ON THE THEORY OF ELECTROCHEMICAL AND CHEMICAL ELECTRON TRANSFER PROCESSES[1]

R. A. MARCUS

ABSTRACT

Kinetic studies of simple electron transfer systems in solution and at electrodes have revealed a number of interesting and simplifying features. The chemical reactions also represent one of the very few cases in kinetics where it has been possible to make reasonable calculations of the absolute rate constant without introducing adjustable parameters or arbitrary assumptions. Because of their comparative simplicity, these processes also serve as a useful kinetic tool for investigating ion–solvent–electrode interactions.

In the present paper the writer's recent theoretical investigations are summarized and used to interpret data obtained from both solution and electrode studies. Various phenomena are discussed in the light of this theory and several predictions of behavior are made. The topics considered include effects of changing the overpotential or the standard free energy of reaction, the ionic structure, temperature, salt concentration, solvent, and electrode material. Both the parallelism between chemical and electrochemical transfers and the role played by the electrostatic image in the latter case are discussed. A classification of reactants is employed throughout, based in part on differences in the theoretical treatment.

INTRODUCTION

In 1952 Libby (19) interpreted the behavior of some isotopic exchange electron transfer reactions in terms of the Franck–Condon principle, a suggestion which served to stimulate much further experimental and theoretical work. About the same time, Randles (31) discussed the rates of simple electron transfer electrode processes in terms of related concepts. This work was followed several years later by Rudolph J. Marcus, Zwolinski, and Eyring's investigation of an electron tunnelling mechanism for electron transfer (28) and by Taube's evidence that a bridge-activated complex may serve as an intermediate in some cases (38). Each of these stimulating contributions was qualitative (19, 31, 38) or semiempirical in nature (28).

More recently the writer has formulated a quantitative theory of electron transfers in solution (20) and at electrodes (26). It is free from arbitrary assumptions and adjustable parameters. In its present form it was devised for *simple* electron transfer reactions in which no rupture or formation of chemical bonds occurs in the transfer step.

THEORY

The basic assumption of the theory is that only a weak electronic interaction of the two reacting species is required for a simple electron transfer process to occur. The reactants may be ions or molecules and, in the electrode system, the electrode and an ion or molecule. Several deductions may be made quantum mechanically from this basic assumption:

(1) The electronic configuration and therefore the charge distribution of the activated complex are inordinately sensitive to the atomic configuration of the medium (as well as to that of the reactants). In this respect and in its consequent mode of treatment it is apparently unique among activated complexes, but it has much in common with the "polaron" (30), the *F*-center (30), and the "solvated electron".

(2) During the course of a reactive encounter, the atomic configuration of the entire

system gradually changes from one characteristic of the reactants to one characteristic of the products. At the same time the electronic configuration undergoes a corresponding change, following this atomic configurational change adiabatically (27).

(3) As in any reaction, the activated complex can possess one of many possible atomic configurations of positions and momenta, but in the present case the configuration must satisfy a severe energy restriction (20). In *this* atomic configuration, a hypothetical system possessing the electronic wave function (and therefore the ionic charges) of the reactants must have the same energy as that of a hypothetical system possessing the electronic wave function of the products in the same configuration.

An infinite number of atomic configurations can satisfy this energy condition, but only a group of these contribute to the macroscopic or "thermodynamic" properties of the activated complex, namely those which minimize its free energy of formation from the reactants.

In setting up an expression for the reaction rate, the atomic configuration of the system outside the co-ordination shell of each reactant was treated as forming a continuous dielectric medium (20, 26). The configuration of the co-ordination shells themselves was expressed in terms of structural properties such as bond force constants and lengths, using statistical mechanics (22). Special methods involving "nonequilibrium" electrostatic considerations were developed for solving the minimization of free-energy problem subject to the energy restriction (21, 25). The group of atomic configurations constituting the activated complex could not be in electrostatic equilibrium with both hypothetical charge distributions at the same time.

