Statistical Factors in Reaction Rate Theories

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Abstract: The use of various statistical factors in absolute rate theory (ART) is examined and criticized. It is concluded that of the various procedures proposed for incorporating statistical factors into ART rate constant expressions, only the conventional one employing a symmetry number ratio is consistent with the classical formulation of ART. A generalization of this latter factor to include the effects of chirality is also given. Finally, the use of statistical factors in other statistical rate theories is examined.

Among reaction rate theories those based on a statistical approach have enjoyed widespread use over the years, in large part because of the enormous popularity of absolute rate theory[1] (ART). Other important statistical theories contributing to this use include RRKM,[2] phase space,[3] and collision[4] theories. In the descriptions of rate constants given by these theories it has been found necessary to use statistical factors to correct for inadequacies in the basic theory. In their original formulation,[1] as part of ART, such factors took the form of a ratio of the product of symmetry numbers of the reactants to that of the activated complex. These symmetry numbers arose naturally from the use of classical rotational partition functions in the derivations and were viewed as purely quantum mechanical correction factors. However, the contemporary view of statistical factors in ART and related theories includes a correction that accounts for the presence of multiple reaction pathways.[5] Schlag,[6] for example, has advocated replacing the conventional symmetry number ratio by a "reaction path degeneracy factor", *n*, derived from an elegant group-theoretical treatment of reaction pathways. To simplify the computation Schlag and Haller[7] have described a modified direct-count method, not involving group theory, for determining the value of *n*. A variant of this method, described by Bishop and Laidler, uses the notation $l^{\ddagger}$ for *n* and describes it simply as a "statistical factor". In addition, these workers defined a "statistical factor", $r^{\ddagger}$, for the reverse process of an activated complex returning to reactants. To further complicate matters, other statistical factors designated $L^{\ddagger}$ and σ_{ch} have been proposed by Elliott and Frey[9] and Johnston,[10] respectively. These latter factors appear to be identical with both $l^{\ddagger}$ and *n*.

In a study predating the development of this contemporary view of statistical factors, Rapp and Weston[11] concluded, from an application of ART to some elementary exchange reactions, that the usual symmetry number ratio is an inadequate statistical factor in certain cases. They went on to describe a basis for modifying the symmetry number ratio which yielded statistical factors comparable to those obtained using the direct-count methods.

A further extension of the original concept of a statistical factor came from examining corrections arising from the effects of chirality. Gold,[12] in extending an earlier treatment,[13] suggested the use of symmetry numbers equal to $\frac{1}{2}$ for species which exist as unresolved mixtures of enantiomers. The reaction path degeneracy factor introduced by Schlag implicitly accounts for such effects. Marcus[14] has extended this treatment somewhat by distinguishing between optically isomeric pathways and optically isomeric activated complexes.

While an undesirable proliferation of redundant statistical factors has occurred, more importantly, an evaluation of the use of statistical factors in rate theories has never been made. In the following, we describe such an evaluation.
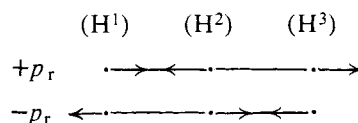
Rapp–Weston Statistical Factors

One of the earliest attempts to revise the use of the con-

ventional symmetry number ratio in ART came from a study by Rapp and Weston.[11] They applied ART to a series of elementary exchange reactions of hydrogen and deuterium and concluded that the corresponding statistical factors were, in certain cases, incorrect. They claimed that the errors arose from the failure of ART to properly account for a particular difference between the partition function of an activated complex and that of a "normal" molecule. The difference that they noted lies in the restriction placed on the integration limits (0 to ∞) of the momentum along the reaction coordinate of the activated complex. They pointed out that this restriction often results in a nonequivalency of certain atoms of an activated complex which would otherwise be equivalent in a normal molecule. For example, one may compare the asymmetry of the terminal atoms in $[H\text{-}\,\text{-}H\text{-}\,\text{-}H]^{\ddagger}$, as formed from $H\cdot + H_2$, in terms of their momentum components along the bond axis relative to the same momentum component of the central atom. This effective lowering of the symmetry of an activated complex was postulated to lead to a parallel lowering of the symmetry number used in calculating the partition function. This changes the statistical factor since ART employs only "normal" symmetry numbers.

