

- (10) See G. C. Pimentel and A. L. McClellan, "The Hydrogen Bond", W. H. Freeman, San Francisco, Calif., 1960, for a discussion of the "deficiencies" of an electrostatic model of the hydrogen bond.
- (11) T. R. Dyke, B. J. Howard, and W. Klemperer, *J. Chem. Phys.*, **56**, 2442 (1972).
- (12) D. R. Yarkony, S. V. O'Neill, and H. F. Schaefer, *J. Chem. Phys.*, **60**, 855 (1975).
- (13) H. Urneyama and K. Morokuma, *J. Am. Chem. Soc.*, **99**, 1316 (1977).
- (14) F. Cotton and G. Wilkinson, "Advanced Inorganic Chemistry", 3rd ed, Wiley-Interscience, New York, N.Y., 1972, describe the different electronegativity scales; we have used the Allred-Rockow scale.
- (15) Of course, we could use any fraction of the van der Waals distance, so these choices are just representative values.
- (16) We used experimental monomer geometries for these molecules; see ref 1.
- (17) As discussed in ref 1 and 2, we evaluated the electrostatic potential around the periphery of the molecule and found suitable "reference positions" to compare the Lewis acidity and basicity of various molecules. For electrophilic regions, we found that an appropriate choice of distances from atoms were H, 2 Å; C, Cl, S, N, F = 2.65 Å. For nucleophilic regions: N, O, F = 2.12 Å and Cl, S, P = 2.65 Å. In each case, we choose the optimum angular orientation at this distance from the atom.
- (18) K. Janda, J. M. Steed, S. E. Novick, and W. Klemperer, submitted for publication.
- (19) According to the vdW model, it is a stronger Lewis base than HF; with the $\frac{1}{2}$ vdW model, it is weaker than HF.
- (20) B. J. Rosenberg, W. C. Ermler, and I. Shavitt, *J. Chem. Phys.*, **65**, 4072 (1976).
- (21) H. Kistenmacher, H. Popkie, and E. Clementi, *J. Chem. Phys.*, **58**, 5627 (1973).
- (22) One might speculate at this point that the tendency for $\text{H}_2\text{PH}\cdots\text{PH}_3$ to have a linear H bond rather than be bifurcated in the 431G calculations is due to charge transfer terms (which would favor a linear A-H \cdots B geometry) canceling the electrostatic tendency to bifurcate. As has been previously noted,² such charge redistribution effects would be expected to be more important in second row (P, Cl, S) than first row (N, O, F) intermolecular complexes.
- (23) P. Kollman and S. Rothenberg, *J. Am. Chem. Soc.*, **99**, 1333 (1977).
- (24) S. Iwata and K. Morokuma, *J. Am. Chem. Soc.*, **95**, 7563 (1973).
- (25) K. G. Spears, *J. Phys. Chem.*, **81**, 186 (1977).
- (26) J. Del Bene, *J. Chem. Phys.*, **62**, 4666 (1975).
- (27) H. Bent, *Chem. Rev.*, **68**, 587 (1968).
- (28) A. Johansson, P. Kollman, S. Rothenberg, and J. McKelvey, *J. Am. Chem. Soc.*, **96**, 3794 (1974).
- (29) The estimate for $(\text{H}_2\text{O})_2$ comes from an analysis by P. Kollman in "Modern Theoretical Chemistry", Vol. 7, H. F. Schaefer, Ed., Plenum Press, New York, N.Y., 1977. For $(\text{HCN})_2$, W. F. Giaque and R. A. Ruhrwein (*J. Am. Chem. Soc.*, **61**, 2626 (1939)) found $\Delta H^{298} = -3.3$ kcal/mol; using an approximate (1 kcal/mol) difference between ΔH^{298} and ΔE° as was found in the above analysis for $(\text{H}_2\text{O})_2$, we conclude that $-\Delta E^\circ$ for $(\text{HCN})_2$ is likely to be ~ 4.3 kcal/mol.
- (30) Comparing the expected distance dependence with that actually calculated with these charge distributions indicates that the electrostatic potential at these distances from the molecule follows approximately the very simple $1/R^2$ dependence.
- (31) STO-3G calculations on $(\text{HCN})_2$ (A. Johansson, P. Kollman, and S. Rothenberg, *Theor. Chim. Acta*, **26**, 97 (1972)) and $(\text{H}_2\text{O})_2$ (J. Del Bene and J. A. Pople, *J. Chem. Phys.*, **52**, 4858 (1970)) suggest that $R(\text{N}\cdots\text{C}) > R(\text{O}\cdots\text{O})$ by ~ 0.4 Å. Thus, we have used the observed O-O distance in $(\text{H}_2\text{O})_2$ ($R = 3.0$ Å) and assumed $R(\text{C}-\text{N}) = 3.4$ Å. This leads to an H \cdots O distance in $(\text{H}_2\text{O})_2$ of 2.047 Å and an H \cdots N distance in $(\text{HCN})_2$ of 2.343 Å. We then scale the Lewis acid ESPOT from Table VI by $(2.0 \text{ Å}/R(\text{H}\cdots\text{X}))^n$, and the Lewis base ESPOT by $(2.12 \text{ Å}/R(\text{H}\cdots\text{X}))^n$ where $n = 2$ for ESPOT and $n = 3$ for $\nabla(\text{ESPOT})$.
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- (35) J. O. Noell and K. Morokuma (*J. Phys. Chem.*, **80**, 2675 (1976)) also found $\theta = 20$ for $(\text{H}_2\text{O})_2$ with atom-centered partial charges and $R(\text{O}-\text{O})$ fixed. However, the experimental fact that $\theta > 20$ for $(\text{H}_2\text{O})_2$ and $\theta \neq 0$ for $(\text{HF})_2$ suggests that a nonsymmetric charge distribution around F and O is required.

Symmetry Numbers, Not Statistical Factors, Should Be Used in Absolute Rate Theory and in Brønsted Relations

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Abstract: For many years there has been some question whether one should correct for the effects of molecular symmetry, in the rate expressions of transition state theory, by simply using symmetry numbers, as one does in the equilibrium expressions of statistical thermodynamics; several authors have asserted that the correct rate expressions should instead contain "statistical factors", which are dynamically defined numbers characteristic of the reaction mechanism. We show that the use of symmetry numbers is always correct, and that statistical factor rate expressions—when they differ from their symmetry number counterparts—are wrong. Special attention is given to reactions involving optically active species, and to symmetric reactions, where it is easy to make mistakes in writing down transition state theory rate expressions. The implications for the Brønsted relations of acid-base catalysis are discussed.

