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Theory of Electron-Transfer Reaction Rates of Solvated Electrons*

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A theory of electron-transfer reactions of solvated electrons is described. Using an electron-transfer theory formulated elsewhere and using polaron theory the rate constant is related to the standard reduction potentials of the two reactants, spectral and other data for the solvated electron, and rate data on ordinary chemical or electrochemical electron-transfer reactions of the second reactant. This calculated rate constant appears in a boundary condition in a diffusion-reaction differential equation. When that constant is high the reaction becomes diffusion controlled, but when the constant is low it becomes the observed rate constant itself. Some comparison is made with existing data. Conditions for possible but as yet unobserved chemiluminescence are also considered. Solvent-electron polarization in the vicinity of a solvated electron is also examined, by application of polaron theory for a high lattice frequency continuum.

INTRODUCTION

IN the present paper a reaction-rate theory is formulated for electron-transfer reactions of solvated electrons. Consideration is restricted to "pure" electron transfers, i.e., to reactions for which chemical bond rupture does not occur or occurs subsequent to electron transfer as in (1) and (2).

$$e(\text{aq})+\text{Ox}\rightarrow\text{Red}, \tag{1}$$

$$\text{Red}\xrightarrow{\text{fast}}\text{products}. \tag{2}$$

An expression for the reaction rate is obtained in terms of standard reduction potentials of the two reactants, spectral data for the solvated electron, and reorganization parameters found from rate data on chemical or electrochemical electron transfers when available. When the calculated rate constant is very high it is not used directly but appears, instead, in a boundary condition in a differential equation for mutual diffusion of the two reactants. For very high rate constants the reaction becomes diffusion controlled.

A major purpose of the present paper is to relate rate constants of solvated-electron reactions to other rate constants and to quite different properties. Many rate constants for reactions of solvated electrons have now been measured in water and in alcoholic solvents.[1,2] More precisely, rate constants have been measured for reaction with some species which, measurements of salt effects in the diffusion-controlled region suggest, has a unit negative charge,[3] and which has an absorption spectrum in water and alcoholic solvents shifted to the blue from that in liquid ammonia.[1,2]

At present, tests of the theoretical rate expression derived in the present paper are somewhat limited by the fact that many of the common redox reactants, for which conventional electron-transfer rates are known, are reduced very quickly by the solvated electron because of the latter's extremely high reduction potential. Thus, many of those reactions of the solvated electron are diffusion controlled, so that only lower bounds for the corresponding activation-controlled rate constants are available from the data. For many reactants whose rates of reaction with the solvated electron are not diffusion controlled, the corresponding redox reactions, chemical or electrochemical, are slow. Nevertheless, by suitable choice of solvents, reactants, and techniques, one may anticipate, this sparsity of comparable data will be reduced.

POTENTIAL-ENERGY SURFACES AND REACTION MECHANISM

The concepts of electron-transfer theory presented elsewhere[4,5] remain applicable here when the overlap of the electronic orbital of the solvated electron and that of the second reactant is weak: One may draw a potential-energy surface as before, the electronic structure of the reacting species being that of the reactants and the surface being plotted as a function of the position of all the atoms in the system. Similarly, a second potential-energy surface in this many-dimensional configuration space may be drawn, the electronic structure of the reacting species being that of the products. When there is zero electronic interaction of the redox orbitals

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[1] For review see E. J. Hart, J. K. Thomas, and S. Gordon, Radiation Res. Suppl. 4, 24 (1964).

[2] For review see L. M. Dorfman and M. S. Matheson, Progr. Reaction Kinetics (to be published).

[3] G. Czapski and H. A. Schwarz, J. Phys. Chem. 66, 471 (1962); E. Collinson, F. S. Dainton, D. R. Smith, and S. Tazuke, Proc. Chem. Soc. 1962, 140 and more recent references described in Ref. 2.

[4] R. A. Marcus, Ann. Rev. Phys. Chem. 15, 155 (1964).

[5] (a) R. A. Marcus, J. Chem. Phys. 24, 966 (1956); (b) Discussions Faraday Soc. 29, 21 (1960); (c) J. Chem. Phys. 43, 679 (1965); (d) J. Phys. Chem. 67, 853 (1963); (e) the assumptions of this electron-transfer theory and of the additional ones used in the present investigation are summarized by the author in Advan. Chem. Ser. 50, 138 (1965).

of the two reacting species these two potential-energy surfaces intersect.

In the absence of an interaction of the redox orbitals a fluctuation of coordinates from ones describing stable spatial configurations of the atoms in the initial system to those characterizing the intersection region and finally to those describing stable spatial configurations of products cannot lead to reaction. It merely represents a fluctuation of coordinates, fluctuations which occur continually. The presence of some electronic interaction between the redox orbitals splits the surfaces at each point of intersection in the usual quantum-mechanical manner. If the "redox interaction" is appreciable so is the splitting. A fluctuation of the above type then causes electron transfer to occur as the system passes through the region of configuration space characterizing the intersection region. The process occurs adiabatically if the splitting is sufficiently large, and nonadiabatically if it is not.[4,5]

The coordinates in this many-dimensional configuration space include ones describing the vibrations of each molecule present, its translations, and its orientations. Fluctuations leading to reaction include those of the separation distance of the reactants, reorientation of the dielectrically polarized solvent molecules, and vibrations in the second reactant. In fact, any favorable changes in a coordinate which has a somewhat different equilibrium distribution in the initial and final states, or which permits the reactants to come close together, helps facilitate reaction, i.e., in the present case permits the system to reach and pass through the intersection region in a place where the redox interaction is appreciable. To be sure, related remarks apply to all chemical reactions, but in the usual chemical reactions one concentrates mainly on the chemical bonds that are broken and those that are formed. The present step (1) involves no such bonds for the reaction being considered.

The electronic wavefunction of the solvated electron is very sensitive to fluctuations of the solvent molecules, unlike the electronic wavefunction of a conventional reactant. This circumstance leads to one principal quantitative difference between the present treatment of its reactions and that given earlier[4,5] for more conventional electron-transfer reactions. A second difference lies in the fact that the number of particles changes in the simple electron-transfer step (1), while in those considered previously there was no such change. Normally in reactions the number of particles changes only because of formation or rupture or new chemical bonds. In the present situation, however, it occurs by absorption of the electron into the second reactant and deorientation of the solvent molecules formerly oriented about it.

For purposes of simplicity in the present paper we formulate the theory using dielectric-continuum theory for the solvent polarization. Any vibrational changes in the other reactant are treated in molecular terms, however. The functional form of the resulting rate equation suggests a functional form for a statistical mechanically derived expression, much as it did in the formulation of an electron-transfer theory: A continuum treatment was given first[5a] and was followed by a statistical-mechanical treatment.[5b,c] Both had a rate expression of the same functional form.

A qualitative summary of the assumptions and of the principal results of the present paper have been given in a recent monograph.[5c] A glossary of the principal symbols employed is given in Appendix III.

THEORY

Since the orientation polarization has a much lower characteristic frequency than the frequency of motion[6] of the solvated electrons, the orientation polarization "sees" a smeared-out charge distribution of the electron. When the environment is in thermal equilibrium with the solvated electron the polarization function and wavefunction are found by minimizing a certain functional, the sum of the kinetic energy of the electron and the free energy of the polarized system.[7] No constraint is imposed in the minimization (other than that of normalization of the wavefunction).

The activated complex for a weak-overlap electron-transfer reaction is a species having the set of spatial configurations that occur at the intersection of the two potential-energy surfaces described earlier. It has the potential energy of the intersection for each point of the set and has an equilibrium distribution of coordinates within this set.[4] The properties of the activated complex have been related elsewhere to those of two other constrained systems[4,5]: One of these two systems has the electronic structure of the reactants and the other has that of the products. Each system is simpler than the activated complex in that each is constrained to be centered on the intersection region rather than confined to it. Each has the same thermodynamic energy (the same as that of the activated complex) and the same Boltzmann distribution of configurations. Since the two systems have the same distribution of coordinates in configuration space they also have the same entropy and, thereby, the same free energy. They have different electronic structures, and the condition that they have the same free energy at all temperatures constitutes an equation of constraint.

Let ΔF^* be the free energy of formation, from reactants fixed in position far apart, of a system in which the system is centered in the above intersection region, as described earlier, and in which the reactants are fixed in position a distance R apart. Then, it has been shown, the bimolecular rate constant is given by[4,5c]

$$k = Z\kappa\rho \exp(-\Delta F^*/kT), \qquad (3)$$

[6] The frequency of motion of the electron ν_e is approximately $\Delta E/h$ where ΔE, the transition energy in water, is about 1.7 eV. Thus, ν_e is about 4×10^{14} sec^{-1}.

