

On the Theory of Oxidation-Reduction Reactions Involving Electron Transfer. I*

R. A. MARCUS

Department of Chemistry, Polytechnic Institute of Brooklyn, Brooklyn, New York

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A mechanism for electron transfer reactions is described, in which there is very little spatial overlap of the electronic orbitals of the two reacting molecules in the activated complex. Assuming such a mechanism, a quantitative theory of the rates of oxidation-reduction reactions involving electron transfer in solution is presented. The assumption of "slight-overlap" is shown to lead to a reaction path which involves an intermediate state X^* in which the electrical polarization of the solvent does not have the usual value appropriate for the given ionic charges (i.e., it does not have an equilibrium value). Using an equation developed elsewhere for the electrostatic free energy of nonequilibrium states, the free energy of all possible intermediate states is calculated. The characteristics of the most probable state are then determined with the aid of the calculus of variations by minimizing its free energy subject to certain restraints. A simple expression for

the electrostatic contribution to the free energy of formation of the intermediate state from the reactants, ΔF^* , is thereby obtained in terms of known quantities, such as ionic radii, charges, and the standard free energy of reaction.

This intermediate state X^* can either disappear to reform the reactants, or by an electronic jump mechanism to form a state X in which the ions are characteristic of the products. When the latter process is more probable than the former, the over-all reaction rate is shown to be simply the rate of formation of the intermediate state, namely the collision number in solution multiplied by $\exp(-\Delta F^*/kT)$. Evidence in favor of this is cited. In a detailed quantitative comparison, given elsewhere, with the kinetic data, no arbitrary parameters are needed to obtain reasonable agreement of calculated and experimental results.

INTRODUCTION

DURING recent years oxidation-reduction reactions involving the transfer of an electron between the reactants have been the subject of many kinetic studies.¹ Several generalizations may be drawn from this data. For example, it was found that isotopic exchange reactions between ions differing only in their valency are generally slow if simple cations are involved and fast if the ions are relatively large, such as complex ions.

This behavior has been qualitatively explained by Libby² on the basis of related ideas of Franck, applying the Franck-Condon principle. The degree of orientation of the solvent molecules toward an ion greatly depends on the charge of that ion. For a given ion, it will therefore be different before and after this ion undergoes an electron transfer. Libby observed that the solvent molecules near the reacting ions cannot adjust themselves immediately to the change in ionic charges resulting from an almost instantaneous electronic jump. A state of high energy, he suggested, is therefore produced. Such a barrier to reaction would be greater for small ions, since they are more highly solvated than large ones. This conclusion is in agreement with the fact that in most cases the smaller ions react more slowly in these isotopic exchange redox reactions.

Another observation which can be drawn from a

summary³ of data on isotopic exchange reactions having simple mechanisms is that the entropy of activation of such reactions is large and negative. It is of interest that all these reactions were between ions of like sign. It was assumed³ that a reorganization of the solvation atmospheres about the reacting ions occurred prior to reaction, but it was believed that this would contribute a positive term to the entropy of activation. It was suggested that the reorganization would involve a partial "melting" of the solvent attached to the ions, and that this would involve an increase in entropy. To explain the observed entropy of activation there would have to be a larger, negative term. It was suggested that this term was due to the low probability of an electron tunnelling⁴ through a solvation barrier, from one reactant to the other in the intermediate state. However, several aspects of this interesting treatment are open to question.⁵ In fact, using the values given

* Marcus (Rudolph J.), Zwolinski, and Eyring, *J. Phys. Chem.* **58**, 432 (1954). These authors summarize some of these data in their Table I. In Table II, reactions are given having apparent positive entropies of activation. However, in at least all but one of the reactions in Table II the mechanism is complex and the concentrations of the actual reactants are unknown. Accordingly, the so-called entropies of activation of such reactions have no immediate theoretical significance. The lone possible exception, incidentally, does not involve reacting ions of like sign.

⁴ J. Weiss, *Proc. Roy. Soc. (London)* **A222**, 128 (1954), has also discussed the electronic jump process. Unlike reference 3 the necessity for the reorganization of the solvent occurring prior to the electronic transition was not considered there.

⁵ The mechanism used there was incomplete in that only one fate of the intermediate state in the reaction was considered. It was tacitly assumed that this state involving the reorganized solvent could only produce products, but not reform the reactants. (The former would occur by an electron jump process, the latter by a disorganizing motion of the solvent.) It is shown later that this omission can significantly affect the role played by the electronic jump process.

The number of times per second that the electron in one of the reactants struck the barrier was not included in the over-all calculation. Effectively, this made electron tunnelling appear about one thousand-fold less frequent than would otherwise have been estimated.

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¹ See review articles: Zwolinski, Marcus (Rudolph J.), and Eyring, *Chem. Revs.* **55**, 157 (1955); C. B. Amphlett, *Quart. Revs.* **8**, 219 (1954); O. E. Myers and R. J. Prestwood, *Radioactivity Applied to Chemistry*, edited by Wahl and Bonner (John Wiley and Sons, Inc., New York, 1951), Chap. 1; Betts, Collinson, Dainton, and Ivin, *Ann. Repts. on Progr. Chem. (Chem. Soc. London)* **49**, 42 (1952); R. R. Edwards, *Ann. Revs. Nuclear Sci.* **1**, 301 (1952); M. Haissinsky, *J. chim. phys.* **47**, 957 (1950); and recent reviews in *Ann. Rev. Phys. Chem.*

² W. F. Libby, *J. Phys. Chem.* **56**, 863 (1952).

there for the probability of electron tunnelling and using the detailed treatment given in the present paper, a different conclusion will be drawn about the origin of the observed entropy of activation.

An object of the present paper is to devise a method of calculating the free energy of reorganization of the solvent molecules about the reactants prior to the electronic jump process, and from this to develop a quantitative theory of electron transfer reactions.

THEORETICAL

General

In most bimolecular reactions, appreciable changes in various interatomic distances within each molecule generally occur during the course of a collision. The potential energy of this system, arising from the stretching and compression of various chemical bonds, usually passes through a maximum in the collision. The configuration of the atoms at the maximum is the well-known activated complex, and a detailed knowledge of it permits an *a priori* calculation of the reaction rate.

In most reactions there usually is a transfer of atoms or groups of atoms between the reactants, and a rearrangement of atoms within each reactant. In order for this to occur, there presumably must be a strong interaction of the electronic structures of the two reactants in the activated complex. That is, there would be a considerable spatial overlap of the electronic orbitals of the two reacting molecules in this complex.

In contrast to such reactions, some reactions may merely involve the transfer of an electron between the reacting molecules. For such reactions to occur, only a slight overlap of the electronic orbitals is perhaps necessary. Only a slight electronic interaction may be sufficient to electronically couple the two molecules and permit the electron transfer to occur. If this is indeed the case, then its consequences are far-reaching. In the present paper a quantitative theory for electron transfer reactions will be developed on the basis of the assumption that there is little overlap of the electronic orbitals of the two reacting particles in the activated complex. The final formula of this paper is therefore not applicable to any electron transfer reaction having a large-overlap activated complex.

Electronic Configuration of the Activated Complex

Just before a collision the electronic configuration of the reacting pair of molecules is the same as that of reactants. Just after a successful collision, their electronic configuration is the same as that of the products. The electronic configuration of the intermediate stage in the reaction, i.e., of the activated complex, is presumably of an intermediate nature. We may readily determine it for activated complexes in which there is but slight overlap of the electronic orbitals of the two reacting particles.

One may write down Schrödinger's wave equation, describing the wave function ϕ of the electrons of the reacting particles in the activated complex, taking into account their interactions with each other and with all the solvent molecules. Let us consider first any given configuration of all the atoms in the system, i.e., of the atoms of the two reacting particles and of the solvent. If there were no overlap of the electronic orbitals of the two reacting particles there would be no electronic interaction of the two molecules. Therefore an exact solution of the wave equation would then simply be that wave function which characterizes the electronic configuration of the two reactants when they are far apart in the solvent. For the given atomic configuration of the reacting particles, let us denote this wave function by ϕ_x . Again, an equally valid solution to the wave equation would be that which characterizes the electronic configuration of the two products when they are far apart in the solvent. For the given atomic configuration of the reacting particles, let this function be ϕ_x^* . In the case of weakly interacting electronic orbitals of the two reacting particles the linear combination $(\phi_x + c\phi_x^*)$, where c is a constant, would be the appropriate wave function for the activated complex, but not ϕ_x or ϕ_x^* alone. It can be shown⁶ that this is the appropriate solution for weakly interacting orbitals only if the *total* energy of the system is the same for each of electronic configurations ϕ_x and ϕ_x^* in any given atomic configuration.