I. Introduction

Over the past 15 years it has become widely accepted that in applications of absolute rate theory the symmetry of a reacting species or transition state is not always correctly taken into account by the use of symmetry numbers.¹⁻⁷ Two particular objections to the use of symmetry numbers have been raised: first, the symmetry number method seems to give clearly incorrect rate expressions for symmetric reactions;^{1-3,6,8} and second, complications arise for reactions that involve optically active species.^{1-3,6,9-12} Several authors have therefore proposed that one should use so-called "statistical factors" or "reaction path degeneracies" instead of symmetry numbers;^{1-3,6} the definition of statistical factors seems to ensure that one obtains correct expressions in these cases.

More recently, however, a number of authors^{6,13-15} have pointed out that the use of statistical factors cannot always be

correct, for in some reactions the ratio of forward to backward rate constant—when these are evaluated using statistical factors—does not equal the equilibrium constant. There is therefore a puzzle: apparently symmetry numbers are not always enough but on the other hand statistical factors can also lead to error; what then is the correct way of accounting for symmetry in transition state theory?

In this paper we show that the symmetry number method, properly applied, will always lead to correct rate expressions. Statistical factor rate expressions, when they differ from their symmetry number counterparts, are therefore wrong.

We emphasize that the suspicious phrase "properly applied", in the paragraph above, is not meant to cover magic or fraud. The rate expressions given by the symmetry number method are unambiguous, and they are correct, but it is easy to make mistakes writing them down for symmetric reactions and for reactions involving optically active species.

Here is the plan of the paper: In section II we give a mathematically precise definition of what we mean by statistical factors; this definition is our interpretation of the 1969 Bishop and Laidler prescription¹⁵ that the statistical factor for a process is the number of "chemically plausible" products that can be formed if all identical atoms in the reactant molecules are labeled. In section III we comment on the violation of detailed balance by the statistical factor method, and we discuss and reject a solution to the problem proposed by Murrell and Laidler¹³ (see also Laidler⁶). Section IV proves the validity of the symmetry number method, by an argument that makes direct use of statistical factors. In sections V and VI we outline the proper application of the symmetry number method to reactions involving optically active species and to symmetric reactions. Symmetry corrections to the Brønsted relations of acid-base catalysis are discussed in section VII. We conclude with a sampling of particular examples, in section VIII, to illustrate the application of the symmetry number method.

Finally, we should mention that while awaiting journal acceptance of this paper we received a preprint from D. R. Coulson¹⁸ on the same subject and with much the same conclusions. The reader should consult Coulson's paper for other arguments to the effect that the symmetry number rate expressions are correct.

II. Symmetry Numbers and Statistical Factors

Suppose that like atoms in a molecule could be distinguished, by labels. Then from one equilibrium configuration of the labeled molecule others could be made, by permutation of like atoms; the total number of configurations generated in this way would be $\prod_i N_i!$, where N_i is the number of atoms of type i in the molecule. Some of these configurations might be related to others by a rotation of the molecule as a whole; we say that two equilibrium configurations of the labeled molecule are physically distinct if one cannot be superimposed on the other by a rigid displacement—by translation and/or rotation. The number of physically distinct configurations of the molecule is $\prod_i N_i!/\sigma$ where σ is the molecule's symmetry number, and this relation may be used as the definition of the symmetry number. For example, labeled methane has just two physically distinct configurations, which are mirror images of each other, and therefore the symmetry number of methane is 12.

Suppose now that the molecule—call it A—participates in a unimolecular reaction $A \rightleftharpoons C$ that proceeds through a "transition state" intermediate T,



The transition state geometry is, of course, just a different arrangement in space of the $\sum_i N_i$ atoms that make up A, and the number of physically distinct configurations of labeled T is $\prod_i N_i!/\sigma_T$ where σ_T is the symmetry number of the transition state.

Statistical factors for reaction 1 are defined with reference to the potential energy surface governing the reaction. Let E_T be the potential energy of the transition state, presumed greater than E_A or E_C , the potential energies of reactant and product, respectively. Suppose that a given configuration of labeled A and a given configuration of labeled T can be connected by a path in nuclear configuration space on which the potential energy is less than E_T at all points but the end point at T; then that configuration of T is an intermediate for reaction from the given configuration of A, in the sense that one can reach it from A without first passing through another transition state or a configuration of even higher potential energy. The statistical factor l_A —the statistical factor for leaving A in the process $A \rightarrow T$ —is the number of physically distinct configurations of labeled T that are intermediates for reaction from one configuration of labeled A.

It is not hard to show that the statistical factor l_A is well defined by the preceding paragraph—that l_A does not depend on the particular configuration of labeled A that one selects as starting point. The essence of the argument is this: two physically distinct configurations of labeled A differ—aside from a rigid displacement—by a permutation of like atoms; if from one configuration of A one can reach l_A physically distinct configurations of labeled T, then from the other configuration of A one can reach those l_A configurations of T obtained by the appropriate permutation of like atoms; these l_A configurations are in fact physically distinct, for a common permutation applied to physically distinct configurations gives physically distinct configurations.

The statistical factor r_A for returning to A from T is defined in similar fashion as the number of physically distinct configurations of labeled A that can be reached, from one configuration of T, by paths on which the unique point of highest potential energy is the starting point at T. To the product side of T we have, with analogous definitions, the statistical factor l_C for leaving C in the process $C \rightarrow T$ and the statistical factor r_C for returning to C from T.

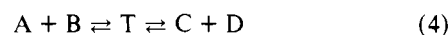
To calculate statistical factors one often needs some knowledge of the potential surface governing the reaction; to calculate symmetry numbers one need only know molecular geometries. Nevertheless, statistical factors and symmetry numbers are not entirely unrelated: Bishop and Laidler^{3,15} showed that

$$l_A/\sigma_A = r_A/\sigma_T \quad (2)$$

$$l_C/\sigma_C = r_C/\sigma_T \quad (3)$$

We shall use eq 2 and 3 in sections III and IV. These equations follow so directly from our definition of statistical factors that we give the proof. Choose $\prod_i N_i!/\sigma_A$ physically distinct configurations of labeled A and $\prod_i N_i!/\sigma_T$ physically distinct configurations of labeled T. Each configuration of A connects to l_A configurations of T by paths on which T is the unique point of highest potential energy, and each configuration of T connects to r_A configurations of A by paths on which T is the unique point of highest potential energy. Connections are reversible: if a configuration of A connects to a configuration of T, then that configuration of T connects to that configuration of A. Therefore the total number of connections from A, $l_A \prod_i N_i!/\sigma_A$, equals the total number of connections from T, $r_A \prod_i N_i!/\sigma_T$, and eq 2 follows. Equation 3 is proved in analogous fashion.

