Electron Transfer Reactions

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With 2 Figures

1. Introduction

Electron transfer processes of chemical interest are of various types: certain homogeneous redox reactions, electron exchange reactions, electrode processes, solvated electron reactions, certain chemiluminescent processes, intramolecular electron transfers, and electron transfers between ions in solution and semiconductor electrodes. The distinction between redox reactions of the atom transfer type and those of the electron transfer type should be noted.

This contribution will discuss theoretical and experimental results in this field and will be based on several recent papers of the author (Ann. Rev. Phys. Chem. **15**, 155 (1964), J. Phys. Chem. **67**, 853, 2889 (1963), J. Chem. Phys. 43, 679 (1965)).

In the present paper, we outline the assumptions, aspects of the derivation, and deductions of a theory of electrochemical and homogeneous reactions of the redox type. The theory has been developed with increase in generality in several recent papers [*1*]. The last of these [*1e*] encompasses the others and is the one summarized here. Because of the techniques devised [*2*] it became possible to present the theory of homogeneous reactions and of electrochemical ones in a single formulation, thereby emphasizing their similarity. We shall follow this procedure here. A variety of applications of the theory has already been described [*3*].

2. Potential Energy Surfaces and Mechanism of Electron Transfer

We consider an electron transfer between two "reacting" species. These species consist of two dissolved ions (molecules) in the homogeneous case and one such ion and electrode in the electrochemical one. Some insight into the mechanism of electron transfer is provided by examination of the behavior of the entire system on its potential energy surface [*1c*, *1d*]. The surface for the system of reactants and surrounding medium is a function of all the translational, rotational, and vibrational coordinates in this system. Similarly, the surface for a system consisting of the products and the medium is a function of these coordinates also.

In the absence of electronic coupling between the orbitals of the two reacting species, the two potential energy surfaces intersect. It is then not possible for the system to go from one surface to the other, i.e., to undergo electron transfer (Fig. 1). A suitable coupling (Fig. 2) removes the degeneracy at this intersection, in the usual quantum mechanical manner [4], and the system may now go from one original potential energy surface to the other by a fluctuation which permits it to pass through the "intersection" region of coordinate space. If the coupling is strong enough the product is thereby formed adiabatically from the reactant; otherwise the formation occurs nonadiabatically. For an adiabatic process in reaction kinetics there is continuous quantum mechanical equilibrium between electrons and nuclei and no abrupt electronic rearrangement. Such processes are primarily of interest here.

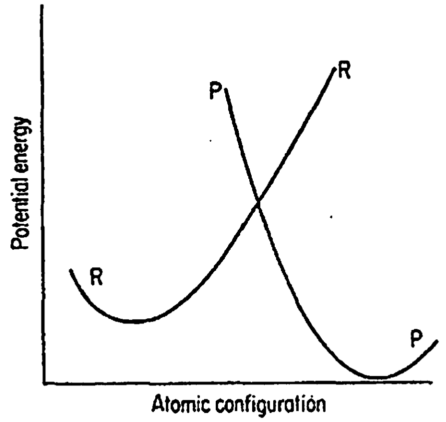

Fig. 1. *R*-reactants, *P*-products, no coupling between the states ψ_R and ψ_P

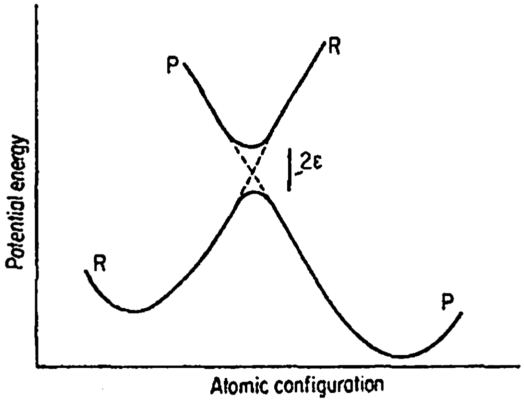

Fig. 2. *R*-reactants, *P*-products, coupling between the states ψ_R and ψ_P, ε-exchange energy

In summary, electron transfer can occur if there is suitable electronic coupling between the reacting species and if there is a suitable fluctuation of coordinates (e.g. bond distances, orientation of solvent molecules, position of ions in atmosphere, including those in the double layer) leading from values appropriate to the reactants to ones appropriate to the products.

