Reprinted from ADVANCES IN CHEMISTRY SERIES, Number 50, Page 138, 1965

Theoretical Study of Electron Transfer Reactions of Solvated Electrons

R. A. MARCUS

Noyes Chemical Laboratory, University of Illinois, Urbana, Ill. 61803

The assumptions, equations and several applications of a recently formulated theory of electron transfer reactions of solvated electrons are outlined. The relationship of the reorganization terms to those of ordinary electron exchange and electrochemical reactions is described, together with the role played by an effective standard free energy of reaction. Applications include prediction of conditions under which chemiluminescence might be found and description of conditions under which reactions might not be diffusion-controlled.

For purposes of this monograph we summarize the concepts and principal assumptions of an electron transfer theory (*5*), together with the additional ones used to formulate a treatment of electron transfer reactions of solvated electrons (*8*). The final equations and several applications are also described, but the detailed mathematical derivation is given elsewhere (*8*).

Electron Transfer Mechanism

The theory stems from the writer's work on simple electron transfer reactions of conventional reactants (*5*). A simple electron transfer reaction is defined as one in which no bonds are broken or formed during the redox step; such a reaction might be preceded or followed by bond-breaking or bond-forming steps in a several-step reaction mechanism. Other chemical reactions involve rupture or formation of one or several chemical bonds, and only a few coordinates suffice to establish their essential features. In simple electron transfers in solution, on the other hand, numerous coordinates play a role. One cannot then use the usual two-coordinate potential energy contour diagram (*4*) to visualize the course of the reaction, but must resort to some other pictorial method such as the use of profiles of a potential energy surface.

In the postulated mechanism of simple electron transfer reactions, a weak coupling of the "redox orbitals" of the two reactants is assumed (*5*), and fluctuations of translational, rotational, and vibrational coordinates leading from those characterizing stable configurations of reactants to those describing stable configurations of products is described in terms of potential energy surfaces. A surface for the reactants, plotted *vs.* the many relevant coordinates of the system, intersects one for the products, and a profile of these surfaces is given in Figure 1. The intersection is split in the usual quantum mechanical manner by a coupling of the redox orbitals (*5*).

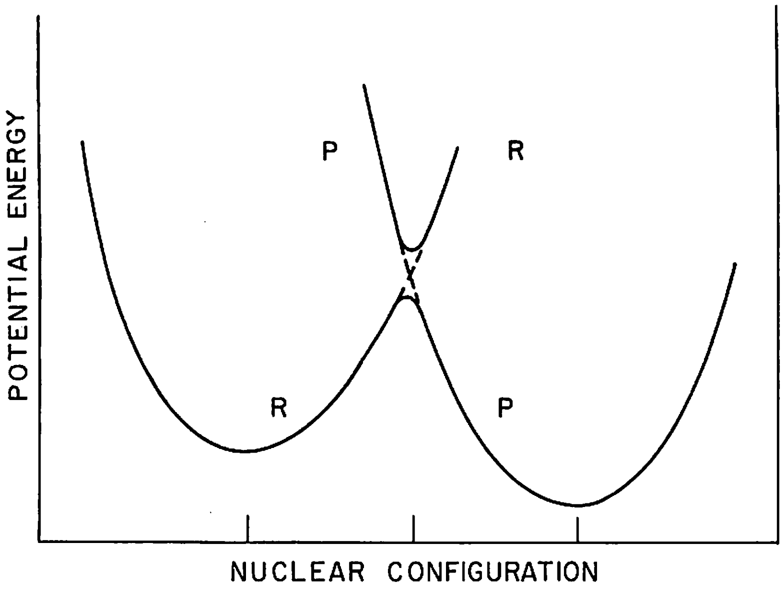

Figure 1. Profile of potential energy surface of reactants (R) and that of products (P) plotted vs. configuration of all the atoms in the system. The dotted lines refer to a system having zero electronic interaction of the reacting species. Each adiabatic surface is indicated by a solid line.