Minor modifications in the definitions above are needed for the case of a bimolecular reaction,



Here an equilibrium configuration of labeled reactants—a minimum on the potential energy surface—is a configuration in which A and B are held in fixed relative orientation and at a fixed distance from one another by weak van der Waals forces. The barrier to free rotation of the separated molecules is usually negligible in comparison with the activation barrier to reaction, so two equilibrium configurations of labeled reactants are considered physically distinct only if they cannot be superimposed by translation and rotation of the individual molecules A and B. If A and B are molecules of different type, the number of physically distinct reactant configurations is then $\prod_i N_i!/\sigma_A \sigma_B$, where N_i is the total number of atoms of type i in molecules A and B and σ_A and σ_B are the symmetry numbers of the individual molecules. Statistical factors are defined as before: l_{A+B} is the number of physically distinct configurations of T that can be reached from a given configuration of A + B, and r_{A+B} is the number of physically distinct configurations of A + B that can be reached from a given

configuration of T, by paths on which T is the unique point of highest potential energy; and

$$l_{A+B}/\sigma_A\sigma_B = r_{A+B}/\sigma_T \quad (5a)$$

If $A = B$, the number of physically distinct reactant configurations is $\prod_i N_i!/2\sigma_A^2$, since the particular permutation of like atoms that interchanges the two molecules can be effected by simply moving each molecule to where the other was. In this case,¹⁹

$$l_{A+A}/2\sigma_A^2 = r_{A+A}/\sigma_T \quad (5b)$$

We close this section by listing various transition state theory rate expressions, to establish notation. For the moment we exclude reactions that involve optically active species (see section V) and symmetric reactions (see section VI). Then according to the symmetry number method the forward and backward rate constants for the unimolecular reaction (1) are

$$k_f = \frac{kT}{h} \frac{Q_T^0/\sigma_T}{Q_A^0/\sigma_A} \quad k_b = \frac{kT}{h} \frac{Q_T^0/\sigma_T}{Q_C^0/\sigma_C} \quad (6)$$

while the statistical factor method gives

$$k_f = \frac{kT}{h} l_A \frac{Q_T^0}{Q_A^0} \quad k_b = \frac{kT}{h} l_C \frac{Q_T^0}{Q_C^0} \quad (7)$$

Here Q^0 denotes partition functions evaluated without symmetry numbers—that is, as if like atoms in A, T, and C were distinguishable—and energies are measured with respect to a common zero, so that Q_T^0 contains a factor $\exp(-E_T/kT)$, Q_A^0 a factor $\exp(-E_A/kT)$, and so on. For the bimolecular reaction (4) the corresponding expressions are of course

$$k_f = \frac{kT}{h} \frac{Q_T^0/\sigma_T}{Q_A^0 Q_B^0/\sigma_A\sigma_B} \quad k_b = \frac{kT}{h} \frac{Q_T^0/\sigma_T}{Q_C^0 Q_D^0/\sigma_C\sigma_D} \quad (8)$$

according to the symmetry number method and

$$k_f = \frac{kT}{h} l_{A+B} \frac{Q_T^0}{Q_A^0 Q_B^0} \quad k_b = \frac{kT}{h} l_{C+D} \frac{Q_T^0}{Q_C^0 Q_D^0} \quad (9)$$

according to the statistical factor method.

III. Violation of Detailed Balance by the Statistical Factor Method

Using eq 2 and 3, one finds that the symmetry number rate equations (6) agree with the statistical factor expressions (7) if and only if $r_A = r_C = 1$; similarly, expressions 8 and 9 agree only if $r_{A+B} = r_{C+D} = 1$.²⁰ The reactions of interest, then, are those in which a given transition state connects to two or more physically distinct configurations of labeled reactant and/or product.

Now whether or not the symmetry number expressions 6 are correct, their ratio gives the correct statistical mechanical expression for the equilibrium constant. This is true of the statistical factor rate expressions 7 only if $r_A = r_C$; otherwise, we have

$$k_f/k_b = (l_A/l_C)(Q_C^0/Q_A^0) \\ = (r_A/r_C)(Q_C^0/\sigma_C)/(Q_A^0/\sigma_A) = (r_A/r_C)K_{eq}$$

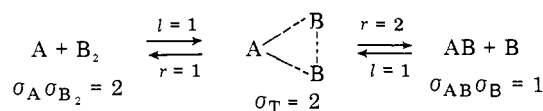
the statistical factor method violates the principle of detailed balance, and k_f or k_b or both must be wrong. This is not a new observation,^{6,13-15} but we have a few comments to make on it before turning to the symmetry number method.

Reactions that proceed through a transition state of sufficiently high symmetry *must* yield such violations of detailed balance by the statistical factor method. In fact, if $\sigma_T > \prod_i N_i!/\sigma_C/\sigma_A$ then necessarily $r_C > r_A$; for

$$r_C = l_C\sigma_T/\sigma_C \geq \sigma_T/\sigma_C > \prod_i N_i!/\sigma_A \geq r_A$$

since r_A cannot be greater than the total number of physically distinct configurations of labeled A. Similarly, if $\sigma_T > \prod_i N_i!/\sigma_A/\sigma_C$ then necessarily $r_A > r_C$. Analogous inequalities apply to bimolecular reactions.

The simplest example of a high-symmetry transition state is a C_{2v} intermediate for reaction of an atom with a homonuclear diatomic,

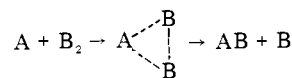


Here $\sigma_T > 2!/\sigma_{AB}\sigma_B/\sigma_A\sigma_{B_2}$, so necessarily $r_{AB+B} > r_{A+B_2}$. (The reader should check that the l 's and r 's must be as shown, for there is only one physically distinct configuration of labeled reactant and only one of labeled transition state.) Since $r_{A+B_2} \neq r_{AB+B}$, the statistical factor rate expressions in this case must violate the principle of detailed balance.

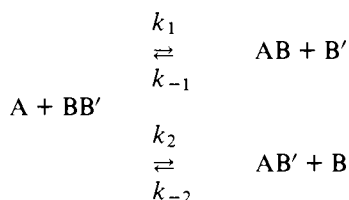
This example has been discussed in detail by Murrell and Pratt.¹⁴ The essential point is not that a C_{2v} structure is necessarily the correct transition state for any given reaction $A + B_2 \rightarrow AB + B$, but rather that it could be—that one can imagine a potential surface (see Murrell and Pratt¹⁴ for pictures) on which a C_{2v} structure is the transition state without breaking any basic rules of physics or mathematics.