[7] S. I. Pekar, *Untersuchungen über die Elektronentheorie der Kristalle* (Akademie Verlag, Berlin, 1954).

where Z is a collision frequency $(8\pi kT/m^*)^{\frac{1}{2}}R^2$ calculated for the most probable separation distance R between the centers of the reactants in the activated complex. Typically, R is the sum of the radii of the reactants, any uncertainty in R leading to a minor uncertainty in k; m^* is approximately the reduced mass for the reaction coordinate; κ is unity for an adiabatic reaction (as we usually assume it to be) and less than unity for a nonadiabatic one; ρ is a factor usually close to unity: it is the ratio of the root-mean-square fluctuation of R in the activated complex to that of s, the displacement normal to the "intersection hypersurface" in the centered distribution.[5c]

We let $F^{*r}(R)$ denote the free energy of a system of reactants, fixed in position, a distance R apart and having the constrained equilibrium distribution of configurations described above; let $F^{*p}(R)$ denote that for the product in a system with the same constrained distribution, and let $F^r(\infty)$ denote the free energy of an unconstrained system of the reactants when they are fixed in position but far apart. We have

$$\Delta F^* = F^{*r}(R) - F^r(\infty). \tag{4}$$

The value of ΔF^* is determined as the solution of the variational problem (5) and (6)

$$\delta F^{*r}(R) = 0, \quad \text{subject to (6)}, \tag{5}$$

$$F^{*r}(R) = F^{*p}(R). \tag{6}$$

The variation in (5) is to be performed with respect to parameters describing the configurational distribution of the system: The orientation polarization is characterized by a continuous parameter, a polarization function, and the distribution of vibrational coordinates of the second reactant is characterized by several parameters, q_*^i the most probable value of each vibrational coordinate q^i in the centered distribution.

The vibrational contribution to ΔF^* is then given by[8]

$$\Delta F^*_{\text{vib}} = \tfrac{1}{2}\sum_{i,j} k_{ij}(q_*^i - q_r^i)(q_*^j - q_r^j), \tag{7}$$

where q_r^i and q_p^i denote the most probable (unconstrained) values of q^i for the reactant and product, respectively; k_{ij} is a symmetrical function,

$$2k_{ij}^r k_{ij}^p/(k_{ij}^r + k_{ij}^p),$$

of the corresponding force constants, k_{ij}^r and k_{ij}^p, of the reactant and product. The vibrational contribution to the free energy of formation of the activated complex from the separated products is the same as (7) but with q_r^i replaced by q_p^i.

Another term in $F^{*r}(R)$ is the kinetic energy of the excess electron, $(-\hbar^2/2\mu)\int\psi^*\nabla^2\psi d\mathbf{r}$. On integration by parts it becomes $\hbar^2\int|\nabla\psi|^2 d\mathbf{r}_1/2\mu$, where $\mathbf{r}_1$ and μ denote the position and the effective mass of the electron.[7] Hence, another contribution to ΔF^* is the change in this kinetic energy arising from a change in ψ.

A final contribution to $F^{*r}(R)$ is the free energy of polarization of the system. It has been suggested[9] that cavity formation does not occur in strongly hydrogen-bonding solvents such as water and alcohols, unlike liquid ammonia. In the present paper we assume cavities to be absent—and so perhaps restrict attention to the strongly hydrogen-bonding solvents. Use of a more elaborate expression for the free energy of polarization would permit the inclusion of cavities.

The usual polaron-type theory[7,10,11] is employed to describe the polarization free energy of the system. However, we do not wish to tie the present reaction-rate formalism too closely to any particular model for the solvated electron. A simple approximate analysis of the effect of using alternative models is described in a later section, therefore.

For each value of $\mathbf{r}_1$ the free energy of polarization of the system is shown in Appendix I to be (8), where $\mathbf{P}(\mathbf{r})$ is a function of the orientation polarization at $\mathbf{r}$:

$$F_{\text{pol}}(\mathbf{r}_1) = -\int \mathbf{P}\cdot\mathbf{D}d\mathbf{r} + \frac{2\pi}{c}\int \mathbf{P}^2 d\mathbf{r} - \frac{e_2^2}{2a_2}\left(1-\frac{1}{D_{\text{op}}}\right) + \frac{e_1 e_2}{D_{\text{op}}|\mathbf{r}_1-\mathbf{r}_2|}, \tag{8}$$

where c is given by (9), $\mathbf{D}$ is the field due to the permanent charges and is given by (10), and the radius a_2 for the second reactant is that of a sphere which includes any inner coordination shell. (One can weaken the spherical assumption, however; then, the final rate expression contains an orientational factor.) Changes in values of the coordinates in that shell contribute to ΔF^*_{vib}.

$$c = D_{\text{op}}^{-1} - D_s^{-1}, \tag{9}$$

$$\mathbf{D} = \mathbf{D}_1 + \mathbf{D}_2, \tag{10}$$

$$\mathbf{D}_1 = -\nabla(e_1/|\mathbf{r}-\mathbf{r}_1|), \qquad \mathbf{D}_2 = -\nabla(e_2/|\mathbf{r}-\mathbf{r}_2|). \tag{11}$$

[8] This result utilizes the experience of the derivation in Ref. 5(c), where it was found that the vibrational coordinates in the centered distribution have a Boltzmann distribution characterized by parameters q_*^i and that the expression can be considerably simplified with little error by introduction of the k_{ij}'s. Instead, one can include in $F^{*r}(R)$ the vibrational free energy, $\int\rho_i(h_i^r + kT\ln\rho_i)d\tau_i$, where ρ_i, h_i^r, and τ_i are the vibrational phase space density, sum of vibrational kinetic and potential energy, and vibrational phase space volume element. The corresponding vibrational term with h_i^r replaced by h_i^p can be included in $F^{*p}(R)$. One then solves the constrained variational problem (5) and (6), the variations being $\delta\rho$ and $\delta\mathbf{P}$, and eventually introduces methods such as those employed in Ref. 5(c), to obtain (7), with q_*^i given by (17), thus achieving the same result as before.

[9] J. Jortner, Radiation Res. Suppl. 4, 24 (1964); Mol. Phys. 5 257 (1962).

[10] R. A. Marcus, J. Chem. Phys. 24, 979 (1956); 38, 1858 (1963); 39 1734 (1963). See the appendix of the present paper for a notational change.

[11] A recent survey of polaron theory is given in *Polarons and Excitons*, edited by C. G. Kuper and G. D. Whitfield (Oliver and Boyd, Ltd., Edinburgh, 1963).

In (11) e_2 is the charge of the second reactant, which is centered at $\mathbf{r}_2$. D_{op} and D_s denote the optical and static dielectric constant of the medium.

The total free energy of polarization is obtained by multiplying (8) by $|\psi|^2 d\mathbf{r}_1$ and integrating over $\mathbf{r}_1$.

If we denote by $\mathfrak{F}_o^r$ the sum of the electron kinetic energy and the free energy of polarization of the unconstrained system of reactants when they are far apart then ΔF^* becomes

$$\Delta F^* = \Delta F^*_{vib} + \frac{\hbar^2}{2\mu}\int |\nabla\psi|^2 d\mathbf{r}_1 + \int F_{pol}{}^r(\mathbf{r}_1)\,|\psi|^2 d\mathbf{r}_1 - \mathfrak{F}_o^r, \tag{12}$$

with ΔF^*_{vib} and $F_{pol}{}^r$ given by (7) and (8) with $\mathbf{D}$, e_1, and e_2 all bearing r superscripts to denote properties of reactants.

We consider next the corresponding free energy of formation of the constrained state with the electronic structure of the product, from an unconstrained state, ΔF^{*p}. Because of the manner in which $F^{*p}(R)$ and $F^{*r}(R)$ were defined ("reacting species fixed in position") there is no translational contribution to this

$$F^{*p}(R) - F^p(\infty).$$

By arguments analogous to those used to derive (12) we obtain

$$\Delta F^{*p} = \tfrac{1}{2}\sum_{i,j} k_{ij}(q_*{}^i - q_p{}^i)(q_*{}^j - q_p{}^j) + \frac{2\pi}{c}\int \mathbf{P}^2 d\mathbf{r} - \int \mathbf{P}\cdot\mathbf{D}^p d\mathbf{r} - \frac{e_2^2}{2a_2}\left(1 - \frac{1}{D_{op}}\right). \tag{13}$$

The expression is somewhat simpler than (12): The charge $e_1{}^p$ vanishes. The electron kinetic energy term is missing, since the electron now resides in the second reactant, where its kinetic energy is insensitive to solvent fluctuations and does not contribute to ΔF^{*p}, therefore.