3. Assumptions

To calculate the rate of the reaction, it is convenient to introduce several assumptions:

1. The rotational, translational and *relevant* vibrational coordinates of both reacting species and of the molecules and ions in the medium are treated classically.
2. The probability of the system being in the intersection region and having any specified molecular velocities is that computed from equilibrium statistical mechanics.
3. Each reacting species in the activated complex has an inner coordination shell [*5*] not shared by the other reactant. Consequently, any "bridging" of the reactants is of the outer sphere type [*6*].
4. The potential energy of the entire system is the sum of *intra* and *inter* particle terms [*2a*], the second term being a quadratic function of the permanent charge distributions on the particles. (This particle description is much more general than the usual one of polar media, which treats solvent molecules as having only induced and permanent *dipoles* and which was used in reference [*1d*]. The entire electrode and the entire medium can each be treated as a single particle [*2a*].
5. The splitting of the doubly degenerate energy level at the intersection surface is sufficiently small that the potential energy of the lowest electronic state of the entire system differs but slightly from that at the original intersection, for each point of the intersection region.
6. Reaction occurs primarily by the system passing over the barrier rather than by a nuclear tunnelling motion through it.
7. The reaction coordinate *in the region near the intersection surface* does not involve the rupture of a chemical bond.

Assumption 1 is reasonable under the usual experimental conditions, since the highest pertinent molecular frequency is usually a metal-ligand one in the inner coordination shell of an ionic reactant [*7*], and available data indicate this frequency to be typically 300–500 cm^{-1}. Assumption 2 is the standard one in activated complex theory. Assumption 3 could be removed by extending the theory. When assumption 5 is not fulfilled, a condition which could conceivably happen sometimes when inner type bridging occurs (i.e. when assumption 3 fails), the theory could again be extended by calculating independently the splitting of the two energy levels, as a function of coordinates of the intersection surface. Assumption 6 will undoubtedly fail at sufficiently low temperatures. Assumption 7 can be removed by calculating the adiabatic potential energy surface for the case of bond ruptures. In the current literature of chemical kinetics such calculations are presently of a semi-empirical nature, and we wish to avoid computations based on adjustable parameters at present.

Supplementing these assumptions, it is convenient to introduce several approximations which convert the equations for the reaction rate into a rather simple functional form, a form particularly useful for theoretical predictions of correlations among the experimental data:

(I) The partial dielectric (or, more precisely, electric) saturation approximation [*2b, c*] for the entire medium outside the inner coordination shells is valid.

(II) The effective potential energy function for coordinates in the inner coordination shell of each reactant is a quadratic function of the coordinate displacements.

(III) In any given species, the force constant of any bond s may differ when that species is a reactant, k_s^r, as compared with when it is a product, k_s^p. These two force constants are expressed in terms of symmetric and antisymmetric functions of them, namely of $2\,k_s^r k_s^p/(k_s^r + k_s^p)$ and of $(k_s^r - k_s^p)/(k_s^r + k_s^p)$, respectively, and it is shown in ref. [*1e*] that the second of these can be neglected. This approximation simplifies the equations of reference [*1e*] considerably.

Using these assumptions and approximations, and using the method of equivalent equilibrium distribution described in reference [*1d*] and further refined in reference [*1e*], one eventually obtains Eq. (3) for the rate constant [*8a*] of the electrochemical reaction (1) or of the homogeneous reaction (2) where 1 and 2 denote different soluble redox couples.

$$Ox + ne \longrightarrow Red \tag{1}$$

$$Ox_1 + Red_2 \longrightarrow Red_1 + Ox_2 \tag{2}$$

$$k_r = Z \gamma \varrho \exp\left(- \Delta F^* / R_g T\right) \tag{3}$$

where

electrochemical:

$$\Delta F^* = \frac{w^r + w^p}{2} + \frac{\lambda_{el}}{4} - \frac{nF(E - E_0')}{2} + \frac{[-nF(E - E^{0'}) + w^p - w^r]^2}{4\lambda_{el}} \tag{4}$$

homogeneous:

$$\Delta F^* = \frac{w^r + w^p}{2} + \frac{\lambda}{4} + \frac{\Delta F^{0'}}{2 N_a} + \frac{(\Delta F^{0'} + w^p - w^r)^2}{4\lambda} \tag{5}$$

$R_g = k N_a$, where k is Boltzmann's constant and N_a is Avogadro's number.

w^r = work required to bring reactants together until they are at the most probable of the separation distances contributing effectively to reaction.

w^p = corresponding quantity for the products, for the same separation distance.