Accordingly, reaction can occur if the system reaches the intersection region during a fluctuation, and if the electronic coupling is large enough to cause the system to remain on the lowest surface during the crossing of the intersection. The configurations occurring at the intersection constitute the "activated complex" for the reaction. They define a hypersurface in this many-dimensional configuration space. The theoretical problem of calculating the reaction rate is largely that of calculating the chance of crossing this hypersurface in unit time. The coordinates undergoing some or appreciable change during the simple electron transfer include the separation distance of the reactants, bond distances in a reactant (those in an inner coordination shell for example), and orientations of solvent molecules. All of these coordinates contribute to the "reaction coordinate" leading from reactants through activated complex to products.

Special Features for Solvated Electron Reactions

In addition to the above features which electron transfer reactions of solvated electrons and ordinary electron transfers have in common, those of the solvated electron possess several novel aspects:

(1) The electronic wave function of a solvated electron, spread over several solvent molecules, should be very sensitive to orientation fluctuations of these molecules, unlike that of an ordinary reactant.

(2) The solvated electron "disappears" into the other reactant so that there is a change in number of reacting particles.

(3) Unlike many of the conventional electron transfers, many reactions of the solvated electron are diffusion controlled.

Because of (1) the mean kinetic energy of the solvated electron changes appreciably during the orientation fluctuations required for the system to reach the intersection hypersurface. Such changes are included in Figure 1, which represents a plot of the total electronic energy of the system as a function of the atomic coordinates.

Item (2) contributes to the calculated free energy of formation of the product from a system coming from the intersection.

Because of (3), the observed rate constant k_{obs} is given by

$$\frac{1}{k_{\text{obs}}} = \frac{1}{k_{\text{diff}}} + \frac{1}{k_{\text{act}}} \tag{1}$$

where k_{diff} and k_{act} are diffusion-controlled and activation-controlled rate constants. According as $k_{\text{diff}} >> k_{\text{act}}$ or $k_{\text{act}} >> k_{\text{diff}}$, k_{obs} equals k_{act} or k_{diff}, respectively (*7*).

Assumptions

The mathematical derivation of the theoretical expression for k_{act} for solvated electron transfers has been given elsewhere (*8*). The following assumptions were the principal ones made, of which (a) to (c) are standard in activated complex theory:

(a) The adiabatic (Born-Oppenheimer) approximation is used to treat the electronic-nuclear motion. (In the vicinity of the intersection hypersurface, nonadiabatic effects arise only if the splitting is very small. The factor κ in Equation 2 is then less than unity and is calculated by various nonadiabatic methods. Normally, the reaction is assumed to be adiabatic ($\kappa \sim 1$).)

(b) Classical equilibrium statistical mechanics is used to calculate the probability of reaching the intersection hypersurface. Any vibrational quantum effects which occur are treated approximately in the usual way for activated complex theory.

(c) The rate is given by the number of "first passages" of a system across the intersection surface per unit time.

(d) Highly specific interactions of the two reactants (—e.g., steric effects) are assumed to contribute primarily to the work w required to bring the reactants together.

(e) The solvent polarization (outside any inner coordination shell) caused by the two reactants is treated by dielectric continuum theory. (Statistical mechanics was used for conventional electron transfers and can be used to replace the continuum theory when this refinement becomes appropriate.)

(f) In the hydrogen-bonded solvents of present interest the electron is assumed to be in a cavity-free medium. Arguments were given to suggest that when a solvent cavity for the electron occurs it will primarily affect the numerical value of λ_e^∞ in Equation 3 rather than the functional form of those final equations (*8*).

In addition, two approximations were introduced (*5*) which simplified the equations considerably. They are easily avoided as described later. The equations then become more complex.

(g) The vibrations of the second reactant are treated as harmonic oscillators.

