrocinium cations, reactions of various aromatic anions with aromatic molecules, among others [1,7,10a,34,35,37-41,48]. A number of examples are given in Table I [1,7,35]. In these and other studies Eq. (5.1) has permitted an extensive correlation of the data, and on the whole the agreement has been quite reasonable. There are a few major exceptions, mostly involving hexaquo cobaltic ion, and we shall return to the latter later. Frequently, Eq. (5.1) has also been used to calculate a value of an unknown self-exchange rate constant k_{11} when the remaining constants are known.

A related test is that of the dependence of ΔG^* on $\Delta G^{o\prime}$ in Eq. (4.2). Tests of this relation have been made with reactions such as the oxidation of a series of substituted ferrophenanthroline complexes by ceric ion, by manganic ion, and by cobaltic ion, and a series of substituted ferriphenanthrolines reduced by cobaltic ion, by Sutin and his coworkers (ref. 34 in [38]), and the reactions of various actinide ions with each other [31]. In each case good agreement was found between theory and experiment. Similar remarks apply, in the regime $|\Delta G^{o\prime}| < \lambda$, to a study of the quenching of fluorescence of various aromatic-type compounds by organic reactants which quench by electron transfer [36]. In the latter study the reactions were also studied at extremely negative $\Delta G^{o\prime}$'s ($|\Delta G^{o\prime}| > \lambda$), a point to which we return later.

Several comparisons have been made between homogeneous redox reactions and reactions at electrodes, including that of Eq. (5.3) and that of (5.4), the former involving various inorganic complex ions [22], and the latter involving the reduc-

TABLE I. Comparison of Calculated and Experimental k_{12}'s

Reaction	k_{12}, M^{-1} sec^{-1} Observed	Calculated
$Fe(CN)_6^{4-} + MnO_4^-$	1.3×10^4	5×10^3
$V(H_2O)_6^{2+} + Ru(NH_3)_6^{3+}$	1.5×10^3	4.2×10^3
$Ru(en)_3^{2+} + Fe(H_2O)_6^{3+}$	8.4×10^4	4.2×10^5
$Ru(NH_3)_6^{2+} + Fe(H_2O)_6^{3+}$	3.4×10^5	7.5×10^6
$Fe(H_2O)_6^{2+} + Mn(H_2O)_6^{3+}$	1.5×10^4	3×10^4
$IrCl_6^{2-} + W(CN)_8^{4-}$	6.1×10^7	6.1×10^7
$IrCl_6^{2-} + Fe(CN)_6^{4-}$	3.8×10^5	7×10^5
$IrCl_6^{2-} + Mo(CN)_8^{4-}$	1.9×10^6	9×10^5
$Mo(CN)_8^{3-} + W(CN)_8^{4-}$	5.0×10^6	4.8×10^6
$Mo(CN)_8^{3-} + Fe(CN)_6^{4-}$	3.0×10^4	2.9×10^4
$Fe(CN)_6^{3-} + W(CN)_8^{4-}$	4.3×10^4	6.3×10^4
$Ce^{IV} + W(CN)_8^{4-}$	1.9×10^8	4×10^8
$Ce^{IV} + Fe(CN)_6^{4-}$	1.9×10^6	8×10^6
$Ce^{IV} + Mo(CN)_6^{4-}$	1.4×10^7	1.3×10^7
$Co(PDTA)^{2-} + Fe(bipy)_3^{3+}$	8.1×10^4	$> 10^5$
$Fe(PDTA)^{2-} + Co(EDTA)^-$	1.3×10^1	1.3×10^1
$Fe(PDTA)^{2-} + Co(ox)_3^{3-}$	2.2×10^2	1.0×10^1
$Cr(EDTA)^{2-} + Fe(EDTA)^-$	$> 10^6$	10^9
$Cr(EDTA)^{2-} + Co(EDTA)^-$	$\simeq 3 \times 10^5$	4×10^7
$Fe(EDTA)^{2-} + Mn(CyDTA)^-$	$\simeq 4 \times 10^5$	6×10^6
$Co(EDTA)^{2-} + Mn(CyDTA)$	0.9	2.1
$Fe(PDTA)^{2-} + Co(CyDTA)^-$	1.2×10^1	1.8×10^1
$Co(terpy)_2^{2+} + Co(bipy)_3^{3+}$	6.4 x 10	3.2 x 10
$Co(terpy)_2^{2+} + Co(phen)_3^{3+}$	2.8×10^2	1.1×10^2
$Co(terpy)_2^{2+} + Co(bipy)(H_2O)_4^{3+}$	6.8×10^2	6.4×10^4
$Co(terpy)_2^{2+} + Co(phen)(H_2O)_4^{3+}$	1.4×10^3	6.4×10^4
$Co(terpy)_2^{2+} + Co(H_2O)_6^{3+}$	7.4×10^4	2×10^{10} (a)
$Fe(phen)_3^{2+} + MnO_4^-$	6×10^3	4×10^3
$Co(phen)_3^{2+} - Fe^{3+}$	1.5×10^3	5.3×10^2
$Cr^{2+} - Co(NH_3)_6^{3+}$	$\leq 1.6 \times 10^{-3}$	1.0×10^{-3}
$Cr^{2+} - Co(en)_3^{3+}$	$\leq 5.1 \times 10^{-4}$	3.4×10^{-4}
$Cr^{2+} - Co(phen)_3^{3+}$	$\leq 1.1 \times 10^4$	3.0×10^1
$V^{2+} - Co(NH_3)_6^{3+}$	$\leq 2.3 \times 10^{-3}$	1.0×10^{-2}
$V^{2+} - Co(en)_3^{3+}$	5.8×10^{-4}	7.2×10^{-4}
$V^{2+} - Co(phen)_3^{3+}$	2.3×10^4	3.8×10^3
$V^{2+} - Co(bipy)_3^{3+}$	7.6×10^3	1.1×10^3