For any given R we then minimize ΔF^* with respect to the quantities $\mathbf{P}$ and $q_*{}^i$, subject to the constraint imposed by (6). When $\mathbf{P}$ is varied ψ in (12) also varies. However, since ψ is determined as that quantity which minimizes the sum of the kinetic energy and $\int F_{pol}\,|\psi|^2 d\mathbf{r}_1$ (and hence, which minimizes ΔF^*) for any given $\mathbf{P}$, the variation of ΔF^* with ψ at fixed $\mathbf{P}$ is zero. In minimizing ΔF^* with respect to $\mathbf{P}$, therefore, ψ can be regarded as constant and, in the final step, is set equal to the ψ appropriate to the given $\mathbf{P}$. We find (14) for the variation at fixed ψ:

$$\delta(\Delta F^*)_\psi = 0 = \int\left(\frac{4\pi}{c}\mathbf{P} - \int |\psi|^2 \mathbf{D}^r d\mathbf{r}_1\right)\cdot \delta\mathbf{P}\, d\mathbf{r} + \sum_{i,j} k_{ij}(q_*{}^i - q_r{}^i)\,\delta q_*{}^j, \tag{14}$$

$$\delta(F^{*r} - F^{*p})_\psi = 0 = \int\left(\mathbf{D}^p - \int |\psi|^2 \mathbf{D}^r d\mathbf{r}_1\right)\cdot \delta\mathbf{P}\, d\mathbf{r} + \sum_{i,j} k_{ij}(q_p{}^i - q_r{}^i)\,\delta q_*{}^j. \tag{15}$$

On multiplying the second equation by a Lagrangian multiplier m, adding to the first equation and setting the coefficients of $\delta\mathbf{P}$ and $\delta q_*{}^j$ equal to zero the properties of the constrained state, the "centered distribution," are obtained

$$\mathbf{P} = \left[(m+1)\int |\psi|^2 \mathbf{D}^r d\mathbf{r}_1 - m\mathbf{D}^p\right] c/4\pi, \tag{16}$$

$$q_*{}^i = (m+1)q_r{}^i - m q_p{}^i. \tag{17}$$

On introducing these results into (12) we obtain (18):

$$\Delta F^* = \frac{\hbar^2}{2\mu}\int |\nabla\psi|^2 d\mathbf{r}_1 + \frac{m^2 c}{8\pi}\int (\mathfrak{D}^r - \mathbf{D}^p)^2 d\mathbf{r} - \frac{c}{8\pi}\int \mathfrak{D}^{r2} d\mathbf{r}, - \frac{e_2{}^{r2}}{2a_2}\left(1 - \frac{1}{D_{op}}\right) - \frac{e e_2{}^r}{D_{op}}\int \frac{|\psi|^2 d\mathbf{r}_1}{|\mathbf{r}_1 - \mathbf{r}_2|} + m^2\lambda_i - \mathfrak{F}_o^r, \tag{18}$$

where $-e$ is the charge on the electron and

$$\lambda_i = \tfrac{1}{2}\sum_{i,j} k_{ij}(q_p{}^i - q_r{}^i)(q_p{}^j - q_r{}^j), \tag{19}$$

$$\mathfrak{D}^r = \int \mathbf{D}^r |\psi|^2 d\mathbf{r}_1. \tag{20}$$

Analogously, ΔF^{*p} is found to be given by (21):

$$\Delta F^{*p} = \frac{(m+1)^2 c}{8\pi}\int (\mathfrak{D}^r - \mathbf{D}^p)^2 d\mathbf{r} - \frac{c}{8\pi}\int \mathbf{D}^{p2} d\mathbf{r} - \frac{e_2{}^{p2}}{2a_2}\left(1 - \frac{1}{D_{op}}\right) + (m+1)^2\lambda_i - \mathfrak{F}_o^p. \tag{21}$$

To determine the parameter m in terms of known quantities we next express $F^{*r} - F^{*p}$ in terms of the "standard" free energy of reaction.

The "standard" free energy of reaction for the elementary electron-transfer step (1) at the prevailing pressure, temperature, and reaction medium is denoted by $\Delta F^{\circ\prime}$, to distinguish it from the standard one ΔF° at 25°C, 1 atm, and unit activities. Let the standard-state translational free energy of the solvated electron in Step (1) be F°_{transl}. If we subtract from $\Delta F^{\circ\prime}$ this translational contribution, $-F^\circ_{transl}$, and note that the rotational contribution of Ox is the same as that of Red, we obtain the internal contribution, $\Delta F^{\circ\prime}_{int}$. The latter is the free energy of formation of products from reactants when all reacting particles are fixed in position:

$$\Delta F^{\circ\prime}_{int} = \Delta F^{\circ\prime} + F^\circ_{transl}. \tag{22}$$

(We note parenthetically that, in contrast to $\Delta F^{\circ\prime}$, $\Delta F^{\circ\prime}_{int}$ is independent of the choice of concentration units in the standard state.)

With $\Delta F^{\circ\prime}_{int}$ one may now rewrite (6). The free-energy change $\Delta F^{\circ\prime}_{int}$ on going from reactants fixed in position to a product also fixed in position can be regarded as the sum of three terms: formation of constrained state of the reactants in activated complex,

ΔF^*; the change due to a change of electronic structure in the constrained state, $F^{*p}(R)-F^*(R)$, i.e., zero because of (6); formation of product from the constrained state of the product $-\Delta F^{*p}$. Thus, we obtain

$$\Delta F^{\circ\prime}{}_{\rm int}=\Delta F^*-\Delta F^{*p}, \tag{23}$$

where $\Delta F^{\circ\prime}{}_{\rm int}$ is given by (22).

For any given m, the function ψ is determined as the ψ which minimizes ΔF^*. To determine the parameter m, Eqs. (18) and (21) are then introduced into (23).

For completeness, we note that k_{-1}, the unimolecular rate constant for the reverse step of Reaction (1), can be obtained from (21) and from the equilibrium constant for Reaction (1). One finds:

$$k_{-1}=Z\kappa\rho\,\exp(-F^\circ{}_{\rm transl}/kT)\,\exp(-\Delta F^{*p}/kT), \tag{24}$$

where Z is about 10^{14} cc·mole sec^{-1}.

CALCULATION FOR LARGE R

In solving (18), (21), and (23) we consider first the form ΔF^* would take if the separation distance R were large in the activated complex. (The case of any R is considered in a later section.) In this situation the "polaron" is isolated and one may make use of known solutions of the polaron problem to evaluate the various integrals.

Where R is large each of the integrals in (18) becomes the sum of two parts, one describing the polaron and the other describing the second reactant. For sufficiently large R, products such as $\mathbf{D}_1\cdot\mathbf{D}_2$ vanish but terms such $\mathbf{D}_1^2$ and $\mathbf{D}_2^2$ do not. Further, $\mathfrak{D}_2{}^r$ equals $\mathbf{D}_2{}^r$ since the latter is independent of $\mathbf{r}_1$. We then find:

$$\Delta F^*=\frac{\hbar^2}{2\mu}\int|\nabla\psi|^2d\mathbf{r}_1+\frac{m^2c}{8\pi}\int(\mathfrak{D}_1{}^r-\mathfrak{D}_1{}^p)^2d\mathbf{r}-\frac{c}{8\pi}\int\mathfrak{D}_1{}^{r2}d\mathbf{r}$$
$$+\frac{m^2c}{8\pi}\int(\mathbf{D}_2{}^r-\mathbf{D}_2{}^p)^2d\mathbf{r}+m^2\lambda_i-\mathfrak{F}_{o_1}{}^r, \tag{25}$$

where $\mathfrak{F}_{o_1}{}^r$ is the contribution of the isolated polaron to $\mathfrak{F}_o{}^r$ and where we have used the fact that $\mathfrak{F}_{o_2}{}^r$, the contribution of the isolated second reactant, is

$$-e_2{}^{r2}/2a_2[1-(1/D_s)].$$

The latter term canceled two of the other terms, when integration over $\mathbf{r}$ in one of them was performed. In (21) $\mathfrak{D}_1{}^p$ vanishes since "product" 1 now has zero charge.

The expression for $\mathfrak{F}_{o_1}{}^r$ is readily obtained from the sum of the other polaron terms on the right-hand side of (25) by setting $m=0$ in them (for that would correspond to a condition of no constraint, as in the initial state of the polaron). If the properties of the isolated unconstrained polaron are denoted by a subscript o we find:

$$\mathfrak{F}_{o_1}{}^r\equiv H_o=\frac{\hbar^2}{2\mu}\int|\nabla\psi_o|^2d\mathbf{r}_1-\frac{c}{8\pi}\int\mathfrak{D}_{o1}{}^{r2}d\mathbf{r}. \tag{26}$$

The wavefunction ψ_o is determined by minimizing H_o.[12]

Since ψ is determined by minimizing ΔF^* at a given m, it is also obtained by minimizing that part of ΔF^* which depends on ψ at this m, namely H:

$$H=\frac{\hbar^2}{2\mu}\int|\nabla\psi|^2d\mathbf{r}_1-\frac{c(1-m^2)}{8\pi}\int\mathfrak{D}_1{}^{r2}d\mathbf{r}. \tag{27}$$

Since $\mathfrak{D}_{o1}{}^r$ and $\mathfrak{D}_1{}^r$ equal $\int|\psi_o|^2\mathbf{D}_1{}^rd\mathbf{r}_1$ and $\int|\psi|^2\mathbf{D}_1{}^rd\mathbf{r}_1$, respectively, comparison of (26) and (27) shows that H is obtained from the well-known values of H_o in the literature merely by replacing c in the formula for H_o by $c(1-m^2)$.

Finally, we note that (25) becomes

$$\Delta F^*=H-H_o+m^2\lambda_2{}^\infty, \tag{28}$$

where $\lambda_2{}^\infty$ is the sum of λ_i and $\lambda_o{}^\infty$, $\lambda_o{}^\infty$ being the value of $c/8\pi\int(\mathbf{D}_2{}^r-\mathbf{D}_2{}^p)^2d\mathbf{r}$, i.e., $-(e_2{}^r-e_2{}^p)^2c/2a_2$.