Presumably, in our activated complex the two electronic configurations, ϕ_x and ϕ_x^* , make equal contributions to the total wave function. The important thing, however, is that for every atomic configuration of the activated complex the *total* energy of a hypothetical system having the electronic configuration of the reactants (ϕ_x) must be the same as that of a hypothetical system having the electronic configuration of the products (ϕ_x^*). Since this is a thermodynamic system, there will be many atomic configurations of all the solvent molecules and of the reacting pair of molecules in the activated complex which will conform to this energy restriction. Thus, the energy in a thermodynamic sense, which is the average of the energies of all the *suitable* atomic configurations, must be the same for both electronic configurations. These two hypothetical thermodynamic states of the system will be called the intermediate states, X^* and X .

⁶ The Schrödinger equation can be written as $H\phi = E\phi$; E is the energy of an atomic configuration. The Hamiltonian operator H includes terms expressing the interaction of the electrons and nuclei of the reacting particles with each other and with the solvent molecules. In the case of no overlap, ϕ_x and ϕ_x^* were shown to be solutions to this wave equation. Let their corresponding energies be E_x and E_x^* , respectively, so that we have: $H\phi_x = E_x\phi_x$ and $H\phi_x^* = E_x^*\phi_x^*$. If c is any constant, a linear combination of ϕ_x and ϕ_x^* is $(\phi_x + c\phi_x^*)$. When introduced into the wave equation this yields: $H(\phi_x + c\phi_x^*) = E_x\phi_x + E_x^*c\phi_x^*$. Only when E_x equals E_x^* is the right-hand side equal to $E_x(\phi_x + c\phi_x^*)$. That is, only under these conditions does $(\phi_x + c\phi_x^*)$ satisfy the equation $H\phi = E\phi$. It is also seen that for such a linear combination, the total energy E equals E_x and therefore E_x^* .

These considerations of the energy restriction are amplified later in an application of the uncertainty principle to a discussion of the validity of assuming a small-overlap activated complex.

The *total* energy condition can readily be shown to place a severe restraint upon the solvation of the activated complex. The degree of orientation of the solvent molecules about any ion will strongly depend on its charge. Accordingly, the *equilibrium* set of configurations of all the atoms of the solvent in the neighborhood of the reacting particles will greatly depend on whether these particles have the ionic charges of the reactants or of the products. Now the average configuration of the solvent was seen to be the same in the two states, X^* and X . These states differ in the charges of the reacting particles. Therefore, the average configuration of the solvent in the activated complex cannot be an equilibrium one. (In this respect it differs from the large-overlap complex, as discussed in a later section.) The average configuration of the solvent in the activated complex must also be such as to satisfy the energy restriction noted earlier. That is, in the activated complex the solvent configuration must be such that the *total* energy of the system, solvent plus reacting particles, must be the same, regardless of whether these particles are the reactants or the products.

It is of interest that the foregoing discussion can be rephrased in terms of the Franck-Condon principle: When one electron configuration is formed from the other by an electronic transition, the electronic motion is so rapid that the solvent molecules do not have time to move during the electronic jump. That is, the reaction proceeds by way of two successive intermediate states, X^* and X , which have the same atomic configurations but different electronic configurations. Conservation of energy leads to the requirement that the total energy of these two states must be the same.

The electronic wave function of the activated complex derived previously, a linear combination of ϕ_{x^*} and ϕ_x , admits of a simple interpretation. The function is a function of the position coordinates of all the electrons of the two reacting particles. It can be plotted in a many-dimensional space as a function of all these coordinates. In such a plot ϕ_{x^*} will be large in certain regions of this many-dimensional coordinate space, and ϕ_x will be large in other regions. The function ϕ_{x^*} will be large when the coordinates of all the electrons are such that the number of electrons in the vicinity of each of the reacting particles is the same as when these particles are reactants. Since the electrons are indistinguishable there will be a number of such regions in the many-dimensional space. Similarly, ϕ_x will be large when the number of electrons in the vicinity of each of the reacting particles is the same as when these particles are products. Again there will be a number of such regions. The wave function for the activated complex, being a linear combination of these two wave functions, is large in all these regions. The reaction

ultimately involves going from the regions characteristic of ϕ_{x^*} to those characteristic of ϕ_x .

Since the wave function is the sum of two wave functions, each corresponding to a different electronic configuration, we can also interpret the wave function as representing a quantum-mechanical resonance of two electron configurations, one being the electronic configuration of the reactants, the other that of the products.

Inasmuch as there will be some overlap of the electronic orbitals of the two reactants, the description of the activated complex given in this section is but a first approximation, which is the better the less the overlap.

Reaction Scheme

The occurrence of a small overlap in the activated complex introduces another consideration which is normally not present in the usual large-overlap activated complexes. Since the electronic interaction between the reacting particles in a small-overlap complex is weak, the rate at which this electronic interaction can effect any change of electronic configuration may become a slow step in the over-all process. We can envisage the over-all reaction as occurring in the following way. As the two reactants approach each other there is a certain probability that a suitable fluctuation of the solvent molecules which satisfies the restriction described in the previous section will occur, such that an activated complex *could* be formed. An electronic interaction of the reacting particles could then result in the correct electronic configuration of the activated complex. A theoretical treatment of this aspect of the problem could involve the use of several quantum-mechanical methods including the use of time-dependent perturbation theory^{2,6a} or electron tunneling formulas.^{3,4} We shall return to this later. We can suppose, then, that when the reactants are near each other a suitable solvent fluctuation can result in the formation of the state, X^* , whose atomic configuration of the reacting pair and of the solvent is that of the activated complex, and whose electronic configuration is that of the reactants. This state X^* can either reform the reactants by disorganization of some of the oriented solvent molecules, or it can form the state X by an electronic transition, this new state having an atomic configuration which is the same as that of X^* but having an electronic configuration which is that of the products. The state X can either reform X^* by an electronic transition, or alternatively, the products in this state can merely move apart, say.

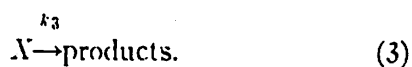
The pair of states X^* and X constitute the activated complex. If the electronic interaction between them were large, the formation of one from the other would be very rapid and one need then not speak of them

^{6a} L. Pauling and E. B. Wilson, *Introduction to Quantum Mechanics* (McGraw-Hill Book Company, Inc., New York, 1935).

separately. An analogous situation also arises in very different reactions, such as some *cis-trans*-isomerizations in which spin-conservation requirements can cause the effective electronic interaction to be very weak.⁷

It may also be remarked that the term *activated complex* was defined earlier in the usual way as the atomic configuration at the potential energy maximum along the reaction coordinate. This does not mean, however, that the reaction rate can be calculated in the usual way simply by calculating the free energy of formation of the activated complex from the reactants and introducing this into the well-known absolute reaction rate theory formula⁷ for the rate constant. Instead, the present reaction has been shown to consist of several elementary steps, several of which may be slow. In such cases the rate constants of all the elementary steps must be evaluated individually, and for this purpose, too, the absolute rate theory formulas will not be used as such.

The reaction scheme described above can be written as the sequence Eqs. (1) to (3). In this treatment it is not necessary that all of the reactants or products have charges. In this reaction sequence *A* and *B* will denote the reactants involved in the electronic transition.



The reverse step of (3) does not have to be considered, even though it may occur when the concentration of products is appreciable, since we are only interested here in calculating the rate constant of the over-all *forward* reaction. The rate constant for the over-all backward reaction could then be calculated from this with the aid of the equilibrium constant for the over-all reaction.