(a) See Table III.

tion of a series of cobaltic pentammino ions $Co^{III}(NH_3)_5X$ by inorganic reductants and by reduction at an electrode (cf. refs. 61, 62 and 74 in [23]). In various studies involving the effect of electrode potential on the reaction rate at an electrode the relation (4.9) has been tested, e.g., refs. in [22]. (In each case the last term in (4.9) was negligible.) The slope α also depends on whether or not an oxide layer is present.

Solvent effects can be quite varied, even including cause of a change in the coordination shell of a reactant. When this effect and other specific solvent effects are absent, and when the solvent orientation contribution to λ can be approximated using dielectric continuum theory, the expression for λ in the Appendix obtains. It has been applied to electron transfers between aromatic anions and aromatic molecules [3] with reasonable agreement between calculated and observed solvent effects, and to reduction of various nitro aromatic anions at an electrode [32], again with reasonable agreement.

Comparison between theory and experiment has also been made via studies of electron transfers at semiconductor electrodes, [29,30] and refs. cited therein. In this case one includes expressions for the electric fields existing within the electrode itself [10].

Rate constants of electron transfer self-exchange reactions can differ by many orders of magnitude, reflecting differences in λ and perhaps in κ. A principal factor influencing λ is the change in bond lengths Δq of corresponding bonds in the two redox forms of a species (Appendix). In the case of the systems in Table I the transfers involve the d-orbitals of the central metal cation, and for reasons which are now understood a change in occupation of an e_g d-orbital (which points along the ligand bonds in hexa-coordinated systems) causes a larger Δq than that by a change in occupation of a t_{2g} d-orbital (which points between the ligands): The loss of an e_g electron from a reductant tends to make the metal-ligand bond become even shorter than it would other-

wise be, as compared with the loss of a t_{2g} electron. Thereby, Δq and λ are larger, and so k_{rate} is smaller. Examples are given in Table II, where the rate constants of several reactions at electrodes at $E=E^{0'}$ are compared with the loss of an e_g or a t_{2g} electron. Again, when the lost electron had been delocalized throughout the complex ion, as in $Fe(CN)_6^{-4}$ and MnO_4^{-2}, Δq should be smaller, and k_{rate} larger than otherwise (cf. Table II). An example of the fact that the metal-ligand bond length depends on whether the extra electron occupies an e_g orbital of the metal ion or a t_{2g} orbital is found in cis-$Fe(bipy)_2(NCS)_2$ (Table II), where the $(t_{2g})^6$ and $(t_{2g})^4(e_g)^2$ states of Fe are compared [17]. (Discussions of electronic structure effects are given in [5,13, 33,40,45,47].

Table II. Effect of Electronic Structure on k_{rate}

System	k_{rate} (cm sec^{-1})[a]	Comment
$Co^{+3,+2}$	2×10^{-7}	e_g involved
$Co(NH_3)_6^{+3,+2}$	5×10^{-6}	e_g involved
$Fe^{+3,+2}$	5×10^{-3}	t_{2g} involved
$V^{+3,+2}$	4×10^{-3}	t_{2g} involved
$Ru(NH_3)_6^{+3,+2}$	ca. 10^{-2}	t_{2g} involved
$Fe(CN)_6^{-3,-4}$	10^{-1}	delocalized
$MnO_4^{-1,-2}$	$> 10^{-2}$	delocalized
$q_{Fe-N}(e_g)^2 - q_{Fe-N}(t_{2g})^2 = 0.12$ Å		

a. e.g., [12], p. 246, for α's of 0.5; Ru est. from Fe and rel. k_{11}'s.

