Theoretical Relations among Rate Constants, Barriers, and Brønsted Slopes of Chemical Reactions[1]

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A simple relation, $\Delta F^* = \lambda(1 + \Delta/\lambda)^2/4$, derived originally for weak-overlap electron transfers, is explored in a slightly modified version for reactions with considerable resonance splitting, such as atom transfers, proton transfers, and strong-overlap electron transfers. A useful additivity property, $\lambda_{12} = (\lambda_{11} + \lambda_{22})/2$, permits barriers ΔF^* for cross-reactions to be computed from those of exchange reactions, $\lambda_{ii}/4$. Some 45 barriers, calculated from some ten others, agreed with BEBO results, within a few kilocalories per mole. The agreement is analyzed and more general models for which it might occur are considered. A functional relationship between barrier and a degree-of-reaction parameter is devised to avoid commitment to too specific a model. An example where breakdown should occur is also given. Experimental data, as well as quantum mechanical calculations of barriers, will permit further tests. Corollaries of the relation include: (1) a classification of reaction barriers in terms of intrinsic (λ_{ii}) and extrinsic ($\Delta F^{0\prime}$) contributions, (2) a rate-constant relation $k_{12} \cong (k_{11}k_{22}K_{12}f_{12})^{1/2}$ and modifications thereof, (3) a calculation of the local Brønsted slope α from the intercept of the ΔF^* *vs.* ΔF^0 plot, $\alpha = (1 + \Delta/\lambda)/2$, (4) a relation between k_H/k_D *vs.* $\Delta F^{0\prime}$ plots and local α's, and (5) other relations among rate constants. Throughout, ΔF^* and $\Delta F^{0\prime}$ refer to an elementary step.

Introduction

A simple relation has been derived for the free-energy barrier and rate constant of weak-overlap electron-transfer reactions[2,3]

$$k = Z \exp(-\Delta F^*/RT) \quad (1)$$

$$\Delta F^* = w^r + \lambda(1 + \Delta F_R^{0\prime}/\lambda)^2/4 \quad (2)$$

where Z is a bimolecular collision frequency in solution ($\cong 10^{11}$ l./mol sec), $\Delta F_R^{0\prime}$ denotes $\Delta F^{0\prime} + w^p - w^r$, $\Delta F^{0\prime}$ is the "standard" free energy of the reaction for the prevailing medium and temperature, w^r (or w^p) is the work required to bring the reactants (or products) together to the mean separation distance in the activated complex, and λ for a cross-reaction is the mean of that for two electron-exchange reactions[4]

$$\lambda_{12} = (\lambda_{11} + \lambda_{22})/2 \quad (3)$$

As a consequence of eq 1–3 one finds[2c,5]

$$k_{12} \cong (k_{11}k_{22}K_{12}f_{12})^{1/2} \quad (4)$$

where k_{12} and K_{12} are the rate constant and equilibrium constant of the cross-reaction, k_{11} and k_{22} are the rate constants of the electron-exchange reaction of the two different redox systems, and $\ln f_{12}$, which equals $-\Delta F_R^{0\prime 2}/2\lambda RT$, is given by eq 5.

$$\ln f_{12} \cong (\ln K_{12})^2/4 \ln (k_{11}k_{22}/Z^2) \quad (5)$$

Equation 4 has been applied in the literature to weak-overlap electron transfers.[6] Recently, as a conjecture, it was applied to a few examples of atom-transfer reactions.[7] Equations 1 and 2 have been similarly used to calculate Brønsted slopes in atom- and proton-transfer reactions.[8] In each case, the results were

(1) Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, and to the National Science Foundation for their support of this research.

(2) (a) *J. Chem. Phys.*, 24, 966 (1956); (b) *Discussions Faraday Soc.*, 29, 21 (1960); (c) R. A. Marcus, *J. Phys. Chem.*, 67, 853, 2889 (1963); (d) *Ann. Rev. Phys. Chem.*, 15, 155 (1964); (e) *J. Chem. Phys.*, 44, 679 (1965); (f) a review of this work and of that of other investigators (*e.g.*, Levich and Dogonadze, Hush) is given in ref 2d. A factor of κ_p, omitted in eq 1, is about unity for an adiabatic reaction and is not relevant for the present purposes.

(3) When the reaction is partially or completely diffusion controlled, k is only one contribution to the observed rate constant. *E.g.*, when the diffusion step is followed by an irreversible reaction step, $k_{obsd}^{-1} = k^{-1} + k_{diff}^{-1}$. Compare R. A. Marcus, *Proc. Exchange Reactions Symp., Upton, N. Y.*, 1 (1965); and R. A. Marcus, *Discussions Faraday Soc.*, 29, 129 (1960).

(4) The cross-reaction is $A_1^{ox} + A_2^{red} \rightarrow A_1^{red} + A_2^{ox}$, where A_1^{ox} and A_1^{red} differ only in their redox state. The exchange reactions are $A_1^{ox} + A_1^{red} \rightarrow A_1^{red} + A_1^{ox}$ and $A_2^{ox} + A_2^{red} \rightarrow A_2^{red} + A_2^{ox}$.

(5) The work terms are omitted in eq 4. When they are included and $f_{12} \cong 1$, the right side of eq 4 has an additional factor $\exp[-(w_{12}^r + w_{12}^p - w_{11}^r - w_{22}^r)/2RT]$. (Note that $w_{ii}^r = w_{ii}^p$.) When f_{12} is not close to unity, the appropriate correction of eq 4 is made using eq 2.

(6) N. Sutin, *Ann. Rev. Phys. Chem.*, 17, 119 (1966).

(7) (a) N. Sutin, *ibid.*, 17, 154 (1966); (b) N. Sutin, *Proc. Exchange Reactions Symp., Upton, N. Y.*, 7 (1965); (c) A. Haim and N. Sutin, *J. Am. Chem. Soc.*, 88, 434 (1966).

(8) A. O. Cohen and R. A. Marcus, unpublished data.

encouraging, but more extensive application is needed.

A semi-empirical, bond energy–bond order (BEBO) method has been used to calculate activation energies of gas-phase atom transfers.[9] The potential energy form of eq 2, slightly modified in a way expected for atom transfers, permitted[10] the calculation of potential-energy barriers for some 45 cross-reactions from those of 10 exchange reactions, with a reasonable agreement of about 2 kcal/mol. (There were 90 cross-reactions, but only 45 were independent.) The results are given in Appendix I.

In the present paper these equations are discussed for "strong-overlap" reactions, such as atom transfers, proton transfers, and strong-overlap electron transfers, and various consequences are noted. In some respects, the present discussion is a quantitative treatment of the common notion in the literature[11] that the Brønsted slope reflects the extent to which the activated complex resembles the reaction products (*e.g.*, our eq 31). The definitions or physical meanings of principal symbols are given in the Glossary.