The sequence (1) to (3) will in many cases represent the complete reaction. In more complex systems, however, *A* and *B* may not be the actual compounds introduced into the reaction system, but would be the active entities formed from them. The over-all rate of this reaction sequence will be written as $k_{bi}c_a c_b$ where *c*'s denote concentrations and k_{bi} is the observed rate constant of this reaction sequence. According to Eq. (3), the rate is also given by $k_3 c_x$. We may therefore write

$$k_{bi}c_a c_b = k_3 c_x. \quad (4)$$

The steady-state equations for the concentrations of X^* and of X , c_{x^*} and c_x , are given by Eqs. (5) and (6).

$$\frac{dc_{x^*}}{dt} = 0 = k_1 c_a c_b - (k_{-1} + k_2) c_{x^*} + k_{-2} c_x \quad (5)$$

$$\frac{dc_x}{dt} = 0 = k_2 c_{x^*} - (k_{-2} + k_3) c_x. \quad (6)$$

Introducing into Eq. (4) the value obtained for c_x by solving these simultaneous equations, we find

$$k_{bi} = k_1 / [1 + (1 + k_{-2}/k_3)k_{-1}/k_2]. \quad (7)$$

The various rate constants appearing in this expression for the over-all rate constant, k_{bi} , will be estimated in the present paper. It is shown later that when the forward step in reaction (2) is more probable, or about as probable, as the reverse step in reaction (1), Eq. (7) reduces to a particularly simple form (neglecting factor of about two, which is of minor importance):

$$k_{bi} \cong k_1. \quad (8)$$

Otherwise, Eq. (7) would be used. Equation (8) will be used extensively in correlating observed and calculated rates of oxidation-reduction reactions.

We proceed now to estimate the properties of the intermediate states X^* and X , in order to be able to calculate their rate of formation.

Solvation of Activated Complexes

As noted earlier, in the activated complex all the solvent molecules are oriented in some nonequilibrium configuration. This is in marked contrast to what is usually assumed for large-overlap activated complexes. In the latter, the solvent configuration is assumed to be in equilibrium with the ionic charges of the activated complex. For example, it is generally assumed that the electrical polarization of the solvent at any point can be calculated from the dielectric constant and the ionic charge and radius of the complex, by standard electrostatic procedures. It is usually assumed, for example, for purposes of calculating the free energy of solvation of the complex, that the complex can be treated as a sphere having a charge equal to the sum of the charges of the reactants.⁷ This theory has proved very useful in interpreting the effect of dielectric constant on the reaction rate. However, we have seen that such a description would be quite inapplicable to electron transfer reactions in which the overlap of the electronic orbitals of the two reacting particles is small in the activated complex.

In order to calculate the thermodynamic properties, such as the energy, of the intermediate states X^* and X it is necessary to use expressions which do not assume that the solvent molecules are oriented toward the ions in an equilibrium manner. More explicitly, the electrical polarization of the solvent at each point is not in elec-

⁷ Glasstone, Laidler, and Eyring, *The Theory of Rate Processes* (McGraw-Hill Book Company, Inc., New York, 1941).

trostatic equilibrium with the electrical field produced by ionic charges. That is, it cannot be predicted from the known ionic charge distribution by standard methods. Recently, however, a method for calculating the thermodynamic function of such systems was devised⁸ and will be used to calculate the free energy of formation of the intermediate states X^* and X from the reactants.

There are an infinite number of pairs of (thermodynamic) intermediate states, X^* and X , just as there are an infinite number of thermodynamic states of any system, each pair satisfying the energy restriction described earlier. Actually it is the most probable pair of intermediate states which constitutes the activated complex. The most probable pair of intermediate states can be determined with the aid of the calculus of variations by minimizing the free energy of formation of X^* from the reactants subject to the energy restriction found earlier, that is, subject to the restriction that X and X^* have the same total energy. This minimization procedure serves to determine the electrical polarization of the solvent at each point of the system in the intermediate state. This can be used to calculate the free energy of formation and rate of formation of the intermediate state from the isolated reactants in the medium.

A Model for the Reactants

The model which will be used for the structure of the reactants will be closely akin to that which is generally employed in the treatment of ionic interactions. It will be assumed that each reactant may be treated as a sphere, which in turn *may* be surrounded by a concentric spherical region of saturated dielectric,⁹ outside of which the medium is dielectrically unsaturated.

We let the sphere bounding the saturated region have a radius a . The radii, a_1 and a_2 , for the two reactants could change somewhat when the two ions approach each other though this effect is invariably ignored in the treatment of ionic interactions and will be ignored here. For a given element of the Periodic Table it will also depend to some extent on the valence of the ion. In the case of monatomic ions, however, a is generally assumed to equal the sum of the crystallographic radius and the diameter of a solvent molecule, since only the innermost layer of solvent molecules is usually assumed to be saturated.⁹ However, since the crystallographic radius varies relatively little with the valence of the ion,¹⁰ a would be expected to vary but little with the ion's valence. A refinement of the present

treatment would take this variation into consideration. In general when a is slightly different before and after the electron transfer reaction a mean value for it will be adopted. To sum up we shall suppose that the region inside a sphere of radius a about a reactant is rigid, all groups within a being fully oriented (saturated dielectric). A refinement of this assumption of constant a will be described in a later paper of this series.

The usual treatment of ionic interactions assumes that the free energy of interaction of two ions of charges q_1 and q_2 a distance R apart in a medium of dielectric constant D is q_1q_2/DR . This implies several assumptions^{11,8} and we shall make analogous ones in the present treatment. We shall treat an ion plus its rigid, saturated dielectric region as a conducting sphere of radius a . Now the free energy of the entire system is the sum of several contributions; one is the free energy of interaction of all the atoms within one sphere with each other and with the central ionic charge in that sphere. A second is the free energy of interaction of all the atoms within the sphere about the second reactant with each other and with the central ionic charge of the second reactant. A third is the free energy of interaction of all the molecules outside of the two spheres with each other and with the charges of the spheres. A fourth is the interaction of the two ionic spheres with each other. As in the treatment of ionic reactions which employs the q_1q_2/DR law, we observe that if, as assumed, the atoms in the spheres are not to change their average positions during the mutual approach of the ions, the first two contributions to the free energy will remain fixed and, therefore, not contribute to the free energy of formation of the state X^* from the reactants, and similarly will not contribute to the free energy of formation of the products from the state X . The remaining two contributions to the free energy are calculated, as previously observed, by treating each ion plus saturated sphere as a conducting sphere of radius a .

We proceed to consider the properties of the dielectric, assumed unsaturated,⁹ *outside of these saturated spheres*.

Electrostatic Characteristics of the Activated Complex

As noted previously, each of the intermediate states X^* and X , can be treated as a macroscopic system having a definite value of the electrical polarization of the medium at each point of the system. The primary problem then becomes one of determining this polarization function in these two intermediate states, in the volume *outside* of that occupied by the two reactants plus saturated spheres.

The polarization of any dielectric medium is generally regarded as consisting of electronic, atomic, and orientation contributions. As observed previously, the two intermediate states X^* and X have similar configurations of all atomic nuclei in the system. Since the atomic

⁸ R. A. Marcus, J. Chem. Phys. 24, 979 (1956).

⁹ Numerous theoretical treatments of the free energy of solvation which have assumed this model include: (a) J. D. Bernal and R. H. Fowler, J. Chem. Phys. 1, 515 (1933); (b) D. D. Eley and M. G. Evans, Trans. Faraday Soc. 34, 1093 (1938); (c) E. J. W. Verwey, Rec. trav. chim. 61, 127 (1942); (d) R. W. Attree, Dissertation Abstr. 13, 481 (1953).

¹⁰ This is especially true when the valence of the ion before and after the reaction differs by only one unit. This will be shown to be the case of greatest interest, in later applications of this paper.