On the basis of theoretical considerations it seems appropriate to classify the reactants somewhat loosely into three groups. Class I consists of those species for which the co-ordination shell of the oxidized form has essentially the same interatomic distances as does that of the reduced form. Class II consists of those in which the bonds of one form have become slightly stretched or compressed compared with the other form. Class III consists of those in which large stretching or compression has occurred.

Examples of Class I include (35) MnO_4^-–MnO_4^{-2} and probably $Fe(CN)_6^{-3}$–$Fe(CN)_6^{-4}$. Examples of Class II include many hydrated metal cations such as $Fe(H_2O)_6^{+3}$–$Fe(H_2O)_6^{+2}$, and those of Class III include (3, 6) $Co(NH_3)_6^{+3}$–$Co(NH_3)_6^{+2}$ and $Cr(H_2O)_6^{+3}$–$Cr(H_2O)_6^{+2}$.

The equations given below were derived for reactants of Class I. Some modifications appropriate to the other classes are noted.

THEORETICAL EQUATIONS

Using as a reaction co-ordinate either a solvent polarization co-ordinate or a movement of either reacting ion relative to the solvent, the following relation can be deduced for both solution and electrode–electron transfer rate constants (20, 26):

[1]
$$k = A' e^{-\Delta F^*/RT}$$

where ΔF^* is defined below and where A' is of the order of 10^{16} cc mole^{-1} sec^{-1} and 5×10^4 cm sec^{-1} for solution and electrode processes, respectively.* Defining the activation energy, E_a, in the usual way as $-\partial \ln k/\partial(1/RT)$ and neglecting the minor temperature dependence of A' we find:

*The exact value of A' is under current study. It depends both on the detailed nature of the reaction co-ordinate and on the value of the collision frequency of two uncharged species. Derivations of a high value (10, 20) for the bimolecular collision frequency in solution can be shown to be overestimates for the system under consideration.

[2]
$$k = A\, e^{-E_a/RT}$$

where

[3]
$$E_a = \Delta F^* + T\Delta S^*$$

[4]
$$A = A'\, e^{\Delta S^*/RT}$$

[5]
$$\Delta S^* = -\partial \Delta F^*/\partial T.$$

ΔF^* represents the change in free energy of ion–ion and ion–solvent interactions accompanying the formation of the activated complex from the reactants:

[6]
solution

$$\Delta F^* = w^* + m^2\lambda$$

[7]

$$-(2m+1)\lambda = \Delta F^0 + w - w^*$$

[8]
electrode

$$\Delta F^* = w^* + m^2\lambda/2$$

[9]

$$-(2m+1)\lambda/2 = -ne\eta_a + w - w^*$$

[10]
$$\lambda = n^2 e^2(1/a - 1/r)\,(1/D_{op} - 1/D_s).$$

The following symbols are employed in these equations:

w^*, w = Work required to bring the two reactants together and the two products together, respectively, from infinity to the positions they would occupy in the activated complex. For the electrode system, w^* and w denote the work required to transport the reactant and the product to the electrode, respectively.

m, λ = Defined by equations [7], [9], and [10].

n = Number of electrons transferred from one reactant to the other (i.e., from a reactant to the electrode, for the electrode case).

e = Unit of electronic charge.

a = Ionic radius (including region occupied by co-ordination shell). If the radii of the two ionic reactants differ, and have values a_1 and a_2, then $2/a = (1/a_1) + (1/a_2)$.

r = Interionic distance in the activated complex or, for the electrode case, twice the distance from the electrode to the center of the ion.

D_{op} = Square of the refractive index.

D_s = Static dielectric constant.

$\Delta F^0 = -RT \ln K$, K being the equilibrium constant for the reaction at the given salt concentration. ΔF^0 will be called the "standard" free energy of reaction.

η_a = Activation overpotential (zero for equilibrium at the given salt concentration).

