EXCHANGE REACTIONS AND ELECTRON TRANSFER REACTIONS INCLUDING ISOTOPIC EXCHANGE

THEORY OF OXIDATION-REDUCTION REACTIONS INVOLVING ELECTRON TRANSFER

PART 4.—A STATISTICAL-MECHANICAL BASIS FOR TREATING CONTRIBUTIONS FROM SOLVENT, LIGANDS, AND INERT SALT

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The mechanism for electron transfer is discussed in terms of an atomic motion on a potential-energy surface in many-dimensional atomic configuration space. In the absence of electronic coupling between the reactants, a surface for the reactants intersects one for the products. Electronic coupling causes the usual removal of this degeneracy and permits the products to be formed adiabatically or nonadiabatically by an atomic motion across the " intersection " surface.

The properties of a system on this latter surface are formulated in terms of statistical mechanics, in order to treat in a consistent manner the ligands microscopically and the exterior solvent macroscopically. A concept of " equivalent equilibrium distribution " is introduced to evaluate the surface integral. A macroscopic quantity is invoked only in the last step of the derivation, replacing its statistical-mechanical equivalent.

A relatively simple expression is obtained thereby for the reaction rate, which reduces to that obtained in part 1 when ligand and salt contributions are omitted. Applications can be made to a number of problems, such as prediction of non-isotopic electron-transfer rates from isotopic ones, relation between chemical and electrochemical electron transfers inert salt effects and possibility of an inverted chemical effect.

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1. INTRODUCTION

In a recent series of papers, the writer has formulated and applied a quantitative theory of the rates of electron transfers in solution.[1-3] In that work the need for reorganization of configuration of the solvent molecules before and after electron transfer was discussed. The free energy of solvent reorganization was then computed using a macroscopic treatment [4] for such a system having " non-equilibrium dielectric polarization ".

In some electron transfers there are also changes in distances in the co-ordination shell as well (cf. ref. (5)-(7)). Clearly, this contribution needs to be estimated in microscopic terms. In order to include both contributions in a consistent manner, we first formulate the entire discussion of the reaction rate in terms of statistical mechanics and only in the last step we replace, for ease of calculation, one of the quantities by its macroscopic equivalent.

2. MANY-DIMENSIONAL POTENTIAL ENERGY SURFACES

(i) NO ELECTRONIC INTERACTION

In discussions of electron transfer, problems which have frequently arisen and have occasioned some uncertainty and confusion concern the charge distribution

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in the transition state, the mode of calculating its interaction with surrounding molecules, and the mechanism of the electron transfer itself. To treat these problems, we first consider a hypothetical case where no electronic coupling between the redox orbitals of the reactants occurs, so that no electron transfer is possible. To anticipate, conclusions reached in § 2 include those reached somewhat more intuitively in part 1 (cf. ref. (8).

In this case, we have two distinctly different electronic states—one having the electronic structure of the reactants, the other having that of the products. The lowest electronic state of each chemical pair has its own potential-energy surface in a many-dimensional atomic configuration space, whose co-ordinates are those of all the atoms of the two reactants, of the solvent, and of any electrolyte.

The two surfaces each have their own valleys but the two sets of valleys occur in quite different regions of the space, reflecting differences in stable bond lengths, solvent orientations, etc. The surfaces intersect, usually along some upper reaches of each, and form thereby a surface of one less degree of freedom. A cross-section of the surfaces and of their intersection is indicated in fig. 1.
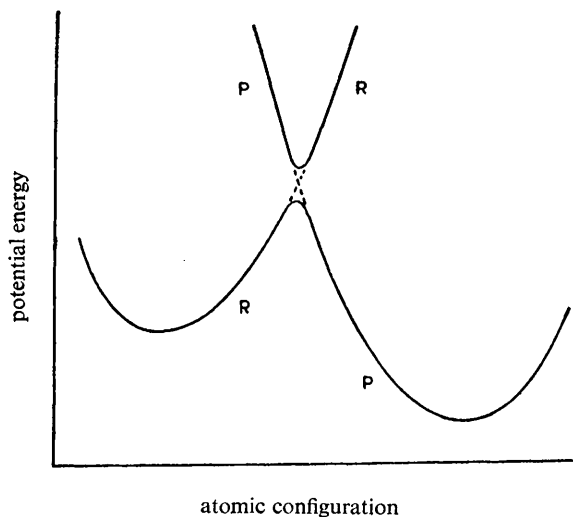

atomic configuration

FIG. 1.—Profile of N-dimensional potential energy surfaces plotted against an atomic configurational co-ordinate of the entire system. Curve R denotes reactants ($ox_1 + red_2$) ; curve P, products ($red_1 + ox_2$). Dotted lines show intersection of surfaces (zero electronic interaction case) and solid lines indicate the splitting for the case of weak interaction.

The intersection surface can be reached by any suitable fluctuation of atomic co-ordinates to produce some atomic configuration which is usually a compromise between the stabler ones of the two electronic states. Because of the absence of electronic interaction of the redox orbitals, such a fluctuation does not cause any electron transfer. The system merely stays on the surface corresponding to the original electronic configuration on passing through the intersection. Fluctuations of this nature involve simultaneous changes in orientation, position and atomic polarization of the solvent molecules, in internuclear distances in the co-ordination shell, in relative motion of the reactants and in configuration of the ionic atmosphere.