Similarly the expression for ΔF^{*p} is found to be (29), upon noting that $\mathfrak{F}_o{}^p$ equals $-[1-(1/D_s)]\int\mathbf{D}_2{}^{r2}d\mathbf{r}/8\pi$.

$$\Delta F^{*p}=\frac{(m+1)^2c}{8\pi}\int\mathfrak{D}_1{}^{r2}d\mathbf{r}+(m+1)^2\lambda_2{}^\infty. \tag{29}$$

A useful virial theorem can be derived for the solution of the nonlinear wave equation for ψ_o, $\delta H_o=0$, using a scale-factor technique[13] similar to the one[14] used to establish the virial theorem for the usual (linear) Schrödinger equation. One finds, thereby,[13]

$$\frac{\hbar^2}{2\mu}\int|\nabla\psi_o|^2d\mathbf{r}_1=-H_o, \tag{30}$$

$$-\frac{c}{8\pi}\int\mathfrak{D}_{o1}{}^{r2}d\mathbf{r}=2H_o. \tag{31}$$

Similarly, the first term of (27) is $-H$ and the second is $2H$. One can always assure satisfaction of this virial theorem by introduction of a scale factor as one of the variational parameters, as one may see from the above proofs[13,14] of the theorem.

On applying these results to Eq. (29) and noting that the integral $\int\mathfrak{D}_1{}^{r2}d\mathbf{r}$ appears in both (27) and (29), one obtains

$$\Delta F^{*p}=[2(m+1)/(m-1)]H+(m+1)^2\lambda_2{}^\infty. \tag{32}$$

The explicit dependence of H on m can be obtained as follows: Since $\mathfrak{D}_{o1}{}^2$ contains a factor e^2 one can show from (26) that H_o/ce^2 depends only on $\hbar^2/\mu ce^2$. The only dimensionless variable composed of these two quantities is $H_o\hbar^2/\mu e^4c^2$. Thus, any solution of (26),

[12] We note, incidentally, that this H_0 is also the same as that used for the isolated, unconstrained polaron by Pekar in Ref. 7 and by Jortner in Ref. 9. (However, Jortner assumed $D_{op}=1$ for the ground-state calculation.)

[13] Reference 7, pp. 38–41 and Eqs. (8.10) and (8.11). Our lhs of Eq. (31) is his $\bar{V}/2$.

[14] E.g., W. Kauzmann, *Quantum Chemistry* (Academic Press Inc., New York, 1957), pp. 229–232.

approximate or exact, can be written as (33), where A is a dimensionless constant.

$$H_o = -A\mu e^4 c^2/\hbar^2. \tag{33}$$

On comparing (26) and (27) we see that H is given by

$$H = -A\mu e^4 c^2 (1-m^2)^2/\hbar^2 = (1-m^2)^2 H_o. \tag{34}$$

We then obtain

$$\Delta F^* = -m^2(2-m^2)H_o + m^2\lambda_2^\infty, \tag{35}$$

$$\Delta F^{*p} = -2(m+1)^2(1-m^2)H_o + (m+1)^2\lambda_2^\infty, \tag{36}$$

and m is a solution of (37).

$$-(2m+1)(-2H_o+\lambda_2^\infty) - m^2(m^2+4m+2)H_o = \Delta F^{o\prime}_{\text{int}}. \tag{37}$$

As (30) and (34) show, H_o and H in (30) to (37) are always negative.

Under typical conditions where these reactions are very fast, one sees from (35) that m^2 is small, a conclusion verified in more detail later for typical values of λ_2, H_o, and $\Delta F^{o\prime}$. One then finds that $m^2 \ll 1$, so that (35) to (37) become

$$\Delta F^* = m^2(-2H_o+\lambda_2^\infty), \tag{38}$$

$$\Delta F^{*p} = (m+1)^2(-2H_o+\lambda_2^\infty), \tag{39}$$

and m is the solution of (40):

$$-(2m+1)(-2H_o+\lambda_2^\infty) = \Delta F^{o\prime}_{\text{int}}. \tag{40}$$

These equations now have the same functional form as those derived for more conventional electron-transfer reactions. (In those cases, however, $\Delta F^{o\prime}_{\text{int}}$ equaled $\Delta F^{o\prime}$.)

EVALUATION OF H_o

Variational functions of the type (41) have been used by Pekar to evaluate H_o.

$$\psi_o = B(1+\alpha r+\beta r^2)e^{-\alpha r}, \tag{41}$$

the best result for A in Eq. (41) being -0.0544.[7] Jortner has used instead a $1s$ wavefunction, $B\exp(-\gamma r)$, which yields a slightly worse result: $A=-0.0488$.[9,15] Quantitative calculations show that the βr^2 is hardly necessary in (41) but that the αr term is useful, since the effective potential for the polaron is found to be of a harmonic-oscillator nature near the origin rather than Coulombic.[7] Results of other variational calculations have also been summarized by Allcock.[16] They include the use of a harmonic-oscillator wavefunction by Pekar *et al.* (1948, 1954) and by Feynman (1955), which yields $A=-0.053$, and the use of a $1s$ wavefunction by Frohlich (1954), which yields $A=-0.0488$. On using a $2p$ wavefunction for the excited state Pekar[7] found the transition energy to be $0.0697\mu e^4c^2/\hbar^2$, i.e., $-1.28H_o$.

Since this transition energy is about 1.7 eV when the solvent is water, H_o is about -1.3 eV in that solvent. This particular result is independent of the value used for c, as long as the same c is used in the ground and $2p$ state. Nevertheless, such an evaluation of H_o is open to some question: one should subtract from 1.3 eV an amount $\Delta\mathcal{A}/1.28$ where $\Delta\mathcal{A}$ is some difference in "electron affinity" (i.e., in short-range interactions) of the solvent molecules for the solvated electron in its ground and excited states. Perhaps, then, this magnitude of 1.3 eV is too high:

A comparison in Appendix II of spectral and solvation data permits one to eliminate the unknown "electron affinity" of the ground state, $\mathcal{A}_g$. When that of the excited state can be neglected, the values of $-H_o$ and of $\mathcal{A}_g$ are estimated to be roughly about 0.7 and 0.8 eV, respectively, but they are quite uncertain since they depend on a small difference ($\sim$5) between fairly large quantities ($\sim$35 kcal mole^{-1}). The actual value of $-H_o$ is larger, and that of $\mathcal{A}_g$ smaller, if the neglected electron affinity of the excited state is positive.

A direct calculation of H_o made by assuming $\mu=$ electron mass and $D_{\text{op}}=(1.33)^2$, yields 0.45 eV for $-H_o$. To explain a particular rate constant we later take $-H_o$ to be some compromise—about 0.65 eV—though the value must be regarded as highly tentative pending accumulation of more data.

The above results suggest that part of the large spectral difference of the solvated electron in ammonia and in water may be due to a difference in $\mathcal{A}_g$, if the affinity is greater for water.

CASE OF FINITE R

On introducing (11) into (18) we find

$$\Delta F^* = \frac{\hbar^2}{2\mu}\int|\nabla\psi|^2 d\mathbf{r}_1 + \frac{(m^2-1)c}{8\pi}\int \mathfrak{D}_1{}^{r2} d\mathbf{r} - \frac{ee_2{}^r}{D_s}\int\frac{|\psi|^2 d\mathbf{r}_1}{|\mathbf{r}_1-\mathbf{r}_2|} + \frac{m^2ce^2}{2a_2} - m^2ce^2\int\frac{|\psi|^2 d\mathbf{r}_1}{|\mathbf{r}_1-\mathbf{r}_2|} + m^2\lambda_i - H_o, \tag{42}$$

where H_o is given by (33).

The first term involving $|\mathbf{r}_1-\mathbf{r}_2|^{-1}$ and, when m^2 is small, the second $|\mathbf{r}_1-\mathbf{r}_2|^{-1}$ term also are small in comparison with the electronic energy of the polaron.[17] The distortion of ψ from the form it has when these terms are absent is assumed small, therefore. In this

[15] This particular result is unaffected by the fact that Jortner assumes $c=1-(1/D_s)$ for the ground state.

[16] G. R. Allcock, Advan. Phys. 5, 412 (1956), p. 450.

[17] For example, when m^2 is small Eqs. (27), (31), and (34) show that the second term in (42) is approximately $2H_o$, i.e., about -2.6 eV according to the value derived earlier for H_o. The third term in (42) is about $-ee_2{}^r/D_sR$, i.e., about -0.03 eV in water when $R=6$ Å and $e_2{}^r=e$. The fifth term in (42) is about $-m^2ce^2/R$, i.e., about -0.15 eV when m^2 has a typical value of about 0.1 (or less) in these very fast reactions.

case ψ is seen from (42) to satisfy the same variational equation, for any given m, as the ψ in the previous section, i.e., as the ψ for the isolated but constrained polaron, for only the first two terms in (42) now depend on ψ. Thus, the first two terms on the rhs of (42) equal $-H$ and $2H$ as before, H being given by (34).

The overlap of the polaron wavefunction and the charge of the second reactant was assumed earlier to be small. In this case the term $\int|\psi|^2 d\mathbf{r}_1/|\mathbf{r}_1-\mathbf{r}_2|$ becomes R^{-1} because of the spherical nature of $|\psi|^2$ in this nondistorted ground state.

We let w^r denote the reversible work required to bring the reactants together. It is the free energy of formation of an unconstrained state at the above R from an unconstrained state at $R=\infty$. This term is obtained from (42) by setting $m=0$, as one may see by recalling the origin of m as a Lagrangian multiplier. (When m vanishes, so does the equation of constraint.)

$$\Delta F^*=w^r-m^2(2-m^2)H_o + m^2\{\lambda_i+e^2c[(1/2a_2)-(1/R)]\}, \quad (43)$$

where H_o is given by (33) and

$$w^r=-ee_2^r/D_sR. \quad (44)$$

Similarly one finds

$$\Delta F^{*p}=-2(m+1)^2(1-m^2)H_o + (m+1)^2\{\lambda_i+e^2c[(1/2a_2)-(1/R)]\} \quad (45)$$

and m is then the solution of (23).