In a paper that preceded the Murrell and Pratt contribution Murrell and Laidler¹³ (see also Laidler⁶) proposed that one should exclude all transition states for which the “return” statistical factors r do not equal unity. This is one way to resolve the disagreement between the statistical factor method and the symmetry number method in absolute rate theory, by restricting the theory to those cases where there is no disagreement, but it is unacceptable, because it would exclude not only reactions that proceed through transition states of peculiarly high symmetry but also, for example, most of organic chemistry. When like atoms are labeled, most organic molecules have physically distinct configurations separated by rather small barriers—usually, barriers to rotation about a single bond—and if one can descend to one of these configurations, from a higher energy transition state, then one can also get down to the others. The Murrell-Laidler proposal would exclude from consideration all nontrivial reactions that consume or produce such molecules.

There is a restriction on transition state theory, which will figure in some of the discussion in sections IV and V; we discuss it here because it relates to the Murrell-Laidler proposal. Murrell and Laidler would restrict transition state theory to those reactions in which a given transition state connects to only one physically distinct configuration of labeled reactant and only one of labeled product. Actually, all we should require, for unambiguous application of the theory, is that a transition state connect to only one species of *unlabeled* reactant and only one of *unlabeled* product, so that we can say with certainty what product is formed by breakup of the transition state and what reactant is responsible for it.²¹ This is an elementary point, but one worth emphasizing. Thus we should expect from transition state theory a definite prediction of the rate constants for the reaction



even though this reaction falls outside the Murrell-Laidler proposal and even though the statistical factor rate expressions for it must be incorrect, since they violate detailed balance. But if we make an isotopic substitution and study the two distinct reactions



and if both reactions proceed through a common transition state



then we cannot expect from transition state theory an unambiguous determination of the forward rate constants k_1 and k_2 or the backward rate constants k_{-1} and k_{-2} . From transition state theory we can calculate the total rate of formation of product,

$$(k_1 + k_2)[\text{A}][\text{BB}'] = \frac{kT}{h} \frac{Q_{\text{T}}}{Q_{\text{A}}Q_{\text{BB}'}} [\text{A}][\text{BB}']$$

but we do not know how much of this rate to assign to reaction 1 and how much to reaction 2—we do not know the branching ratios for breakup of the transition state. Similarly, in the backward direction we can calculate the total rate of formation of $\text{A} + \text{BB}'$ from an equilibrium mixture of AB' , AB , B , and B' ,

$$\begin{aligned}
 & k_{-1}[\text{AB}][\text{B}'] + k_{-2}[\text{AB}'][\text{B}] \\
 &= \frac{kT}{h} \frac{Q_{\text{T}}}{Q_{\text{AB}}Q_{\text{B}'}} [\text{AB}][\text{B}'] = \frac{kT}{h} \frac{Q_{\text{T}}}{Q_{\text{AB}'}} [\text{AB}'][\text{B}]
 \end{aligned}$$

but this tells us only that

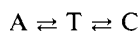
$$Q_{\text{AB}}Q_{\text{B}'}k_{-1} + Q_{\text{AB}'}Q_{\text{B}}k_{-2} = (kT/h)Q_{\text{T}}$$

IV. The Symmetry Number Method

Although the rate expressions of the statistical factor method are not, in general, correct, statistical factors do have a place in rate theory: here we show that they can be used to derive the rate expressions of the symmetry number method!

As before, we exclude for the moment processes that involve optically active species, and symmetric reactions such as internal rotation or symmetric atom exchange (e.g., $\text{H} + \text{H}_2 \rightarrow \text{H}_2 + \text{H}$).

Consider the unimolecular reaction 1,



We imagine, as before, that like atoms are distinguished by labels. Suppose further that labeled molecules could be separated, by an omnipotent chemist; then the number of different A molecules possible would be the number of physically distinct configurations of labeled A, $\prod_i N_i!/\sigma_{\text{A}}$. Let us call these distinct A molecules A_j , $j = 1$ to $\prod_i N_i!/\sigma_{\text{A}}$. Similarly, the distinct transition states are T_k , $k = 1$ to $\prod_i N_i!/\sigma_{\text{T}}$, and the distinct products are C_l , $l = 1$ to $\prod_i N_i!/\sigma_{\text{C}}$.

The symmetry number of each A_j , T_k , or C_l is of course unity, since all atoms in these molecules are distinguished by labels.

Now imagine the reaction mixture at complete chemical equilibrium. The concentration of each of the reactants A_j is the same and proportional to Q_{A}^0 ; the concentration of each of the products C_l is the same and proportional to Q_{C}^0 ; and we have, for any l and any j ,

$$[C_l]/[A_j] = Q_{\text{C}}^0/Q_{\text{A}}^0$$

If $[C]$ is the total concentration of C molecules, regardless of type, and $[A]$ the total concentration of A molecules, then

$$\begin{aligned}
 [C]/[A] &= \sum_l [C_l]/\sum_j [A_j] \\
 &= \left(\prod_i N_i! Q_{\text{C}}^0/\sigma_{\text{C}} \right) / \left(\prod_i N_i! Q_{\text{A}}^0/\sigma_{\text{A}} \right) = (Q_{\text{C}}^0/\sigma_{\text{C}})/(Q_{\text{A}}^0/\sigma_{\text{A}})
 \end{aligned}$$

as should be.

Now consider the rate of passage through a particular transition state T_k , in the direction of product. By familiar arguments,⁶ this is

$$\frac{kT}{h} \frac{Q_{\text{T}}^0}{Q_{\text{A}}^0} [A_j] \quad (10)$$

No symmetry numbers appear because all species involved have symmetry numbers of unity.

T_k connects to r_{C} different products C_l . To calculate the rate of formation of each of these products from T_k we need to know, as emphasized in the last section, how much of the rate (10) leads to each product—that is, the branching ratios for decomposition of the transition state T_k . Let us make the simplest assumption, that these branching ratios are all the same and therefore equal to $1/r_{\text{C}}$. It will be evident later that our conclusion, eq 13, in no way depends on this assumption.

Consider, then, a given product C_l . At equilibrium, it is being produced by l_{C} distinct transition states, at a rate from each that is $1/r_{\text{C}}$ times the rate (10). Therefore the rate of formation of C_l is

$$\frac{l_{\text{C}}}{r_{\text{C}}} \frac{kT}{h} \frac{Q_{\text{T}}^0}{Q_{\text{A}}^0} [A_j] \quad (11)$$

The total rate of formation of C molecules, irrespective of type, is $\prod_i N_i!/\sigma_{\text{C}}$ times this rate,

$$\frac{\prod_i N_i!}{\sigma_{\text{C}}} \frac{l_{\text{C}}}{r_{\text{C}}} \frac{kT}{h} \frac{Q_{\text{T}}^0}{Q_{\text{A}}^0} [A_j] = \prod_i N_i! \frac{kT}{h} \frac{Q_{\text{T}}^0/\sigma_{\text{T}}}{Q_{\text{A}}^0} [A_j] \quad (12)$$