While, in a certain sense, the symmetry of an activated complex may be affected by limiting the value of a momentum coordinate, it does *not* follow that such an effect changes the statistical factor for the reaction. Consider, for example the partition function, $Q_n^{\ddagger}$, of the activated complex for the simple hydrogen exchange reaction, $[H\text{-}\,\text{-}H\text{-}\,\text{-}H]^{\ddagger}$, as given in the classical approximation[15] by
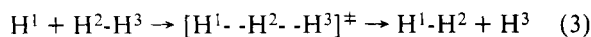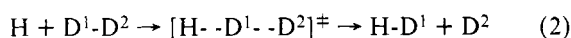
$$Q_N^{\ddagger} = \frac{1}{\sigma_{\pm}h^9} \int_{p_1} \cdots \int_{q_9} e^{-H^{\ddagger}/kT} dp_1 dq_1 \cdots dp_9 dq_9$$
$$\infty \leq p_i, q_i \leq \infty \tag{1}$$

where $H^{\ddagger}$ is the total Hamiltonian of the activated complex and $\sigma_{\pm}$ is its symmetry number. If we assume, for the moment, that there are no limit restrictions on any of the coordinates, then the required symmetry number, $\sigma_{\pm}$, equals 2. Introduction of limit restrictions on q_r, the reaction coordinate ($q_r = q_0$ to $q_0 + \delta$ where q_0 is a value of q_r near the saddle point), and on p_r, the conjugate momentum coordinate ($p_r = 0$ to $p_r = \infty$) yields the appropriate partition function for an activated complex moving toward products. These restrictions do not, however, lead to a change in the required symmetry number. With these limits the integral in eq 1 still counts the two rotational isomers, say $[H^1\text{-}\,\text{-}\,\text{-}H^2\text{-}\,\text{-}\,\text{-}H^3]^{\ddagger}$ and $[H^3\text{-}\,\text{-}\,\text{-}\,\text{-}H^2\text{-}\,\text{-}\,\text{-}H^1]^{\ddagger}$, as belonging to separate phase space volumes. This may be seen by associating p_r with the normal antisymmetric stretching mode.

$$(H^1) \qquad (H^2) \qquad (H^3)$$

$$+p_r \quad \cdot\longrightarrow\!\!\longleftarrow\cdot\text{------}\cdot\longrightarrow$$

$$-p_r \quad \longleftarrow\cdot\text{------}\cdot\longrightarrow\!\!\longleftarrow\cdot$$

The arrows in these diagrams may be viewed as representing the momentum components along the bond axis. For positive values of p_r both H^1 and H^3 will always have equal, positive values for their respective momentum components. Also, for any given elemental phase space volume surrounding a positive value of p_r there exists an equal volume corresponding to the species where the positional coordinate values of H^1 and H^3 have been interchanged. Since the two corresponding species are physically identical, the usual symmetry number correction ($\sigma_{\ddagger} = 2$) must still be made instead of using the value of unity as suggested by Rapp and Weston. Finally, we may conclude that the introduction of the limit restrictions, while affecting the value of the integral, does so without changing the value of the statistical factor. These conclusions may be generalized to include any activated complex and hence lead directly to the rejection of the use of Rapp-Weston statistical factors in ART.