If m is small we again may set $m^2\ll 1$ and write:

$$\Delta F^*=w^r+m^2\lambda, \quad (46)$$

$$\Delta F^{*p}=(m+1)^2\lambda, \quad (47)$$

where m is given by (48) and λ by (49).

$$-(2m+1)\lambda=\Delta F^{\circ\prime}{}_{\text{int}}-w^r, \quad (48)$$

$$\lambda=-2H_o+\lambda_i+e^2[(2a_2)^{-1}-R^{-1}](D_{\text{op}}{}^{-1}-D_s{}^{-1}). \quad (49)$$

If we define λ_e by (50) and call it the λ for the polaron and write λ_2 as in (51), Eq. (52) follows:

$$\lambda_e=-2H_o-(e^2/2R)(D_{\text{op}}{}^{-1}-D_s{}^{-1}), \quad (50)$$

$$\lambda_2=\lambda_i+\tfrac{1}{2}e^2(D_{\text{op}}{}^{-1}-D_s{}^{-1})(a_2{}^{-1}-R^{-1}), \quad (51)$$

$$\lambda=\lambda_e+\lambda_2. \quad (52)$$

This λ_2 appears as a characteristic parameter for the second reactant in ordinary chemical and electrochemical transfers. The R may vary somewhat from reaction to reaction but correction can be made for this variation.

A value for $\Delta F^{\circ\prime}{}_{\text{int}}$ is given in the next section.

STANDARD POTENTIAL AND $\Delta F_{\text{int}}{}^{\circ\prime}$

From an estimate of the forward and reverse rate constants of Reaction (53), Baxendale estimated the latter's equilibrium constant.[18a]

$$e(\text{aq})+\text{H}_2\text{O}\rightleftharpoons\text{H}+\text{OH}^-. \quad (53)$$

This constant was then combined with the autoprotolysis constant of water and with the equilibrium constant for $2\text{H}\rightleftharpoons\text{H}_2$ to yield a ΔF° of -61.5 kcal mole^{-1} for Reaction (54) and, hence, an E° of $+2.7$ V

$$e(\text{aq})+\text{H}^+(\text{aq})\rightleftharpoons\tfrac{1}{2}\text{H}_2. \quad (54)$$

A review of the argument employed reveals two errors.[18b] On making corrections for them and on using very recent data for the equilibrium constant of (53) the ΔF° for (54) is found to be -62.7 kcal mole^{-1} and the new E° to be $+2.7$ V.

To calculate $F^\circ{}_{\text{transl}}$ for the electron in Reaction (1) we may proceed as follows:

On the right-side of the equilibrium, the excess electron resides in the reduced reactant and its motion is correspondingly restricted, while on the left-hand side this electron has three translational degrees of freedom. On recalling the definition of $\Delta F^{\circ\prime}{}_{\text{int}}$ and denoting the translational partition function of the solvated electron by $(\text{pf})_{\text{transl}}$, the equilibrium constant of Reaction (1), K, is given by (55) (we have canceled the translational partition functions of Red and Ox).

$$K=\exp(-\Delta F^{\circ\prime}{}_{\text{int}}/kT)\,(\text{pf})_{\text{transl}}{}^{-1}. \quad (55)$$

Any volume change is supposed to be included in $\Delta F^{\circ\prime}{}_{\text{int}}$ through electrostriction. That is, $\Delta F^{\circ\prime}{}_{\text{int}}$ is a "Gibbs free-energy" change.

The energy of the polaron, $H(v)$, calculated by solving the Schrödinger equation for a dynamical polaron moving with velocity v, is assumed to have the form[7]

$$H(v)=H_o+\tfrac{1}{2}m_pv^2, \quad (56)$$

where m_p is the reduced mass for the polaron and H_o is the energy (or really, in part, free energy) of the stationary polaron.

We now obtain

$$(\text{pf})_{\text{transl}}=(2\pi m_pkT)^{\frac{3}{2}}V/h^3, \quad (57)$$

[18] (a) J. H. Baxendale, Rad. Research Suppl. 4, 139 (1964); (b) The value used for the equilibrium constant of water should be $(10^{-14}/55)M$ instead of $10^{-14}M^2$, since $55M$ is the molarity of water. [Alternatively, in a water medium a pseudo first-order rate constant for the forward step in (53) can be used and the ordinary autoprotolysis constant employed.] Secondly, to obtain proper cancellation of units the ΔF° used for $\text{H}\rightleftharpoons\frac{1}{2}\text{H}_2$ should be that for a standard state of H atoms of $1M$ rather than of 1 atm. (c) M. S. Matheson, Advan. Chem. Ser. **50**, 45 (1965): These latest values of the rate constants of forward and reverse reactions in (53) are 16 ± 1 $M^{-1}\cdot\text{sec}^{-1}$ and $1.8\pm0.6\times10^7$ $M^{-1}\cdot\text{sec}^{-1}$, respectively.

where V is 1 cc when the units of K are molecules per cubic centimeter. On recalling the definition of F°_{transl} by Eq. (22) we obtain

$$\exp(-F^\circ_{\text{transl}}/kT) = (\text{pf})_{\text{transl}}. \tag{58}$$

At present the value for m_p is somewhat uncertain. It does not seem quite appropriate to use a value computed for a solid-state system.[19] On the other hand, the estimated diffusion constant[20] of $\sim 10\times 10^4$ cm^2 sec^{-1} for the polaron is substantially higher than that of a water molecule (2.45×10^4 cm^2 sec^{-1}), indicating a considerable freedom of motion. Perhaps a value for m_p of the order of $\frac{1}{4}$ to 10 molecular weight units would be appropriate.

On using (57) and (58) we obtain -5.3 kcal mole^{-1} for F°_{transl} when $m_p \sim 3$ and the standard state in (58) and for K is 1 mole/liter.

It is convenient to define an effective $E^{\circ\prime}_1$, $E^{\circ\prime}_{\text{eff}}$, for the solvated electron by means of (59), since $\Delta F^{\circ\prime}_{\text{int}}$ (and, hence, $E^{\circ\prime}_{\text{eff}} - E^{\circ\prime}_2$) describes the effective driving force of the reaction, according to (46) to (48).

$$\Delta F^{\circ\prime}_{\text{int}} = -eF(E^{\circ\prime}_{\text{eff}} - E^{\circ\prime}_2), \tag{59}$$

where $E^{\circ\prime}_2$ is the "standard" reduction potential of the second reactant. Using the above value for F°_{transl} and (22) we find

$$E^{\circ\prime}_{\text{eff}} = +2.9 \text{ V}.$$

ACTIVATION AND DIFFUSION CONTROL

The observed rate constant of a reaction can be expressed in terms of D, the sum of the diffusion coefficients of the reactants, and in terms of the activation-controlled rate constant k_{act} as in (60).[21]

$$k_{\text{obs}}^{-1} = k_{\text{act}}^{-1} + k_{\text{diff}}^{-1}, \tag{60}$$

where

$$k_{\text{diff}} = 4\pi D \Big/ \int_R^\infty e^{w/kT} \frac{dr}{r^2}. \tag{61}$$

The activation-controlled constant k_{act} is the one calculated by Eq. (3). When $k_{\text{act}} \ll k_{\text{diff}}$, k_{obs} equals k_{act}, and when $k_{\text{diff}} \ll k_{\text{act}}$, k_{obs} equals k_{diff}. The diffusion-controlled constants for the solvated-electron reactions are quite high, a result which is attributed to a high diffusion coefficient ($\sim 10^{-4}$ cm^2 sec^{-1}) for the solvated electron,[20] comparable to that of H_3O^+. These rate constants ranged from $13\times 10^{10} M^{-1}\cdot\text{sec}^{-1}$ for reaction with a large, positively charged cation [$Cr(en)_3^{3+}$], where en is ethylene diamine, through 2.0×10^{10} for a neutral species (O_2) to 0.3×10^{10} for reaction with a negative species [$Fe(CN)_6^{3-}$].[2]

CALCULATIONS OF k_{act}

For water as solvent at room temperature $ce^2/2R$ is $90/R$ kcal mole^{-1}, with R in angstroms. Thus, if R is about 6 Å, this contribution to λ_e in (50) is about 15 kcal mole^{-1}. [Such a choice of R is a possible one since the radius for e(aq), it has been suggested,[22a] is about 2.5 to 3.0 Å, while the radius of a small hydrated cation is typically about 3.5 Å.] However, the value for H_o itself is presently uncertain, as we saw earlier, and the value for λ_e is tentatively taken as 15 kcal mole^{-1} to explain the Sm^{3+} data described later. [This λ_e corresponds to an H_o of -15 kcal mole^{-1}, according to (50).] A lower bound to λ_e appears to be about 6 kcal mole^{-1}.[22b] Calculations based on a λ_e of 45 kcal mole^{-1} are also given for comparison.