(ii) ADIABATIC AND NON-ADIABATIC MECHANISMS FOR ELECTRON TRANSFER

Consider next the weak electronic interaction between the redox orbitals which occurs, for example, when the reactants are not too far apart. Their interaction leads to the usual splitting of the surfaces, as indicated in fig. 1.

For sufficient electronic interaction, a system passing across the intersection during a fluctuation will always stay on the lowest surface. We see from fig. 1, therefore, that the products have been formed from the reactants adiabatically (in the quantum-mechanical sense) as a result of this atomic motion. This motion, then, is one which produces an atomic configuration of the system more favourable to the electronic charge distribution of the products.

When the electronic interaction is extremely weak, on the other hand, for example when the reactants are far apart, the system tends to retain its original electronic configuration on passing across the intersection, i.e., the system " jumps " to the upper surface at such times and jumps back on its return. Each time no electron transfer tends to occur. There is, nevertheless, in such cases a small probability of " transition ". For this system, we have thereby a " non-adiabatic " mechanism for electron transfer.

As long as the interaction is not too strong, the splitting is relatively small, and little error is made in regarding the correct potential energy at the " intersection " surface as being essentially equal to that for the zero-interaction system. *Thus, both the potential energy and the probability distribution on the intersection surface can be computed for the weak interaction system by the simple expedient of regarding the system as being the conceptually simpler zero-interaction one.* Moreover, it may be emphasized here that in the computation, the charge distribution for the *zero-interaction* case should be used. It is the one for the reactants (or products) and not some compromise.

In both cases, adiabatic and non-adiabatic, it is necessary for the system to pass through the intersection surface. In the first approximation the theoretical rate expression deduced below for the adiabatic mechanism will apply to a non-adiabatic one if, in the latter case, it is multiplied by some factor denoting an average transition probability per passage through the intersection region. (Nuclear tunnelling through the barrier in fig. 1 is neglected here in both cases.)

3. Quantitative formulation of the theory

(i) Equations for rate and for intersection surface

We shall use an equation for rate of passage through a surface in many-dimensional space, in our case the intersection surface. It is similar to the usual transition state theory equation (e.g. ref. (9) and unpublished results). If $\Delta F^{\ddagger}$ denotes the difference in free energy of the reactants when they are constrained to exist on this $(N-1)$ dimensional surface as compared with their existing in all atomic configurations, the rate constant, k_r, is

$$\dot{k}_r = (kT/h) \exp(-\Delta F^{\ddagger}/kT). \tag{3.1.1}$$

For defining the intersection surface in terms of molecular properties, we introduce the following notation :

$k =$ any atomic configuration of the entire system in N-dimensional space,
$p =$ superscript to designate throughout a property of the products (a change of notation from part 1),
$\mathscr{E}_k =$ potential energy of reactants in configuration k,
$\Delta\mathscr{E} =$ difference between electronic energy of the lowest electronic state of the products and that of the reactants when each is at its own zero of potential energy.

Since the electronic energies of the reactants and products are equal along the intersection surface, the latter obeys the relation,

$$\mathscr{E}_k = \mathscr{E}_k^p + \Delta\mathscr{E} \tag{3.1.2}$$

at the intersection.

The potential energy of the reactants on the intersection surface, $\mathscr{E}_k^{\ddagger}$, say, equals $\mathscr{E}_k$ and because of (3.1.2) could also be written as

$$\mathscr{E}_k^{\ddagger} = \mathscr{E}_k + m(\mathscr{E}_k - \mathscr{E}_k^{\,p}) - m\Delta\mathscr{E}, \qquad (3.1.3)$$

where m is any constant. The usefulness of (3.1.3) will be shown in § 3.4.

(ii) POTENTIAL-ENERGY EXPRESSION

We assume that the potential energy of the reactants is essentially the sum of two contributions:

$$\mathscr{E}_k = \mathscr{E}_{k^i} + \mathscr{E}_{k^\circ} \qquad (3.2.1)$$

where $\mathscr{E}_{k^i}$ depends on the internal co-ordinates, k^i, of the co-ordination shells alone ($\mathscr{E}_{k^i}$ being defined as zero at the equilibrium values of these co-ordinates), and $\mathscr{E}_{k^\circ}$ depends on all other co-ordinates, k°, of the entire system. Thus, k, the totality of all co-ordinates,* is an abbreviation for k^i plus k° (" inner " and " outer ").

We treat the jth particle as possessing a permanent dipole moment μ_j, an isotropic polarizability α_j, and a charge e_j, some of which may be zero. We introduce the following additional notation:

$\mathbf{E}$ = electric field strength at any point, arising from all the ionic charges and from the permanent and induced dipoles.

ϕ = potential arising directly from all ionic charges = $\Sigma_j e_j / r_j$.

$\mathbf{D}$ = contribution to $\mathbf{E}$ arising solely from the charges. $\mathbf{D} = -\nabla\phi$.