It is of interest to note that Rapp and Weston's original motivation for their treatment of statistical factors came from the "untenable conclusion" that certain exchange reactions, such as those given in eq 2 and 3, must have different statistical factors ". . . at the classical limit of high temperatures where all quantum effects have vanished . . .".

$$H + D^1\text{-}D^2 \rightarrow [H\text{-}\text{-}D^1\text{-}\text{-}D^2]^{\ddagger} \rightarrow H\text{-}D^1 + D^2 \qquad (2)$$

$$H^1 + H^2\text{-}H^3 \rightarrow [H^1\text{-}\text{-}H^2\text{-}\text{-}H^3]^{\ddagger} \rightarrow H^1\text{-}H^2 + H^3 \qquad (3)$$

The ART statistical factors for eq 2 and 3 are 2 and 1, respectively. Their premise that "all quantum effects have vanished" is obviously incorrect since the quantum mechanically determined wave function symmetry properties appear at all temperatures and underlie the difference shown between the two statistical factors given here. Specifically, the antisymmetry of the total wave function of the activated complex of eq 3 requires that a statistical factor be included to account for the prohibition of rotational functions possessing symmetry properties incompatible with this total wave function. Naive "collisional" arguments that equate a statistical factor with the number of ways that an activated complex might be formed also do not take into account these essential symmetry properties.

Reaction Path Degeneracy Factors

In the calculation of ART rate constants a simple reaction path based procedure, whereby the symmetry numbers are equated to unity and the rate constant expression is simply multiplied by the number of ways reaction may occur (i.e., reaction pathways), gives, in many cases, the same results as the conventional one using symmetry numbers. As pointed out by Schlag,[6] this fact led many early workers to assume their complete equivalence. However, it was apparently the previously discussed study of Rapp and Weston[11] that first implied a *preference* for a reaction path based procedure. This notion resulted from their derivation of a new method of determining statistical factors that gave apparent agreement with those calculated using a direct-count method.

In a follow-up to this study, Schlag[6] gave his elegant derivation of the reaction path degeneracy factor and showed its use as a statistical factor in a reaction path based treatment of ART rate constants. This factor, n, was given as

$$n = kg/h \qquad (4)$$

where g and h are the orders of point groups associated with reactants and activated complex, respectively. The quantity k is the number of permutations of identical atoms in reactants, resulting from a hypothetical equilibrium between activated complexes and reactants, which are not also equivalent to a symmetry operation contained in the point group associated with g. Concerning the use of n in ART, Schlag did not attempt

to prove the validity of a reaction path based procedure, apparently feeling that its validity followed from the work of Rapp and Weston. However, Bishop and Laidler[8a] did attempt to justify this procedure using an elementary argument that bears examining.

These workers considered a general, bimolecular reaction

$$A + B \rightleftharpoons X^{\ddagger} \rightarrow C + D \qquad (5)$$
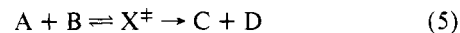
in which the activated complex, $X^{\ddagger}$, formed from A and B was hypothetically prevented from passing into products. This means that $X^{\ddagger}$ is in equilibrium with A and B. The assumption was then made that the rate of return, R_r, of the activated complex, $X^{\ddagger}$, to reactants is given by

$$R_r = r^{\ddagger}\nu[X^{\ddagger}] \qquad (6)$$

where ν is the ordinary frequency of crossing the reaction potential barrier and $r^{\ddagger}$ is the reaction path degeneracy factor associated with $X^{\ddagger}$ returning to products. A Maxwell-Boltzmann distribution for $X^{\ddagger}$ yields

$$[X^{\ddagger}] = [A][B] \left(\frac{f^{\ddagger}}{f_A f_B}\right) e^{-E_0/kT} \qquad (7)$$

where the f's are the system partition functions, including symmetry numbers. Extraction of a vibrational factor from $f^{\ddagger}$, evaluated[16] at small values of the associated frequency, gives

$$[X^{\ddagger}] = [A][B] \left(\frac{kT}{h\nu}\right)\left(\frac{f_{\ddagger}}{f_A f_B}\right) e^{-E_0/kT} \qquad (8)$$

They then applied a theorem[8,17] (cf. Appendix) relating the forward and reverse reaction path degeneracy factors, $l^{\ddagger}$ and $r^{\ddagger}$, respectively, to the symmetry numbers of A, B, and $X^{\ddagger}$.