A Modification of Eq 2

Because of an expected difference in potential-energy surfaces, discussed in Appendix II, any applicability of eq 2 to gas-phase atom-transfer reactions is expected to be limited to $|\Delta F_R^{0\prime}| \leqslant \lambda$. Outside that interval, eq 6 is to be used. The same remarks apply to reactions in solution (Appendix II) if most of the reorganization comes from the bonds being broken and formed, rather than from all the other coordinates.[12]

$$\begin{aligned} \Delta F^* &\cong w^r \quad (-\Delta F_R^{0\prime} \geqslant \lambda) \\ \Delta F^* &\cong \Delta F^{0\prime} + w^p \quad (\Delta F_R^{0\prime} \geqslant \lambda) \end{aligned} \tag{6}$$

The λ in eq 2 and 6 is seen from eq 2 to equal approximately $4\Delta F_0^*$, where ΔF_0^* is the value of ΔF^* at $\Delta F^{0\prime} = 0$.

The following potential-energy counterparts (for gas-phase reactions) of eq 2 and 6 were used to calculate the energy barriers for gas-phase atom transfers mentioned earlier. (The work terms, w^r and w^p, usually coulombic, are absent now.) Let E_{ij} be the potential energy barrier of the atom transfer (7)

$$A_iB + A_j \longrightarrow A_i\cdots B\cdots A_j \longrightarrow A_i + BA_j \tag{7}$$

and let ΔE^0 be the net potential-energy change when $i = 1$ and $j = 2$. Then

$$E_{12} = E(1 + \Delta E^0/4E)^2 \quad (|\Delta E^0| \leqslant 4E) \tag{8a}$$

$$\begin{aligned} E_{12} &= 0 \quad (\Delta E^0 \geqslant 4E) \\ E_{12} &= \Delta E^0 \quad (\Delta E^0 \geqslant 4E_1) \end{aligned} \tag{8b}$$

In (8a) and (8b)

$$E = (E_{11} + E_{22})/2 \tag{8c}$$

Outline of Treatment

Before proceeding with detailed derivations, aspects of the paper are first reviewed. In weak-overlap electron-transfer reactions, it may be recalled, reactants experience work terms w^r, which are of coulombic and, in some cases,[2c] "hydrophobic–hydrophilic" origin (solvent structural effects). These reactants also experience a readjustment of bond lengths, of bond angles when appropriate, and of orientations of solvent molecules outside the reactants' coordination shells. Typically, the need for making these readjustments, more than w^r, constitutes the principal barrier to reaction. They occur because the system not only has to undergo electron transfer, but also has to eventually adopt values of these coordinates which are appropriate to the reaction products.

In the present paper, the arguments are extended to reactions in which bonds are broken and formed. Initially, a very simple bond energy–bond order model for gas-phase reactions (eq 9), is considered and eq 12 is derived. The main purpose of using eq 12 is to provide a simple, plausible vehicle for considering atom transfers and for comparing with eq 8, not for making a detailed calculation for these reactions. More elaborate quantum-mechanical calculations of E_{12}, E_{11}, and E_{22} would be useful for testing eq 8 or for testing eq 20, a result derived from eq 12.

For some purposes, it is not necessary to employ an equation which contains the specific assumptions present in eq 12 or 8. A more general, functional equation (16) is therefore introduced to generalize a portion of the subsequent treatment. Equation 16 includes eq 8 and 12 as special cases and, like them, relates barriers of cross-reactions to exchange reactions and serves also as a basis for a discussion of Brønsted slopes.

A comparison of these equations is then given. At low $\Delta E^0/4E$, they are found to give exactly the same first-order term for the barrier, and the latter term is found to contain no intrinsic asymmetry. When eq 8 and a symmetrized eq 12 are compared at arbitrary $\Delta E^0/4E$, they are found to give fairly similar results.

Reactions in solution are considered next. The coordinates of the reactants and solvent molecules in such systems can be roughly grouped as follows: (1) several bond distances, for bonds undergoing rupture or formation, and (2) coordinates describing more minor

(9) C. Parr and H. S. Johnston, *J. Am. Chem. Soc.*, 85, 2544 (1963).

(10) I am indebted to Mrs. Audrey Cohen for these calculations. The mean-square deviation was 1.5 kcal/mol.

(11) (a) *E.g.*, J. E. Leffler and E. Grunwald, "Rates and Equilibria of Organic Reactions," John Wiley and Sons, Inc., New York, N. Y., 1963, p 157; (b) see also R. P. Bell, "The Proton in Chemistry," Cornell University Press, Ithaca, N. Y., 1959, Chapter 10; J. O. Edwards, "Inorganic Reaction Mechanisms," W. A. Benjamin, Inc., New York, N. Y., 1964, Chapter 3.

(12) We note that eq 6 and 2 form a continuous function for ΔF^* for all values of $\Delta F_R^{0\prime}$. Also, in each case in eq 6 the rate constant or that of the reverse reaction is now essentially diffusion controlled in solution, and one calculates k_{obsd} accordingly.[3]

adjustments in bond lengths and angles in reactants, of which the solvent may be one, and orientations of solvent molecules. A simple treatment of group 1 could parallel the one used to obtain eq 8 and, simultaneously, group 2 could be treated by the method used to obtain eq 2. The details of the latter would differ somewhat from that for weak-overlap electron transfers,[13] and so the contribution of group 2 coordinates to intrinsic terms g_i in eq 21 would differ. However, the basic approach could be made rather similar. A discussion of steric and statistical factors is also given. (They were absent in weak-overlap electron transfers.)

Equation 4 relating rate constants of cross-reactions to those of exchange reactions is next examined, and the implications of the preceding results are given. The discussion suggests that eq 4 comes through fairly intact, particularly at low $\Delta F^{0\prime}/4\Delta F_0^*$. In several subsequent sections, the meaning and magnitude of the Brønsted slope are considered, as is its relation to a kinetic isotope effect. The various findings are then summarized and, in a concluding section, the classification of activation free energies into intrinsic and extrinsic contributions is noted.

One Model for Atom Transfers

In the BEBO method,[14] the energy of the A_iB bond in a gas-phase reaction (7) is written empirically as $-V_i n_i^{p_i}$, where n_i is the instantaneous bond order of A_iB, V_i is the A_iB bond energy when $n_i = 1$, and p_i is a quantity determined from bond energy–bond order relations in the literature; p_i is quite close to unity. Thus, E_i, the potential energy of formation of the system from the initial configuration is eq 9 when $n_1 = 1$ and $n_2 = 0$ initially.

$$E_i = (-V_1 n_1^{p_1} - V_2 n_2^{p_2}) + V_1 \qquad (9)$$

In the cited model of the gas-phase reaction, it is then assumed that the total bond order $n_1 + n_2$ is constant along the reaction path; it is unity in the present case. By setting $dE_i/dn_2 = 0$ at the energy maximum along the reaction path, the activation energy is calculated from empirically known V_i's and p_i's.