$\mathbf{D}_\mu$ = contribution to $\mathbf{E}$ arising solely from the permanent dipoles.

Ω_{k° = van der Waals' potential energy of interaction of all the particles (repulsive, dispersive, permanent dipole-dipole). Ω_{k° is taken to depend only on k°, i.e. $\Omega_{k^{\bar\circ}} = \Omega_{k^\circ}^p$.

j = subscript to also denote fields at particle j, minus the latter's contribution.

It can then readily be shown that $\mathscr{E}_{k^\circ}$ is given by

$$\mathscr{E}_{k^\circ} = \Omega_{k^\circ} + \Sigma_j(e_j\phi_j/2 - \mu_j \cdot \mathbf{D}_j - \alpha_j\mathbf{E}_j \cdot (\mathbf{D}_j + \mathbf{D}_{\mu j})/2). \qquad (3.2.2)$$

To establish (3.2.2), arguments related to those in appendix IV of ref. (4) may be used (cf. ref. (10)). The second term is the interaction between the charges. The third is that between the charges and the permanent dipoles. The remainder is a composite one. It includes ion-induced dipole interactions, $-\Sigma_j\alpha_j\mathbf{E}_j \cdot \mathbf{D}_j$; an induced-permanent dipole term, $-\Sigma_j\alpha_j\mathbf{E}_j \cdot \mathbf{D}_{\mu j}$; induced-induced, $-\frac{1}{2}\Sigma_j\alpha_j\mathbf{E}_j \cdot (\mathbf{E}_j - \mathbf{D}_j - \mathbf{D}_{\mu j})$; and the energy stored up in the induced dipoles $\Sigma_j\alpha_j\mathbf{E}_j^2/2$. The Ω_{k° term includes the permanent dipole-dipole term, $-\Sigma_j\mu_j \cdot \mathbf{D}_{\mu j}/2$.

$\mathbf{E}_j$ obeys the relation:

$$\mathbf{E}_j = \mathbf{D}_j + \mathbf{D}_{\mu j} - \nabla_j \sum_{m \neq j} \alpha_m\mathbf{E}_m \cdot \nabla_m\frac{1}{r_{jm}}. \qquad (3.2.3)$$

(Cf. ref. (11) for non-polar and ref. (10) for polar molecules between parallel electrodes in a non-electrolyte system.) Unlike the D in ref. (11), say, ours is not the dielectric displacement, a quantity with little molecular significance here, but is the microscopic equivalent of $^4\mathbf{E}_c^*$).

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* There would be no real loss of generality if one now omitted from k°, k and further consideration those co-ordinates whose behaviour is entirely the same in each of the two electronic states (e.g. some solvent vibrations).

(iii) POTENTIAL ENERGY FOR TRANSITION STATE

Introducing the above quantities into (3.1.3), an expression is obtained for $\mathscr{E}_k^\ddagger$ which simplifies considerably when the linearity property of (3.2.3) is applied.* We obtain

$$\mathscr{E}_k^\ddagger = \mathscr{E}_{k^i}^+ + \mathscr{E}_{k^\circ}^+ + C, \tag{3.3.1}$$

where

$$\mathscr{E}_{k^\circ}^+ = \Omega_{k^\circ} + \Sigma_j[e_j^+\phi_j^+/2 - \mu_j \cdot \mathbf{D}_j^+ - \alpha_j\mathbf{E}_j^+ \cdot (\mathbf{D}_j^+ + \mathbf{D}_{\mu j})/2]. \tag{3.3.2}$$

ϕ_j^+, $\mathbf{D}_j^+$, $\mathbf{E}_j^+$ and $\mathscr{E}_{ki}^+$ are abbreviations for functions of the type

$$X^+ = X + m(X - X^p); \tag{3.3.3}$$

$$C = m(m+1)\Sigma_j[\alpha_j(\mathbf{E}_j - \mathbf{E}_j^p) \cdot (\mathbf{D}_j - \mathbf{D}_j^p) + (e_j - e_j^p)(\phi_j - \phi_j^p)/2] - m\Delta\mathscr{E}. \tag{3.3.4}$$

C depends essentially only on the positions of the two reacting species : for $\mathbf{D}_j - \mathbf{D}_j^p$ and related factors depend only on these co-ordinates, while $\mathbf{E}_j - \mathbf{E}_j^p$ is independent of molecular orientations and of positions of atmospheric ions. Because a liquid is closely packed, the energy term involving $\mathbf{E}_j - \mathbf{E}_j^p$ can be taken as effectively independent of the much less important variables, the positions of the solvent molecules.

(iv) EQUIVALENT EQUILIBRIUM DISTRIBUTION (e.e.d.) :

It is instructive, for evaluating $\Delta F^\ddagger$, to first compare the transition state, in which exp $(-\mathscr{E}_k^\ddagger/kT)$ is integrated over the intersection surface, with a state in which this factor is integrated over all of space. We shall term the configurational distribution of the latter state the " equivalent equilibrium distribution " (e.e.d.).