We have used eq 3. But $\prod_i N_i! [A_j] = \sigma_{\text{A}} [A]$, and we have finally that the total rate of formation of C is

$$\frac{kT}{h} \frac{Q_{\text{T}}^0/\sigma_{\text{T}}}{Q_{\text{A}}^0/\sigma_{\text{A}}} [A] \quad (13)$$

This is just the rate expression (6) of the symmetry number method.²²

We conclude that the correct rate expressions of transition state theory must be those of the symmetry number method. Indeed, it could not be otherwise without violating the laws of statistical thermodynamics. At equilibrium the concentration of transition state intermediates is given in terms of partition functions that involve symmetry numbers, not statistical factors. The rate at which intermediates move into the product region, along the reaction coordinate, is then just the symmetry number rate. This is the correct rate of reaction, given the two dynamical assumptions of transition state theory²³—the “no return” assumption that systems that leave the transition state in either product or reactant direction in fact make it all the way to product or reactant, and the “equilibrium” assumption that the observed rate of product formation, in a nonequilibrium kinetics experiment, is equal to the rate of product formation calculated as if reactants were at equilibrium.

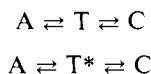
The cases in which the symmetry number rate expressions are “obviously” wrong are usually reactions involving optically active species or symmetric reactions. We discuss these now in more detail.

V. Reactions Involving Optically Active Species

There is no possibility of confusion, in dealing with reactions involving optically active species, if one keeps in mind that optical enantiomers, although symmetry related, are different

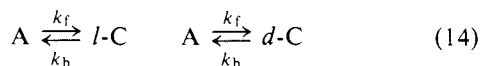
molecules. The correct rate expressions are then given directly by the symmetry number method, without special factors, for each elementary reaction in which the transition state connects to only one species of reactant and only one of product (see the discussion at the end of section III); but with reactions of optically active species it is often possible to deduce branching ratios from symmetry and therefore extend transition state theory beyond its "natural" limits; and one has also to take account of all elementary reactions going on. We illustrate these points with a brief discussion of the three possible cases.

1. If the transition state is optically active but reactants and products are not, the reaction rate is twice that calculated from either transition state enantiomer alone, for both are accessible to reactants and products and by symmetry contribute equally to the rate. There are in fact two elementary reactions going on; in the unimolecular case, these are



where T^* is the mirror image of T , and the rate constants for each elementary reaction are given by the symmetry number expressions.

2. If reactants and/or products are optically active but the transition state is not, the branching ratios for breakup of the transition state to the reactant and/or product enantiomers must be $1/2$, by symmetry. It is therefore possible to calculate the various rate constants from enantiomer to enantiomer even though the transition state connects to more than one reactant and/or product (see the remarks at the end of section III). Consider, for example, the reactions



Here the total rate through the transition state, in product direction, is

$$\frac{kT}{h} \frac{Q_T^0/\sigma_T}{Q_A^0/\sigma_A} [A]$$

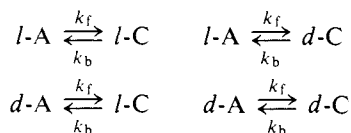
From eq 14 this is also equal to $2k_f[A]$. The total rate through the transition state, in reactant direction, from a racemic mixture of $l-C$ and $d-C$, is

$$\frac{kT}{h} \frac{Q_T^0/\sigma_T}{Q_C^0/\sigma_C} [l-C] = \frac{kT}{h} \frac{Q_T^0/\sigma_T}{Q_C^0/\sigma_C} [d-C]$$

where Q_C^0 and σ_C are the partition function and symmetry number of one enantiomer of C ; from eq 14 this is also equal to $k_b([l-C] + [d-C]) = 2k_b[l-C] = 2k_b[d-C]$. Therefore

$$k_f = \frac{kT}{2h} \frac{Q_T^0/\sigma_T}{Q_A^0/\sigma_A} \quad k_b = \frac{kT}{2h} \frac{Q_T^0/\sigma_T}{Q_C^0/\sigma_C}$$

Similar considerations give the rate constants k_f' and k_b' for the set of unimolecular reactions



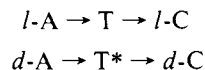
namely,

$$k_f = \frac{kT}{4h} \frac{Q_T^0/\sigma_T}{Q_A^0/\sigma_A} \quad k_b = \frac{kT}{4h} \frac{Q_T^0/\sigma_T}{Q_C^0/\sigma_C}$$

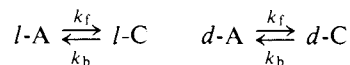
The reader should work through the various possibilities for bimolecular reactions. Here there are cases for which transition state theory cannot unambiguously predict all rates; for example, if both product molecules C and D are optically active and the transition state connects to all four possible products

($l-C + l-D$, $l-C + d-D$, $d-C + l-D$, $d-C + d-D$), one knows from reflection symmetry of the transition state only that the rate to $l-C + l-D$ equals the rate to $d-C + d-D$ and the rate to $l-C + d-D$ equals that to $d-C + l-D$, but not how much of the total rate through the transition state leads to each alternative.

3. If both transition state and reactants and products are optically active, rate constants can be calculated in straightforward fashion provided that a given transition state enantiomer connects to only one reactant and product enantiomer. For example, if the reaction scheme, from optically active A to optically active C , is



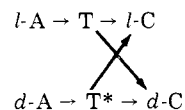
the rate constants for the reactions



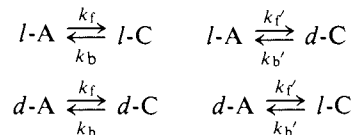
are

$$k_f = \frac{kT}{h} \frac{Q_T^0/\sigma_T}{Q_A^0/\sigma_A} \quad k_b = \frac{kT}{h} \frac{Q_C^0/\sigma_C}{Q_C^0/\sigma_C}$$

where Q_A^0 and σ_A (Q_T^0 and σ_T , Q_C^0 and σ_C) are the partition function and symmetry number of one enantiomer of A (T , C). On the other hand, if T and T^* both give some of each product,



then from transition state theory we cannot determine the rate constants for the reactions

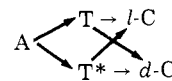


but only the combinations

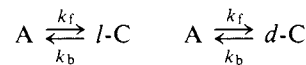
$$k_f + k_f' = \frac{kT}{h} \frac{Q_T^0/\sigma_T}{Q_A^0/\sigma_A} \quad k_b + k_b' = \frac{kT}{h} \frac{Q_C^0/\sigma_C}{Q_C^0/\sigma_C}$$

(see the discussion at the end of section III).