The pre-exponential factor in the rate constants for self-exchange electron transfers, given by (5.6), is in principle of considerable interest. However, while many have been measured, the relative contributions of $\varkappa$ and of the entropy change associated with bringing two highly charged reacting ions together in a high ionic strength medium have not been adequately disentangled in the majority of instances (cf. [23]). Salt effects are marked when the ionic charges are large, as expected.

pre-exponential factors (usually reported indirectly as an "entropy of activation" $\Delta S^{\ddagger}$) for cross-reactions are also influenced by $\Delta S^{o\prime}$, which is no longer zero. The magnitude and sign of $\Delta S^{o\prime}$ can have a major effect on $\Delta S^{\ddagger}$ (and A), as can that of $\Delta H^{o\prime}$ have on $\Delta H^{\ddagger}$ (and E_a). A negative heat of activation $\Delta H^{\ddagger}$ can even occur when $\Delta H^{o\prime}$ is sufficiently negative [2,28].

The expressions given in Secs. IV and V for k_{rate} for the homogeneous bimolecular reactions refer to the case where the reaction rate is not controlled by diffusion. When the collision efficiency of the reaction becomes high, e.g., in water when it approaches ca. 0.01 or higher, the slow step in the reaction is the diffusion of the two species towards each other. In this case, when the diffusion is followed by reaction, with no back reaction, the rate constant k_{rate} for a homogeneous reaction is given by [26]

$$\frac{1}{k_{rate}} = \frac{1}{k_{act}} + \frac{1}{k_{diff}} \quad , \tag{6.1}$$

where k_{act} is the "activation controlled rate constant, and is given by the expressions in Sec. III-V, and k_{diff} represents the well-known expression for the rate constant of a purely diffusion controlled reaction. It is sometimes necessary to make use of (6.1) for very fast reactions. According as $k_{act} >> k_{diff}$ or $k_{diff} >> k_{act}$, we have $k_{rate} \cong k_{diff}$ or $k_{rate} \cong k_{act}$, respectively. (For an application see [13a].)

Thus far, we have considered outer sphere electron transfers. A variety of interesting and specific effects occur in inner sphere electron transfers. The cross-relation (5.1) has been applied to a number of inner sphere electron transfers [38, 49]. Applications have also been made to biological systems involving electron transfer [21,39,40].Other interesting effects in redox systems which have been studied are the effect of pressure on the spin state and on the oxidation state [5] and the spectral properties of intervalency compounds [15].

We return, finally, to two apparent anomalies mentioned earlier: (a) In the main experiment available a very large

negative $\Delta G^{o\prime}$ ($-\Delta G^{o\prime} > \lambda$) did not ultimately cause the k_{rate} to become smaller [36]. This discrepancy has been attributed, in part and in one form or another, to a nuclear tunneling from the R to the P curve in Fig. 2 [6,14,46] and/or to the occurrence of alternate pathways for k_{rate}, such as formation of electronically excited states of one of the reactants. (b) A large discrepancy occurs for (5.1) in the case of reactions of $Co^{+3}(aq)$ (cf. Table III given later). It was found that an increasingly negative $\Delta G^{o\prime}$ does not reduce to zero or nearly zero the effective barrier to reaction [16]. Two explanations, both consistent with this observation and with the fact that there is an extensive difference in electronic configuration between $Co^{+3}(aq)(t_{2g}^6)$ and $Co^{+2}(aq)$ $(t_{2g}^5 e_g^2)$, are (A) $\varkappa$ may be very small or (B) there is a pre-equilibrium (6.2), unaffected by $\Delta G^{o\prime}$, and followed by (6.3).

$$Co^{+3}(aq)(t_{2g}^6) \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} Co^{+3}(aq)^* \qquad (6.2)$$

$$Co^{+3}(aq)^* + A_2(red) \xrightarrow{k_{12}'} Co^{+2}(aq)(t_{2g}^5 e_g^2) + A_2(ox) \ . \qquad (6.3)$$

$Co^{+3}(aq)^*$ may be an electronically excited state† or a very transient form of the ground state (existing for no more than a vibration) in which the metal-ligand bond angles are bent so as to mix the e_g and t_{2g} orbitals. (In contrast, reaction (6.3) probably involves mainly stretching of the metal-ligand bonds.) The self-exchange reaction would be (6.2) followed by

$$Co^{+3}(aq)^* + Co^{+2}(t_{2g}^5 e_g^2) \xrightarrow{k_{11}'} Co^{+2}(t_{2g}^5 e_g^2) + Co^{+3}(aq)^*, \qquad (6.4)$$

and the latter by $Co^{+3}(aq)^* \rightarrow Co^{+3}(aq)(t_{2g})^6$. By assuming an equilibrium constant $K \cong 10^{-5}$ for (6.2) in explanation B, stipulating $k_{-1} > k_{12}'A_2$, and assuming $\varkappa \cong 10^{-5}$ for explanation A, the results in Table III were obtained. (Details are given in Appendix B.) The large discrepancies are reduced.