The values of λ_2 may be estimated from electrochemical or chemical electron transfer rates, though in some cases the magnitude of the correction of the rate for a work term is somewhat uncertain. According to a recent tabulation[23] we find λ_2 to be about 35, 40, and 60 kcal mole^{-1} for a single ion in the $Fe^{2+,3+}$, $Tl^{3+,2+}$ and $Co(NH_3)_6^{2+,3+}$ systems, for example. (λ_2 values for many other ions are available.) On recalling that the E°_2's for these reactants are -0.77, $\sim +0.34$, and ~ -0.1 V one then finds from (48) that the calculated ΔF^*'s are small, regardless of whether λ_e is taken to be 15–20 or 45 kcal mole^{-1}: For a λ_e of 15 kcal mole^{-1} the calculated ΔF^*'s are about 1, -2, and -1.5 kcal mole^{-1}, respectively, and for a λ_e of 45 kcal mole^{-1} they are about -2, -1, and $+2.5$ kcal mole^{-1}. The $Co(NH_3)_6^{3+}$ reaction has been investigated and is diffusion controlled.

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[19] The mass m_p for the solid-state system equals 0.020 α^4, where α equals $e^2c(\mu/2\omega\hbar^3)^{\frac{1}{2}}$. (Compare Ref. 7 or survey by G. R. Allcock.)[16] The value of m_p depends, therefore, on the magnitude of the angular frequency of the "lattice polarization", ω. If $\omega/2\pi$ were 10^{13} sec^{-1} and γ equalled the ratio of μ to the electron mass, α for such a model would equal 18 $c\gamma^{\frac{1}{2}}$. If one chose a value of $c\gamma^{\frac{1}{2}}$ of 0.65 (to fit the H_o of Appendix II) then m_p would be about one quarter of a molecular weight unit, and would be larger if the appropriate frequency for the liquid motion were less.

[20] H. A. Schwarz, Radiation Res. Suppl. 4, 89 (1964).

[21] R. A. Marcus, Discussions Faraday Soc. 29, 129 (1960).

[22] (a) Reference 9. In Ref. 7, pp. 35–38, Pekar estimates a different radius on the basis of a different criterion, which leads to a radius of 8 Å when $c=0.65$[19] and μ=electron mass; (b) N. Sutin, in *Symposium on Exchange Reactions* (International Atomic Energy Agency, Brookhaven, New York, June 1965) calculated this value of λ_e by assuming that the diffusion of the solvated electron in water occurs as a site-to-site electron transfer (jump distance of 2 Å) and by using an expression for ΔF^* for a unimolecular electron-transfer reaction. The value is an upper bound, since the mean jump distance l may be shorter than 2 Å for then the solvent reorganization barrier would be smaller. Indeed, if the diffusion constant depends on l roughly as $l^2 \exp[-\Delta F^*(l)/RT]$, the most probable value of l is that which maximizes this expression.

[23] Reference 5(d). The value of λ_2 equals $\lambda/2$ in Eq. (2) there, when Eq. (2) refers to a chemical electron exchange reaction, and to λ when it refers to electrochemical exchange. (λ_2 is the λ per ion and there are two reactants in the chemical and one in the electrochemical exchange.) Values of λ are estimated from the data in Table I there, with the aid of this Eq. (2). (Both the λ_2 and the E_2° for the $Tl^{3+,2+}$ are somewhat uncertain since there are known to be two consecutive one-electron transfers in the electrochemical reaction $Tl^{3+,1+}$: The value given is obtained from a geometric mean of the rate constants. The latter k's are close together, and therefore we have assumed for simplicity that the E_2°'s for the two reactions probably are also.)

We consider next a hydrated cation with a λ_2 of about 40 kcal mole^{-1} and inquire as to how positive its standard reduction potential E_2° should be in order that the reaction no longer be diffusion controlled. When its E_2° is about 2.0 V $m^2\lambda$ is estimated to be about 6 or 12 kcal mole^{-1} according as λ_o is 15–20 or 45 kcal mole^{-1}, neglecting w^r. Even with a favorable w^r of several kilocalories per mole, this reaction should be activation controlled. Similar remarks apply to an E_2° or 1.5, except that the reaction should be partially in the diffusion-controlled region if the lower λ_o is used. Interesting from this point of view is a recent study of reactions with rare earths.[24] E°'s ($M^{3+,2+}$) for Eu^{3+}, Yb^{3+}, and Sm^{3+} are known. They are about +0.43, +1.15, and +1.55 V, respectively.[25] The corresponding E°'s for the others are not known but are probably higher since these other rare earths do not form stable divalent states. Reactions for the first two and perhaps for the third appear to be diffusion controlled (k=6.1, 4.3, and $2.5\times10^{10}M^{-1}\cdot\text{sec}^{-1}$, respectively). The rate constants of the other rare earths are definitely activation controlled, the rate constant for Tm^{3+} being $3\times10^{9}M^{-1}\cdot\text{sec}^{-1}$, for example.

Judging from an electrochemical rate constant the value of λ_2 for $Eu^{2+,3+}$ is about 40 kcal mole^{-1}.[23] In the cases of Eu^{+3} and Yb^{3+} the theoretical rate is so high that the reaction is predicted to be diffusion controlled for a λ_o of 15–20 kcal mole^{-1}. (For Yb^{+3} ΔF^* is 4 kcal mole^{-1} if λ_o is 45 kcal mole^{-1}.) In the case of Sm^{3+}, ΔF^* is estimated to be about 1, 1.5, or 7 kcal mole^{-1} according as λ_o is taken to be 15, 20, or 45 kcal mole^{-1}. (For w^r a Coulombic term, $-3e^2/D_oR$, is assumed.) If k_{diff} in Eq. (60) is taken to be $6.1\times10^{10}M^{-1}\text{sec}^{-1}$ (the value for Eu^{3+}) then the experimental k_{act} is estimated to be $4\times10^{10}M^{-1}\cdot\text{sec}^{-1}$ for Sm^{3+}, which corresponds to a ΔF^* of about 0.5 kcal mole^{-1}. Thus, a value for λ_o of around 15 kcal mole^{-1} seems slightly favored at this time, but the various uncertainties in the λ's and in the E°_{eff} for the solvated electron must be borne in mind in such comparisons with the data. In turn, further kinetic and equilibrium data involving the solvated electron and further kinetic data on ordinary chemical and electrochemical exchanges should provide more precise E°_{eff}, λ_o, and λ_2's. An important region for such investigations would be one with E°_2's in the vicinity of 1.5 to 2.0 V.

These calculations are further discussed in Ref. 5e.

POSSIBILITY OF CHEMILUMINESCENCE

With a strong reducing agent such as the solvated electron, $\Delta F^{\circ\prime}_{int}$ can be extremely negative. For example, when $E_2^{\circ\prime}$ is as negative as −1.9 V, $\Delta F^{\circ\prime}_{int}$ is −110 kcal mole^{-1}. In such cases there is a possibility of formation of the product in an excited state, and then chemiluminescence becomes possible. The possibility of forming an excited state is enhanced when reaction leading to the ground state of the product is made less favorable. In principle such a circumstance can arise when the reorganization parameter λ is made sufficiently small by suitable choice of reactant: When $|\Delta F^{\circ\prime}_{int}/\lambda|$ is large (somewhat greater than unity) the conventional type of crossing of the two potential surfaces becomes difficult. The surfaces no longer cross at configurations which are compromises between reactants and products, and then the value of the reorganizational barrier $m^2\lambda$ actually increases as $\Delta F^{\circ\prime}_{int}$ becomes more negative.[5b]

For example, when λ_2 is 20 or 40 kcal mole^{-1} and $\Delta F^{\circ\prime}_{int}$ is −110 kcal mole^{-1}, $m^2\lambda$ is about 35 or 15 kcal mole^{-1}, respectively, if λ_o is 15 kcal mole^{-1}. It is still large even if λ_o is 45 kcal mole^{-1}, if λ_2 is 20. Then, $m^2\lambda$ equals 8 kcal mole^{-1}. If there is a readily accessible excited state of the product available the product might then be formed in the excited state and, under favorable conditions, fluoresce. The rate of Reaction (1) to form the product in an excited state, Ox* is again given by Eq. (3), but $\Delta F^{\circ\prime}_{int}$ is now the associated free energy change for the reaction leading to Ox*. Other things being equal, low λ_2's are favored by ligands such as *o*-phenanthroline and bipyridyl or by having an aromatic molecule as one of the reactants. For example, λ_2 for an iron *o*-phenanthroline ion appears to be about 15–20 kcal mole^{-1}, or less.[26]

USE OF ALTERNATIVE MODELS FOR THE POLARON

Comparison of Eqs. (38) and (46) for the values of ΔF^* at $R=\infty$ and at finite R reveals one feature identical with that in the equations derived earlier[5] for conventional electron-transfer reactions: The expression for ΔF^* has the form of m^2 times an intrinsic term (the value of λ at $R=\infty$) plus m^2 times a term e^2c/R. As the derivation for the conventional transfers reveals, this particular c is a property of the medium outside of the region occupied by the two reactants, regardless of what value one may eventually use for c appearing in the expressions for H_o and for λ at $R=\infty$.

Accordingly, use of some other model for the polaron is expected to lead to Eqs. (46) and (49) for ΔF^*, but with a somewhat different expression for part of λ, namely the $-2H_o$ term. That is, we have (50) and (51) as before but with a value of H_o which may differ somewhat from (33).