Comparison of (3.3.1) with (3.2.1.) and of (3.3.2) with (3.2.2) reveals that the e.e.d. is one which would be obtained in a corresponding *equilibrium* system in which the charges on the two central ions were e_n^+, i.e. $e_n + m(e_n - e_n^p)$, $(n = 1, 2)$, and which had $\mathscr{E}_{ki}^+$ as a potential function for the co-ordination shell.

The transition state of the zero-interaction system differs from this system in only two respects : the charges of the two central ions are those of the reactants, and it has one less dimension of freedom than an N-dimensional system.

4. EVALUATION OF THE REACTION RATE CONSTANT

(i) GENERAL

For exact evaluation of the surface integral, we should examine in detail the motion along the surface, for example, by examining the atomic motion normal to it, i.e., the reaction co-ordinate. We hope to analyze this dynamical problem at a later date. For the present, we use instead the following procedure.

By a suitable choice of m (see § 4.4. and appendix 1), the e.e.d. is made to centre on the intersection surface, and thereby to die away fairly rapidly along the normal. Since (3.3.1) applies both to e.e.d. and to the transition state, we may then set the surface integral over exp $(-\mathscr{E}_k^\ddagger/kT)$ equal to the volume integral for the e.e.d., divided by a partition function along the normal, as found in appendix 1. (If some of the motions along the surface are quantized, this statement could be expressed

* For any given j and k°, $\mathbf{E}_j$ is the same function of the $\mathbf{D}_m + \mathbf{D}_{\mu m}$ as $\mathbf{E}_j^p$ is of the $\mathbf{D}_m^p + \mathbf{D}_{\mu m}$ and as $\mathbf{E}_m - \mathbf{E}_m^p$ is of the $\mathbf{D}_m - \mathbf{D}^p$. This relationship becomes evident when the n simultaneous vector eqn. (3.2.3) are written in matrix form and inverted to obtain a formal explicit expression for the matrix of E_js. (The procedure is analogous to that employed in eqn. (4) of ref. (10) for a simpler system.) A similar procedure is then used to obtain E_j^p and, by subtraction, $E_j - E_j^p$.

in terms of equating corresponding free energies of the two systems.) Most of the likely motions along the normal to the transition state surface, such as some of those mentioned in § 2.1 have a "frequency" of motion of about 10^{13} sec^{-1}. We anticipate, therefore, that the partition function just noted, which may be written as kT/hv, will be of the order of unity, and that the procedure just outlined makes the rate constant uncertain only by a small numerical factor.

(ii) APPLICATION OF e.e.d.

The e.e.d. was seen to have "inner" co-ordinates which behave as though the potential function were $\mathscr{E}_{ki}^{+}$ (or as we shall now denote it, $\mathscr{E}_{kl}^{\ddagger}$). Let the latter's minimum relative to the zero of $\mathscr{E}_k i$ be called $\Delta\mathscr{E}_i^{\ddagger}$ and the corresponding vibrational energy levels be $\mathscr{E}_v^{\ddagger}$ (totality of quantum numbers, v). Let F denote the free energy of the reactants.

Using (3.3.1.) we then deduce for $\Delta F^{\ddagger}$:

$$\exp\left(-\Delta F^{\ddagger}/kT\right) = \frac{\exp\left(F/kT\right)}{h^{N_0}} \int \cdot \cdot \int_{v=0}^{\infty} \sum \exp\left[-(\mathscr{E}_v^{\ddagger} + \Delta\mathscr{E}_i^{\ddagger}\right.$$
$$\left. + \mathscr{E}_{k^o}^{\ddagger} + C + K)/kT\right]\mathrm{d}\tau_0, \qquad (4.2.1)$$

where K is the kinetic energy of the N_0 outer co-ordinates and $\mathrm{d}\tau_0$ is their volume element in phase space. Summation over all v immediately yields the vibrational partition function, $Q_{\mathrm{vib}}^{\ddagger}$, for the inner co-ordinates, and integration over the N_0 momenta cancels a corresponding momentum integral in an expression for F (as does the h^{N_0} factor). The residual integrand depends only on the relative "outer" co-ordinates (position and orientational) of all the particles. We next hold all of these relative co-ordinates fixed within two fairly large spheres, one about each central ion (large enough so that the long range ion-ion-solvent interactions are negligible on their surfaces). We then integrate over the co-ordinates of the centre of gravity of these two ions and over the orientations of their line of centres, translating and rotating, respectively, the entire system within the large spheres to ensure constancy of the important relative co-ordinates during integration. Holding the distance r between the ions fixed, we next integrate over all other outer co-ordinates, the integral being denoted later by $\exp\left(-F_0^{\ddagger}(r)/kT\right)$. In integrating finally over r, we first note two factors which favour small rs in spite of any coulombic repulsion: the solvent reorganization barrier is smaller there (cf. below) and, at the larger rs, the electronic interaction becomes so weak that out there the integral should be multiplied by some small non-adiabatic transition probability. We presumably err relatively little if we simply take r as the distance of closest approach and set the corresponding r-partition function equal to unity, i.e. $kT/hv_r{\sim}1$ (cf. also § 4.1). We obtain after some cancellation:

$$k_r = Z \exp\left[-(\Delta F_i^{\ddagger} + \Delta F_0^{\ddagger})/kT\right], \qquad (4.2.2)$$

where

$$\Delta F_i^{\ddagger} = \Delta\mathscr{E}_i^{\ddagger} - kT \ln Q_{\mathrm{vib}}^{\ddagger}/Q_{\mathrm{vib}}, \qquad (4.2.3)$$

$$\Delta F_0^{\ddagger} + F_0 = F_0^{\ddagger}(r) = -kT \ln \int \cdot \cdot \int \exp\left(-\mathscr{E}_{k^o}^{\ddagger}/kT\right)\mathrm{d}k_0'. \qquad (4.2.4)$$