It is interesting to note that if either reactant or product is optically inactive the rate constants are unambiguously determined, even when each transition state enantiomer connects to both enantiomers of product or reactant. Consider, for example, the reaction scheme



Since A is optically inactive, T and T^* are produced at the same rate, and symmetry demands—no matter what the branching ratio from T to $l-C$ and $d-C$ —that for a racemic mixture of T and T^* the products $l-C$ and $d-C$ are formed at the same rate. The rate constants for the reactions



are therefore

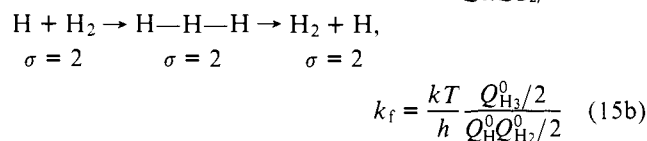
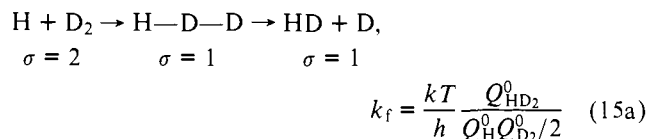
$$k_f = \frac{kT}{h} \frac{Q_T^0/\sigma_T}{Q_A^0/\sigma_A} \quad k_b = \frac{kT}{h} \frac{Q_C^0/\sigma_C}{Q_C^0/\sigma_C}$$

where Q_T^0 and σ_T (Q_C^0 and σ_C) are the partition function and symmetry number of one enantiomer of T (C).

VI. Symmetric Reactions

Symmetric reactions are those in which reactants and products are indistinguishable unless like atoms are labeled. Hindered rotation of a methyl group, about the bond linking it to the rest of the molecule, is a unimolecular symmetric reaction; the atom exchange $\text{H} + \text{H}_2 \rightarrow \text{H}_2 + \text{H}$ is the archetypal bimolecular symmetric reaction.

The subtlety, in dealing with symmetric reactions, lies in the proper definition of the rate, since it is not so obvious what the rate of reaction is when, really, there is no reaction at all. Failure to appreciate this can lead to error. Consider, for example, the following comparison which makes it "obvious" that the symmetry number method for calculating rate constants is incorrect:



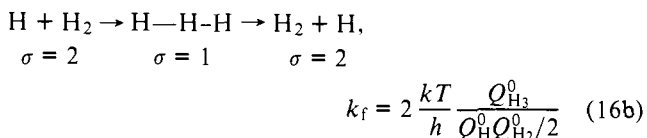
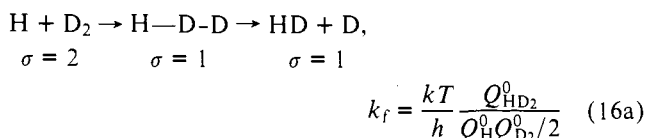
Aside from differences in the partition functions Q^0 , reaction 15a is evidently favored by a factor of 2 over reactions 15b; but that is absurd—at given H atom concentration D_2 and H_2 molecules collide with H atoms at essentially the same rate.

The mistake we have made, in this example, is the application by rote of the transition state formula to the symmetric reaction 15b. Transition state theory calculates the rate of passage through the transition state in one direction, from reactant to product; here reactant equals product and passage through the transition state in *either* direction results in an H atom exchange.⁸ If we want to calculate the lifetime of an H_2 molecule against H atom exchange, the relevant rate is the total rate of passage through the transition state, in either direction; the appropriate rate constant is then twice that given in eq 15b, and the paradox, in comparing $\text{H} + \text{D}_2$ with $\text{H} + \text{H}_2$, disappears.

Similar considerations apply to any symmetric exchange reaction $\text{A} + \text{B} \rightarrow \text{B} + \text{A}$: the fraction of A molecules that undergo exchange, in time interval dt , is $2k_f[\text{B}]dt$ where k_f is the rate constant for passage through the transition state in one direction, $k_f = (kT/h)(Q_{\text{T}}^0/\sigma_{\text{T}})/(Q_{\text{A}}^0/\sigma_{\text{A}})(Q_{\text{B}}^0/\sigma_{\text{B}})$. Similarly, in a unimolecular symmetric reaction $\text{A} \rightarrow \text{A}$ the fraction of A molecules that rearrange, in a time interval dt , is $2k_f dt$ where k_f is the rate constant for passage in one direction through the transition state, $k_f = (kT/h)(Q_{\text{T}}^0/\sigma_{\text{T}})/(Q_{\text{A}}^0/\sigma_{\text{A}})$.

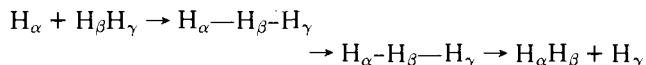
So much for the simple rule, "Double the rate for a symmetric reaction"; now for the exceptions to the rule.

Consider the H atom exchange again, but on a potential surface with a well rather than a saddle point at the symmetric H_3 configuration; the transition state for exchange is now unsymmetric $-\text{H}-\text{H}-\text{H}$, perhaps. Compare the reactions $\text{H} + \text{D}_2 \rightarrow \text{HD} + \text{H}$ and $\text{H} + \text{H}_2 \rightarrow \text{H}_2 + \text{H}$:



where the factor of 2 in eq 16b comes from the rate doubling for a symmetric reaction. Evidently reaction 16b is now favored by a factor of 2!

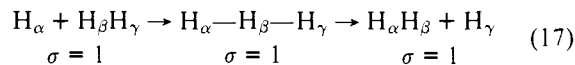
The mistake we have made this time is the application of elementary transition state theory to a complex reaction. Label the hydrogens; the reaction sequence for eq 16b is



The system must pass through two physically distinct configurations of labeled transition state to accomplish H atom exchange, and in between may rattle around a while in the potential well.

Standard transition state theory and the doubling rule for symmetric reactions do *not* apply to this exchange or to any reaction where more than one physically distinct labeled transition state must be crossed on the way to product. Standard theory applied only if one can find a "reaction path" from reactants to products along which the transition state configuration is the unique point of highest potential energy. For the $\text{H} + \text{H}_2$ exchange it is easy to show that, no matter what the potential surface, the transition state must then have a mirror plane that interchanges the exchanging hydrogens. In general, though, mirror planes are not necessary. For example, standard transition state theory and the doubling rule for symmetric reactions can be used to calculate the rate of hindered rotation of a methyl group, even when the group is attached to an asymmetric carbon, so long as only one transition state configuration lies between each of the three rotational minima.

Finally, we emphasize that when like atoms are distinguished by labels—as, for example, in a classical trajectory calculation of reaction rate—a symmetric reaction is no longer symmetric, and transition state rate constants must be evaluated in standard fashion. For example, the forward rate constant for the labeled hydrogen atom exchange



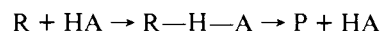
is

$$k_f = \frac{kT}{h} \frac{Q_{\text{T}}^0}{Q_{\text{H}}^0 Q_{\text{H}_2}^0}$$

half that for the symmetric reaction of unlabeled hydrogens. This is of course as it should be, since reaction 17 proceeds through hydrogen attack at only one end of the hydrogen molecule.