INTERPRETATION OF THE EQUATIONS

Experimentally, various properties of the electron transfer rate constants of both processes can be measured: their dependence on standard free energy or activation overpotential; their dependence on ionic structure; the extent of parallelism between both rate constants for a series of reactants; the frequency factor and activation energy; the dependence of rate constants on added salts, on the solvent medium, and on the electrode material and surface contamination. The equations will be examined with these features in mind.

The theoretical equations of the two processes are closely related. Typically in each

case, ΔF^* decreases with increasing a, decreasing ne, decreasing r, increasing D_{op}, decreasing D_s (except for the latter's effect, more important perhaps, on w^* and w), and increasingly negative ΔF° or $-ne\ \eta_a$. This behavior has a simple physical interpretation related to the ease with which the energy restriction discussed earlier can be satisfied (23, 24).

For example, ion–solvent interactions decrease with increasing ionic radius a, so that there would be a smaller energy difference between the two hypothetical charge distributions in the original atomic configuration of the reactants and therefore a smaller reorganization would be needed to equalize the two energies. Similarly, the smaller the charge transferred, ne, or the smaller the distance between the reactants (or between the ion and its electrostatic image in the electrode), the less the medium can discriminate energywise between the two hypothetical charge distributions and therefore the less the reorganization needed for energy equalization. A larger optical dielectric constant, D_{op}, serves to partially neutralize the electrostatic fields of the charges and therefore to reduce their energy difference for a given atomic configuration. The more D_s approaches D_{op}, the smaller the dipolar contribution to the electrical polarization of the medium and the less the necessary rearrangement of the atoms (at least for zero ΔF° or zero η_a).

The RHS of equations [7] and [9] has an interesting interpretation. The effective driving force of the reaction is not really the free energy difference (ΔF° or $-ne\ \eta_a$) between reactants and products when the reacting species are far apart but rather when they are in the positions they occupy in the activated complex. These quantities are simply the $\Delta F^\circ + w - w^*$ and $-ne\ \eta_a + w - w^*$ of equations [7] and [9]. By lowering the free energy of the final state of the system relative to that of the initial state, these terms reduce the amount of necessary reorganization of atomic configuration of the initial state in order to satisfy the energy restriction (24).

One difference between the two sets of equations is that λ in equations [6] and [7] for the homogeneous system has become $\lambda/2$ for the electrode system. This difference can be attributed to the absence of one half of the dielectric medium in the electrode case. (Effectively, the charge is transferred from the ion to its electrostatic image, and the metal surface bisects the line drawn between the two.)

The theoretical expressions for ΔF^* and ΔS^* of Classes II and III naturally would contain additional terms. Interesting suggestions concerning these classes have been made by several groups (e.g., 1, 3, 6, 9, 14, 29).

INTERPRETATION OF THE DATA

The data will be discussed from the point of view of the various factors influencing the reaction rate.

"Standard" Free Energy Change or Activation Overpotential

The influence of this factor alone on the rate constant, holding the other factors essentially constant, is more easily investigated for the electrode process. When w and w^* are sufficiently small, it can be deduced from equations [1], [8], and [9] that the transfer coefficient—$\partial \ln k/\partial\ (ne\ \eta_a)$—is 0.5, a value found in a number of simple electron transfer processes (11, 14, 33). Complexation of the reacting species with added salt can change this coefficient (11) but equation [8] does not apply to such systems.

The quantitative effect of ΔF° on the homogeneous bimolecular rate constants has been measured experimentally for some nonspherical reactants (4, 5). While ion–solvent interactions in these systems (oxidation of hydroquinone-like compounds) were not as simple as assumed in equation [6] and an atom transfer mechanism could not be ruled out, reasonable agreement with the experimental rate constants was found (24).