In these equations, Q_{vib}, the vibrational partition function of the inner co-ordinates of the reactants, was extracted from F: $F_0^{\ddagger}(r)$ is the configurational free energy of the reactants due to all ion-solvent-ion interactions in (3.2.4), at fixed positions of the central ions; $\mathrm{d}k_0'$ is the configuration volume element of the remaining $(N-6)$ outer co-ordinates. Z is the same as the usual collision frequency of two non-polar molecules in solution (probably about 10^{11} l./mole sec rather than the value suggested in ref. (2) and (12)).

(iii) Evaluation of $\Delta F_0^{\ddagger}$ and $\Delta F_i^{\ddagger}$

It follows from § 3.4 that (4.2.4) for $F_0^{\ddagger}(r)$ is simply the free energy of a system having the charges of the reactants a distance r apart but a distribution of orientations of solvent molecules and of positions of ions in the ionic atmosphere which would be in equilibrium with the hypothetical charges, $e_n + m(e_n - e_n^p)$, $(n = 1, 2)$, on the two central ions. It is at this point that we introduce the macroscopic expression [4] for the free energy of this type of non-equilibrium system. We obtain *

$$\Delta F_0^{\ddagger} = w + m^2 \lambda, \tag{4.3.3}$$

$$\lambda = (\Delta e)^2 \left(\frac{1}{2a_1} + \frac{1}{2a_2} - \frac{1}{r} \right) \left(\frac{1}{n^2} - \frac{1}{D_s} \right), \tag{4.3.4}$$

where w is the coulombic work required to bring the reactants together at the prevailing salt concentrations and equals $e_1 e_2 / D_s r$ at infinite dilution; Δe is the charge transferred; a_1 and a_2 are the ionic radii of the ions (including their co-ordination shells); we take $r = a_1 + a_2$; n and D_s are the refractive index and static dielectric constant, respectively.

We evaluate the contributions to $\Delta F_i^{\ddagger}$ when the vibrations are harmonic, the anharmonic values being somewhat more complex. If q_s denotes a bond co-ordinate of the reactants, having equilibrium value q_s° and force constant K_s, we have

$$\mathscr{E}_{k_i} = \Sigma_s K_s (q_s - q_s^{\circ})^2 / 2. \tag{4.3.5}$$

Upon finding the minimum of $\mathscr{E}_{k_i}^{\ddagger}$ and evaluating $\partial \mathscr{E}_{k_i}^{\ddagger} / \partial q_s$ there (at $q_s^{\ddagger}$), we deduce for the transition state:

$$q_s^{\circ \ddagger} = [(m+1)K_s q_s^{\circ} - m K_s^p q_s^{\circ}] K_s^{\ddagger}, \tag{4.3.6}$$

$$K_s^{\ddagger} = (m+1)K_s - m K_s^p, \tag{4.3.7}$$

$$\Delta \mathscr{E}_i^{\ddagger} = (m^2/2) \Sigma_s K_s (\Delta q_s^{\circ})^2 (K_s^p / K_i^{\ddagger})^2, \tag{4.3.8}$$

where

$$\Delta q_s^{\circ} = q_s^{\circ p} - q_s^{\circ}.$$

In appendix 2, these equations are obtained approximately for a normal co-ordinate treatment, the $q_s - q_s^{\circ}$ then becoming normal co-ordinates and the $\sqrt{K_s}/2\pi$ becoming vibration frequencies of the normal modes.

(iv) Equation for m

The equation for m is obtained by equating the difference between free energies of activation for the forward and reverse reactions to the standard free energy of reaction at the prevailing electrolyte concentration, $\Delta F^{\circ\prime}$. In the process, we tacitly set the free energy of the reactants on the intersection surface equal to that of the products there (by making both equal $F_i^{\ddagger}$) and so satisfy the energy condition (A1) in appendix 1, since the entropies of two systems similarly distributed on the

* Eqn. (25) and (25a) of ref. (4) were used in conjunction with certain macroscopic properties ($\mathbf{P}_u$ and c_i) of the e.c.d. system. Two minor approximations were made: " image effects " were neglected. We estimate [13] that their inclusion would raise $\Delta F_0^{\ddagger}$ by less than 10 % (see also ref. (14)). In calculating the salt effect, an additional approximation was made but leads to no error in the Debye-Hückel region and is probably unimportant otherwise. Incidentally, the ions are *not* treated as conducting spheres, as suggested on p. 986 of ref. (4). The mathematical details of these calculations will be described elsewhere.

same surface are also equal. Thereby the e.e.d. is made to centre on the inter-section surface.