Further analysis of the dynamical polaron may well again lead to an expression of the type (56) in the

[24] J. K. Thomas, S. Gordon, and E. J. Hart, J. Phys. Chem. 68, 1524 (1964); compare J. H. Baxendale *et al.* Nature 201, 468 (1964).

[25] These values are those listed in Ref. 24 and may be compared with polarographic half-wave potentials (0.43, 0.93, and 1.56, respectively) given by I. M. Kolthoff and J. J. Lingane, *Polarography* (Interscience Publishers, Inc., New York, 1952), Vol. 2, p. 440.

[26] There is some uncertainty as the exact value of w^r when two organiclike ions react or when an organiclike ion reacts with an inorganic one. Compare data of G. Dulz and N. Sutin, Inorg. Chem. 2, 917 (1963).

first approximation but with a value for the effective mass of the polaron derived from the behavior of polarons in polar liquids. The exact value for m_p can also affect somewhat the pre-exponential factor ρ in Eq. (3). This factor is a ratio of the root-mean-square fluctuation of R to that of the perpendicular displacement s from the intersection region in the centered distribution, it is recalled. A small value of m_p may lead to a somewhat larger $[(\delta R)^2]^{\frac{1}{2}}$, although this could be partially offset by a larger $[(\delta s)^2]^{\frac{1}{2}}$. The exact value of ρ depends on the nature of the typical motion along the reaction coordinate.[5o]

FURTHER DISCUSSION

In the derivation of expression (7) for ΔF^*_{vib} the vibrations of the reactant were treated as harmonic oscillators. In these strongly negative $\Delta F^{\circ\prime}_{\text{int}}$ systems the activated complex resembles the reactants much more than the products, so that the second reactant may have a vibrational configuration considerable strained from that which it will later have as a product. In such cases the harmonic-oscillator approximation may be less accurate than it normally is. One can readily avoid the approximation, though the resulting expressions become more complex, as in Ref. 5(b). Alternatively, some estimate of the error can be made *a posteriori* by comparing a harmonic term,

$$\tfrac{1}{2}\sum k_{ij}{}^p(q_*{}^i-q_p{}^i)(q_*{}^j-q_p{}^j),$$

with the corresponding change of vibrational potential energy for the actual product molecule when the q^i are stretched from $q_p{}^i$ to $q_*{}^i$.

The factor $Z\exp(-F^\circ_{\text{transl}}/kT)$ appearing in the unimolecular rate constant (24) is of some interest. If, for the sake of simplicity, the reaction coordinate is assumed to be one purely of relative motion of the polaron and the second reactant, then because m_p is small Z becomes effectively $(8\pi kT/m_p)^{\frac{1}{2}}R^2$ and $Z\rho\exp(-F^\circ_{\text{transl}}/kT)$ becomes $(kT/h)(8\pi^2IkT/h^2)\rho$, where I equals m_pR^2 and ρ is unity. This factor in the unimolecular rate constant becomes the usual 10^{13} sec^{-1} factor multiplied by a rotational partition function. To be sure, if m_pR^2 were small this rotational partition function would be replaced by its quantum value and a corresponding correction would be made in Eq. (24): the latter would be multiplied by

$$\sum_{j=0}^{\infty}(2j+1)\exp(-J^2\beta)\beta,$$

where $\beta=\hbar^2/2IkT$. However, R^2 is very large.

Finally, it may be noted, the value of R in Eq. (49) for λ is by no means established and, in the case of solvated-electron reactions, might depend on the reaction. When $-\Delta F^{\circ\prime}_{\text{int}}/\lambda$ or, more precisely, when $-(\Delta F^{\circ\prime}_{\text{int}}-w^r)/\lambda$ becomes more positive than 1, ΔF^* actually increases as $-\Delta F^{\circ\prime}_{\text{int}}$ increases [Eqs. (46) and (48)]. This situation occurs only at very negative $\Delta F^{\circ\prime}_{\text{int}}$'s. In such a case, the most favorable R might be that which makes λ a little larger, namely by being larger itself (Eq. 49) and hence makes $|\Delta F^{\circ\prime}_{\text{int}}/\lambda|$ a little smaller. However, too large an R would make κ too small in Eq. (3). Again, it should be emphasized, we have considered only weak-overlap electron transfers. We have not permitted the solvated electron wavefunction to overlap the orbital of the second reactant appreciably, partly because the resulting desolvation might not be economical and partly because the theoretical calculations become more involved. The present work is intended to be a first approximation for comparing with and interpreting the experimental data.

An alternative atom-transfer mechanism for some reactions is discussed in Ref. 5e.

ELECTRON POLARIZATION OF THE SOLVENT

An aspect of the theory of the unconstrained polaron of particular interest involves the extent of electron polarization of the solvent. Purely from the viewpoint of the frequency of motion of the solvated electron alone (about 4×10^{14} sec^{-1})[6] there would appear to be on the surface no difficulty in the solvent electrons following the motion of the solvated electron: When the frequency of a light wave is 1.5, 3, 4, 5, and 13×10^{14} sec^{-1} the refractive index of water at 25°C is quite high[27]: $n=1.30$, 1.32, 1.33, 1.33, and 1.38_5, respectively. ($D_{\text{op}}=n^2$). In fact, refractive-index dispersion data for typical solvents can be interpreted[28] by regarding the valence and inner electrons of the solvent as having a mean frequency of about 3×10^{15} sec^{-1}, which is much larger than that of the solvated electron. Their corresponding angular frequency ω is 2π times this value.

However, an exclusion of solvent-electron polarization nevertheless must occur in the immediate vicinity of the solvated electron. This particular exclusion has not explicitly been discussed in the literature from the viewpoint of continuum theory, but can be treated by applying to the electron polarization analogous arguments[29] made in the literature for high-frequency lattice polarization. We consider first a system free of solvent orientation and vibrational polarization and consider the qualitative behavior and then in (62) the quantitative result.

Electrons of the solvent which are too close to the solvated electron cannot respond instantaneously to its motion no matter how high their natural frequency ω, namely electrons within a distance[30] $d\cong v/\omega$, where v is

[27] H. H. Landolt and R. Börnstein, *Zahlenwerte und Functioner*, edited by K.-H. Hellwege and A. M. Hellwege (Springer-Verlag, Berlin, 1962), 6th ed., Vol. 2, Part 8, pp. 5–562 to 5–566.

[28] Reference 14, p. 692.

[29] H. Frohlich, in Ref. 11, pp. 6–7.

[30] The solvent electrons outside of a sphere of radius d, centered at the solvated electron, will see the solvated electron as a static charge if the fractional change of field D is small in the time required ω^{-1} for appreciable change of electron polarization. This change in D at a point on this sphere is small if in time ω^{-1} the path length of the moving solvated electron subtends only a small angle at that point, i.e., if $(v/d)\omega^{-1}\lesssim1$.

the velocity of the solvated electron. This d is small when v is small. Yet, v cannot be very small and at the same time the electron be localized with a distance d less than $\sim\hbar/\mu v$ according to the uncertainty principle. Thus, we can at best have $v/\omega\cong\hbar/\mu v$ as a condition defining a distance outside of which the solvent electrons are polarized by the solvated electron. That is, $v\cong(\hbar\omega/\mu)^{\frac{1}{2}}$ and, hence $d\cong(\hbar/\omega\mu)^{\frac{1}{2}}$. The energy of polarization is then of the order of $-(e^2/2d)(1-1/D_{op})$ (Born formula).

A quantitative solution of the Schrödinger equation for the motion of the solvated electron and of a polarizable continuum of angular frequency ω leads in fact to Eq. (62) for the energy in this high-frequency limit:

$$\mathcal{E}=-e^2/2d[1-(1/D_{op})], \tag{62}$$

where

$$d=(\hbar/2\mu\omega)^{\frac{1}{2}}. \tag{63}$$

This result can be derived from that given by Allcock[16,31] by noting that in the present case of zero-orientation polarization and a frequency ω for motion of the solvent electrons, the formalism for the problem is identical with the one given there in the high-frequency approximation but that the D_s and D_{op} appearing there should now be replaced by D_{op} and unity, respectively.

When $\omega/2\pi$ has the value cited earlier of 3×10^{15} sec^{-1}, d equals 0.55 Å. Related remarks concerning an exclusion sphere of solvent-electron polarization should apply in systems containing orientation and vibrational polarization. The size of this exclusion sphere in either case is relatively small: The radius of the $1s$ polaron orbit[16] is about 1.80 Å ($16\hbar^2/5ce^2\mu$) so that the circumference of the orbit is about 11 Å or about 10 times the diameter of the exclusion sphere. Thus, one is inclined to suspect that this exclusion sphere, which occurs both in orientation free and the orientation polarization systems, has relatively little effect on H_o, which is the free energy of formation of the orientation polarization system from the orientation-free one.

With the framework of this continuum approximation this problem could of course be investigated precisely: A Schrödinger equation could be set up for this dynamical motion of the solvent electrons, the solvated electron, and the lattice polarization. The lattice polarization would be treated in the low-frequency approximation and the electron polarization in the high-frequency approximation. The foregoing arguments suggest, however, that the net change from the simple polaron theory calculation of H_o is small, although a molecular treatment of the electron polarization might yield a somewhat different conclusion. Since d is smaller than the "lattice" distance, the above continuum estimate cannot be an accurate one.