(h) A symmetrized vibrational potential energy function is used for reactants and products. The minor error introduced thereby has been estimated elsewhere (*5*).

A solvated electron in a polar solvent has a high classical frequency of motion in its "orbit." Accordingly, the rotating or librating solvent molecules of the system see it primarily as some diffuse charge distribution. The molecules orient themselves toward this diffuse charge in a way consistent with their thermal motion and with their bonding to other molecules. The valence and inner electrons of these molecules are polarized by the instantaneous field of the solvated electron when they are some distance from the electron. If they are too close to it they cannot follow the motion of the instantaneous field, as uncertainty principle arguments show (*8*). A quantum mechanical continuum estimate of the radius of this dynamical sphere of exclusion of electron polarization and of the contribution to the interaction energy was made (*8*). When the radius is small relative to the circumference of the "orbit" of the electron the radius does not influence the numerical value of λ_e^∞ in Equation 3. More refined models for the solvated electron would also recognize any vibronic effects, since the estimated frequency of electronic motion (*8*) is not far from that of polar OH vibrations of the medium.

Calculation of k_{act}

The rate constant k_{act} is given by Equation 2, on the basis of assumptions (a) to (c) and the introduction of certain comparatively minor approximations (*5, A*). (In the present paper a reference labelled by a letter refers to a comment in the Appendix.)

$$k_{\text{act}} = Z\kappa\rho e^{-\Delta F^*/kT} \tag{2}$$

where ΔF^* is the free energy of formation from reactants of a system centered on the intersection hypersurface and Z is a collision frequency between uncharged species. (Z is about 10^{11} liters/mole/sec. The charge effects on collision frequency are included in ΔF^*.) ΔF^* is computed for the most probable separation distance contributing to reaction. ρ is a ratio of certain root mean square displacements and is taken to be about unity (*5, A*).

Statistical mechanics was used to calculate the probability of occurrence of the necessary fluctuations in vibrational coordinates. Continuum theory was used to calculate the free energy of formation of any nonequilibrium state of polarization of the medium in the presence of the electron, and quantum mechanics to calculate changes in the kinetic energy and solvation free energy of the electron owing to changes in solvent polarization (*8*). In this way the free energy was calculated for a system having the electronic charge distribution of the reactant and having Boltzmann-type polarization and vibrational distribution functions. Similarly, for the same distribution of coordinates the free energy was calculated for a system having the electronic configuration of the product. However, as Figure 1 illustrates, these two free energies are equal when each system is constrained to be centered on the intersection hypersurface: the potential energy, averaged over the given distribution, is the same, because of the intersection, and the entropy of a system is determined only by the configurational distribution and so must also be the same for two systems having the same such distribution. The kinetic energy of any nucleus is also the same in the two systems.

Minimization of the free energy of this arbitrary state of a system containing the reactants, subject to the condition of equality of the two free energies, yields an expression for the free energy of the reactants in this centered distribution and, thereby, for ΔF^*. The functional form of the equation for ΔF^* is given by Equation 3, and that for ΔF^{*p}, the free energy of formation of the centered distribution from the product, is given by Equation 4 (*8*).

$$\Delta F^* = w + m^2\left[\left(1 - \frac{m^2}{2}\right)\lambda_e^\infty + \lambda_2^\infty + \Delta\lambda_R\right] \qquad (3)$$

$$\Delta F^{*p} = (m + 1)^2[(1 - m^2)\lambda_e^\infty + \lambda_2^\infty + \Delta\lambda_R], \qquad (4)$$