The term $(F^\ddagger - F^p)$ can either be calculated directly or simply by using the following transformation property to obtain it from $F^\ddagger - F$; any property of the transition state is invariant with respect to a simultaneous replacing of $-m$ by $m+1$ and interchange of " p " and " no p " superscripts (the property can be established from (3.1.3)—valid now for all k of the e.e.d.—with some caution, remembering that $\mathscr{E}_k^\ddagger$ is relative). We obtain for m:

$$-(2m+1)\lambda + \Delta\mathscr{E}_i^\ddagger - \Delta\mathscr{E}_i^{p\ddagger} = \Delta F^{\circ'} - \Delta F_{vib}^\circ + w^p - w, \qquad (4.4.1)$$

where $\Delta\mathscr{E}_i^{p\ddagger}$ is $\Delta\mathscr{E}_i^\ddagger$ with $m+1$ and K_s replaced by $-m$ and K_s^p, and where $-\Delta F_{vib}^\circ$ is defined as $kT \ln Q_{vib}^p/Q_{vib}$. When $K_s = K_s^p$, $\Delta\mathscr{E}_i^\ddagger - \Delta\mathscr{E}_i^{p\ddagger}$ becomes simply $-(2m+1)\Sigma_s K_s(\Delta q_s^\circ)^2/2$.

5. CONCLUDING REMARKS

Eqn. (4.2.2) and (4.4.1) reduce to those of part 1 when any effects from co-ordination shell distances and from electrolyte are omitted. Eqn. (4.2.3) for the contribution of the " inner " co-ordinates reduces to that obtained by George and Griffith [15] if ΔF° is set equal to zero, the partition function omitted and the normal co-ordinates replaced by bond co-ordinates.

Among the topics to which the results of the present analysis could be applied are the following:

   (i) Relation between chemical and electrochemical electron transfer rates: cf. ref. (3) for solvent reorganization only. This discussion could now be generalized.

  (ii) Prediction of electron transfer rates of non-isotopic exchanges from iso-topic ones: e.g., taking $K_s \cong K_s^p$, one finds from (4.2.2) that when correc-tions are made for any differences of coulombic repulsion, the mixed rate constant is related to the isotopic ones (k_1 and k_2) and to the equilibrium constant K in the given electrolyte medium by $k_{12} \cong (k_1 k_2 K)^{\frac{1}{2}}$ if ΔF° is not too large.

 (iii) Numerical estimate of contribution to activation free energy from the co-ordination shells when the necessary force constants and internuclear distances are available * (cf. ref. (7)).

  (iv) Inert salt effects (subject to an assumed treatment of the ionic atmosphere as a continuous distribution, however).

   (v) Possibility of " inverted " chemical behaviour. If ΔF° becomes too negative, intersection of the two surfaces becomes possible only at high potential energies, unless in such cases a more favourable reaction mech-anism is found. In (4.3.3) and (4.3.8) m^2 eventually increases with in-creasing $-\Delta F^\circ$, and the rate constant decreases.

  (vi) Analysis of assumptions made when electron transfers are interpreted in the terms of the Franck-Condon principle (cf. analysis in ref. (8)).

APPENDIX 1

PROPERTY OF THE e.e.d.

If the e.e.d. is indeed " centred " on the intersection surface, a system having the e.e.d. and the electronic configuration of the reactants would have the same

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* A similarly made estimate for $D_2O + H_2O$ effects using (4.2.3) would be valid only if the contribution of the OH frequencies to the reaction co-ordinate were negligible (cf. discussion of uncertainty in k_r in § 4.1) and only if one added to $\Delta F^\ddagger$ any additional con-tribution from changes in hydrogen bonding as the charged reactants approach each other, if any.

average energy as a system having the same e.e.d. and the electronic configuration of the products. That is, it would satisfy

$$\langle \mathscr{E}_k \rangle_{\mathrm{av}} = \langle \mathscr{E}_k^p + \Delta\mathscr{E} \rangle_{\mathrm{av}},\tag{A1}$$

each averaged over the e.e.d. (They would also have the same free energy too.)

It is easy to show that such an e.e.d. exists. Consider the expression $-kT \ln \int \ldots \int \exp(-\mathscr{E}_k^{\ddagger}/kT)\mathrm{d}\tau_k$, as a function of m and minimize it with respect to m. One obtains immediately, using (3.1.3):

$$\frac{\int \ldots \int \exp(-\mathscr{E}_k^{\ddagger}/kT)\mathscr{E}_k \mathrm{d}\tau_k}{\int \ldots \int \exp(-\mathscr{E}_k^{\ddagger}/kT)\mathrm{d}\tau_k} = \frac{\int \ldots \int \exp(-\mathscr{E}_k^{\ddagger}/kT)(\mathscr{E}_k^p + \Delta\mathscr{E})\mathrm{d}\tau_k}{\int \ldots \int \exp(-\mathscr{E}_k^{\ddagger}/kT)\mathrm{d}\tau_k}.\tag{A1}$$

This is the desired property. Thus, there is an e.e.d. centred on the intersection surface. It has the property that the ln term, i.e. the free energy, is a minimum with respect to m. (4.4.1), the equation in the text for m, satisfies the above equation.