¹¹ See R. Platzman and J. Franck, Z. Physik 138, 411 (1954).

and orientation polarization are associated with the polarized motion of the nuclei, the first being associated with the relative positions of the atoms within a molecule and the second with the orientation of the molecule as a whole, we see that each of these two contributions will be the same in both intermediate states, X^* and X . The electronic polarization, on the other hand, is associated with the electronic motion of the solvent's molecules. Just as the electronic structure of either reacting particle differs in states X^* and X , the electronic polarization can differ, and is presumably that which is produced by the electric field generated by the ionic charges plus the atomic and orientation polarization.

It is seen that in the intermediate states X^* and X , the electrical polarization of the medium can be classified into two types. One type, which is the electronic polarization in the present case, varies with position in a way dictated by the local electric field strength. That is, it is in "electrostatic" equilibrium with the field. The other type, which is atomic plus orientation polarization in the present case, is independent of the local electrical field strength, i.e., it is not in electrostatic equilibrium with it. These two types of polarization were termed⁸ E -type and U -type, respectively. At any point in the system outside of the two spheres occupied by the saturated dielectric let these types of polarization have a magnitude and direction given by the vectors $\mathbf{P}_e(\mathbf{r})$ and $\mathbf{P}_u(\mathbf{r})$, respectively, where the coordinates of the point are indicated by the vector $\mathbf{r}$ drawn from any arbitrary origin to the point. As observed previously the intermediate states X^* and X have the same vector point function, $\mathbf{P}_u(\mathbf{r})$, but will have different values of the function $\mathbf{P}_e(\mathbf{r})$. The total polarization $\mathbf{P}(\mathbf{r})$ at any point is the vector sum of these.

$$\mathbf{P}(\mathbf{r}) = \mathbf{P}_e(\mathbf{r}) + \mathbf{P}_u(\mathbf{r}). \quad (9)$$

As observed previously, the medium outside of the two saturated spheres is assumed to be unsaturated. Accordingly outside of these spheres $\mathbf{P}_e(\mathbf{r})$ is at each point proportional to the electric field strength $\mathbf{E}(\mathbf{r})$. On the other hand $\mathbf{P}_u(\mathbf{r})$ is unrelated to $\mathbf{E}(\mathbf{r})$ in these nonequilibrium states. We shall let

$$\mathbf{P}_e(\mathbf{r}) = \alpha_e \mathbf{E}(\mathbf{r}) \quad (10)$$

where α_e is the polarizability associated with the E -type polarization.

In treating the electrostatic behavior of states in which all or part of the polarization is not in equilibrium with the electric field produced by the charges in the system, a vector $\mathbf{E}_r$ was defined.⁸ This is the electric field strength which the spheres would exert if they were in a vacuum rather than in a polarized medium. It is given by Eq. (11).

$$\mathbf{E}_r(\mathbf{r}') = -\nabla_{r'} \left\{ \int \frac{\rho(\mathbf{r}) dV}{|\mathbf{r} - \mathbf{r}'|} + \int \frac{\sigma(\mathbf{r}) dS}{|\mathbf{r} - \mathbf{r}'|} \right\} \quad (11)$$

where $\rho(\mathbf{r})$ and $\sigma(\mathbf{r})$ denote the volume and surface charge densities in the system, and where the subscript r' on the gradient operator $\nabla_{r'}$ indicates differentiation with respect to the coordinates of $\mathbf{r}'$. The first integral is over the entire volume of the system, and the second integral is over every surface present. An ion, for example, is generally treated as a sphere bearing a uniform surface charge density.

In any system, equilibrium or not, it was observed⁸ that the potential $\psi(\mathbf{r}')$ at any point $\mathbf{r}'$ in the system depended on the polarization, $\mathbf{P}$, and the vector, $\mathbf{E}_c$, according to Eq. (12).

$$\psi(\mathbf{r}') = \int (\mathbf{P} - \mathbf{E}_c/4\pi) \cdot \nabla \frac{1}{|\mathbf{r} - \mathbf{r}'|} dV \quad (12)$$

where only in an equilibrium system can $\mathbf{P}$ be immediately expressed in terms of the electric field strength, $\mathbf{E}$. In the absence of dielectric saturation (outside the region occupied by the two spheres) the relation between $\mathbf{P}$ and $\mathbf{E}$ is given by Eq. (13), since $\mathbf{E}(\mathbf{r})$ is $-\nabla\psi$.

$$\mathbf{P}(\mathbf{r}) = \alpha \mathbf{E} = -\alpha \nabla \psi \quad (13)$$

where α is the total polarizability of the medium. The values of $\mathbf{E}_c$, $\mathbf{P}_e$, $\mathbf{P}_u$, $\mathbf{P}$, and $\mathbf{E}$ which obtain in the intermediate state X^* will be designated by an asterisk, while those characteristic of state X will bear no asterisk. Since the U -type polarization is the same in both states, $\mathbf{P}_u^*$ equals $\mathbf{P}_u$.

The electrostatic free energy of any state is generally defined as the reversible work required to charge up that state. Expressions have been derived elsewhere⁸ for the electrostatic free energy of nonequilibrium systems of the type discussed here. Using the results given by Eq. (25) of reference 8 we have for the electrostatic free energy of states X^* and X .

$$F^* = -\frac{1}{2} \int \left\{ \frac{\mathbf{E}_c^{*2}}{4\pi} - \mathbf{P}^* \cdot \mathbf{E}_c^* + \mathbf{P}_u \cdot \left(\frac{\mathbf{P}_u}{\alpha_u} - \mathbf{E}^* \right) \right\} dV \quad (14)$$

$$F = -\frac{1}{2} \int \left\{ \frac{\mathbf{E}_c^2}{4\pi} - \mathbf{P} \cdot \mathbf{E}_c + \mathbf{P}_u \cdot \left(\frac{\mathbf{P}_u}{\alpha_u} - \mathbf{E} \right) \right\} dV \quad (15)$$

where the dot, $\cdot$, denotes the dot product of two vectors and where α_u is the polarizability for the U -type polarization. This can be expressed⁸ in terms of the static dielectric constants D_s and optical dielectric constant D_{op} (i.e., the square of the refractive index in the visible region of the spectrum, say):

$$4\pi\alpha_u = D_s - D_{op}. \quad (16)$$

For water as solvent, D_s and D_{op} equal 78.5 and about 1.8, respectively, at 25°C. The electrostatic contribution ΔF^* to the free energy of formation of the intermediate state X^* from the reactants may be found by subtracting from F^* the reversible work, W_{iso}^* , say, required to charge up the spheres when they are iso-

lated (i.e., far apart) in the dielectric medium.

$$\Delta F^* = F^* - W_{iso}^*. \quad (17)$$

Similarly, the electrostatic contribution to the free energy of formation of X from the products is F minus the work W_{iso} required to charge up the isolated products in the medium.

Before applying these considerations to the determination of the solvent polarization in the intermediate state, the restraint imposed by the fact that the states X^* and X have the same total energy and the same $\mathbf{P}_u(\mathbf{r})$ will be examined in greater detail.

Restraint Imposed upon the Activated Complex

As observed previously, the intermediate states X^* and X will have the same total energy. Again, two states which have the same set of atomic configurations will also have the same entropy term arising from their atomic motions. (The magnitude of this entropy term has been discussed elsewhere.⁸) In fact, their only difference in entropy will arise from a possible difference in the electronic degeneracy between the products and the reactants, and will be denoted by ΔS_e , say. If the product of the electronic degeneracies of each of the reactants is Ω^* and if that of the product is Ω , then ΔS_e is given by Eq. (18).

$$\Delta S_e = k \ln \Omega / \Omega^*. \quad (18)$$

Generally, ΔS_e will be equal to or essentially equal to zero.

Since the energies of the states X^* and X are the same and since their entropies only differ by an amount of ΔS_e , it is seen that the free energy difference between the two states is $-T\Delta S_e$.

A common type of electron transfer reaction is one in which no valence bonds are broken in the reaction sequence (1) to (3). In many reactions of this nature corresponding valence bonds in the products and in the reactants are probably not appreciably different in length, so that they do not have to be stretched or compressed in the formation of the intermediate state. This rephrases in part what was previously stated, namely that in the present paper we will consider a reactant in which all atoms within the sphere of radius a maintain their same relative positions throughout the reaction. It is reactions of this type which will be treated in the present paper. A treatment of reactions which also involve bond ruptures or other changes in bond lengths will be described later.