$$\frac{l^{\ddagger}}{r^{\ddagger}} = \frac{\sigma_A \sigma_B}{\sigma_{X^{\ddagger}}} \qquad (9)$$

Use of this theorem leads to the expression

$$[X^{\ddagger}] = [A][B] \left(\frac{kT}{h\nu}\right)\left(\frac{l^{\ddagger}}{r^{\ddagger}}\right)\left(\frac{f_{\ddagger}^0}{f_A^0 f_B^0}\right) e^{-E_0/kT} \qquad (10)$$

where the f^0's are the partition functions from which the symmetry numbers have been omitted. Substitution of eq 10 into eq 6 yields

$$R_r = l^{\ddagger}[A][B]\left(\frac{kT}{h}\right)\left(\frac{f_{\ddagger}^0}{f_A^0 f_B^0}\right) e^{-E_0/kT} \qquad (11)$$

Since the system is at equilibrium, eq 11 also gives the rate with which the reactions enter the activated state. Replacing the barrier restriction by the hypothesis[18] that all activated complexes become products results in R_r becoming the rate associated with product formation, in accordance with the reaction path based procedure discussed previously.

While appearing straightforward, this argument is flawed by the initial assumption that R_r is given by eq 6. The correct expression should be
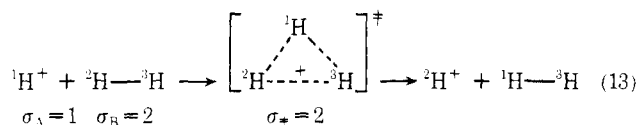
$$R_r = \nu[X^{\ddagger}] \qquad (12)$$

To understand this requires a brief examination of the properties of an activated complex. Within the quadratic approximation, the barrier-crossing frequency, ν, may be identified with a vibrational normal mode corresponding to the reaction coordinate. Since the force constant matrix of an activated complex must possess only one negative eigenvalue,[19] this eigenvalue must be associated with ν. It follows that an activated complex may possess only one normal mode of decomposition. This implies that the rate of decomposition to reactants of an activated complex is determined solely by ν; if the factor for $[X^{\ddagger}]$ were $r^{\ddagger}\nu$ instead of ν then there would exist $r^{\ddagger}$ independent decomposition modes corresponding to $r^{\ddagger}$ additional

normal modes. In the case where $r^{\ddagger} > 1$ the structure would no longer be an activated complex.[20]

Use of eq 12 in Bishop and Laidler's argument leads to a modification of eq 11 in which $l^{\ddagger}$ is replaced by $l^{\ddagger}/r^{\ddagger}$. This modified rate constant expression is equivalent to the conventional ART expression since this latter ratio is equivalent to the conventional symmetry number ratio (cf. eq 9). In addition to vindicating the original symmetry number treatment this modified argument also shows the proper use of reaction path degeneracy factors in ART rate constant calculations.

The use of reaction path degeneracy factors in the analysis of reaction pathways has occasionally led to difficulties. For example, a recent study[22] discussing the use of statistical factors in reaction systems containing "valley bifurcations" [23] on the associated potential energy surfaces concluded that the relative merits of using single reaction path degeneracy factors vs. symmetry number ratios depended upon the detailed kinematics near these bifurcations. However, since ART is not concerned with species intermediate (e.g., at a bifurcation) between reactant and activated complex it follows that the kinematics associated with such a species are irrelevant to choosing a statistical factor. Had these workers realized this, their remaining arguments would have led them to reject their use of reaction path degeneracy factors in describing these reactions.