We now examine in more detail the approximation of replacing the $(N-1)$-dimensional surface integral by an N-dimensional volume integral over the e.e.d., N being large. A co-ordinate system is introduced as follows.

We note first that the intersection of the two potential surfaces in fig. 1 defines a surface of $(N-1)$ degrees of freedom and that shifting the potential-energy surface of the products vertically by an amount Γ without change of shape, produces a different intersection which defines a new $(N-1)$-dimensional surface parallel to the first one. In this way a family of parallel surfaces can be generated, each member associated with a particular value of Γ and obeying (A2) (cf. § 3.1).

$$\mathscr{E}_k = \mathscr{E}_k^p + \Delta\mathscr{E} + \Gamma.\tag{A2}$$

Let σ denote the totality of $(N-1)$ orthogonal curvilinear co-ordinates defining position on any given surface and let γ be the co-ordinate normal to the family of surfaces, so that k in $\mathscr{E}_k$ consists of σ and γ. Let the origin of γ be at the actual intersection surface, for which $\Gamma = 0$. $\Gamma(\gamma)$ is a strictly monotonic function of γ and $\Gamma(0) = 0$.

Consider now the volume integral over the e.e.d.,

$$\int \ldots \int \exp(-\mathscr{E}_{\sigma\gamma}^{\ddagger}/kT)\mathrm{d}\sigma\mathrm{d}\gamma,$$

where $\mathscr{E}_{\sigma\gamma}^{\ddagger}$ satisfies (A3) (cf. 3.1.3)) and m was selected so that (A4) is satisfied (cf. (A1), using A2)).

$$\mathscr{E}_{\sigma\gamma}^{\ddagger} = \mathscr{E}_{\sigma\gamma} + m\Gamma,\tag{A3}$$

$$\int \ldots \int \Gamma \exp(-\mathscr{E}_{\sigma\gamma}^{\ddagger}/kT)\mathrm{d}\sigma\mathrm{d}\gamma = 0.\tag{A4}$$

In the vicinity of $\gamma = 0$, Γ equals $\gamma(\mathrm{d}\Gamma/\mathrm{d}\gamma)_0$, the derivative being non-zero. (A4) thus becomes

$$\int_{-\infty}^{\infty} \gamma \exp(-F_{(\gamma)}^{\ddagger}/kT)\mathrm{d}\gamma = 0,\tag{A5}$$

where $F_{\gamma}^{\ddagger}$, the free energy of a system constrained to exist on the surface γ, is given by (A6):

$$\exp(-F_{(\gamma)}^{\ddagger}/kT = \int \ldots \int \exp(-\mathscr{E}_{\sigma\gamma}^{\ddagger}/kT)\mathrm{d}\sigma.\tag{A6}$$

Since (A5) is applicable to all T, we infer that $F_{\gamma}^{\ddagger}$ is an even function of γ and write therefore the Taylor's series (A7), retaining only terms up to γ^2 for physical reasons based on fig. 1:

$$F_{(\gamma)}^{\ddagger} = F_{(0)}^{\ddagger} + (\gamma^2/2!)F_{(0)}'' + \ldots.\tag{A7}$$

Using (A7) the N-dimensional volume integral becomes

$$\int_{-\infty}^{\infty} \exp(-F_{(\gamma)}^{\ddagger}/kT)\mathrm{d}\gamma = \exp(-F_{(0)}^{\ddagger}/kT)\sqrt{\overline{2\pi kT/F_{(0)}''}}. \qquad (A8)$$

But $\exp(-F_{(0)}^{\ddagger}/kT)$ equals $\int \ldots \int \exp(-\mathscr{E}_{\sigma 0}/kT)\mathrm{d}\sigma$, using (A6) and (A3) at $\gamma = 0$, and so equals the desired $(N-1)$-dimensional surface integral. Thus, if the " vibrational-like partition function " $\sqrt{2\pi kT/F_{(0)}''}$ is of the order of unity, the basic approximation enunciated in § 4.1 is seen from (A8) to be justified.

We next estimate $F_{(0)}''$ and incidentally investigate the significance of m. Differentiating (A6) with the aid of (A3), we find

$$F_{(0)}' = m(\mathrm{d}\Gamma/\mathrm{d}\gamma)_{\gamma=0} + \langle(\mathrm{d}\mathscr{E}_{\sigma\gamma}/\mathrm{d}\gamma)_0\rangle_0, \qquad (A9)$$

$$F_{(0)}'' = \langle(\mathrm{d}^2\mathscr{E}_{\sigma\gamma}^{\ddagger}/\mathrm{d}\gamma^2)_0\rangle_0 + [\langle(\mathrm{d}\mathscr{E}_{\sigma\gamma}^{\ddagger}/\mathrm{d}\gamma)_0\rangle_0^2 - \langle(\mathrm{d}\mathscr{E}_{\sigma\gamma}^{\ddagger}/\mathrm{d}\gamma)_0^2\rangle_0]/kT, \qquad (A10)$$

where $\langle f\rangle_0$ denotes any function f averaged over the intersection surface,

$$\int \ldots \int f\exp(-\mathscr{E}_{\sigma 0}/kT)\mathrm{d}\sigma / \int \ldots \int \exp(-\mathscr{E}_{\sigma 0}/kT\mathrm{d}\sigma.$$

Since $F_{(0)}' = 0$, we find

$$-m = \langle(\mathrm{d}\mathscr{E}_{\sigma\gamma}/\mathrm{d}\Gamma)_0\rangle_0.$$

It can thereby be seen that for any fixed shape of the two potential energy surfaces (i.e. for fixed ΔS°), m is the increase in activation energy per unit increase in standard energy of reaction. Accordingly, if m were 0, the activated complex would resemble the reactants. It would resemble the products if m were -1 and would be as much like one as the other if m were $-\frac{1}{2}$. These remarks can also be inferred from (3.3.3).