Because of this restriction the over-all standard free energy of formation of the products from the reactants can be written simply as the sum of three terms: the contribution $(F^* - W_{iso}^*)$ to the free energy of formation of the state X^* from the reactants, the free energy change accompanying the formation of X from X^* , which we have seen to be $-T\Delta S_e$, and the contribution to the free energy of formation of the products from the

state X , $-(F - W_{iso})$. There is one other term involved in the free energy of formation of X^* from the reactants, which is associated with the fact that in the state X^* , unlike the initial state in which the reactants are far apart, the relative motion of the centers of gravity of the two reactants is restricted. However, the corresponding free energy term, which is discussed later, is exactly canceled by a similar term in the free energy of formation of the products from the state X .

It may be concluded that the standard free energy of reaction ΔF^0 is given by Eq. (19).

$$\Delta F^0 = (F^* - W_{iso}^*) - T\Delta S_e - (F - W_{iso}). \quad (19)$$

The derivation of this equation is seen to include, and in fact to summarize quantitatively, the restraints imposed upon the two intermediate states.

Minimization of the Free Energy Subject to the Free Energy Restriction, Eq. (19)

It was observed in an earlier section that there are an infinite number of intermediate states X^* and X which could satisfy the free energy restriction given by Eq. (19), each pair having the previously stated charge distributions but a different vector point function, $\mathbf{P}_u(\mathbf{r})$. The problem is to determine that pair which has the maximum probability of formation from the reactants, i.e., to determine the pair (X^* and X) with minimum free energy, subject to the restraint on $\mathbf{P}_u(\mathbf{r})$ imposed by Eq. (19). To do this the variation of the free energy of the state X^* corresponding to a variation in the function $\mathbf{P}_u(\mathbf{r})$ is first computed. The computation is made at fixed charge distribution, so that the variation in $\mathbf{E}_c^*$, $\delta \mathbf{E}_c^*$, equals zero. The temperature is also held fixed. The only contribution to the free energy of formation of the state X^* from the reactants which can vary under these conditions is seen from Eq. (17) to be F^* . Computing δF^* from Eq. (14) we obtain

$$\delta F^* = \frac{1}{2} \int \left\{ -\delta \mathbf{P}^* \cdot \mathbf{E}_c^* + \frac{2\mathbf{P}_u}{\alpha_u} \cdot \delta \mathbf{P}_u - \mathbf{P}_u \cdot \delta \mathbf{E}^* - \mathbf{E}^* \cdot \delta \mathbf{P}_u \right\} dV. \quad (20)$$

The quantity $\delta \mathbf{P}^*$ which appears in Eq. (20) may be expressed in terms of $\delta \mathbf{P}_u$ and $\delta \mathbf{E}^*$ by introducing into this equation the analog of Eqs. (9) and (10) which obtains for state X^* ,

$$\mathbf{P}^*(\mathbf{r}) = \mathbf{P}_u(\mathbf{r}) + \alpha_u \mathbf{E}^*(\mathbf{r}). \quad (21)$$

We obtain in this manner,

$$\delta F^* = \frac{1}{2} \int \left\{ \left(-\mathbf{E}_c^* + \frac{2\mathbf{P}_u}{\alpha_u} - \mathbf{E}^* \right) \cdot \delta \mathbf{P}_u - (\alpha_u \mathbf{E}_c^* + \mathbf{P}_u) \cdot \delta \mathbf{E}^* \right\} dV. \quad (22)$$

The variations in $\mathbf{P}_u$ and $\mathbf{E}^*$ in this equation are not independent since the variation in $\mathbf{P}_u$ throughout the medium will affect the variation in $\mathbf{E}^*$ at any point. A relation between the integrals involving $\delta\mathbf{P}_u$ and $\delta\mathbf{E}^*$ has been developed elsewhere.⁸ Using this relation it has been shown in Eq. (40) of reference 8 that Eq. (22) of the present paper is equivalent to

$$\delta F^* = \int \left(\frac{\mathbf{P}_u}{\alpha_u} - \mathbf{E}^* \right) \cdot \delta \mathbf{P}_u(\mathbf{r}) dV. \quad (23)$$

The U -type polarization $\mathbf{P}_u(\mathbf{r})$ in the most probable pair of intermediate states X^* and X , is to be determined by setting δF^* equal to zero. Accordingly, this $\mathbf{P}_u(\mathbf{r})$ satisfies the relation,

$$\int \left(\frac{\mathbf{P}_u}{\alpha_u} - \mathbf{E}^* \right) \cdot \delta \mathbf{P}_u(\mathbf{r}) dV = 0. \quad (24)$$

In passing it is observed that if there were no restraints on $\delta\mathbf{P}_u(\mathbf{r})$ the quantity in parentheses in Eq. (24) would be everywhere equal to zero, since the integral itself must equal zero for all arbitrary variations, $\delta\mathbf{P}_u(\mathbf{r})$. That is, we would obtain, as expected, $\mathbf{P}_u(\mathbf{r}) = \alpha_u \mathbf{E}^*$, the equilibrium relation. However, in the present problem the variation $\delta\mathbf{P}_u(\mathbf{r})$ is to be performed subject to the restraint on $\mathbf{P}_u(\mathbf{r})$ expressed by Eq. (19). Since ΔF^0 , W_{iso}^* , ΔS_e , and W_{iso}^* of that equation are unaffected by a variation in $\mathbf{P}_u(\mathbf{r})$, the equation of restraint is also given by Eq. (25), obtained by taking variations of the terms in Eq. (19),

$$\delta F^* - \delta F = 0. \quad (25)$$

The variation δF^* is given by Eq. (23), and δF is given by a similar equation without the asterisks. Accordingly, we obtain

$$\delta F^* - \delta F = \int (\mathbf{E} - \mathbf{E}^*) \cdot \delta \mathbf{P}_u dV = 0. \quad (26)$$

Equations (24) and (26) are to be satisfied simultaneously. Multiplying the latter equation by a constant, the Lagrangian multiplier, m say, and adding these equations we have

$$\int \left\{ \frac{\mathbf{P}_u}{\alpha_u} - \mathbf{E}^* + (\mathbf{E} - \mathbf{E}^*)m \right\} \cdot \delta \mathbf{P}_u dV = 0. \quad (27)$$

This is an identity for all arbitrary variations of $\mathbf{P}_u$ in each volume element. Accordingly the expression in brackets is everywhere equal to zero and we have in each volume element,

$$\mathbf{P}_u = \alpha_u \{ \mathbf{E}^* + (\mathbf{E} - \mathbf{E}^*)m \}. \quad (28)$$

It is now desirable to express the field strengths $\mathbf{E}^*$ and $\mathbf{E}$ in terms of the quantities $\mathbf{E}_c^*$ and $\mathbf{E}_c$ since the latter can very easily be calculated from the known charge distributions. In the appendix it is shown that

using the usual assumptions made in treatment of ionic interactions we obtain for the present case

$$\mathbf{E}^* - \mathbf{E} = (\mathbf{E}_c^* - \mathbf{E}_c)/D_{0p} \quad (29)$$

and

$$\mathbf{E}^* = \frac{\mathbf{E}_c^*}{D_s} - m(\mathbf{E}_c^* - \mathbf{E}_c) \left(\frac{1}{D_{0p}} - \frac{1}{D_s} \right) \quad (30)$$

where the dielectric constants D_{0p} and D_s have been defined previously. With the aid of these equations, Eq. (28) for $\mathbf{P}_u$ becomes

$$\mathbf{P}_u(\mathbf{r}) = \alpha_u \left\{ \frac{\mathbf{E}_c^*}{D_s} - m(\mathbf{E}_c^* - \mathbf{E}_c) \left(\frac{1}{D_{0p}} - \frac{1}{D_s} \right) + \frac{m(\mathbf{E}_c^* - \mathbf{E}_c)}{D_{0p}} \right\}. \quad (31)$$

Introducing these equations for $\mathbf{E}^*$, $\mathbf{E}$, and $\mathbf{P}_u$ into Eq. (14) for the electrostatic free energy of state X^* , and into Eqs. (14) and (15) for $(F^* - F)$ we obtain

$$F^* = \frac{1}{8\pi} \int \left\{ \frac{\mathbf{E}_c^{*2}}{D_s} + m^2(\mathbf{E}_c^* - \mathbf{E}_c)^2 \left(\frac{1}{D_{0p}} - \frac{1}{D_s} \right) \right\} dV \quad (32)$$

and

$$\begin{aligned} F^* - F &= \frac{1}{8\pi} \int \left\{ \frac{\mathbf{E}_c^{*2} - \mathbf{E}_c^2}{D_s} \right. \\ &\quad \left. - (2m+1)(\mathbf{E}_c^* - \mathbf{E}_c)^2 \left(\frac{1}{D_{0p}} - \frac{1}{D_s} \right) \right\} dV \\ &= \Delta F^0 + T\Delta S_e + W_{iso}^* - W_{iso} \quad (33) \end{aligned}$$

where in the latter equation we have also introduced Eq. (19). Equation (33) serves to determine the Lagrangian multiplier, m .