It has been tacitly assumed by some workers[6,11] that the reaction path degeneracy factors and the Rapp-Weston factors are equivalent. That this is not a correct assumption may be shown most directly by a simple example that demonstrates the contrary. Consider the proton exchange reaction given in eq 13. A hypothetical activated complex of C_{2v} symmetry is

$$
{}^{1}\mathrm{H}^{+} + {}^{2}\mathrm{H}{-\!\!\!-}{}^{3}\mathrm{H} \longrightarrow \left[{}^{2}\mathrm{H} \overset{\overset{\textstyle {}^{1}\mathrm{H}}{\diagup \diagdown}}{\cdots \overset{+}{\cdots}} {}^{3}\mathrm{H} \right]^{\ddagger} \longrightarrow {}^{2}\mathrm{H}^{+} + {}^{1}\mathrm{H}{-\!\!\!-}{}^{3}\mathrm{H} \quad (13)
$$

$$
\sigma_{\mathrm{A}} = 1 \quad \sigma_{\mathrm{B}} = 2 \qquad \sigma_{\ddagger} = 2
$$

postulated. While it is symmetry allowed,[21] its reasonableness is irrelevant to the following considerations. A trivial calculation shows the symmetry number ratio, $\sigma_{\mathrm{A}}\sigma_{\mathrm{B}}/\sigma_{\ddagger}$, to equal unity. The reaction path degeneracy factor $l^{\ddagger}$, calculated by Laidler's procedure, is equal to 3. Finally, owing to the inequivalence of atoms 2 and 3 along the reaction coordinate, the symmetry number of the activated complex, by Rapp and Weston's reasoning, must be reduced to unity resulting in a modified symmetry number ratio of 2. Thus, all three statistical factors are different!

Effects of Chirality on Statistical Factors

Since the partition function of a chiral species represents that of only one enantiomer, in reactions involving unresolved mixtures of enantiomers a corrected ART rate constant expression is often needed to account for the presence of the other enantiomer. Thus, Gold[12] suggested assigning a symmetry number equal to $\frac{1}{2}$ to any species, which is also an unresolved mixture of enantiomers, involved in a reaction. This, in effect, doubles the value of the corresponding partition function thus accounting for both enantiomers. For reactions involving *diastereomeric* species only one of these should be counted since the others are best viewed as belonging to separate reaction systems.

Gold's ad hoc procedure of accounting for enantiomeric species in reactions may be generalized to include *all* species if the symmetry number of a species is simply replaced by the factor $h/2$, where h is the order of the point group of the species. Thus, in the case of achiral species, this factor reduces to the symmetry number,[7] σ, since the order of the point group is 2σ. The only exceptions occur for the cases of linear molecules possessing $D_{\infty h}$ or $C_{\infty v}$ symmetry, where the symmetry

numbers are 2 and 1, respectively. Similarly, for chiral species this factor reduces to $\sigma/2$ since the order of the corresponding point group is σ owing to the absence of improper rotation axes in point groups of chiral systems. Thus, Gold's factor of $\frac{1}{2}$ is automatically included here for all chiral species with symmetry numbers of unity. In addition, this procedure accounts for chiral species possessing symmetry numbers greater than unity. This generalization also applies to statistical factors in equilibrium constant expressions.

Statistical Factors in Other Rate Theories

Most work on statistical factors has concentrated on applications to ART. We now give an outline of extensions of this work to other important statistical theories.

A. RRKM Theory.[2] Since RRKM theory is based on ART the same considerations apply. Hence, the appropriate statistical factor, S, is given by

$$
S = h_{\mathrm{R}}/h_{\mathrm{X}^{\ddagger}} \quad (14)
$$

where h_{R} and $h_{\mathrm{X}^{\ddagger}}$ refer to the group orders of reactant (R) and activated complex ($\mathrm{X}^{\ddagger}$), respectively. In the usual case where only achiral species are involved this ratio of group orders reduces to the familiar ratio of the corresponding symmetry numbers. This same reduction also applies to reaction involving *only* unresolved chiral species.