Ionic Structure

The effect of ion size on the rates of homogeneous reactions is most conveniently studied using isotopic exchange reactions whose reactants merely exchange their charges, for then ΔF° and $w^* - w$ are both zero, and m of equation [6] is simply $\frac{1}{2}$. The factor of ion size has been extensively investigated by Wahl and co-workers (8, 35, 39, 40). The rates of large ions, probably of Class I, were found to be much larger than those of the smaller ions, $MnO_4^{-1,-2}$ and $Fe(CN)_6^{-3,-4}$. Again, the latter two systems had comparable rates in spite of the greater Coulombic repulsion in the second case, perhaps because of the larger size of the iron cyanide ion (4.5 vs. 2.9 Å). Rather good agreement was obtained between experimental and calculated rate constants using the theoretical equations, taking into consideration the absence of adjustable parameters (16).

The cobalt–nitrogen bonded complexes probably are members of Class III (3, 6) and the rates are therefore extremely slow. The marked increase in rate (3, 18) in the sequence $Co(NH_3)_6^{+3,+2}$, $Co(en)_3^{+3,+2}$, and $Co(phen)_3^{+3,+2}$ may be partly a reflection of increasing ionic size, and partly a reflection of ligand field (29) effects.

The ferrous–ferric system is probably of Class II, and its rate (36) is correspondingly much less than that of the MnO_4^- or $Fe(CN)_6^{-3}$ systems. Nevertheless, its rate greatly exceeds that (1) of $Cr(H_2O)_6^{+3,+2}$, a probable member of Class III (3). Reasonable agreement between calculated and experimental results for the $Fe(H_2O)_6^{+3,+2}$ was found by adapting the theory to Class II reactants (22). Thus far, there is no experimental evidence which definitely establishes either an electron or an atom transfer mechanism for these homogeneous isotopic exchange reactions of hydrated cations. The general parallelism of various rates in the two processes discussed below suggests, however, a common electron transfer mechanism.

Parallelism Between Rates in Solution and at Electrodes

When similar mechanisms are operative, the theoretical equations suggest a close parallelism between the rates of the two processes, particularly when ΔF° and η_a are zero and the work terms are small. The parallelism becomes very close, therefore, when the rates of isotopic exchange reactions are compared with the corresponding electrochemical exchange currents.

The distance of closest approach for the electrode case will depend on the surface contamination and on the strength of metal–solvent binding. Let us write, therefore, $r = 2a + 2b$ for this system and $r = 2a$ for the homogeneous system. When the work terms are negligible, we obtain

[11]
$$\Delta F^*_{\text{solution}} = \lambda_s^2/4, \quad \Delta F^*_{\text{electrode}} = \lambda_e^2/8$$
where

[12]
$$\lambda_e/\lambda_s = (1 + 2b/a)/(1 + b/a).$$

The chemical and electrochemical electron transfer rates of the systems (3, 32, 36, 39) $Cr(H_2O)_6^{+3,+2}$, $Fe(H_2O)_6^{+3,+2}$, and $Fe(CN)_6^{-3,-4}$ both increase in the order given as do those of the systems (15, 16, 18) $Co(NH_3)_6^{+3,+2}$ and $Co(en)_3^{+3,+2}$. The absolute rates of various electrochemical processes (32) are in the general range expected from the values of the chemical rate constants, but further work is desirable, both theoretically on Class II and Class III systems as well as experimentally on salt effects and hydrolysis effects.

Frequency Factor and Activation Energy

While some application (24) of the theory has been made to the hydroquinone oxidations referred to earlier, the frequency factors, A, of the simpler isotopic exchange

reactions have been much more revealing. For the latter systems, ΔF^* equals $w^* + \lambda/4$. Correspondingly, ΔS^* is the sum of two terms. The first, $-\partial w^*/\partial T$, is the usual entropy change which results when two ions are brought together. The second, $-(d\lambda/dT)/4$, is the entropy of formation of the "nonequilibrium" atomic configurations from the equilibrium ones at the same r in order to satisfy the energy restriction. Its value may be computed from equation [10]. It proves to be very small for reactants of Class I.