In passing we observe that a special case of this equation obtains when the reacting ions differ only in their valency and when the electronic jump simply effectively exchanges the charges of these ions. In this case it is readily verified that the solution of this equation is $m = -\frac{1}{2}$: First, in the case ΔF^0 and ΔS_e are zero. Moreover W_{iso}^* and W_{iso} are equal, since the over-all reaction produces no net change in the numbers of each ionic species. For the same reason and by symmetry the integral involving $\mathbf{E}_c^{*2}$ equals that involving $\mathbf{E}_c^2$. Further, the integral in Eq. (33) involving $(\mathbf{E}_c - \mathbf{E}_c^*)^2$ must be positive. Introducing these results into Eq. (33) we see that m equals $-\frac{1}{2}$.

These equations for the electrostatic free energy F^* of the intermediate state X^* , and for the Lagrangian multiplier, m , will now be expressed in terms of the ionic charges and radii. We let the charges of the first reactant be e_1^* and e_1 in states X^* and X , respectively, and the corresponding charges of the second reactant will be denoted by e_2^* and e_2 . The radii of the saturated

dielectric spheres about these reactants, a_1 and a_2 , are, as previously stated, taken to be essentially unchanged by the reaction.

The vector $\mathbf{E}_c^*$ is the negative gradient of the potential which the reacting ions in state X^* would exert if they were in a vacuum rather than in a polarized medium. In a discussion elsewhere⁸ it has been observed that the potential tacitly used in the usual treatment of ionic interactions between ions of charges e_1 and e_2 in a vacuum is given by the following equations:

$$\left. \begin{aligned} \psi(r) &= \frac{e_1}{r_1} + \frac{e_2}{r_2}, & r_1 \geq a_1 \text{ and } r_2 \geq a_2 \\ \psi(r) &= \text{constant}, & r_1 < a_1 \text{ or } r_2 < a_2 \end{aligned} \right\} \quad (34)$$

where r_1 and r_2 are the distances of the field point $\mathbf{r}$ to the centers of these ions. The vector $\mathbf{E}_c$ is simply $-\nabla\psi$, ψ being given by these equations. Thus, we have

$$\left. \begin{aligned} \mathbf{E}_c &= -e_1 \nabla \frac{1}{r_1} - e_2 \nabla \frac{1}{r_2}, & r_1 \geq a_1 \text{ and } r_2 \geq a_2 \\ \mathbf{E}_c &= 0, & r_1 < a_1 \text{ or } r_2 < a_2 \end{aligned} \right\} \quad (35)$$

The vector $\mathbf{E}_c^*$ is obtained from $\mathbf{E}_c$ simply by replacing e_1 by e_1^* and e_2 by e_2^* .

These expressions for $\mathbf{E}_c$ and $\mathbf{E}_c^*$ are introduced into Eq. (32) for F^* and into Eq. (33) for the Lagrangian multiplier m , and the integrations are performed. The following integrals which are readily verified are used for this purpose:

$$\left. \begin{aligned} \int \nabla \frac{1}{r_1} \cdot \nabla \frac{1}{r_2} dV &= \frac{4\pi}{R} \\ \int \nabla \frac{1}{r_i} \cdot \nabla \frac{1}{r_i} dV &= \frac{4\pi}{a_i} \end{aligned} \right\} \quad (36)$$

where R is the distance between the centers of the ions, and where the integration volume excludes the volume physically occupied by the two ionic spheres (i.e., we have $r_1 \geq a_1$ and $r_2 \geq a_2$, simultaneously).

The work required to charge up conducting sphere of radius a in a dielectric medium is given by the well-known expression,¹² $e^2/2aD_s$, where e is the ionic charge. Accordingly W_{iso}^* and W_{iso} are given by

¹² E.g., if during some point of the charging process the ion has a charge q , then the potential at any point in the dielectric medium distant r from the center of the ion is $q/D_s r$. The potential at the surface of the sphere is $q/D_s a$. The work required to add an infinitesimal charge dq to the ion is therefore $(q/D_s a)dq$. Upon integrating this from $q=0$ to $q=e$, the total work required to charge up the ion is seen to be $e^2/2aD_s$. In passing it is observed that when one subtracts from this the work, $e^2/2a$, required to charge up the sphere in a vacuum ($D_s=1$), one obtains the usual expression for the contribution to free energy of solvation of an ion, $-(e^2/2a)(1-1/D_s)$, arising from the dielectric outside of the sphere. See reference 9.

Eq. (37).

$$\left. \begin{aligned} W_{iso}^* &= \frac{e_1^{*2}}{2a_1 D_s} + \frac{e_2^{*2}}{2a_2 D_s} \\ W_{iso} &= \frac{e_1^2}{2a_1 D_s} + \frac{e_2^2}{2a_2 D_s} \end{aligned} \right\} \quad (37)$$

With the aid of Eqs. (17), (32), (35), (36), and (37), we obtain for the contribution, ΔF^* , to the free energy of formation of the intermediate state X^* from the isolated reactants in the dielectric medium,

$$\Delta F^* = F^* - W_{iso}^* = \frac{e_1^* e_2^*}{RD_s} + m^2 (\Delta e)^2 \left(\frac{1}{2a_1} + \frac{1}{2a_2} - \frac{1}{R} \right) \left(\frac{1}{D_{0p}} - \frac{1}{D_s} \right) \quad (38)$$

where we have introduced the conservation of charge relation,

$$e_1^* - e_1 = -(e_2^* - e_2) = \Delta e, \text{ say.} \quad (39)$$

Similarly, with the aid of Eqs. (33), (35), (36), and (37), we obtain as the equation for m

$$\begin{aligned} -(2m+1)(\Delta e)^2 \left(\frac{1}{2a_1} + \frac{1}{2a_2} - \frac{1}{R} \right) \left(\frac{1}{D_{0p}} - \frac{1}{D_s} \right) \\ = \Delta F^0 + T\Delta S_s + \frac{e_1 e_2 - e_1^* e_2^*}{D_s R} \end{aligned} \quad (40)$$

where ΔS_s is given by Eq. (18).

The standard free energy of formation of the intermediate state X^* from the isolated reactants in the dielectric medium is the sum of ΔF^* and of a term describing the motion and positions of the centers of gravity of each of the two reactants in the initial state and in the state of the system, X^* . This contribution is evaluated in a later section.

Rate Constants of the Elementary Steps

(a) Estimation of k_{-1} and k_3

The rate constant k_{-1} is associated with the disappearance of the state of the system X^* to reform the reactants. There are several possible modes of decomposition and each of these will be considered.

The first mode involves an escape from the solvent cage. In the intermediate state, as in any collision complex in solution, the reactants may be considered to be in a solvent cage. Within this cage they vibrate with respect to each other, striking the cage walls about 10^{13} times a second. The chance that one of them will escape from the cage is α per collision with the walls of the cage. Accordingly, the unimolecular rate constant for this mode of dissociation would be about $10^{13}\alpha \text{ sec}^{-1}$ where α is less than one.