$F_{(0)}''$ contains first an average force constant term $\langle(\mathrm{d}^2\mathscr{E}_{\sigma\gamma}^{\ddagger}/\mathrm{d}\gamma^2)_0\rangle_0$. The sum of the second and third terms is found from approximate calculations based on (4.3.5) to be of a magnitude comparable with the first. Accordingly, it seems reasonable to expect that the results of more detailed calculations will show that the value of $F_{(0)}''$ is of the order of that of a typical force constant, and that therefore the partition function is of the order of unity. The results for the calculated free energy of activation are, it follows from (A8), relatively insensitive to the exact value of $F_{(0)}''$.

APPENDIX 2

NORMAL CO-ORDINATES AND $\Delta F_i^{\ddagger}$

As before, $\mathscr{E}_{\dot{k}i}^{\ddagger}$ is minimized and $\Delta\mathscr{E}_i^{\ddagger}$ and the vibration frequencies $\nu_s^{\ddagger}$ are then computed.

A reactant whose structure has a similar symmetry in the two redox states will also have similar types of normal co-ordinates, Q_s. The dependence of certain of these co-ordinates (particularly stretching co-ordinates) on the internal co-ordinates of displacement, $S_t = x_t - x_t^\circ$, will also be essentially the same in spite of any changes in equilibrium bond lengths. Moreover, comparing molecules of similar geometry, it may be deduced from the pertinent transformation equations [16] that each Q_s is unaffected by changes in corresponding force constants when only one type of force constant contributes appreciably to that Q_s or when all contributing ones change by the same factor. The former appears to be true for many vibrations, as inferred from the valency force field approximation [17] and perhaps from the

relative constancy of vibration frequencies associated with the relative motion of two atoms or of two groups. We shall, for simplicity, make this approximation here.

Thus, writing

$$Q_s = \sum_t l_{st}(x_t - x_t^\circ) \quad \text{and} \quad Q_s^p = \sum_t l_{st}^p(x_t - x_t^{\circ p}),$$

we shall let $l_{st}^p = l_{st}$. Denoting $4\pi^2 v_s^2$ by λ_s, we also have

$$\mathscr{E}_{ki}^{\ddagger} = \tfrac{1}{2}\sum_s \lambda_s Q_s^2 (m+1) - \tfrac{1}{2}\sum_s \lambda_s^p (Q_s^p)^2 m.$$

We next define a new set of coordinates q_s (equilibrium values q_s°):

$$q_s = \sum_t l_{st} x_t^\circ, \quad q_s^\circ = \sum_t l_{st} x_t^\circ.$$

Therefore,

$$Q_s = q_s - q_s^\circ \quad \text{and} \quad Q_s^p = q_s - q_s^{\circ p}.$$

Regarding $\mathscr{E}_{ki}^{\ddagger}$ as a function of the q_s now, we may expand it about its minimum at $q_s = q_s^{\circ \ddagger}$ say) by the usual process of computing derivatives with respect to the q_s. Eqn. (4.3.6) to (4.3.8) are then obtained, with the Ks replaced by λs and the q's having the above meaning. The $\lambda_s^{\ddagger}$ are related to the frequencies $v_s^{\ddagger}$ by the equation,

$$\lambda_s^{\ddagger} = 4\pi^2 v_s^{\ddagger 2}.$$

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[2] Marcus, *J. Chem. Physics*, 1957, **26**, 867, 872 (parts 2 and 3).

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[4] Marcus, *J. Chem. Physics*, 1956, **24**, 979.

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[6] Hush, *Faraday Society Discussions*, 1958, **26**, 145.

[7] cf. Marcus, *Trans. N.Y. Acad. Sci.*, 1957, **19**, 423 for numerical estimate.

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[9] e.g. Horiuti, *Bull. Chem. Japan*, 1938, **13**, 210 (cf. eqn. (2)).

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[14] Levine, *Faraday Soc. Discussions*, 1957, **24**, 43.

[15] George and Griffith, *The Enzymes*, Boyer, Lardy and Myrback, ed. (Academic Press Inc., New York, 1959), p. 364 (cf. ref. (5)).

[16] cf. Wilson, Decius and Cross, *Molecular Vibrations* (McGraw-Hill Book Company Inc., New York, 1955), p. 72 ff.

[17] cf. Herzberg, *Infra-red and Raman Spectra* (Van Nostrand and Co., Inc., New York, 1945), for calculations.