λ, λ_{el} = reorganization factors, described in reference [3] and, with more generality, in reference [1e]. They are independent of E, E_0' and $\Delta F^{0'}$. λ as well as λ_{el} is a sum of the contributions from the inner coordination shell (λ_i) and of the contributions from the medium outside this coordination shell (λ_0). λ_i is dependent on the changes in bond distances and bond angles and on the force constants of all the vibrational coordinates of each reacting species in its reacting state and in its product state. λ_0 is given for a dielectric continuum treatment (D_{op} – square of the refractive index, D_s – static dielectric constant) by

$$\lambda_0 = \left(\frac{1}{2a_1} + \frac{1}{2a_2} - \frac{1}{r}\right)\left(\frac{1}{D_{op}} - \frac{1}{D_s}\right)(n\,e)^2\ ;$$

a_1 and a_2 are the radii of the spherical particles undergoing reaction including the coordination shell and $r = a_1 + a_2$ is taken as the mean distance between the centers of the reactants in the activated complex. In the electrochemical case $a_1 = a_2$, and r is twice the distance from the center of the reacting particle to the electrode surface. A formal statistical mechanical expression for λ_0 is given in reference [1e].

n = number of electrons transferred,

F = Faraday,

E= potential of half-cell (American convention, sign bivariant),

E_0' = standard potential of half-cell,

$\Delta F^{0'}$ = the apparent standard free energy of reaction [9], equal to nF times the difference of standard potentials of the two redox systems, 1 and 2.

Z = collision number in solution (10^{11} l mole^{-1} sec^{-1}) or, in the electrochemical case, the collision frequency with the electrode (10^4 cm sec^{-1}).

γ = an averaged probability of remaining on the lowest potential energy surface per passage across the intersection region [1d] ($\gamma = 1$ for an adiabatic reaction).

$\varrho = \langle\Delta r\rangle/\langle\Delta q\rangle$, where $\langle\Delta r\rangle$ is the average range of separation distances contributing effectively to reaction, and $\langle\Delta q\rangle$ is the average range of distances along reaction coordinate effectively occupied by the equivalent equilibrium distribution. Explicit formal expressions for ϱ are given in reference [1e]. Typically, it is probably of the order of magnitude of unity; an exception would occur if a low frequency orientation dielectric relaxation coordinate were the major component of the reaction coordinate, thereby making ϱ less than one. We shall take $\varrho\gamma$ to be unity. Further work on its evaluation is in progress. In all cases, a weaker assumption suffices to predict the correlations below.

Sometimes reactions (1) and (2) are preceded or followed by other reactions, so that then neither *Ox* nor *Red* denote the stable species present, merely those participating in the electron transfers (1) and (2). Then, k_r is the rate per unit concentration of these species rather than of the stable ones, and w^r, w^p, $\Delta F^{0'}$, nFE_0', λ and λ_{el} refer to the free energy terms involving such species and not to the stable ones.

4. Deductions

The characteristics of λ most important for predicting correlations are:

(I) In a homogeneous reaction λ is essentially an additive property [10] of the two redox couples, 1 and 2.

$$\lambda = \lambda_1 + \lambda_2 \tag{6}$$

(II) Let λ_{ex} be the value of λ for the homogeneous isotopic exchange reaction:

$$Ox_j^* + Red_j = Ox_j + Red_j^* \tag{7}$$

where the starred species denote isotopic labelling. If this reaction corresponds to an electrode reaction (1) then

$$\lambda_{el} = \frac{1}{2}\lambda_{ex}\,, \tag{8}$$

when the most probable distance of the reactant from the electrode in the pre-electrode layer equals twice that between the reactants in the homogeneous reaction.