where w is the work required to bring the reactants together to a mean separation distance R in the activated complex. (Both coulombic and noncoulombic terms can contribute to w.) λ_e^∞ is an "intrinsic reorganization factor," which can be expressed in terms of the properties of the solvated electron (*8*). λ_2^∞ is an "intrinsic reorganization factor" of the second reactant and depends only on the properties of that reactant, such as differences in equilibrium bond lengths and orientation polarization in the oxidized and reduced forms (*8*). The ∞ superscript indicates that the quantities are evaluated for reactants far apart, and $\Delta\lambda_R$ is the change in the sum of intrinsic reorganization factors from $(\lambda_e^\infty + \lambda_2^\infty)$ to $(\lambda_e^R + \lambda_2^R)$. In terms of continuum theory $\Delta\lambda_R$ for the one-electron transfer equals $-e^2(D_{op}^{-1} - D_s^{-1})/R$, where D_{op} and D_s denote the optical and static dielectric constants, respectively, and where e is the electronic charge (*8*). The quantity m is the solution of

$$\Delta F^* - \Delta F^{*p} = \Delta F^{\circ\prime}{}_{\text{int}} - w. \tag{5}$$

In this last equation $\Delta F^{\circ\prime}{}_{\text{int}}$ is the "standard" free energy of reaction $\Delta F^{\circ\prime}$ in the prevailing medium, corrected for the translational free energy loss when the "oriented center," in which the electron formerly resided, disappears during the formation of product from the centered distribution on the hypersurface. This corrected $\Delta F^{\circ\prime}$ constitutes the "driving force" for reaction at the mean separation distance R:

$$\Delta F^{\circ\prime}{}_{\text{int}} = \Delta F^{\circ\prime} - \Delta F^{\circ}{}_{\text{trans}} \tag{6a}$$

$$= \Delta F^{\circ\prime} - RT\ln[(2\pi m_p kT)^{3/2}1000/h^3\text{N}_a] \tag{6b}$$

for a standard state of $1M$, where m_p is the effective mass for translation of the solvated electron (the "polaron") and N_a is Avagadro's number. The value of $\Delta F^{\circ}{}_{\text{trans}}$ is 5.3 kcal./mole if m_p is $3/\text{N}_a$ grams/molecule (*B*).

The functional form of Equations 3 and 4 differs somewhat from that found earlier (*5*) for conventional electron transfers, the difference arising from the sensitivity of the wave function to changes in solvent polarization. Equations 3 and 4 simplify on close examination: These reactions are extremely rapid because the solvated electron is a very strong reducing agent, so that $\Delta F^{\circ\prime}$ is very negative. In this case, ΔF^* is very small and, therefore, m^2 is seen from Equation 3 to be small. In fact, for the usual reactions of the solvated electron *a posteriori* numerical calculations from the observed rates show that $m^2 << 1$, and so m^2 can be neglected in the coefficients of λ_e^{∞} in Equations 3 and 4.

The equations then become

$$\Delta F^* = w + m^2\lambda \tag{7}$$

$$m = -\frac{1}{2}\left(1 + \frac{\Delta F^{\circ\prime}{}_{\text{int}} - w}{\lambda}\right) \tag{8}$$

where

$$\lambda = \lambda_e^R + \lambda_2^R \tag{9}$$

These equation are now similar to those derived earlier for conventional electron transfer reactions (*5*).

The value for λ_2^R is the same as that for this same reactant in an ordinary homogeneous or electrochemical electron transfer occurring at the same R and can be estimated from them, as described later (*6*). $\Delta F^{\circ\prime}{}_{\text{int}}$ is known for many reactions of the solvated electron, and w can be estimated approximately. Accordingly, a theoretical value of ΔF^* can be calculated from Equation 7 once λ_e^R is known. Either λ_e^R can be calculated from other sources (it depends on the model of the solvated electron) or a value can be used which best fits data on k_{act} for several reactions, or both. In making such calculations it should be noted that ΔF^* is not highly accurately given by Equation 7, because of the various approximations. It is more realistic to compare theoretical and experimental values for ΔF^*, therefore, rather than those for k_{act}.