Application of the theoretical equations to Class I reactants by the writer led to good agreement between experimental and calculated frequency factors for the $MnO_4^{-1,-2}$ system and (within a factor of 50) for the $Fe(CN)_6^{-3,-4}$ system, the latter system having an extremely small frequency factor (40).† These results suggest that the probability of adiabatic reaction may be of the order of unity, at least for these systems. The frequency factors of Class I reactants provide the most direct measure of this probability factor.

Many of the hydrated metal cations, which are mainly of Class II, tend to hydrolyze and form other complexes easily. In a careful investigation Silverman and Dodson (36) unravelled the rate constant of the $Fe^{+3,+2}$ system from those involving $FeOH^{+2}$ and others. The frequency factor was very small. If $-\partial w^*/\partial T$ is fairly small at the high ionic strengths (high acidity) needed to minimize hydrolysis, this low A-value indicates an additional negative contribution to ΔS^*.

Recently, Baker, Basolo, and Neumann (3) have reported a most interesting result of a very high frequency factor, 5×10^{16} cc mole^{-1} sec^{-1}, for a Class III system, $Co(phen)_3^{+3,+2}$. One simple extension of the present theory for Class I systems to those of Class III can provide an explanation of this possible behavior if the following reaction has an appreciably positive entropy change:

$$Co(phen)_3^{+3} + M(phen)_3^{+2} = Co(phen)_3^{+2} + M(phen)_3^{+3},$$

where $M(phen)_3^{+2}$ is some reactant of Class I or II, such as $Fe(phen)_3^{+2}$. No entropy data appear to have been reported for this process. A similarly high frequency factor has been reported for another Class III system (2a), $Cr(H_2O)_6^{+3,+2}$, but this reaction may be complicated by hydrolysis effects.

The frequency factors of the electrochemical systems have not been measured in the same detail. However, in a recent study, Randles and Somerton (32) found them to be typically in the range 3×10^2 to 3×10^4 cm sec^{-1}. The reactants were primarily hydrated metal cations and so were mostly of Class II. In one system, $Cr(CN)_6^{-3,-4}$, a rather low frequency factor (10 cm sec^{-1}) was found. The electrostatic repulsion between ion and electrode was estimated to be large for this system, and the low A-value was attributed to a small transition probability factor because of the increased r. However, we see from equation [10] that there is also an image term present. This term would tend to favor small r's. An alternative explanation for the A-value could be given on the basis of the usual sign of $-\partial w^*/\partial T$. When two reactants of like sign approach each other, the enhanced electrostatic field polarizes the solvent more strongly and causes a negative ΔS^*. A different region for testing the appropriateness of assuming simple Coulombic interactions and their consequent effects on ΔS^* is suggested in the concluding section.

Activation energies for several electrochemical electron transfers have been measured (32). While these results cannot be precisely compared with those of the isotopic exchange reactions (36, 40), partly because there was no detailed examination of hydrolysis and

†The data were extrapolated to infinite dilution, taking cognizance of the comparative insensitivity of the theoretical activation energy to salt effects.

salt effects, the results tentatively indicate the activation energies of the electrode reactions to be more than one-half those of the corresponding exchange processes. Should this result prove to be generally true (at least for Class I and Class II reactants) one possible interpretation would be that the distance between the ion in the activated complex and its electrical image exceeds twice the ionic radius (cf. equations [10] and [11]). An independent, approximate estimate of this distance may be obtainable from an experiment suggested in the concluding section.

Salt Effects

Using a rough model for ionic interactions the w and w^* terms were calculated by the writer for several Class I reactions and compared with the data of Wahl and co-workers (35, 40). Fair agreement was obtained using no adjustable parameters.