To later compare eq 8 with 9, we first note that the former depends on only three quantities, E_{11}, E_{22}, and ΔE^0, while the latter depends on four, V_1, V_2, p_1, and p_2. We may remove this difference as follows. Since $p_i \cong 1$, a Taylor's expansion of eq 9 can be made and powers of $(p_i - 1)$ higher than the first neglected. The instantaneous bond energy of A_iB is then

$$-V_i n_i^{p_i} \cong -V_i[n_i + (p_i - 1)\, n_i \ln n_i] \qquad (10)$$

Maximization of eq 9 using eq 10 yields $n_i = 1/2$ for an exchange reaction.[15] One finds

$$E_{ii} = V_i(p_i - 1) \ln 2 \qquad (11)$$

$$E_i = n_2\Delta E^0 - E_{11}\frac{n_1 \ln n_1}{\ln 2} - E_{22}\frac{n_2 \ln n_2}{\ln 2} \qquad (12)$$

Since $n_1 + n_2$ equals unity, and since n_2 is determined from $dE_i/dn_2 = 0$, one sees E_i now depends only on three properties, E_{11}, E_{22}, and ΔE^0.

It is useful to introduce E, the symmetric combination of E_{11} and E_{22} given by eq 8c, and an antisymmetric combination ϵ defined by

$$\epsilon = (E_{11} - E_{22})/(E_{11} + E_{22}) \qquad (13)$$

The terms intrinsic asymmetry, measured by ϵ, and extrinsic asymmetry, measured by $\Delta E^0/4E$, will be employed throughout this paper.

In the region of small intrinsic and extrinsic asymmetry eq 12 can be expanded about the symmetric condition $n_2 = 1/2$, and powers of $(n_2 - 1/2)$ higher than the second neglected. Maximization of E_i with respect to n_2 yields

$$E_i = E + 1/2\Delta E^0 + (2x^{\pm 2}E/\ln 2) + \cdots \qquad (14)$$

where $x^{\pm}$ $(= n_2^{\pm} - 1/2)$ is

$$x^{\pm} = \{-\Delta E^0 + 2\epsilon E[1 - (1/\ln 2)]\}(\ln 2)/4E \qquad (15)$$

A More General Equation

Equations 8 and 12 are special cases of a more general one

$$E_i = n\Delta E^0 + 1/2E_{11}g_1(n) + 1/2E_{22}g_2(1 - n)$$
$$dE_i/dn = 0 \ (n = n^{\pm}) \qquad (16)$$

where n is some degree-of-reaction parameter, being zero initially, unity finally, and $n^{\pm}$ for the activated complex. E_{11} and E_{22} retain their earlier definitions. The term $g_i(n)$ is any function[16,17] of n, normalized so that $g(1/2) = 1$.

In the region of small intrinsic and extrinsic asymmetry, eq 16 may be expanded in powers of $n = 1/2$ and terms beyond the second power neglected. One obtains eq 17

(13) In this reaction, there is a relatively abrupt charge transfer, namely near a value of the reaction coordinate defining the intersection of reactants' and products' potential-energy surfaces. In the case of proton or strong-overlap electron transfers, the change of charge distribution is expected to occur more gradually, *i.e.*, over a wider interval along the reaction coordinate.

(14) For simplicity, the method discussed is the one originally used in H. S. Johnston, *Advan. Chem. Phys.*, 3, 131 (1960).

(15) While $(p_i - 1)\ln 2$ varies widely from bond to bond, it averages around 0.05 to 0.1, so that the energy barrier (11) of an atom-exchange reaction might be about 5–10% of the bond energy, a reasonable figure. In a few cases $p_i - 1$ was negative, so the maximum occurred at the end points and one sets $E_{ii} = 0$ instead of eq 11.

(16) In this notation, the n and $1 - n$ in the last two terms of eq 16 are the arguments of the functions g_i, rather than multiplying factors.

(17) (a) Equation 8a follows from eq 16 by setting $g_i(n) = 4n(1 - n)$ in the interval $(0 < n < 1)$ and so outside of the infinitesimal regions around $n = 0$ and $n = 1$. In those regions, one could choose the g_i to approach zero extremely rapidly and, thereby, approximate eq 8b as closely as desired. The details of this choice of g_i are unimportant for our purposes, but a study of the g_i in footnote 17b is revealing; (b) to obtain eq 12, one sets $n = n_2$, $g_1(n) = g_2(n) = -2(1 - n)\ln(1 - n)/\ln 2$.

$$E_t = E + {}^1/_2\Delta E^0 - \frac{x^{\pm 2}}{4}[E_{11}g_1'' + E_{22}g_2''] \quad (17)$$

where $x^{\pm}$ ($= n^{\pm} - {}^1/_2$) is

$$x^{\pm} = 2[-\Delta E^0 - {}^1/_2(E_{11}g_1' - E_{22}g_2')]/(E_{11}g_1'' + E_{22}g_2'') \quad (18)$$

The primes denote derivatives evaluated at $n = {}^1/_2$.

Relation among Eq 8, 12, and 16

It has already been noted that eq 8 and 12 are special cases of eq 16. Unlike eq 8, eq 12 and 16 do have an intrinsic asymmetry term. However, a rather striking result can be proven when the intrinsic and the extrinsic asymmetry ($\Delta E^0/4E$) are both small: the intrinsic asymmetry makes no contribution to the first-order term in those equations for E_t. For example, in eq 14 and 17, the first-order term is $E + {}^1/_2\Delta E^0$, the same as it is in eq 8. It contains no intrinsic asymmetry, ϵ. Thus, all three equations agree at low $\Delta E^0/4E$. (A consequence of this absence of ϵ is noted under Remarks in eq 4.)

We next consider the relation between eq 8 and 12 at any value of $\Delta E^0/4E$. In both equations, E_t becomes 0 or ΔE^0, accordingly, as $\Delta E^0/4E$ becomes very negative or very positive. For other $\Delta E^0/4E$, eq 8 is most easily compared with eq 19, the symmetrized form of eq 12, since 8 contains no intrinsic asymmetry.

$$E_t = n\Delta E^0 - E[n \ln n + (1 - n) \ln (1 - n)]/\ln 2 \quad (19)$$

The value of n which solves $dE_t/dn = 0$ is found and inserted into eq 19. Manipulation yields[18]

$$E_t = E + {}^1/_2\Delta E^0 + ({}^1/_2\Delta E^0/y) \ln \cosh y \quad (20)$$

where $y = (\Delta E^0/2E) \ln 2$. The $\Delta E^{02}/16E$ term in eq 8a can be written for comparison, as ${}^1/_2\Delta E^0 y/4 \ln 2$.