The work term w makes a relatively minor contribution to ΔF^*. In numerical calculations it is usually assumed to be electrostatic in origin and to be given roughly by the shielded coulombic formula, $w^r = (e_1e_2/DR) \exp(-\kappa R)$, where e_1 and e_2 are the charges of the reactants, D is the dielectric constant and κ the Debye kappa. (In very dilute solutions $\exp(-\kappa R) \cong 1$.)

Dependence of k_{act} on $\Delta F^{\circ\prime}$. Possible Chemiluminescence.

To explore the behavior of ΔF^* with $\Delta F^{\circ\prime}$ it is convenient to rewrite Equations 7 and 8 as

$$\Delta F^* = w + \frac{\lambda}{4}\left[1 + \frac{\Delta F^{\circ\prime}{}_{\text{int}} - w}{\lambda}\right]^2 \tag{10}$$

The value of $\Delta F^* - w$ is seen to decrease at first as $\Delta F^{\circ\prime}$ becomes increasingly negative, to pass through a minimum at $(\Delta F^{\circ\prime}{}_{\text{int}} - w) = -\lambda$, and then to increase as $\Delta F^{\circ\prime}$ becomes still more negative. The physical origin of the behavior is seen from Figure 1: As $\Delta F^{\circ\prime}$ is made more negative the product surface in Figure 1 is lowered relative to the R surface, and ΔF^* becomes smaller at first, because the intersection occurs at lower energies on the R surface. This effect of $\Delta F^{\circ\prime}$ on ΔF^* is the normal one, and the configurations at the intersection are seen to be a compromise between the stable ones of the initial state and the stable ones of the final state. When $\Delta F^{\circ\prime}$ becomes still more negative, the intersection is seen to occur to the left of the minima of the R and P surfaces in Figure 1, at higher and higher parts of the initial R surface as $\Delta F^{\circ\prime}$ becomes increasingly negative. The configurations at the intersection are no longer compromise ones. This latter $\Delta F^{\circ\prime}$ region might be called the abnormal $\Delta F^{\circ\prime}$ region.

When $\Delta F^{\circ\prime}$ is sufficiently negative ΔF^* becomes large, and either the reaction with the solvated electron should become very slow or a reaction should occur by other paths, two of which are the following:

(a) Formation of electronically-excited states and possible chemiluminescence (*8*):

Although the intersection of the R surface with the surface for the electronic ground state of the product occurs at high ΔF^*'s when $\Delta F^{\circ\prime}/\lambda$ becomes very negative (slightly more negative than -1), the calculations given below indicate that an intersection with a surface in which the product is excited may then occur at low ΔF^*; chemiluminescence may therefore result:

For formation of the excited state of the product ΔF^* is again given by Equation 10, with λ_2^R and $\Delta F^{\circ\prime}{}_{\text{int}}$ now referring to formation of this excited state. For example, in a reaction for which $\Delta F^{\circ\prime}{}_{\text{int}}$ is as negative as -4 e.v., and in which the fluorescence occurs at say 6000 A. (2 e.v.), the $\Delta F^{\circ\prime}{}_{\text{int}}$ for formation of the excited state is then only -2 e.v. or even less. If $\lambda/4$ for both reactions is about 0.4 e.v. and if, for present purposes we neglect w, then ΔF^* for a reaction leading to the ground and excited state of the product is 0.9 e.v. and 0.025 e.v., respectively. In the first case the reaction is much too slow for measurement in these systems and in the second case it would occur with ease, the barrier ΔF^* being about 0.6 kcal./mole.