VII. Brønsted Relations

Brønsted relations¹⁶ correlate the catalytic power of an acid or base with its acid or base strength as measured by the dissociation constant. Consider, for example, an acid-catalyzed isomerization that proceeds by partial transfer of a proton from acid HA to reactant R:



The second-order catalytic rate constant k_{HA} is

$$k_{\text{HA}} = \frac{kT}{h} \frac{Q_{\text{T}}}{Q_{\text{R}} Q_{\text{HA}}}$$

Because formation of the transition state $\text{R}-\text{H}-\text{A}$ requires partial ionization of HA, it is reasonable to suppose that the free energy of formation of the transition state is some fraction α of the free energy of dissociation of HA, plus a contribution from reactant R that is independent of the particular acid HA; then

$$k_{\text{HA}} = G(K_{\text{HA}})^\alpha \quad (18)$$

where K_{HA} is the acid dissociation constant and G is independent of HA. To the extent that the fraction α does not vary from acid to acid, the Brønsted relation (18) correlates the catalytic power of various acids, in effecting the transformation $R \rightarrow P$, with their acid strengths as measured by K_{HA} .

Modifications are necessary when one wants to compare acids that differ, say, in the number of acidic hydrogens available for catalysis. Brønsted reasoned as follows: let p be the number of equivalent acidic hydrogens in HA and q the number of equivalent sites for proton attachment in the conjugate base A^- ; the forward rate for dissociation of HA should be proportional to p , the backward rate to q , so the equilibrium constant K_{HA} should be proportional to p/q ; then $K_{HA}q/p$ should measure the strength of the acid *per elementary dissociation*, and the catalytic power of HA, *per acidic H*, should correlate with $K_{HA}q/p$:

$$k_{HA}/p = G(K_{HA}q/p)^\alpha \quad (19)$$

The modern version of this argument, due to Benson,¹⁷ is couched in terms of symmetry numbers and asserts that linear free energy relations should be applied to equilibrium expressions from which the symmetry numbers have been removed; thus,

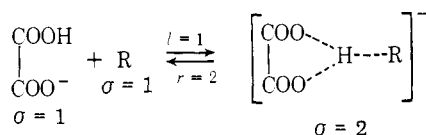
$$k_{HA} = (\sigma_R \sigma_{HA} / \sigma_T) \frac{kT}{h} \frac{Q_T^0}{Q_{HA}^0 Q_R^0} \approx (\sigma_R \sigma_{HA} / \sigma_T) G(K_{HA}^0)^\alpha \\ = (\sigma_R \sigma_{HA} / \sigma_T) G(K_{HA} \sigma_{A^-} / \sigma_{HA})^\alpha \quad (20)$$

The Benson version of the Brønsted relation was criticized by Bishop and Laidler,³ who proposed a statistical factor Brønsted relation which differs from eq 20 only in that k_{HA} is taken proportional to the statistical factor l for forming the transition state rather than to the ratio of symmetry numbers:

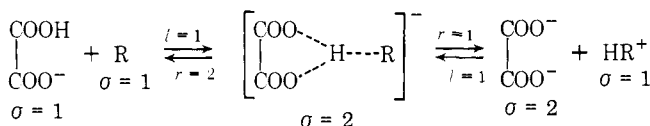
$$k_{HA} = l_{HA} G(K_{HA} \sigma_{A^-} / \sigma_{HA})^\alpha \quad (21)$$

The difference between eq 20 and 21 is the same difference between symmetry number and statistical factor rate constants that we have discussed above, and we reject the statistical factor Brønsted relation for the same reason that we reject the statistical factor rate constant. Granted the basic assumption, common to both eq 20 and 21, that linear free energy relations apply to equilibrium expressions from which symmetry numbers have been removed, Benson's modification of the Brønsted relation to take account of molecular symmetry is correct.

As an example, consider the following hypothetical catalysis, discussed by Bishop and Laidler:³



Here R is supposed to be sufficiently symmetric that the symmetry number of the transition state is 2. The statistical factor method then predicts a forward rate constant twice that given by the symmetry number method, just as it would if the reaction in fact led to complete proton transfer to R:



In the latter instance the statistical factor method is wrong and in fact would give an incorrect equilibrium constant since the statistical factor r for returning to reactant from the transition state differs from the factor r for returning to product.

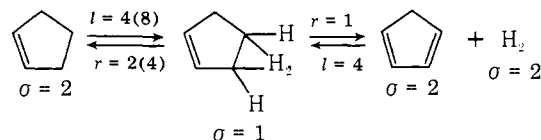
In Brønsted's notation, Benson's Brønsted relation for the catalysis (18) has $p = 1/2$, $q = 1$. One can understand this from

Brønsted's point of view: if acid catalysis (18) is in fact analogous to acid dissociation, then acid dissociation must proceed through a symmetric transition state in which the proton is shared by two carboxylates; therefore the number q of sites available for proton attachment in the conjugate base $(\text{CO}_2)_2^{2-}$ is not 2 but 1; and then if the ratio q/p is to be equal to $\sigma_{A^-} / \sigma_{HA} = 2$ —as it is in both the symmetry number eq 20 and the statistical factor eq 21—we must set $p = 1/2$.

VIII. Examples

In this section we consider several reactions that have been discussed by other writers on the subject. The reader should not be distracted by the implausible transition state structures that appear below; it is the principle of the thing that matters.

1. Schlag,¹ Bishop and Laidler,³ and Murrell and Laidler¹³ considered dehydrogenation of cyclopentene via a transition state in which the departing hydrogens lie in the plane of the ring:

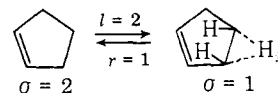


The symmetry factor in the forward rate—that is, σ_A / σ_T , in the notation of previous sections—is 2; the symmetry factor in the backward rate, $\sigma_C \sigma_D / \sigma_T$, is 4.

According to the statistical factor method, the symmetry factor in the backward rate is 4—in agreement with the symmetry number method—since H_2 can attack either double bond, with either end of the H_2 closer to the CH_2 group.