When y tends to $\pm\infty$, ln cosh y tends to $\pm y - \ln 2$. Thereby, E_t in eq 20 tends to 0 or ΔE^0, according as ΔE^0 tends to $-\infty$ or to $+\infty$, respectively, in agreement with eq 8b. When $\Delta E^0 = 2E$, which is midway between the extremes of small $\Delta E^0/4E$ and of $\Delta E^0/4E \sim 1$, $(1/y)$ ln cosh y is about ${}^1/_8$, while $y/4$ ln 2 is ${}^1/_4$. The difference of eq 8a and 20 is, therefore, ${}^1/_{24}\Delta E^0$, which is small.

E, defined by eq 8c, is sometimes of the order of 10 kcal/mole, so that a ΔE^0 of about $2E$ is then about 20 kcal/mole.

Reactions in Solution

Two quite different gas-phase models of a reaction obeyed eq 16, one being BEBO and the other (see Appendix II) having a pair of intersecting potential energy parabolas. In the free-energy analog of eq 16, to be used for reactions in solution, E_t, ΔE^0, and E_{tt} are replaced by their analogs at a mean separation distance, R, in the activated complex, $\Delta F^* - w^r$, $\Delta F_R^{0'}$, and $\Delta F_{tt}^* - w_{tt}$

$$\Delta F^* - w^r = n\Delta F_R^{0'} + {}^1/_2(\Delta F_{11}^* - w_{11})\, g_1(n) + {}^1/_2(\Delta F_{22}^* - w_{22})\, g_2(1 - n) \quad (21)$$

$$\partial\Delta F^*/\partial n = 0 \quad (n = n^{\pm})$$

where $w_{tt} = w_{tt}^r = w_{tt}^p$ and $\Delta F_R^{0'} = \Delta F^{0'} + w^p - w^r$.

The quadratic expression (2) can in fact be written as in eq 21, with $g_1(n) = g_2(n) = 4n(1 - n)$ and $\Delta F_{tt}^* - w_{tt} = \lambda_{tt}/4$. In Appendix III the results of ref 2e are used to show that weak-overlap electron transfers in solution obey eq 21, even before some approximations present in eq 2 are introduced.

As noted earlier, the nuclear coordinates in electron-transfer reactions are of two types: (a) vibrational coordinates (bond lengths and angles) in reactants, including those of any solvent molecules in the coordination shell, and (b) orientational coordinates of solvent molecules outside the coordination shell. For the former, a quadratic potential-energy function is appropriate. For the latter, it is not. Instead, the statistical mechanical equivalent of dielectric unsaturation for partial saturation was introduced into the free-energy expression for the solvent system.[2e,19] The free energy of the solvent then became a quadratic function of fluctuations in solvent polarization, just as the harmonic potential energy for vibrational coordinates is a quadratic function of fluctuations in those coordinates. The total of the two contributions to ΔF^* leads, as noted in Appendix III, to eq 21.

In the case of an atom, proton, or strong-overlap electron transfer reaction in solution, it was noted that there are: (a) bonds being broken or formed, including any involving addition or removal of a solvent molecule to or from a reactant; (b) vibrational coordinates undergoing smaller changes; and (c) orientations of solvent molecules changing their distribution because of a change in charge distribution in the reactants. The first group might be treated as in eq 12 or 16, the second as in the preceding paragraph, and the third by the statistical mechanical dielectric unsaturation method noted there. The final result for the latter two contributions would differ somewhat from that found for weak-overlap electron transfers, because the change in charge distribution as the system moves along the reaction coordinate is now less abrupt. However, since quite different models led to eq 16, there is little doubt that a reasonable theory consistent with eq 21 can be formulated.

Steric and Statistical Factors

In atom or proton transfers, steric and statistical factors may contribute to the rate constant in a manner which depends on details of the potential-energy surface.

(18) *E.g.*, one finds $(\Delta E^0 \ln 2)/E = \ln [n/(1 - n)]$. Thus, $n = \exp(2y)/[1 + \exp(2y)] = \exp(y)/2 \cosh y$ and $1 - n = \exp(-y)/2 \cosh y$. Substitution in eq 19 yields eq 20.

(19) R. A. Marcus, *J. Chem. Phys.*, 38, 1858 (1963); 39, 1734 (1963).

Several models can be considered in such a way as to permit the preceding formalism to be utilized intact, as for example the following. (1) The reactants come together, requiring the coulombic or other work term, w^r. They reorient, with a steric and statistical factor of S^r and s^r, respectively.[20] (2) The system undergoes the pertinent changes of bond lengths and solvation and so reaction occurs. (3) The products separate, the relevant terms for the reverse process being w^p, S^p, and s^p.

The free-energy change in steps 1 and 3 is $w^r - RT \ln S^r s^r$ and $w^p - RT \ln S^p s^p$, respectively, and we write

$$W^r = w^r - RT \ln S^r s^r \tag{22}$$

The over-all "standard" free energy of reaction in steps 1–3 is $\Delta F^{0\prime}$, so that in step 2 is $\Delta F_R^{0\prime} = \Delta F^{0\prime} + W^p - W^r$. The configurational free-energy barrier to form the activated complex is $^1/_4\lambda(1 + \Delta F_R^{0\prime}/\lambda)^2$ when $|\Delta F_R^{0\prime}/\lambda| \leqslant 1$, according to the arguments which led to eq 2; λ has the additivity in eq 3.

The "translational" contribution[21] to the free energy of activation $\Delta F^{\ddagger}$ is $-kT \ln (hZ/kT)$, where Z is the collision number of uncharged species in solution ($\sim 10^{11}$ l./mol sec). Thus from $k_{rate} = (kT/h) \exp(-\Delta F^{\ddagger}/RT)$, one again obtains eq 1-3, where now the w^r and w^p are replaced by W^r and W^p. *E.g.*

$$\Delta F^{*} = W^r + \frac{\lambda}{4}(1 + \Delta F_R^{0\prime}/\lambda)^2 \tag{23}$$

$|\Delta F_R^{0\prime}/\lambda| \leqslant 1$, where $\Delta F_R^{0\prime} = \Delta F^{0\prime} + W^p - W^r$ now.

Remarks on Eq 4

In this section, a modification of eq 4 based on the free-energy analog of eq 20 is first given. We also consider a case where eq 4 could break down.