(b) Atom transfer reaction: In principle, it is possible that an atom transfer reaction such as Equation 11 can occur when the second reactant is an atom transfer acceptor or is otherwise reactive to the atom. To be sure, there is no evidence as yet for such reactions of the solvated electron. By suitable choice of reactant they could be avoided.

$$e(H_2O)^- + Fe(CN)_6^{-3} \rightarrow OH^- + Fe(CN)_5CNH^{-3} \qquad (11a)$$

$$Fe(CN)_5CNH^{-3} \rightarrow Fe(CN)_6^{-4} + H^+ \qquad (11b)$$

Estimating $\Delta F^{\circ\prime}_{\text{int}}$ and λ

From measured forward and reverse rate constants of the reaction of a solvated electron with water Baxendale (*1*) estimated the standard potential for the solvated electron. Use of a more recent rate constant (*3*) and correction (*8*) for a certain omitted entropy change yields a value, $E^{\circ\prime}_e = +2.7$ volts, for the standard oxidation potential of the solvated electron. To calculate $\Delta F^{\circ\prime}_{\text{int}}$ for a reaction from a difference of the standard oxidation potentials of the two reactants, $E^{\circ\prime}_e - E^{\circ\prime}_2$, the $\Delta F^{\circ\prime}$ must be corrected for the $\Delta F^{\circ}_{\text{trans}}$ of about 5 kcal./mole. This correction can be made (*8*) by taking the effective $E^{\circ\prime}_e$, $E^{\circ\prime}_{\text{eff}}$, for a solvated electron to be 2.9 volts.

$$\Delta F^{\circ\prime}_{\text{int}} = -eF(E^{\circ\prime}_{\text{eff}} - E^{\circ\prime}_2) \qquad (12)$$

In homogeneous electron exchange reactions between two species differing only in their valence states, ΔF^* is given by Equation 10 with λ equal to $2\lambda_2^R$ and $(\Delta F^{\circ\prime}_{\text{int}} - w)$ replaced by $\Delta F^{\circ\prime} - w^r + w^p$ (*5*). (w^r and w^p denote the work required to bring the reactants together to the mean separation distance R, and the products to this R, respectively.) $\Delta F^{\circ\prime}$ is zero for a simple electron exchange reaction and w^r equals w^p for it, since the products are chemically indistinguishable from the reactants.

$$\Delta F^*_{\text{ex}} = w^r + \frac{\lambda_2^R}{2} \qquad (13)$$

The separation distance R should affect primarily the orientation polarization contribution to λ rather than the vibrational contribution from the inner coordination shell (*5*). If R is about the same for this reaction as it is for reaction with the solvated electron then λ_2^R is the same. The difference in λ_2^R would probably be relatively minor in any case for typical R's.

Since ΔF^*_{ex} equals $-RT \ln(k_{\text{ex}}/10^{11}\ M^{-1}\ \text{sec.}^{-1})$, λ_2^R can be estimated from the electron exchange rate constant k_{ex} when correction of ΔF^*_{ex} is made for w^r or when w^r is small enough to be neglected. Values of ΔF^*_{ex} have also been obtained indirectly from measurements of rate constants of other redox reactions involving the species, particularly in (*2*), where tests of this evaluation are described.

In electrochemical electron transfer reactions, the value of the rate constant k_{el} at zero activation overpotential yields a value of ΔF^*_{el}. The latter equals $-RT \ln(k_{el}/10^4 \text{ cm. sec.}^{-1})$, and the theoretical expression for ΔF^*_{el} is (*5*)

$$\Delta F^*_{el} = \frac{w^r + w^p}{2} + \frac{\lambda_2^R}{4} \tag{14}$$

Correction of this ΔF^*_{el} for the work terms then yields a value of λ_2^R. The consistency of Equations 13 and 14 has received some experimental support (*9*), though further work is desirable. Examples of some approximate values of λ_2^R computed in these ways are (*C*): $Co(NH_3)_6^{+2,\,3}$ (~60 kcal./mole), $Fe(phen)_3^{+2,3}$ (~15 kcal./mole), $Eu^{+2,\,+3}$ (~40 kcal/mole).