†The state would be $Co^{+3}(t_{2g}^4 e_g^2)$ [N. Sutin, private communication], and then (6.3) and (6.4) would involve the transfer of a t_{2g} electron. A possible shortcoming of B for the two phenanthrolines (Table III) is its result for the ratio of k's in the footnote.

Table III. Values of k_{12} for Reactions of $Co^{+3}(aq)$ (M^{-1} sec^{-1})

Reagent	k_{obs}	k_{calc} (new,A)[a]	k_{calc} (old)
Fe(II)	2.5×10^2	4×10^4	4×10^7
V(II)	($\sim 10^6$)	10^6	10^{10}
Cr(II)	1.3×10^4	$<7 \times 10^5$	$<10^{10}$
$Co(terpy)_2^{+2}$	7.4×10^4	5×10^3	$\sim 10^{10}$
$Fe(5\text{-}NO_2\text{-}phen)_3^{+2}$	1.5×10^3	10^3	3×10^8
$Fe(5\text{-}Me\text{-}phen)_3^{+2}$	1.5×10^4	4×10^3	3×10^9

[a] In B, $k_{calc} \cong 10^5$, 10^5, 10^5, 5×10^3, 4×10^3, 5×10^3, respectively.

Appendix A. Expressions for λ's

The λ's in Eqs. (4.2) and (4.9) can be written as the sum of two terms [22-24]

$$\lambda = \lambda_i + \lambda_o \quad , \tag{A1}$$

where λ_i is the vibrational contribution from the bonds in each reactant. It is given approximately by

$$\lambda_i = \frac{1}{2} \sum_j k_j (\Delta q_j)^2 \quad , \tag{A2}$$

when stretching motions of the bonds are principally involved. Δq_j is the difference of equilibrium lengths of the corresponding j'th bond on both sides of reaction (4.4), k_j is the bond force constant, and the sum is over all bonds. In the case that the fluctuations in solvent polarization are treated by dielectric continuum theory, λ_o is given by

$$\lambda_o = (ne)^2 \left(\frac{1}{2a_1} + \frac{1}{2a_2} - \frac{1}{R}\right)\left(\frac{1}{D_{op}} - \frac{1}{D_s}\right) \tag{A3}$$

in the homogeneous reaction and by

$$\lambda_{o,e} = \frac{1}{2}(ne)^2 \left(\frac{1}{a} - \frac{1}{R_e}\right)\left(\frac{1}{D_{op}} - \frac{1}{D_s}\right) \tag{A4}$$

in the electrode reaction case. Here, the a's are the radii of the reactants (including coordination shells), and ne is the charge transferred. Data in [9,17] may indicate the $1/R_e$ term to be small.

Appendix B. Calculations for Table III

For explanation B the reaction rate constant is $k_{calc} = Kk_{12}' = K(k_{11}'k_{22}K_{12}'f_{12}')^{1/2}$, with $k_{11}' = k_{11}/K$, $K_{12}' = K_{12}/K$ and f_{12}' calculated from k_{11}', k_{22}, K_{12}'. For explanation A k_{calc} $[= \varkappa k_{12}"] = \varkappa(k_{11}"k_{22}K_{12}"f_{12}")^{1/2}$, with $k_{11}" = k_{11}/\varkappa$ and $K_{12}" = K_{12}$. When the relevant $|\Delta G/\lambda|$ in these highly exothermic reactions, namely $|\ln K_{12}'/2 \ln(k_{11}'k_{22}/Z^2)|$ for case B and with double primes for A, exceeded unity, k_{12}' and $k_{12}"$ were replaced by their maximum, Z, because of the data in [36] referred to in the text. In the case of reactions between an inorganic ion, here $Co^{+3}(aq)$, and the three organic-like ions in Table III a noncancelled work term w has been used in the past [22] to account for other cross-relation results, with $\exp(-w/kT) \sim 0.005$, and so the above k_{12}' and $k_{12}"$ were multiplied by 0.005 for these three ions. Finally, the maximum value of any k_{12}' is k_{diff}, by (6.1), i.e., ca 10^{10} M^{-1} sec^{-1}. Therefore, since $K = 10^{-5}$, the maximum k_{calc} for case B in Table III is 10^5 M^{-1} sec^{-1}.

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