To account for chirality effects Marcus[14] suggested multiplying RRKM rate constant expressions by the factor α, defined as "the number of optically isomeric reaction paths". Paths were chosen instead of activated complexes to account for the situation where two optically isomeric paths intersect in configuration space at a single achiral activated complex. However, within the quadratic approximation,[20] an activated complex cannot exist at the intersection of two independent reaction paths with still a third path leading to products. Thus, one should alter the definition for such systems of α to read "number of optically isomeric activated complexes" in keeping with an earlier definition given by Marcus.[14b] Explicit inclusion of α in rate constant expressions is not necessary since it is already included in eq 14.

B. Collision Theory. The possibility of using a single reaction path degeneracy factor as a statistical factor occurs in this theory. This theory is discussed here mainly to demonstrate this possibility. Eliason and Hirschfelder,[4a] in their general collisional treatment of bimolecular reactions, derived the following rate constant expression for a reaction between a and b,

$$
k_{\mathrm{r}} = \frac{(2/kT)^{3/2}}{(\Pi\mu)^{1/2}Q_{a}{}^{\mathrm{int}}Q_{b}{}^{\mathrm{int}}} \sum_{ij} \sum_{mn} e^{[-|\epsilon_{ai}+\epsilon_{bj}|/kT]}
$$

$$
\int_{0}^{\infty} C_{ij}{}^{mn}(E)Ee^{-E/kT}\mathrm{d}E \quad (15)
$$

where $Q_{a}{}^{\mathrm{int}}$ and $Q_{b}{}^{\mathrm{int}}$ are the respective internal partition functions of a and b, ϵ_{ai} and ϵ_{bj} are the respective ith and jth energy states of a and b, and $C_{ij}{}^{mn}$ is the reaction cross section at initial relative kinetic energy E for reactant states i and j going to product states m and n. An obvious statistical factor is obtained by extracting the symmetry numbers of a and b from the partition functions $Q_{a}{}^{\mathrm{int}}$ and $Q_{b}{}^{\mathrm{int}}$. It also seems reasonable to associate a statistical factor with $C_{ij}{}^{mn}$ if there exists an equivalency among the various orientations of a and b that lead to the same products. Assuming that identical atoms in a and b are labeled, we may define $S_{ij}{}^{mn}$, the specific reaction cross section, to be the reaction cross section associated with the range of relative orientations of a and b that lead to the *same* labeled product(s). From one of these relative orientations of a and b there may be obtained l equivalent ones, by symmetric rotations of a and/or b, that each lead to *different* labeled product(s). If these l orientations represent all

possible orientation ranges for a given reaction between a and b then

$$lS_{ij}{}^{mn} = C_{ij}{}^{mn} \tag{16}$$

The factor l is defined here to be identical with the factor l described by Bishop and Laidler[8] as being the number of differently labeled sets of given products that can be formed if all identical atoms in reactants are labeled. Factoring of both the partition functions and the reaction cross section in eq 15 leads to an overall statistical factor, S_c, given by

$$S_c = \frac{l h_a h_b}{4} \tag{17}$$

For the usual case of achiral reactants, this expression reduces to a simple product of l and the corresponding symmetry numbers.

The specific reaction cross section, $S_{ij}{}^{mn}$, should prove to be a more meaningful quantity than $C_{ij}{}^{mn}$ in discussing relative reactivities since statistical factors are essentially absent from the former factor.

C. Variational Theory. Building on earlier treatments,[24] Keck[25] has described a rate theory based on the assumption that a reacting system can be described by the motion of a representative point in phase space. Division of this phase space by a trial "surface" separates reactants from products. The best approximation to the true reaction rate is obtained by varying this trial surface until a minimum flow through the surface is obtained. An equivalent theory, expressed in a different language, is the so-called phase space theory as formulated by Light and co-workers[3a] and Nikitin.[3b]

Keck's classical expression[25a] for a general rate constant of a reaction of order v leading from an initial chemical state i to a final state f through a dividing surface $S(f,i)$ in phase space is given by

$$k(f,i) = Q_i^{-1} \int_{S(f,i)} e^{-E/kT} \left(\sum_l^{3n-3} J_j/|J_l| \right) dE \prod_2^{3n-3} dp_j dq_j \tag{18}$$

where

$$Q_i = V^{1-v} \int_{\Omega(i)} e^{-E/kT} \prod_i^{3n-3} dp_j dq_j \tag{19}$$

Q_i is the classical partition function per unit volume for a system in the state i, corresponding to the phase space volume $\Omega(i)$, and E is the total energy in the center of mass. The quantity J_j is the Jacobian of the coordinate transformation from (H,S), where H is the system Hamiltonian, to (p_j,q_j).