The value of λ_e^R for the solvated electron has been estimated in several ways (*8, 10*). By assuming that diffusion of the solvated electron in water occurs as a site-to-site electron transfer and using an expression for ΔF^* for a unimolecular electron transfer reaction (*5*); Sutin estimated (*10*) a lower bound of 5 kcal./mole for λ_e^R from the known diffusion constant. The writer has estimated (*8*) a value of roughly 15 kcal./mole to fit the rate constant for reaction of the solvated electron with Sm^{+3}, assuming that λ_2^R was about the same as that for another rare earth, Eu^{+3}. An estimate of λ_e^R can also be made from spectral and solvation data, but depends on the detailed model used for the solvated electron (*8*) and neglects the "electron affinity" of the first excited state of the solvated electron. (This electron affinity describes local interactions; these are not covered by simple polaron theory.) The latter estimated value of λ_e^R is rough but is consistent with the value just cited and with a value estimated *a priori* (*8*). At the same time this second estimate from the data yields a rough and perhaps not reliable value of the "electron affinity" of the ground state of the solvated electron (*8*).

From Equation 10 an estimate can be made of an error in calculated ΔF^* owing to an error in λ. If the errors are denoted by δ's we have

$$\delta\Delta F^* = -\left(1 + \frac{\Delta F^{\circ\prime}_{\text{int}} - w}{\lambda}\right) \frac{\Delta F^{\circ\prime}_{\text{int}}}{2\lambda}\,\delta\lambda \tag{15}$$

For example, an error of 5 kcal./mole in λ introduces an error of 0.6 kcal./mole in ΔF^*, when $\Delta F^{\circ\prime}_{\text{int}}/\lambda \cong -0.6$. Similarly the error in ΔF^* owing to an error in $\Delta F^{\circ\prime}_{\text{int}}$ is

$$\delta\Delta F^* = \left(1 + \frac{\Delta F^{\circ}_{\text{int}} - w}{\lambda}\right) \frac{\delta\Delta F^{\circ\prime}_{\text{int}}}{2} \tag{16}$$

An error of 2 kcal./mole in $\Delta F^{\circ\prime}_{\text{int}}$ introduces an error of 0.9 kcal./mole in ΔF^* when $\Delta F^{\circ\prime}_{\text{int}}/\lambda \cong -0.6$. However, one sees from Equations 15 and 16 that the sensitivity of ΔF^* to a change in λ or $\Delta F^{\circ\prime}_{\text{int}}$ depends on the value of $\Delta F^{\circ\prime}_{\text{int}}/\lambda$. We have selected a typical value.

Further Applications

The prediction (*8*) of possible chemiluminescence at suitable $\Delta F^{\circ\prime}_{\text{int}}/\lambda$'s has already been discussed. Applications of the equations have also been made to calculations of rate constants for reactions of solvated electrons, using λ_2^R's estimated as above (*8, 10*). If, when $\Delta F^{\circ\prime}_{\text{int}}$ is very negative, the calculated rates are too low, the explanation may lie in the formation of excited states or, in some cases, in atom transfers. A search for the predicted chemiluminescence is under way (*11*). It would be favored by a reaction for which λ_2^R is small enough that $\Delta F^{\circ\prime}_{\text{int}}/\lambda$ is quite negative for formation of the ground state of the product. Interestingly enough, it is possible to vary ΔF° systematically without varying λ, simply by varying a substituent in a large organic ligand (*2*). Thus, a control of the relative values of ΔF^*'s for reactions leading to ground and excited states becomes possible and so, thereby, does the yield of any chemiluminescence.