Another mechanism for the dissociation of X^* to reform the reactants is a disorganizing motion of the

solvent, destroying the polarization appropriate to the intermediate state. This state was treated as a macroscopic state in which the polarization was not in equilibrium with the charge distribution. Once this state is formed, it seems reasonable to suppose that a time of the order of magnitude of the relaxation time would be required for the system to assume some other, almost certainly unsuitable, value of the polarization function $P_u(r)$. The relaxation time for atomic polarization is of the order of 10^{-13} sec and that for orientation polarization is about 10^{-11} sec. The atomic polarization is associated with the polarized motion of the atoms in each solvent molecule and constitutes an appreciable fraction of the U -type polarization. If it reverts to an unsuitable value, the state X^* can be considered to be destroyed. The unimolecular rate constant for this mode of dissociation would therefore be about 10^{13} sec $^{-1}$. This is seen to be not less than that for the solvent cage escape mechanism, and therefore to correspond to a prevalent mode of decomposition.

Similar remarks apply to the rate constant k_3 for the dissociation of the other intermediate state, X , to products. Accordingly, we may write approximately

$$k_{-1} = k_3 = 10^{13} \text{ sec}^{-1}. \quad (41)$$

(b) *Estimation of k_1*

The equilibrium constant of reaction (1) is k_1/k_{-1} . The rate



constant k_1 will be calculated by estimating this equilibrium constant and using the value of k_{-1} determined in the previous section.

$$\frac{k_1}{k_{-1}} \cong \frac{(2\pi\langle m_1+m_2 \rangle kT/h^2)^{3/2} (V_f/V) (8\pi^2 \mu R^2 kT/h^2) \exp(-\Delta F^*/kT)}{(2\pi m_1 kT/h^2)^{3/2} (V_f/V) (2\pi m_2 kT/h^2)^{3/2} (V_f/V)} \quad (42)$$

Now k_{-1} is approximately equal to kT/h , since each is about equal to 10^{13} sec $^{-1}$. Introducing this into Eq. (42) we obtain after some cancellation

$$k_1 = (8\pi kT/\mu)^{1/2} R^2 (V/V_f) \exp(-\Delta F^*/kT) \quad (43)$$

where ΔF^* is given by Eq. (38). This expression for k_1 is simply the collision number in solution,¹³ Z , multiplied by $\exp(-\Delta F^*/kT)$. That is,

$$k_1 = Z \exp(-\Delta F^*/kT). \quad (44)$$

(c) *Estimation of k_2 and k_{-2}*

According to Eq. (2), the equilibrium constant for the interconversion of the intermediate states, X^* and X , is k_2/k_{-2} . As noted earlier the free energy difference of these states is $-T\Delta S_e$, where ΔS_e is given by Eq. (18). Accordingly, the equilibrium constant for Eq. (2)

Each of the two reactants have three translational degrees of freedom. In the intermediate state X^* , these six coordinates become three translational degrees of freedom of the center of gravity of the two reactants, two rotational degrees of freedom about this center of gravity, and one degree of freedom involving the vibration of the reactants with respect to each other in the solvent cage. The partition function for the three translational degrees of freedom of the first reactant in the solution is generally written on the basis of the free volume theory as

$$(2\pi m_1 kT/h^2)^{3/2} (V_f/N_1),$$

where V_f is the free volume and N_1 is the number of molecules or moles (depending on the units of the equilibrium constant) of reactant 1. The corresponding factors for reactant 2 and for the state X^* are obtained by replacing m_1 and N_1 by m_2 and N_2 , and by (m_1+m_2) and N_{X^*} , respectively. Actually to calculate the equilibrium constant, the values of the translational partition functions when the species are in their standard states are needed. That is, in these partition functions we set $N_1/V=1$, $N_2/V=1$, and $N_{X^*}/V=1$, the units determining those of the equilibrium constant. The rotational partition function is $8\pi^2 \mu R^2 kT/h^2$, μ being the reduced mass $m_1 m_2 / (m_1 + m_2)$ and R being the distance between the centers of gravity of the two reactants. The vibrational partition function for motion within the cage equals unity, within a factor of about three, say.

The remaining contribution to the standard free energy of formation of the intermediate state X^* from the reactants is ΔF^* , given by Eq. (38). Introducing these results into an expression for the equilibrium constant, we obtain

is given by

$$k_2/k_{-2} = \exp(\Delta S_e/k) = \Omega/\Omega^*. \quad (45)$$

In general this ratio will be approximately, or exactly, equal to unity.

The individual estimation of each of these constants k_2 and k_{-2} can be made assuming some model for the electronic jump process. This has been treated³ as an electron tunnelling process. On the basis of some approximate calculations the probability of an electron tunnelling through a barrier from one reactant to the other, κ_e , was estimated³ to depend exponentially, essentially, on the tunnelling distance, r_{ab} , i.e., $\kappa_e = \exp(-\beta r_{ab})$. According to the calculations given there, we find $\beta = 1.23 \text{ \AA}^{-1}$ for the ferrous-ferric isotopic exchange reaction in water, for example. We would expect this tunnelling distance to be about twice the diameter of a water molecule, i.e., 5.5 Å, since the small cations, ferrous and ferric, each have water molecules

¹³ E.g., A. A. Frost and R. G. Pearson, *Kinetics and Mechanism* (John Wiley and Sons, Inc., New York, 1953), Chap. 7.

strongly bound to them, and the innermost layer of them is presumably quite difficult to remove. We calculate that κ_e is 10^{-3} for this distance. However, the numerical value of β is to be regarded as quite tentative pending a more detailed treatment of the tunnelling process than is given in reference 3. For example, the effect of the water molecules on the extension in space of the electronic cloud of these ions is of particular interest.

The rate constant k_2 is κ_e multiplied by the number of times per second that the electron strikes the barrier. This number is presumably the frequency of motion of the valence electron in the ground state of the ferrous ion. This is of the order of the frequency of excitation of this electron to the next higher principal quantum number. From some data on the energy levels of the ferrous ion¹⁴ we estimate this to be about $2 \times 10^{15} \text{ sec}^{-1}$. Multiplying this by the value of κ_e , we obtain for k_2

$$k_2 \cong 2 \times 10^{12} \text{ sec}^{-1}. \quad (46)$$

Comparison with Eq. (41) shows that this is of the same order of magnitude of k_{-1} , within the error of the calculations.

Validity of the Assumed Small-Overlap Activated Complex

These calculations of k_2 , k_{-2} , k_3 , and k_{-1} , and hence of the lifetimes of each of the intermediate states X^* and X , can be used to examine more closely the basic assumption of this paper, namely, the assumption that some electron transfer reactions, at least, will have a small-overlap activated complex. The calculations can also be used to examine the relation of this complex to the large-overlap one.

A consequence of the assumption of the small-overlap activated complex was⁶ the statement that the energies of the two states X^* and X were equal. Any limitation of this statement is a limitation on the assumption of a small-overlap activated complex. A limitation exists in the form of the uncertainty principle. The energy of any state, X^* , is broadened by an amount $\Delta\epsilon$ which is related to the lifetime τ of that state according to the uncertainty principle, $\Delta\epsilon \cdot \tau = h/4\pi$. *The greater the overlap the shorter will be the lifetimes of X^* and of X .* The lifetime of the state X^* , for example, is about equal to $1/(k_2 + k_{-1})^{-1}$. (It is essentially, therefore, the same as that of the state X .) If τ is about 10^{-13} sec then $\Delta\epsilon$ is found to be about $0.075 \text{ kcal mole}^{-1}$. Thus the energy restriction, summarized by Eq. (19), would have to be modified to state that the energies of the states X^* and X must be equal only within an amount prescribed by the uncertainty principle. This amount would be $2\Delta\epsilon$ or $0.15 \text{ kcal mole}^{-1}$ if $\tau = 10^{-13} \text{ sec}$. Thus, in Eq. (19) which was derived on the basis of the exact equality of energies of X^* and X , we should really replace ΔF^0 ,

say, by $\Delta F^0 \pm 0.15 \text{ kcal mole}^{-1}$. However, this is a negligible correction, and it is evident that this can readily be verified to have a negligible effect on the calculated value of ΔF^* . Even if the lifetimes of the individual states X^* and X were, as a result of large values of k_2 and k_{-2} , as small as 10^{-14} sec , $2\Delta\epsilon$ would be only $1.5 \text{ kcal mole}^{-1}$ and this again would only have a relatively small effect on the calculated value of ΔF^* . On the other hand in a large-overlap activated complex the frequency with which one electronic configuration would be formed from the other would be the order of the electronic frequencies in molecules. These frequencies are about 10^{15} sec^{-1} . Thus τ would be about 10^{-16} sec and $2\Delta\epsilon$ would have the large value of $15 \text{ kcal mole}^{-1}$. The restriction involved in Eq. (19) would no longer be very strong, since ΔF^0 would have to be replaced by $\Delta F^0 \pm 15 \text{ kcal mole}^{-1}$.