Applying the usual quantum mechanical correction, the partition function Q_i corresponding to the v reactants is simply multiplied by the familiar product of reciprocal symmetry numbers, $\prod_i^v 1/\sigma_i$. The phase space volume element in eq 18 corresponds to the species on the surface $S(f,i)$ less one degree of freedom (in addition to the lack of the three translational degrees of freedom). This missing degree of freedom is essentially contained in dE since $dE = J_1 dp_1 dq_1/dS$. Hence, a similar correction applied to this integral yields the reciprocal symmetry number $1/\sigma_*$ corresponding to the surface species, X^*. Obviously, the symmetry number σ_* is critically dependent upon the location of the dividing surface. Depending upon the location of this dividing surface, the symmetry number may, in general, be best represented as a product of w symmetry numbers corresponding to w loosely associated fragments in X^*. The resulting, overall statistical factor, S_v, for achiral species is given by

$$S_v = \frac{\prod\limits_i^v \sigma_i}{\prod\limits_j^w \sigma_j} = \frac{\prod\limits_i^v h_i}{v - w \prod\limits_j^w h_j} \tag{20}$$

The generalization of this expression to the group order form is necessary to account for chirality effects in both reactants and surface species. Keck has also shown that eq 18 reduces to the ART rate constant expression when the energy of the system is separable between the coordinates p_i, q_i and the remaining coordinates. The surface species is then the activated complex and the statistical factor S_v reduces to the ratio of symmetry numbers characteristic of ART.

Conclusions

From this study we conclude that the recent use of reaction path degeneracy factors[6-8] and the Rapp-Weston factors[11] in place of the conventional symmetry number ratios in ART-based rate expressions is inconsistent with the basic assumptions of ART. The conventional symmetry number ratio remains as the proper statistical factor to use in ART. However, while the Rapp-Weston factor arose from an incorrect derivation within ART, the reaction path degeneracy factor stands on its own and may be used as a legitimate statistical factor in, for example, collision theory rate expressions. In examining the effects of chirality on statistical factors it was found that a simple replacement of a symmetry number by the factor $h/2$, where h is the order of the point group associated with a species, leads to a general procedure that accounts for the chirality of all species in reaction systems. Finally, we have extended these conclusions to include the case of statistical factors in the related RRKM and variational rate theories.

Note Added in Proof. E. Pollak and P. Pechuckas (*J. Am. Chem. Soc.*, preceding paper in this issue) discuss the question of using reaction path degeneracy factors in ART. While their approach differs somewhat from ours, they are in agreement with our conclusion that such factors should be replaced by symmetry number ratios. Only in their treatment of symmetric reactions (i.e., those reactions where products are identical with reactants) do our conclusions differ. Our position on this matter is essentially contained in the discussion surrounding eq 2 and 3; vide supra.

Appendix

The relationship of reaction path degeneracy factors to symmetry numbers given by Bishop and Laidler[8] (cf. eq 9) may also be derived from a graph-theoretical result given by Gordon and Temple.[17] These workers showed that the product of the quotients, n_{fi}/n_{ri}, of the forward and reverse reaction path degeneracy factors for a series of y steps leading to a given molecule from its constituent atoms is proportional to the reciprocal symmetry number, $1/\sigma$, of the molecule:

$$g \prod_{i=1}^{y} \frac{n_{fi}}{n_{ri}} = \frac{1}{\sigma}$$

The proportionality constant, g, is a statistical factor equal to the number of equivalent ways the intermediate graph-like particle may be converted into the actual molecular configuration. Applying this relationship to a general, unimolecular reaction, $A \rightarrow T^{\ddagger} \rightarrow B$, yields the equations