To investigate reactions of solvated electrons in the borderline region of diffusion and activation control there are two regions of $E^{\circ\prime}$ for the second reactant which are of interest, for typical λ's. Estimated from Equation 10, neglecting w, these are: $E^{\circ\prime}_2 >$ *ca.* 1.5 to 2 volts (*8*) and $E^{\circ\prime}_2 <$ *ca.* -0.5 to -1.0 volts for a typical λ of about 55 kcal./mole. The former region, particularly, would be expected to yield the most reliable empirical values of λ_e^R, since they involve compromise configurations in the activated complex, just as k_{ex} and k_{el} do. The resulting λ_e^R's *may* be compared with those obtained from the second $E^{\circ\prime}_2$ region. In cases which involve appreciable changes in bond lengths of a reactant, it may be necessary to replace the harmonic oscillator approximation (g) by use of anharmonic potential energy functions. (Approximation (h) is automatically replaced at the same time.) For this purpose one may replace Equation 10 by an equation derived earlier for ordinary electron transfer reactions (*6*) as the derivation of Equation 10 from Equation 3 and as the similarity of Equation 10 to the equation for conventional electron transfers both indicate.

Appendix

(A) In activated complex theory the rate constant can be expressed in terms of the free energy $F^\ddagger$ of a system hypothetically constrained to exist on a certain hypersurface, the "activated complex," cf. Marcus, R. A., *J. Chem. Phys.* 41, 2624 (1964). $F^\ddagger$ can be expressed in terms of the free energy F^* of a system centered on that hypersurface (*5*). The difference between $F^\ddagger$ and F^* contributes a factor to ρ. A second factor in ρ arises from the fluctuations in the separation distance of the reactants in the activated complex (*5*).

(B) Theoretical values of m_p and λ_e^∞ would depend on the model of a solvated electron. The value of m_p used in the text is at best rough (*8*), but $\Delta F^\circ_{\text{trans}}$ is relatively insensitive to it in the region of interest.

A theoretical value of $\Delta F^{\circ\prime}$ would also depend on the model, but fortunately its experimental value is known instead.

(C) Values of λ_2^R for $Co(NH_3)_6{}^{+2,\ +3}$ and for $Eu^{+2,\ +3}$ were estimated from k_{el} in (*9*), neglecting w because of the high salt concentrations. The value of $Fe(phen)_3{}^{+2,\ +3}$ was estimated from the value assigned to k_{ox} in (*2*), neglecting w. Only a lower limit for k_{ox}, quoted in (*2*), is known. A possible noncoulombic source of w for certain $Fe(phen)_3{}^{+3}$ reactions is noted in (*2*) and (*9*) and, if correct, may apply to reaction between e(aq) and $Fe(phen)_3{}^{+3}$. Data on other k_{ox}'s and k_{el}'s are given in (*2*) and (*9*) and in various other articles.

Literature Cited

(1) Baxendale, J. H., *Radiation Res. Suppl.* **4,** 139 (1964).
(2) Campion, R. J., Purdie, N., Sutin, N., *Inorg. Chem.* **3,** 1091 (1964).
(3) Dorfman, L. M., Matheson, *Progr. Reaction Kinetics* **3** (in press).
(4) e.g. Glasstone, S., Laidler, K. J., Eyring, H., "The Theory of Rate Processes," p. 96, McGraw-Hill, New York, 1941.
(5) Marcus, R. A., *Ann. Rev. Phys. Chem.* **15,** 155 (1964); *J. Chem. Phys.* **43,** (1965).
(6) Marcus, R. A., *Discuss. Faraday Soc.* **29,** 21 (1960). (The term involving $(\Delta e)^2(D_{op}{}^{-1} - D_{op}{}^{-1})/2a_1$ there is to be replaced by $\lambda_o{}^{\infty}$ and the Δq_i's now refer only to the second reactant.)
(7) Marcus, R. A., *Discuss. Faraday Soc.* **29,** 129 (1960).
(8) Marcus, R. A., *J. Chem. Phys.* **43,** (1965).
(9) Marcus, R. A., *J. Phys. Chem.* **67,** 853, 2889 (1963).
(10) Sutin, N., in "Symposium on Exchange Reactions," International Atomic Energy Agency, Brookhaven, June 1965.
(11) Sutin, N., Schwarz, H. A., private communication.

RECEIVED May 3, 1965. Supported by a grant from the National Science Foundation.