The free-energy analog of eq 20 yields eq 4, but with

$$f_{12} = K_{12}^{(1/y \ln \cosh y)} \tag{24a}$$

where

$$y = (\ln K_{12})(\ln 2)/\ln (k_{11}k_{22}/Z^2) \tag{24b}$$

For comparison, eq 5 can be rewritten as

$$f_{12} = K_{12}^{y/4 \ln 2} \tag{25}$$

When, as in a previous section, $\Delta E^0/2E \sim 1$ and so $y = \ln 2$, and when $K_{12} = 10^{-12}$, the $f_{12}^{1/2}$s in eq 24a and 25 differ only by a factor of 3.

The breakdown of eq 4 can be investigated by examining the breakdown of the first-order term in eq 8a, $E + {}^1/_2\Delta E^0$, because of the related theoretical origin of both equations. Equation 4 rests on the dependence of all terms in the energy change on any degree-of-reaction variable n. Even a natural asymmetry in the potential-energy surface did not affect this equation in the region of small $\Delta E^0/4E$, because of a compensation.

Correspondingly, some breakdown will occur in these equations when an important term in the free-energy barrier does not vary with n. For example, in the case of eq 16, let a fraction c of the ΔE^0 occur before the principal reorganization. Then E_t is zero initially, and is given by eq 16, subsequently, with $n\Delta E^0$ replaced by $c\Delta E_0 + (1 - c)\, n\Delta E^0$. Manipulation as before leads to

$$E_t = E + {}^1/_2(1 + c)\Delta E^0 - \frac{x^{\mp 2}}{2} Eg''({}^1/_2) + \cdots \tag{26}$$

where $x^{\mp}$ is given by eq 18, with ΔE^0 replaced by $(1 - c)\Delta E^0$, and where we have let $g_1(n) = g_2(n)$ for simplicity of illustration.

From eq 26, or really from its free-energy counterpart, one finds

$$k_{12} \cong (k_{11}k_{22}K_{12}^{1+c})^{1/2} \tag{27}$$

When c is small, $K_{12}^{c/2}$ becomes a second-order term. *E.g.*, if $c = 0.1$ and $K_{12} = 10^{10}$, $K_{12}^{c/2} \cong 3$.

When steric and statistical effects are included, eq 4 becomes

$$k_{12} \cong (k_{11}k_{22}K_{12}f_{12})^{1/2}(\zeta_{12}^2/\zeta_{11}\zeta_{22})^{1/2} \tag{28}$$

where ζ for a reaction is

$$\zeta = (S^r s^r S^p s^p)^{1/2} \tag{29}$$

and f_{12} is

$$\ln f_{12} = (\ln K_{12})^2/4 \ln (k_{11}k_{22}/\zeta_{11}\zeta_{22}Z^2) \tag{30}$$

(Similarly, eq 24b can be corrected for the ζ's by dividing $k_{11}k_{22}$ by $\zeta_{11}\zeta_{22}$.)

Meaning of the Brønsted Slope

The Brønsted slope, α, is $\partial\Delta F^*/\partial\Delta F^{0\prime}$ and, according to eq 21, equals $n + (\partial\Delta F^*/\partial n)_{\Delta F^{0\prime}}(\partial n/\partial\Delta F^{0\prime})$, evaluated at $n = n^{\mp}$. Since $(\partial\Delta F^*/\partial n)_{\Delta F^{0\prime}}$ vanishes at $n = n^{\mp}$, we obtain

$$\alpha = n^{\mp} \tag{31}$$

For the BEBO model described earlier for a gas-phase reaction, $n^{\mp}$, and hence α, is the bond order of the bond being formed. For weak-overlap transfers

(20) S^r can be expressed in terms of a ratio of a vibrational partition function of the activated complex to the rotational–vibrational one of the reactants. s^r can be expressed several ways, one being intuitive and all of which give a similar answer. Compare ref 11a, p 133. See also R. A. Marcus, *J. Chem. Phys.*, 43, 1601 (1965), eq 17; E. W. Schlag and G. L. Haller, *ibid.*, 42, 584 (1965); D. M. Bishop and K. J. Laidler, *ibid.*, 42, 1688 (1965).

(21) Of the six translational degrees of freedom of the two reactants (masses m_1, m_2), five coordinates become three translations and two principal rotations of the activated complex, and a sixth may mix with other coordinates to yield the reaction coordinate and others. The partition function ratio of the five coordinates of the activated complex to the six of the reactants is $[2\pi(m_1 + m_2)\, kT]^{3/2}(8\pi^2 IkT')/\sigma(2\pi m_1 kT 2\pi m_2 kT)^{1/2}(h^3/h^6)$, where I is the relevant principal moment of inertia, written suggestively as μR^2, σ is a symmetry number ($\sigma = 1$ or 2 according as the reactants are unlike or like), and $\mu = m_1m_2/(m_1 + m_2)$. This ratio equals hZ/kT, where Z is defined as $(8\pi kT/\mu)^{1/2}R^2/\sigma$ and equals about 10^{11} l./mol sec.

in solution, discussed in Appendix III and involving no bond ruptures, the distribution of coordinates in the activated complex is determined by a potential-energy function $(1 - n^{\ddagger})\ U^{r} + n^{\ddagger}U^{p}$; *i.e.*, $n^{\ddagger}$ and, thereby, α represents the products' contribution to this function. For an atom or proton transfer or strong-overlap electron-transfer solution, if some method, such as that briefly touched on in a preceding section, were employed to calculate the terms in eq 21, $n^{\ddagger}$ and hence, α would characterize the product-like character of both types of coordinates.

As exemplified by the equations of the following section, and in accordance with the usual notion, the Brønsted plot should be curved when $\Delta F^{0\prime}$ is varied over a sufficiently wide range. For any compound the α and, hence, the $n^{\ddagger}$ equals the instantaneous slope of this plot at the given $\Delta F^{0\prime}$ for this compound.

Magnitude of the Brønsted Slope

Since α is $\partial\Delta F^{*}/\partial\Delta F^{0\prime}$, eq 2 yields

$$\alpha = {}^{1}/_{2}(1 + \Delta F_{R}^{0\prime}/\lambda) \tag{32}$$

when $|\Delta F_{R}^{0\prime}| \leqslant \lambda$. If ΔF_{0}^{*} denotes the intercept at $\Delta F^{0\prime} = 0$ of a plot of ΔF^{*} *vs.* $\Delta F^{0\prime}$, then

$$\Delta F_{0}^{*} = w^{r} + \frac{\lambda}{4}[1 + (w^{p} - w^{r})/\lambda]^{2} \cong \frac{w^{r} + w^{p}}{2} + \frac{\lambda}{4} \tag{33}$$

since $\lambda \gg (w^{p} - w^{r})$. Thus[22]

$$\alpha \cong (1 + \Delta F_{R}^{0\prime}/4\Delta F_{0}^{*})/2 \tag{34}$$

When statistical and steric factors are included, eq 34 again follows, but with w^{r} and w^{p} in $\Delta F_{R}^{0\prime}$ and ΔF_{0}^{*} replaced by W^{r} and W^{p}.