As noted in reference [3], a very common condition experimentally is that the last term in Eqs. (4) and (5) can be neglected. From the resulting equation and the above properties of λ and λ_{el} one would then predict:

1. When the effect of E on the work terms can be ignored the electrochemical transfer coefficient should be 1/2. The slope of the electrochemical plot of $(R_g T/nF)\ln k_r$ vs. electrode potential is called the electrochemical transfer coefficient.

2. The k_{el} deduced from the electrochemical exchange current at standard conditions should bear a simple relation to rate constant of the homogeneous isotopic exchange reaction, k_{ex} for the case that the work terms are small in both experiments.

$$k_{el}/Z = \sqrt{k_{ex}/Z_{ex}} \tag{9}$$

3. In the comparison of the redox reaction of a series of reagents with a given chemical agent and with an electrode at a given E, the ratio of rate constants should be the same for each member of the series, regardless of whether or not the reaction is irreversible.

4. The "chemical transfer coefficient" [*3*] – defined as the slope of the ΔF^* vs. ΔF^0 plot in a series of homogeneous redox-reactions – should be 1/2, a result which provides some insight into the electrochemical coefficient when the work terms cannot be ignored.

5. The bimolecular rate constant k_{12} of the cross-reaction of two redox systems, 1 and 2,

$$Ox_1 + Red_2 = Red_1 + Ox_2, \tag{10}$$

is related to the rate constants of the isotopic exchanges in the two systems, k_{11} and k_{22}, and to the equilibrium constant K_{12}, as in (11), when the work terms in $\Delta F^*_{12} - (\Delta F^*_{11} + \Delta F^*_{22})/2$ cancel or can be ignored.

$$k_{12} = \sqrt{k_{11} k_{22} K_{12}} \tag{11}$$

When these work terms cannot be ignored, the appropriately corrected form of (11) is given in Eq. (12) of reference [*3*]. A more elaborate equation based on Eq. (5) itself, rather than on the approximate form of (5), is given in Eq. (13) of reference [*3*].

Any numerical calculation of the rate constant k_r itself requires a knowledge of equilibrium bond distances and force constants in the coordination shells of the reactant and the product, as well as of certain properties of the medium, for these contribute to λ. Some illuminating calculations based on uncertain values of these constants have been given [*6a, 11*] and provide some insight into the problem of *a priori* calculation of reaction rates. In the present paper, we are particularly interested in correlations, however, for they are independent of the present uncertainties of a *priori* estimates of k_r's.

Eqs. (3) to (5) apply when each reacting species has a given inner coordination shell. However, sometimes a species may be present in several forms which differ in their inner coordination shell. Again, fluctuations in the number of strongly adsorbed ions on the electrode correspond to fluctuations in the "inner coordination shell" of the electrode [*5*]. Subject to conditions summarized in footnote 9 of reference [*3*], the above five deductions still apply when these fluctuations in composition of the inner shells occur.

Comparison of the five deductions with the experimental data has been given [*3*]. The agreement with the data may be considered encouraging. A considerable quantity of data supporting deduction 5 has since been obtained [*12*].

References

1. a) MARCUS, R. A.: J. Chem. Phys. 24, 966 (1956), Part I;
  b) O.N.R. Technical Report No. 12. Project NR 051-337 (1957);
  c) Trans. Symposium Electrode Processes, May 1959, p. 239. E. YEAGER, ed., New York: John Wiley and Sons, 1961.
  d) Discussions Faraday Soc. 29, 21 (1960), Part IV of reference [*1a*].

e) J. Chem. Phys., **43**, 679 (1965), Part VI of reference [1a].
In a) the contribution of the medium (outside the inner coordination shells of the reacting species) to the free energy of activation of homogeneous electron transfers was computed, using nonequilibrium polarization theory and treating the medium as a continuum. In b), a similar calculation was made for electrochemical reactions. The problem was then formulated for electrode reactions in c) and for homogeneous ones in d) in terms of the behavior on many-dimensional potential energy surfaces. A detailed treatment, including the contributions of the inner coordination shells and of the medium outside to the free energy of activation, was given for homogeneous reactions in d), which automatically included a). A unified treatment for both homogeneous and electrochemical reactions, encompassing and generalizing a) to d), is given in e).