In summary, if the overlap of the electronic orbitals of the two reactants is such that the lifetimes of the two intermediate states are greater than 10^{-14} sec , say, we have a small-overlap activated complex. On the basis of the calculations of k_3 and of k_2 given previously we infer that a small-overlap activated complex may well prevail for many electron transfer reactions.

The Over-All Bimolecular Rate Constant

We have seen that k_{-1} is essentially equal to k_3 , according to Eq. (41), and k_2 is essentially the same as k_{-2} . Therefore, when k_2 and k_{-1} are of the same order of magnitude, it follows from Eq. (7) for the over-all bimolecular rate constant, k_{bi} , that

$$k_{bi} \cong k_1 = Z \exp(-\Delta F^*/kT) \quad (47)$$

where we have introduced Eq. (44) for k_1 , Z being the collision number in solution. If k_2 were appreciably less than k_{-1} , this approximation would tend to break down, and the more exact expression for k_{bi} , given by Eq. (7), would have to be employed. The calculations of k_2 and k_{-1} given previously tentatively support the approximate equation, and some success has been obtained in correlating experimental and theoretical results on the basis of this equation.

If k_2 were about five-fold smaller than k_{-1} , say, then according to Eq. (7) and the earlier discussion the approximate equation for k_{bi} , Eq. (47), should be divided by a factor of seven. However, this constitutes a relatively minor correction.

The Interionic Distance, R

The interionic distance, R , in the pair of intermediate states, X^*X , can affect the over-all reaction rate in several ways. For example, the rate of the electronic jump process, reaction (2), decreases exponentially with increasing R . It was seen that when the rate constant of this step, k_2 , was greater than or about equal to 10^{13} sec^{-1} , the over-all reaction rate was independent of k_2 . However, for larger R 's, k_2 will become small and

¹⁴ C. E. Moore, *Atomic Energy Levels* (National Bureau of Standards, 1952), circular 467, Vol. II.

will then affect the magnitude of the over-all rate. Accordingly, the exponential decrease of the rate of the electronic jump process with increasing R is one of the main factors tending to make R a minimum in the intermediate states, X^* and X .

The size of the interionic distance will also affect the over-all reaction rate through its effect on ΔF^* . For example when the ions come closer together, the solvation atmospheres about each ion tend to overlap and to become more similar. Accordingly when a major barrier to reaction lies in the difference of the solvation atmospheres about the reactants, the reaction will occur most readily when these atmospheres are most similar, that is, when the interionic distance R is least. This may also be verified from Eq. (38) for ΔF^* ; when the major barrier to reaction lies in the difference of the solvation atmospheres about the reactants, the second term in that equation is greater than the first term, the Coulombic repulsion. It is seen that the second term decreases as R decreases.

The most appropriate value of R is to be found by maximizing with respect to R Eq. (7) for the over-all rate constant. However, the present limitations of our quantitative knowledge of the electronic jump process make this procedure have doubtful utility. For the present it appears reasonable to suppose that the most suitable value of R is the minimum value. A first approximation to R is therefore the sum of the radii of the two reactants, $a_1 + a_2$.

The Radius, a

The radius a appears in the expression for ΔF^* and therefore in the rate constant k_1 for the formation of the intermediate state X^* . As previously stated, this radius is that of a sphere about the reactant inside of which the dielectric is saturated and outside of which it is assumed to be unsaturated. In this section some tentative suggestions for such radii will be discussed.

As a first approximation it has been assumed for monatomic ions that the innermost layer of solvent is dielectrically saturated.⁹ Accordingly, for such ions the radius a is the sum of the crystallographic radius of the ion plus the diameter of a water molecule.^{9b,c,d} A similar assumption was also used in a recent theoretical treatment of the spectra of halide ions in water.¹¹ Some recent work on the dielectric constant of aqueous ionic salt solutions appears to indicate, however, that the solvent is less saturated in the vicinity of anions¹⁵ than in the vicinity of cations and this should be taken into account. An interesting explanation for this was given in terms of the difference in freedom of a water molecule, in the innermost solvation layer about an ion, to rotate when the ion is a cation and when it is an anion.^{15,16}

Some special circumstances which may occur when a monatomic ion loses its charge completely during an electron transfer process will be discussed in Part III of this series of papers.

The dielectric saturation in the vicinity of many polyatomic ions would be expected to be much less than that near monatomic ions, because of their larger size: the orienting electric field arising from the ionic charge is responsible for the saturation and varies roughly as the inverse square of the distance from the center of the ion. It seems reasonable to assume as a first approximation for polyatomic ions such as MnO_4^- and $\text{Fe}(\text{CN})_6^{3-}$, that the radius a is simply equal to the crystallographic radius of the ion in each case. In fact this is consistent with the assumption that only the first solvation layer of monatomic ions is saturated. The size of a hydrated monatomic cation is about the same as that of one of these polyatomic ions.

APPENDIX

In this appendix, Eqs. (29) and (30), expressing E and E^* in terms of E_c and E_c^* , will be established.

As discussed previously,⁸ the usual treatment of the interaction of ions in a dielectric medium leads to an especially simple relation between the electric field strengths exerted by the ions in a dielectric medium, $E^\dagger$ and in a vacuum, $E_c^\dagger$. According to Eq. (53) of reference 8 this relation is¹⁷

$$E^\dagger(\mathbf{r}) = E_c^\dagger(\mathbf{r}) / (1 + 4\pi\alpha) \quad (48)$$

where α is the polarizability of the dielectric medium and where we have used the superscript $\dagger$, to avoid possible confusion with later substitutions which will be made in this equation. This relation will be used in order to establish Eqs. (29) and (30).

In Eq. (12) of the present paper an expression has been given for the potential at any point in a medium for any state whether it is in equilibrium or not. The potential $\psi^*(\mathbf{r}')$ at each point $\mathbf{r}'$ in the state of the system X^* may be obtained from this equation simply by adding an asterisk to each symbol. Subtracting the resulting equation from Eq. (12), which incidentally can be regarded as the potential in the intermediate state X , we obtain as the difference of potential at the point $\mathbf{r}'$ in these two states,

$$\begin{aligned} \psi(\mathbf{r}') - \psi^*(\mathbf{r}') \\ = \int \left\{ \mathbf{P} - \mathbf{P}^* - \left(\frac{E_c - E_c^*}{4\pi} \right) \right\} \cdot \nabla \frac{1}{|\mathbf{r} - \mathbf{r}'|} dV. \end{aligned} \quad (49)$$

Now, subtracting Eq. (9) for $\mathbf{P}$ from a corresponding equation for $\mathbf{P}^*$ we have

$$\mathbf{P} - \mathbf{P}^* = \mathbf{P}_c + \mathbf{P}_u - (\mathbf{P}_c^* + \mathbf{P}_u) \quad (50)$$

¹⁷ Equation (48) of the present paper may be obtained from Eq. (53) of reference 8 by observing that in that equation, (a) $E = -\nabla\psi$, (b) $D = 1 + 4\pi\alpha$, (c) E_c is the value of E when $D = 1$ (vacuum).

¹⁵ Hasted, Ritson, and Collie, *J. Chem. Phys.* **16**, 1 (1948).

¹⁶ See D. H. Everett and C. A. Coulson, *Trans. Faraday Soc.* **36**, 633 (1940).