For a reaction whose functional dependence of ΔF^{*} on $\Delta F^{0\prime}$ is given instead by eq 20 (with E_{f} and ΔE^{0} replaced by ΔF^{*} and $\Delta F_{R}^{0\prime}$, etc.) α would be

$$\alpha = (1 + \tanh y)/2 \tag{35}$$

where $y = (\Delta F_{R}^{0\prime}/2\Delta F_{0}^{*}) \ln 2$. When $\Delta F_{R}^{0\prime}/\Delta F_{0}^{*}$ is 2, this α is 0.8, while that obtained from eq 34 is 0.75.

Comparisons of experimental plots of ΔF^{*} *vs.* $\Delta F^{0\prime}$ with these equations are appropriate when λ is constant for all points in the plot.

Kinetic Isotopic Effect k_{H}/k_{D} and Brønsted Slope

A maximum in plots of k_{H}/k_{D} *vs.* pK's has sometimes been reported. A useful simple explanation has been given,[23] based on little isotopic effect on ΔpK and on the reaction's forward or reverse step becoming fast (diffusion controlled) at either extremity of the plot.[23] With the aid of eq 2, we can formulate the suggestion in quantitative terms. We consider, then, reactions for which there is little isotopic effect on $\Delta F^{0\prime}$ (and W^{r} or W^{p}). The barrier difference for hydrogen and deuterium isotopes is then found from eq 2 to be [24]

$$\Delta F_{H}^{*} - \Delta F_{D}^{*} \cong {}^{1}/_{4}(\lambda_{H} - \lambda_{D})\left[1 - \left(\frac{\Delta F_{R}^{0\prime}}{\lambda_{H}}\right)^{2}\right] \tag{36}$$

when $|\Delta F_{R}^{0\prime}| \leqslant \lambda_{H}$. We have used the fact that $\lambda_{H}\lambda_{D} \cong \lambda_{H}^{2}$. The barrier difference is seen to pass through a maximum. Since $\alpha - {}^{1}/_{2}$ is $\Delta F_{R}^{0\prime}/2\lambda_{H}$, the last factor in eq 36 is $[1 - 4(\alpha - {}^{1}/_{2})^{2}]$.

Summary of Findings for Cross-Relation and for Brønsted Slope

We summarize our findings regarding eq 4. (1) Except as noted in Appendix II, the application of eq 4 to atom or proton transfers is probably limited to $|\Delta F^{0\prime}/4\Delta F_{0}^{*}| < 1$, a normally minor limitation. (2) Several models, including the BEBO one and a generalization thereof, lead to eq 4 in the vicinity of small $\Delta F^{0\prime}/4\Delta F_{0}^{*}$. Intrinsic asymmetry does not alter this equation when $\Delta F^{0\prime}/4\Delta F_{0}^{*}$ is small. (3) The difference of the BEBO and quadratic approximations, eq 20 and 8, is rather small where we have tested it. (4) Since eq 4 rests ultimately upon a continuous dependence of the main configurational free-energy change on some reaction parameter, the equation will break down when some appreciable fraction of the total free-energy change becomes independent of n, to the extent given by eq 27. (5) When steric and statistical effects occur, several models can be considered, one of which replaces eq 4 by 28. (6) Any effects which are specific only for the cross-reaction or only for one of the exchange reactions are excluded in eq 16, and so tend to cause eq 4 to break down.

The Brønsted slope, α is expected to be 0.5, when $\Delta F^{0\prime} = 0$. However, deviations would occur (a) if $c \neq 0$ in eq 27, *i.e.*, if an appreciable fraction of the free-energy change were independent of the reaction parameter n, or (b) if $g_{i}' \neq 0$ in eq 18 and, at the same time, the asymmetry ϵ is large. Equation 34 is a simple, approximate expression for α for any $\Delta F^{0\prime}$ for which $|\Delta F^{0\prime}/4\Delta F_{0}^{*}| < 1$. It yielded a value (0.75) close to that obtained (0.8) from a quite different model (eq 35) even when $\Delta F^{0\prime}/\Delta F_{0}^{*}$ had the fairly large value of 2. An interpretation of α for a certain class of models, those for which eq 21 is applicable, is given by eq 31 and the associated discussion.

Remark on Intrinsic Barriers

Reaction barriers have been considered here in terms of intrinsic (λ_{ii}) and thermodynamic ($\Delta F^{0\prime}$) contributions, as well as of steric (ζ) and statistical ones. Some test of the intrinsic–extrinsic separation can be made with data on Brønsted slopes and with the cross-relation, *e.g.*, with tests of eq 4 and 34.

(22) In writing eq 34, ${}^{1}/_{2}(w^{r} + w^{p})$ was neglected relative to ΔF_{0}^{*}, since it is normally much smaller. To avoid this approximation, the ΔF_{0}^{*} in eq 34 can be replaced by $\Delta F_{0}^{*} - {}^{1}/_{2}(w^{r} + w^{p})$.

(23) E. S. Lewis and C. H. Funderburk, *J. Am. Chem. Soc.*, 89, 2322 (1967); eq 33 shows that the diffusion-control aspect is incidental, rather than necessary.

(24) All zero-point effects have been included in the λ's.

Table I: Comparison of BEBO Calculations with Eq 8

A_i	A_j: F	HO	H	CF_3	Cl	CH_3	Et	Me_2CH	Me_3C	Br	D_{A_iH}
F	6										140
HO	0.3	4									115
	(0)										
H	2	6	10								109
	(0)	(4)									
CF_3	3	7	12	13							107
	(0.2)	(5)	(11)								
Cl	0.3	0.3	5	8	0						106
	(0)	(0)	(4)	(6)							
CH_3	3	6	11	12	7	13					105
	(0.1)	(5)	(10)	(12)	(6)						
Et	2	4	8	9	4	10	12				100
	(0)	(2)	(7)	(9)	(3)	(10)					
Me_2CH	2	4	8	9	3	9	11	12			98
	(0)	(2)	(6)	(8)	(3)	(9)	(11)				
Me_3C	2	3	6	7	2	7	9	10	12		93
	(0)	(1)	(5)	(7)	(1)	(7)	(9)	(10)			
Br	0	0.4	2	3	0	3	4	4	5	0	90
	(0)	(0)	(0)	(1)	(0)	(1)	(2)	(3)	(5)		

In interpretations of Brønsted slopes, λ has been assumed constant as a conjecture for a reaction series when the substituent is not part of the reaction site.[6,8] When a similar assumption is valid for other reactions, such as those involved in the Hammett $\sigma\rho$ relation, there is an interesting consequence. In the region of $\alpha = {}^1/_2$, σ and ρ then depend only on variations in $\Delta F^{0\prime}$. For other α's they depend on variations in $\Delta F^{0\prime}$ $(1 + \Delta F^{0\prime}/2\lambda)$ at constant λ. Then, with λ estimated from the data, discussions of substituent effects reduce purely to a discussion of effects on $\Delta F^{0\prime}$ and so fall within a broader class of problems concerning the effect of substituents on thermodynamic properties.