2. a) Marcus, R. A.: J. Chem. Phys. **38**, 1335 (1963);
b) **38**, 1858 (1963);
c) Part III of b), **39**, 1734 (1963);
d) Part II of a), **39**, 460 (1963). Reference [2c] is the statistical mechanical counterpart of [2b].

3. Marcus, R. A.: J. Phys. Chem. **67**, 853 (1963), Part V of ref. [1a] η_a there should be replaced by $E - E^{0'}$.

4. e.g. Glasstone, S., K. J. Laidler, and H. Eyring: The Theory of Rate Processes, New York-London: McGraw-Hill 1941.

5. When one of the "reacting" species participating in an electron transfer is an electrode, any strongly adsorbed solvent molecules and ions can be considered as the "inner coordination shell" of this "reactant".

6. a) Discussions of inner sphere and outer sphere reactions are given in several recent reviews: Sutin, N.: Ann. Rev. Nuclear Sci. **12**, 285 (1962);
b) Halpern, J.: Quart. Rev. (London), **15**, 207 (1961);
c) Taube, H.: Advances Inorg. Chem. Radiochem. **1**, 1 (1959).

7. When an equilibrium bond length in a reacting species differs in the reactant and product forms of that species, the corresponding stretching or compressing of the bond will contribute to the reaction coordinate. For recent data on force constants and frequencies, see Shimanouchi, T., and I. Nakagawa: Spectrochim. Acta **18**, 89, 101 (1962); International Symposium on Molecular Structure and Spectroscopy (September 1962, Tokyo). Kakiuti, Y., S. Kida, and T. V. Quagliano: Spectrochim. Acta **19**, 201 (1963).

8. a) When no "dynamic ψ-effect" [8b] occurs, it is convenient to define an electrochemical rate constant k_r as the rate per unit concentration of soluble reactant just outside the electrical double layer region [8c]. When the dynamic ψ-effect occurs, a rate constant k_r, defined as the rate per unit concentration of soluble reactant in some defined pre-electrode layer, is more useful since it can be incorporated into the theory of the dynamic ψ-effect. k_r is given by Eq. (3) and k'_r equals $k_r \exp(w^r/kT)$. Analogous remarks apply to the rate constants of homogeneous reactions, as noted elsewhere [8d]; the one defined by Eq. (3) is the rate for unit concentrations of both reactants in the bulk of the solution;
b) See R. Parsons, in Advances in Electrochemistry and Electrochemical Engineering, ed. P. Delahay, (New York: Interscience 1961), pp. 52–54, for references to the work of Levich and of Sparnaay on the dynamic ψ-effect; *cf* Gierst, L.: in Trans. Symposium Electrode Processes, ed. E. Yeager, (New York: John Wiley and Sons 1961), p. 109.
c) Occasionally, it is asserted in the literature that reaction rate should rigrously beexpressed in terms of the activity of the reacting ion. This state-

ment is not only incorrect but also presupposes a knowledge of the single ion activity coefficient. Rather, the rate should be expressed operationally in terms of concentrations, and all *pertinent* salt effects should be incorporated into the theory of the proportionality constant, i.e. of the rate constant. It is readily verified that in careful transition state theory formulations of the latter constant no single ion activity coefficients appear.

d) Marcus, R. A.: Discussions Faraday Soc. 29, 129 (1960).

9. For brevity, $\Delta F^{0'}$ was denoted by ΔF^0 in reference [*1a–1d*].

10. This additivity is described in detail in reference [*1e*], but is evident from the less general equations in reference [*3*]. The presence of one term there, λ_r, depending on the most probable separation distance r of the two homogeneous reactants make λ not quite additive, because of differences in size of the reactants. It is easily shown that this deviation from additivity is small, using the dielectric continuum expression for λ_r. It is then assumed that the same small deviation from additivity will obtain in the statistical mechanical evaluation.

11. Hush, N.: Trans. Faraday Soc. 57, 557 (1961).

12. See work of N. Sutin et al., cited in Ann. Rev. Phys. Chem. 15, 155 (1964), and subsequent work of Sutin. Exceptions are cited in the Ann. Rev. article.

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