No detailed study of salt effects for simple electron transfers at electrodes appears to have been reported. Therefore it is not yet possible to adequately test the usual assumption (one not made here) that the work required to transport an ion from the body of the solution to the electrode, w^* or w, equals the ionic charge multiplied by the difference of potential at the initial and final positions of the ion, these potentials being computed in the absence of the ion. This assumption is clearly valid when the ionic charge is so small that it does not perturb the configuration of the remaining ions. It is also clearly invalid at the point of zero electrode charge. At this point, the work term estimated on the basis of the above assumption is zero, whereas it actually equals the free energy of interaction of the ion with the image. For infinite dilution, the latter term is $-q^2/2D_s r$, q being the ionic charge, while for dilute salt solutions, an approximate (unpublished) estimate of it is $(-q^2/2D_s r)\exp(-\kappa r)$, κ being the usual Debye κ.

Solvent Effects

Solvent effects for simple electron transfers will occur, according to the theory, whenever there is a change in dielectric constant, refractive index, ionic radius, or standard free energy of reaction. Changes in composition of the co-ordination shell, which may include the solvent, naturally alter a, $\Delta F°$, and the ease of intramolecular compression or stretching. In addition, there are effects which were not incorporated in the theory, effects such as changes in ion-pairing, selective solvation of solvent mixtures, and a change of the mechanism itself. A possible example of selective solvation (7) has been described (2).

Heavy water has been used as a solvent in several studies (e.g., 13, 37). Hudis and Dodson (13) have demonstrated the importance, when hydrolyzed species and other complexes are present, of determining the various equilibrium constants so that meaningful electron transfer rate constants for the different species can be obtained and solvent effects evaluated. The rate constant for $Fe^{+3,+2}$ was smaller by a factor of 2 in D_2O (13), while that of $NpO_2^{+2,+1}$ was smaller by a somewhat smaller factor (37). A qualitative interpretation of the solvent effects can be given in terms of atom transfer (13, 37) or electron transfer (23) theories. Thus far, however, comparative studies in the two solvents do not permit either mechanism to be distinguished from the other. This situation results from the fact that ions have different solvation energies in the two media (17), so that water does not behave as an inert solvent.

The rate of the $Co(NH_3)_6^{+3,+2}$ reaction appears to be faster in liquid ammonia (12) than in water, where it was immeasurably slow (18). The activation energy was high, being in the range found for two other Class III compounds (2a, 3). Possible explanations

for the solvent effect include a change of mechanism, such as a dissociation (12) or possibly a hydrolyzed intermediate, $Co(NH_3)_5NH_2^{+2}$. However, the effect of pH on the reaction rate is not known.

Effects of Electrode Material

A dependence of rate constant on electrode material will occur if there is any change in surface contamination (32) and possible metal–solvent binding, or if electrode charge density at a given η_a changes sufficiently to alter w^* or w. The rate constants measured for one system with several solid electrodes underwent no great variation (within a factor of 10) but were much smaller than that found for a mercury electrode (32).

The Image Force Law and Its Implications

The role of the electrostatic image has been generally ignored in electrochemical theories. A recent investigation (34) of the quantum limitations of the image force law for a vacuum is reassuring. It has been applied by the writer to dielectric media and to electrochemical theory.

The effect of this image is to partially neutralize the field of the ion and to reduce, thereby, the configurational rearrangement free energy needed to satisfy the energy restriction. It is noteworthy that its calculated effect remains, even at salt concentrations sufficiently large as to make w^* and w negligible. This is because it is impossible for the ionic atmosphere in the activated complex to neutralize the ion–image interactions of the two different hypothetical charge distributions at the same time. A compromise configuration results. A similar behavior exists in the homogeneous case, where the $1/r$ term remains even if w^* and w are zero.

At the point of zero electrode charge there is a net, shielded Coulombic attraction between the ion and its image, which is quite large for very dilute solutions. According to the theory a positive ΔS^* would result, since the attraction lowers the entropy of the solvation. A measurement of the frequency factor in this region would permit a determination of this ΔS^*.

If this prediction is verified for Class I reactants, it will be interesting to compare ΔS^* with the theoretical estimates.

ACKNOWLEDGMENTS

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