Appendix I. Comparison of BEBO Calculations and Eq 8

Equation 8 relates the barriers of cross-reactions [$i \neq j$ in eq 7], to exchange reactions [$i = j$ in eq 7]. Table I gives a comparison with calculations made for a BEBO model more complicated than eq 9. The reactions in this table are hydrogen-atom transfers, *i.e.*, B in eq 7 is H now. The diagonal elements in Table I provide the values of the exchange barriers E_{ii}. Values of ΔE^0 are obtained by subtracting the dissociation energies of the A_iH used in the BEBO calculations, D_{A_iH}, given in the last column. Use of eq 8 then permits the nondiagonal elements of the table to be computed. They are given in parentheses. For brevity, only values below the diagonal are given. Those above the diagonal refer to the reverse reaction and are not independent of the former.

The values based on eq 8 are seen to be close to the BEBO ones. The two sets of results show about the same agreement with the experimental data.

Appendix II. Potential Energy Surfaces in Reactions

If the potential energy of a reaction along the reaction coordinate involves a pair of intersecting parabolas, eq 8a is obtained. In this case, the predominant motion along the reaction coordinate is a vibrational or pseudo-vibrational one. In the case of a weak-overlap electron transfer in solution, numerous coordinates are involved and this plot is a profile of the potential energy along a reaction coordinate in many dimensional configuration space (*e.g.*, Figure 1 of ref 2b). The reaction coordinate is expected to be associated in part with vibrational motion of the ligands and dielectric relaxation of the solvent polarization.[2c]

In a gas-phase atom transfer, the reaction coordinate involves a concerted motion of a compressing of one bond and a stretching of the other. Here, using the usual potential contour diagrams, one can plot the potential energy along the reactants' valley, up to the saddle point, and down to the products' valley. Here, the curve, potential energy *vs.* reaction coordinate, is initially constant, then rises to a maximum, like an Eckart barrier, and then falls to another constant value.[25] One can no longer, therefore, obtain the "inverted chemical effect"[2b] possible with eq 2 at large $|\Delta F^{0\prime}/\lambda|$, and so the added equation (6) is imposed.

When the bond rupture–bond formation in atom or proton transfers in solution is the principal contributor to the reaction coordinate, as one would expect, the remarks of the last paragraph apply here as well. However, when most of the reorganization is associated

(25) *E.g.*, I. Amdur and G. G. Hammes, "Chemical Kinetics: Principles and Selected Topics," McGraw-Hill Book Co., New York, N. Y., 1966, p 47.

with coordinates not involved in bond rupture or formation, eq 6 would no longer be applicable. The "inverted chemical effect" could again occur, and the unrestricted eq 2 would again be relevant.

Appendix III. Weak-Overlap Electron Transfers and the Free Energy Analog of Eq 16

We denote by ΔF_R^* the configurational contribution to ΔF^* at any separation distance, *i.e.*

$$\Delta F_R^* = \Delta F^* - w^r \quad \text{(A1)}$$

Similarly, for formation of activated complex from products at a separation distance R, we write

$$\Delta F_R^{*p} = \Delta F^{*p} - w^p \quad \text{(A2)}$$

In ref 2b and 2e, it was noted (i) that the distribution of activated complex configurations for weak-overlap reactions was centered at the intersection of two potential energy functions U^r and U^p in many dimensional configuration space, (ii) that the distribution can be expressed in terms of an equivalent equilibrium distribution for which the configurations are distributed in accordance[26] with the function $f^* = A \exp\{-[(1 - n)U^r + nU^p]/kT\}$, where A is a normalizing constant, and (iii) that f^* is unchanged when the symbols (r, p, and n) are changed to (p, r, and $1 - n$), respectively.

ΔF_R^* can be written as $(1 - n)\ \Delta F_R^* + n\Delta F_R^{*p} + n\Delta F_R^{0'}$, since $\Delta F_R^{0'}$ equals $\Delta F_R^* - \Delta F_R^{*p}$. There is now a useful symmetry property. Because of property iii, examination of an expression for ΔF_R^* shows at once that when (r, p, and n) is replaced by (p, r, and $1 - n$), respectively, ΔF_R^* goes over to ΔF_R^{*p}, ΔF_R^{*p} goes over to ΔF_R^*, and, thus, $(1 - n)\Delta F_R^* + n\Delta F_R^{*p}$ remains unchanged. This result is used later to obtain eq A4.

We shall first show that $\partial\Delta F_R^*/\partial n = 0$. From the definition of F_R^*, *i.e.*, $\langle U^r\rangle + kT\langle \ln f^*\rangle$, [eq 35, ref 2e], where $\langle\ \rangle$ denotes average with respect to f^*, and from the equation reflecting the centered distribution, $\langle U^r\rangle = \langle U^p\rangle$ [eq A1, ref 2e], one finds that $\partial F_R^*/\partial n = 0$. Thus, $\partial\Delta F_R^*/\partial n = 0$, and part of eq 21 has been derived.

We next derive eq A4.

If, for the moment, we regard the ions as far apart, the distribution function f^* can be factored into two parts, one for each ion and its environment. So can that of the initial reactants. Thereby, the expression $(1 - n)\Delta F_R^* + n\Delta F_R^{*p}$ can also be written as the sum of two functions, $f_{11}(r, p, n)$ and $f_{22}(r, p, n)$, one for each reactant. Thus, we may write

$$\Delta F_R^* = n\Delta F_R^{0'} + f_{11}(A_1^{ox}, A_1^{red}, n) + f_{22}(A_2^{red}, A_2^{ox}, n) \quad \text{(A3)}$$

since the reactants are A_1^{ox} and A_2^{red}. In virtue of the symmetry property proven earlier, the last term also equals $f_{22}(A_2^{ox}, A_2^{red}, 1 - n)$. For brevity, we denote this term by $f_{22}(1 - n)$ and the term before it in eq A3 by $f_{11}(n)$

$$\Delta F_R^* = n\Delta F_R^{0'} + f_{11}(n) + f_{22}(1 - n) \quad \text{(A4)}$$

We consider now the case where the ions are close together in the activated complex rather than separated. Their vibrational contributions to U^r and U^p are largely additive, so this contribution to the distribution function f^* factors as before. The solvent-polarization contributions from the two ions are not independent. However, as noted on p 693 of ref 2e, deviation from an *apparent* additivity can be estimated to be small. Thus, eq A3 applies even for interacting cases.