$$g_A \prod_{i=1}^{y-1} \frac{n_{fi}(A)}{n_{ri}(A)} = \frac{1}{\sigma_A} \qquad g_{T^{\ddagger}} \prod_{i=1}^{y} \frac{n_{fi}(T^{\ddagger})}{n_{ri}(T^{\ddagger})} = \frac{1}{\sigma_{T^{\ddagger}}}$$

where the first $y - 1$ steps are common to both. Hence, factoring the left side of the second of these equations yields the identity

$$\left[\frac{n_{fy}(A)}{n_{ry}(A)} \right] g_A \prod_{i=1}^{y-1} \left(\frac{n_{fi}(A)}{n_{ri}(A)} \right) \equiv g_{T^{\ddagger}} \prod_{i=1}^{y} \frac{n_{fi}(T^{\ddagger})}{n_{ri}(T^{\ddagger})}$$

where $n_{ry}(A)/n_{ry}(A)$ is simply the quotient of reaction path degeneracy factors for the transformation $A \rightleftharpoons [T]^{\ddagger}$. Using these relationships it follows that

$$\frac{n_{fv}(A)}{n_{rv}(A)} = \frac{\sigma_A}{\sigma_{T^{\ddagger}}}$$

as shown earlier by Bishop and Laidler.[8] A similar result may be derived for bimolecular reactions.

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Vibronic Coupling Model for Calculation of Mixed Valence Absorption Profiles

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Abstract: A vibronic coupling model for mixed valence systems is developed which provides explicit eigenvalues and eigenfunctions based on the formalism previously developed by Fulton and Gouterman to discuss the excited states of symmetrical dimers. The mixed valence (intervalence) absorption profile is obtained by calculating transition intensities from populated vibronic levels to all higher vibronic levels within the manifold. The parameters of the model are directly related to properties of the "monomeric" units. The theory is first applied to the case of two identical and pseudooctahedral constituent units ("monomers") assuming equal force constants in both oxidation states of the monomer. A number of synthetic profiles are presented for a range of parameters. The unique Creutz–Taube complex ($[(NH_3)_5Ru\text{-pyr-}Ru(NH_3)_5]^{5+}$) is singled out for analysis. The room temperature absorption spectrum is fit well by a pair of quite closely defined parameters. These parameters indicate that the lower potential surface has a small (~57 cm^{-1}) barrier ("valence trapping"). *However*, the lowest vibronic state is calculated to be about 30 cm^{-1} above the top of this barrier. Furthermore, the calculated probability distribution in configuration space shows complete valence delocalization (no trapping) at low temperature, but there is a small hint of trapping at room temperature. The model is extended to unsymmetrical mixed valence systems (nonidentical "monomers"). The consequences both of including spin–orbit coupling and allowing unequal force constants are examined.

I. Introduction

Systems containing ions in two different oxidation states often have intense absorption bands which cannot be attributed to the absorption of either constituent ion. The classic example is Prussian blue, an insoluble crystalline solid containing both six-coordinate ferricyanide [Fe(III)–C–N coordination] and six-coordinate ferrocyanide (Fe(II)–N–C coordination) in a regular cubic array.[2a] Neither of these monomeric species alone gives rise to the intense blue color which apparently results from excitations involving *both* the Fe(II) and Fe(III)

centers. Such transitions are termed mixed valence or intervalence transitions.[2b,c]

In recent years, a new mixed valence complex,

$$[(NH_3)_5Ru\!\!\underset{}{\overparen{}}\!\!NRu(NH_3)_5]^{5+}$$

has been synthesized by Creutz and Taube.[3] This ion is particularly interesting theoretically because the two Ru atoms have identical coordination spheres but different oxidation states; one is Ru(II) and the other Ru(III). In the visible absorption region the Creutz–Taube (C–T) complex shows the

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