APPENDIX I. DERIVATION OF EQ. (8) FOR $F_{pol}(r_1)$

It is convenient to decompose the total polarization at $\mathbf{r}$, $\mathbf{P}_{tot}(\mathbf{r})$, into the sum of two parts[10]:

$$\mathbf{P}_{tot}(\mathbf{r})=\mathbf{P}_e+\mathbf{P}_u, \tag{A1}$$

where

$$\mathbf{P}_e(\mathbf{r})=(D_{op}-1)\,\mathbf{E}(\mathbf{r})/4\pi, \tag{A2}$$

and $\mathbf{E}(\mathbf{r})$ is the electric field at $\mathbf{r}$. If the orientation polarization is held fixed and a charge is changed, the change in polarization is in fact $(D_{op}-1)/4\pi$ times the change in $\mathbf{E}(\mathbf{r})$. Thus, the change in $\mathbf{P}_e(\mathbf{r})$ describes the response at fixed orientation polarization. Therefore, $\mathbf{P}_u(\mathbf{r})$ is some function of the orientation polarization: It is automatically held fixed when the latter is held fixed, since the change in $\mathbf{P}$ is fully accounted for by that in $\mathbf{P}_e$.

If one neglects dielectric image effects it can be shown that $\mathbf{E}(\mathbf{r})$ depends on the field directly due to the charges, $\mathbf{D}(\mathbf{r})$, and on $\mathbf{P}_u(\mathbf{r})$ according to (A3):

$$\mathbf{E}=(\mathbf{D}-4\pi\mathbf{P}_u)/D_{op}. \tag{A3}$$

In this case the reversible work required to charge the system to any given nonequilibrium state described by functions $\mathbf{D}(\mathbf{r})$ and $\mathbf{P}_u(\mathbf{r})$ is[10]

$$W_{rev}=-\frac{1}{8\pi}\left(1-\frac{1}{D_{op}}\right)\int\mathbf{D}^2d\mathbf{r}-\int\mathbf{P}\cdot\mathbf{D}d\mathbf{r}+2\pi c\int\mathbf{P}^2d\mathbf{r}, \tag{A4}$$

where $\mathbf{P}$ denotes $\mathbf{P}_u/D_{op}$ and is again fixed once the orientation polarization is specified. The term $F_{pol}(\mathbf{r}_1)$ is obtained by subtracting from (A4) its value, $W_{rev}(\infty, \text{eq})$, when the reactants are far apart and when the orientation polarization vanishes. Thus $W_{rev}(\infty, \text{eq})$ equals $-1/8\pi[1-(1/D_{op})]\int\mathbf{D}^2d\mathbf{r}$ calculated at $R=\infty$. In this manner one obtains Eq. (8) for F_{pol}. We again neglect dielectric image effects in evaluating integrals. They are small.[50]

APPENDIX II. ESTIMATE OF H_o AND ELECTRON AFFINITY FROM SOLVATION AND SPECTRAL DATA

A rough estimate of these quantities can be attempted from spectral and solvation data as follows.

Noyes[32] has suggested a value of 103.8 kcal mole^{-1} for the ΔF° of the following hypothetical process.

$$\tfrac{1}{2}H_2(g)\rightarrow H^+(aq)+[e^-](aq), \tag{A5}$$

[31] This result, together with higher-order terms which are small in our case (α there is about 0.5 for electron polarization) has been obtained for lattice polarization by S. W. Tiablikov (1952, 1954) T. D. Lee, F. E. Low, and D. Pines (1953), M. Guari (1953), G. Höhler (1955), and R. P. Feynman (1955). The results are summarized largely in Ref. 16 and, in part, in 11.

[32] R. M. Noyes, J. Am. Chem. Soc. 86, 971 (1964). I am indebted to the reviewer for calling this reference to my attention and for suggesting that some comparison be made with solvation data.

where $[e^-]$(aq) denotes a hypothetical electron at the bulk electrostatic potential of the solvent, and having zero entropy and zero energy. For a standard state of $1M$ for H_2, this ΔF° becomes 102.9 kcal mole^{-1}. Subtraction of this value from that for the actual process (54) yields a value of 40.2 kcal mole^{-1} for the free energy of a solvated electron. If the translational free energy of this solvated electron is about -5.3 kcal mole^{-1}, as discussed earlier, the solvation portion is -34.9 kcal mole^{-1}. The difference of this value and the spectral transition energy (1.72 eV) is about 4.7 kcal mole^{-1}. It is independent of the electron affinity of the electron in the ground state and equals 0.28 H_o when the electron affinity of the excited state can be neglected. In that case, H_o would be about 0.7 eV, which is close to the value estimated from rate data in the text, and the electron affinity of the ground state would be about 0.8 eV. However, the considerable uncertainties in these values should be emphasized.

APPENDIX III. GLOSSARY OF PRINCIPAL SYMBOLS

$F^{*r}(R)$	Free energy of system when reactants are fixed in position a distance R apart and are in the distribution centered on the intersection region
$F^{*p}(R)$	Corresponding term for product fixed in position and in the above distribution centered on intersection region
$F^r(\infty)$	Free energy of system when reactants are fixed in position far apart and are otherwise unconstrained
$F^p(\infty)$	Free energy of system when product is fixed in position and is otherwise unconstrained
ΔF^*	$F^{*r}(R)-F^r(\infty)$
ΔF^{*p}	$F^{*p}(R)-F_p(\infty)$
w^r	Work required to bring reactants together, a contribution to ΔF^*
Z	Collision frequency calculated for the above R and for uncharged and otherwise noninteracting species (charge effects, etc., are included in w^r)
q^i	ith vibrational coordinate of reactants (and products), whose equilibrium value in reactant is $q_r{}^i$, in product is $q_p{}^i$, and whose most probable value in the centered distribution is $q_*{}^i$
ΔF^*_{vib}	Vibrational contribution to ΔF^*
$k_{ij}{}^r$, $k_{ij}{}^p$	Force constant of ij cross term in vibrational potential energy of reactant and of product, respectively [reduced force constant k_{ij} is $2k_{ij}{}^r k_{ij}{}^p/(k_{ij}{}^r+k_{ij}{}^p)$]
ψ, ψ_o	Wavefunction of electron when the reactants are in the centered distribution and when they are unconstrained plus far apart, respectively
$F_{\text{pol}}(\mathbf{r}_1)$	Polarization free energy as a function of the electron position $\mathbf{r}_1$
$\mathbf{P}(\mathbf{r})$	A particular function of the orientation polarization of the medium
a_2	Radius of second reactant, including any inner coordination shell
e_1, e_2	Charge of electron and of second reacting species, respectively (superscript r indicates reactants; p, products; hence, $e_1{}^p=0$, $e_1{}^r=-e$)
D_{op}, D_s	Optical and static dielectric constants of the medium, respectively
c	$(D_s-D_{\text{op}})/D_sD_{\text{op}}$
$\mathbf{D}_1$, $\mathbf{D}_2$	Field due directly to the electron at $\mathbf{r}_1$ and to the second reactant at $\mathbf{r}_2$, respectively [Eq. (11)] $\mathbf{D}=\mathbf{D}_1+\mathbf{D}_2$
$\mathfrak{D}_i{}^r$	Value of $\mathbf{D}_i$, averaged over $\lvert\psi\rvert^2$ [Eq. (20)] $\mathfrak{D}^r=\mathfrak{D}_1{}^r+\mathfrak{D}_2{}^r$
$\mathfrak{F}_o{}^r$	Sum of electron kinetic energy and of polarization free energy of system of separated reactants
$H_o\equiv\mathfrak{F}_{o_1}{}^r$	$\mathfrak{F}_o{}^r$ minus contribution of second reactant
$\mathfrak{F}_o{}^p$	Polarization free energy of system containing the product
μ, m_p	Effective mass of electron and of polaron, respectively
m	A Lagrangian multiplier, determined by Eq. (23)
$\Delta F^{\circ\prime}$, K	"Standard" free energy of Reaction (1) at prevailing temperature and for prevailing medium, K being the corresponding equilibrium constant
F°_{transl}, $(\text{pf})_{\text{transl}}$	Translational free energy and translational partition function of the solvated electron, calculated for a state of unit concentration
$\Delta F^{\circ\prime}{}_{\text{int}}$	The internal contribution to $\Delta F^{\circ\prime}$ [Eq. (22)]

λ_i	A factor in ΔF^*_{vib}, $\Delta F^*_{vib} = m^2\lambda_i$
λ_o^∞	An intrinsic orientation polarization reorganization term for second reactant when the reactants are far apart [Eq. (28) ff.]
λ_2^∞	$\lambda_i + \lambda_o^\infty$
H	The kinetic energy of the electron plus the contribution of the electron and its environment to the polarization free energy in the centered distribution when the reactants are far apart
λ	An intrinsic reorganization term [Eq. (46)]
λ_e, λ_2	"Contribution" of the electron and of the second reactant to λ [Eq. (49) ff.]
$E_2^{\circ\prime}$	"Standard" reduction potential of second reactant
$E^{\circ\prime}_{eff}$	Effective standard reduction potential of solvated electron (~2.9 V)
k_{diff}	Diffusion controlled rate constant, Eq. (61)
k_{act}	Activated controlled rate constant, Eq. (3)
k_{obs}	Observed rate constant, Eq. (60)
ω	Classical angular frequency of solvated electron in its orbit.