For an exchange reaction, $f_{22}(n) = f_{11}(n)$. For these systems, according to the analysis, $n = {}^1/_2$. (There is no double maximum for barrier *vs.* reaction coordinate in this treatment.) Thus, for an exchange we have

$$\Delta F_{11}^* = 2f_{11}({}^1/_2) \quad \text{(A5)}$$

If we denote $f_{11}(n)/f_{11}({}^1/_2)$ by $g_1(n)$, the free energy analog of eq 16 follows.

In summary, there are two basic ingredients to this free energy analog of eq 16: (1) a dependence of ΔF^* on a parameter n, and (2) an additivity, which is partly apparent and partly actual, of intrinsic barrier for the changes of configuration around each center, A_1 and A_2, *i. e.*, for the changes that would occur if $\Delta F_R^{0'}$ were zero.

Glossary of Principal Symbols

Symbols	Physical Meaning or Definition
ΔF^*	Gibbs free energy barrier to reaction, related to rate constant k by 1.
$\Delta F^{\ddagger}$	Gibbs free energy of activation ($= \Delta F^* - RT \ln kT/hZ$; compare footnote 21).
$\lambda/4$	Intrinsic contribution to the barrier for electron transfers. It equals the average of the reorganizational barriers ($\lambda_{11}/4$, $\lambda_{22}/4$) of two exchange reactions, as in eq 3.
$\Delta F^{0'}$	Gibbs "standard" free energy of reaction for the prevailing medium and temperature. It differs slightly from the standard free energy change, which refers to STP and to infinite dilution.
K_{12}	Equilibrium "constant," given by $\exp(-\Delta F^{0'}/RT)$.
$\Delta F_R^{0'}$	"Standard" free energy of reaction at a typical separation distance R for the prevailing medium and temperature

(26) We have replaced the $-m$, in ref 2 by n, to conform with present notation.

	($\Delta F_R^{0\prime} = \Delta F^{0\prime} + w^p - w^r$ in eq 2 and $= \Delta F^{0\prime} + W^p - W^r$ in eq 23).
w^r, w^p	w^r is work required to bring reactants together to mean separation distance R; w^p is the similar quantity for the products.
f_{12}	Defined by eq 5. Compare also eq 25.
k_{12}, k_{11}, k_{22}	Rate constants of the cross-reaction (k_{12}) and of the exchange reactions (k_{11}, k_{22}).
ΔF_0^*	Value of ΔF^* extrapolated, in a ΔF^* *vs.* $\Delta F^{0\prime}$ plot, to $\Delta F^{0\prime} = 0$.
E_{12}	Potential-energy barrier of a gas-phase cross-reaction (7).
E_{11}, E_{22}	Potential-energy barriers of gaseous exchange reactions (7) (with $i = j$).
E	Average barrier for the two exchange reactions, as in eq 8c.
ΔE^0	Potential-energy change in the reaction.
V_1, V_2	Bond energies of A_1B and A_2B single bonds.
n_1, n_2	Bond orders of A_1B and A_2B.
p_1, p_2	Exponents in bond energy *vs.* bond order plots.
E_t	Potential energy in atom transfer (7) relative to initial potential energy.
ϵ	Intrinsic asymmetry defined by eq 13.
$x^{\ddagger}$	$n_2^{\ddagger} - 1/2$ in eq 14 or $n^{\ddagger} - 1/2$ in eq 18.
g_1, g_2	Intrinsic barrier terms in eq 16.
n	Degree-of-reaction parameter in eq 16.
$n^{\ddagger}$	Value of n at barrier maximum.
g_t', g_t''	dg_t/dn and d^2g_t/dn^2 at barrier maximum.
ΔF_{11}^*, ΔF_{22}^*	Free-energy barriers in two exchange reactions.
w_{11}, w_{22}	Work terms in two exchange reactions ($w_{tt}^r = w_{tt}^p$).
S^r, S^p	Steric factors for forward and reverse reactions.
s^r, s^p	Statistical factors for forward and reverse reactions.
W^r, W^p	Contributions to ΔF^* before (W^r) and after ($-W^p$) the rearrangements, defined in eq 22.
y, c, ζ	See eq 24b, paragraph before eq 26, and 29, respectively.
α	Brønsted slope. For its variation with $\Delta F^{0\prime}$, see eq 34 or 35.

The Effect of Solutes and Temperature on the Structure of Water

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The spectrum of liquid water has been observed over the range 600–1800 mμ by a differential method in which water at 25° is compared either with an aqueous solution at the same temperature or water at an elevated temperature. Five overtones have been observed, which may be identified with the same ones occurring in the vapor phase, and are believed to be due to the presence of nonbonded liquid water. The band at 958 mμ was chosen for quantitative studies, and solvation numbers have been calculated for a series of simple electrolytes and also for several organic solutes. The numbers obtained for electrolytes differ only slightly from those which appear as parameters in certain equations, but the sequence for the alkali halides is not the same. Water-structure enhancement by organic solutes is experimentally confirmed. Temperatures studies show that the concentration of monomeric water increases approximately linearly with temperature and doubles over the range from 25 to 80°. The strength of the hydrogen bond, based upon this temperature dependence of the monomer concentration, is estimated to be 2.67 kcal/mol. A combination of these data with those from the literature yields a calculated value of the concentration of nonbonded water at 25° of 3.5 mol/l. or about 6%.

Introduction

The structure of water has been the subject of numerous investigations and of much controversy for many years. Various techniques, such as infrared and Raman spectroscopy, nmr, X-ray diffraction, and dielectric relaxation measurements, have been used in these studies, which have also been extended to aqueous solutions. An extensive bibliography on water structure will not be presented in this paper, since excellent ones are available in Kavanau's monograph and in the book published by Pimentel and McClellan.[1] Some of

(1) (a) J. L. Kavanau, "Water and Solute-Water Interactions," Holden-Day, San Francisco, Calif., 1964; (b) "The Hydrogen Bond," G. C. Pimentel and A. L. McClellan, W. H. Freeman and Co., San Francisco, Calif., 1960.