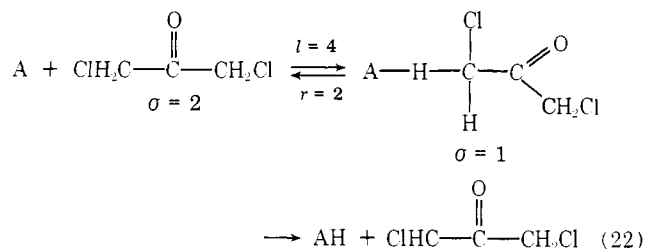
In the forward direction the statistical factor method is ambiguous. If the departing hydrogens must be cis with respect to the ring, in the reactant cyclopentene, then $l = 4$ —there are four such hydrogen pairs—and $r = 2$. If the departing hydrogens can be either cis or trans with respect to the ring, then $l = 8$ and $r = 4$. Which is the case depends on the potential surface, and this is an excellent illustration of the point that in general we need more than just the structure of reactants and transition state to determine a statistical factor, but in either case the statistical factor method is wrong and the statistical factor rate expressions would not give the correct equilibrium constant for the reaction.

If the transition state is nonplanar, and the departing hydrogens must be cis to the ring,



the statistical factor and symmetry number methods agree; the symmetry factor in the forward rate is 4, since the transition state is optically active.²⁴

2. Schlag¹ considered hydrogen abstraction from *sym*-dichloroacetone by an atom A (eq 22); the transition state is

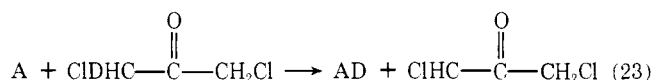


supposed to be planar, except for the two hydrogens at the right end which are symmetrically placed with respect to the plane.

According to the symmetry number method the symmetry

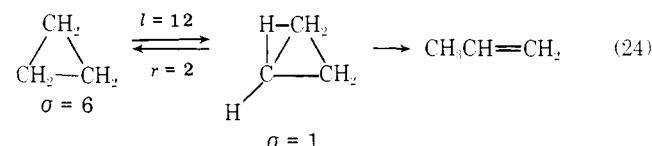
factor in the forward direction is 2; the statistical factor method gives 4, since any one of the four hydrogens can be attacked by A.

The symmetry number method is correct, but one is inclined to disbelief: should not the symmetry factor be 4, since there are four hydrogens to abstract? No; by this reasoning we can conclude only that the rate constant for reaction 22 must be four times as large as that for the monodeuterated compound, neglecting effects due to the mass difference between D and H. The reader may verify that this is the case when the rate constants are calculated by the symmetry number method, remembering that in eq 23 the reactant molecule is optically



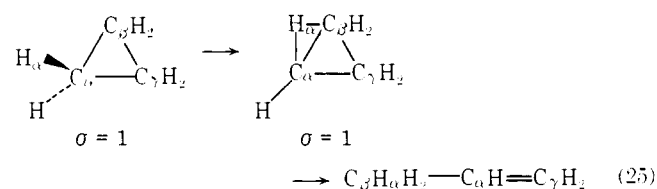
active and the transition state is not. There is no contradiction between the symmetry number method and our certainty that in reaction 22 the four hydrogens are attacked at the same rate.

3. Here is another example in the same vein, isomerization of cyclopropane to propene via a transition state in which the transferring hydrogen and the hydrogen it leaves behind both lie in the plane of the ring^{1,3,13} (eq 24). The symmetry factor



in the forward rate is 6 according to the symmetry number method, 12 according to the statistical factor method. The symmetry number method is correct, but one wonders why, since there are clearly 12 different ways of effecting isomerization—any hydrogen can transfer to either adjacent carbon—and the rate for reaction 24 ought to be 12 times that for a single transfer of a definite H to a definite C.

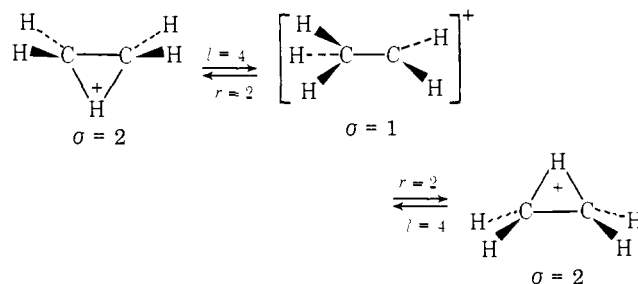
To see that it is, label the three carbons and one of the hydrogens and consider reaction 25. There is only one way of



effecting this reaction, and the rate constant for eq 25 is $1/12$ that for reaction 24, according to the symmetry number method, for the reactant in eq 24 is optically active and the transition state is not.

4. The mechanism of cyclohexane inversion from the chair to the boat configuration has been discussed in the literature.²⁵⁻²⁸ Two transition state structures have been suggested, one with C_s symmetry and the other with C_2 symmetry (for nice diagrams see ref 28). The symmetry number of chair cyclohexane (D_{3d}) is 6; the symmetry number of a C_s structure is 1, the symmetry number of a C_2 structure is 2 but the structure must be optically active; therefore in either mechanism the symmetry factor for chair to boat inversion is 6, in accord with our intuition that any one of the six carbons in the chair can "flip up" to become the prow of the boat.

5. Here, finally, is an example of a symmetric reaction, inversion of ethyl cation through a transition state with a plane of symmetry defined by the CH_2 group:²⁹⁻³¹



Notice that the return factor r from the transition state is 2 since either of the nonplanar H's in the transition state can form a three-center bond with the two carbons; one bond gives "reactant", the other gives "product", but in this symmetric reaction reactants are products.

The symmetry factor in the inversion rate constant is 2, according to the symmetry number method, but then the rate constant must be doubled since this is a symmetric reaction, and accordingly the symmetry number method and the statistical factor method agree that the appropriate symmetry factor for this inversion is 4.

Acknowledgments. This work was supported by a grant from the National Science Foundation. Helpful conversations with J.-T. Hwang are gratefully acknowledged.

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- (19) Bishop and Laidler³ (see also Laidler³) define the statistical factor for leaving $A + A$ as half our l_{A+A} . This definition preserves eq 5a for the case that $B = A$, but we see no other reason for it.
- (20) For simplicity, in this section we ignore bimolecular reactions where $A = B$ or $C = D$.
- (21) There is an exception to this rule, in the case of reactions that involve optically active species; see the discussion below.
- (22) The calculation in the text leading to eq 13 is more drawn out than is strictly necessary. Already from eq 10 one sees that the total rate through unlabeled transition state T is as given by the symmetry number method (multiply eq 10 by the number of physically distinct labeled transition states, $\prod_i N_i!/\sigma_T$, and proceed as from eq 12 to eq 13). We leave the calculation in the "long" form because it illustrates the proper role of statistical factors in chemical kinetics.
- (23) P. Pechukas in "Modern Theoretical Chemistry", Vol. 2, W. H. Miller, Ed., Plenum Press, New York, N.Y., 1976, Chapter 6.
- (24) In this case Bishop and Laidler³ would presumably calculate $l = 4$ directly, for their definition of statistical factors lumps together enantiomeric transition states, while we prefer to emphasize that optical enantiomers are different molecules.
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