Rate Constants and Molecular Structure

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The methods of relating parameters in the Arrhenius rate equation to fundamental molecular properties are briefly reviewed. The limited applicability of purely theoretical methods is noted, the use and limitations of the standard semiemprical method are surveyed, and recent work based on empirical molecular structure and spectroscopy is described in detail. The recent method makes no attempt to calculate activation energy, but within a limited range of cases it does provide a reliable method of estimating the preexponential factor in the Arrhenius equation and calculating the kinetic isotope effect. In this way the method provides a check on the credibility of experimental data and on the assignment of mechnaism. If the mechanism is correct, it provides a method of estimating activation energy from rate data taken at only one temperature. Further developments of this method are anticipated.

Although the equilibrium state of a chemical reaction

$$A + B = C + D \qquad (1)$$

does not depend on the mechanism or the rate of attainment of equilibrium, the rate may be of great practical importance as well as of theoretical interest. In Figure 1 there is proposed a mechanism for reaction [Equation (1)] involving eight rates and three structural intermediates, excited reactant pairs (A, B)*, excited product pairs (C, D)*, and the *transition state,* or *activated complex* (*1*). The activated complex is some structure intermediate between excited reactants and excited products, processing the same energy. A unique specification of the activated complex is made possible from considerations of a reaction coordinate. The excited pair (A, B)* undergoes violent internal motions, vibrations, and internal rotations. A component of these motions is a change in atomic arrangements which causes (A, B)* to go over to (C, D)*. This structural rearrangement is opposed by a potential energy barrier which however eventually reaches a maximum and decreases toward the formation of (C, D)*. The distance along the path of lowest potential energy which effects this structural change is the *reaction coordinate.* The activated complex is the complex for which the reaction coordinate is localized as closely as possible above its maximum in potential energy, while the rest of the structure has any configuration open to it. Most of the excitation energy of (A, B)*, largely internal kinetic energy, has in the activated complex gone into the potential energy of the reaction coordinate. Thus the rest of the activated complex is typically not highly distorted or highly agitated; it is in fact largely like a normal molecule except for the reaction coordinate.

A few examples of reaction coordinate will be given. For the reaction

$$D + H_2 = DH + H \qquad (2)$$

the activated complex is linear; the reaction path is the simultaneous extension of the H–H distance and the shortening of the D–H distance; the reaction coordinate is the difference in D–H and H–H distances and very closely resembles the antisymmetric-stretching normal mode of the linear D–H–H structure. For the reaction

$$H_2 + I_2 = 2HI \qquad (3)$$

the activated complex is planar, and the reaction path is a simultaneous stretching of H–H and I–I bonds with the shortening of two H–I distances. For substitution with inversion about a tetrahedral carbon atom

$$X + H_3CY = XCH_3 + Y \qquad (4)$$

the reaction path is the shortening of the X–C distance, the lengthening of the C–Y bond, and the left-to-right advancing of the three hydrogen atoms. This illustrates that atoms may participate in the reaction coordinate, even though they are not directly involved in the bonds formed or broken.

REVIEW OF CHEMICAL EQUILIBRIUM

If reaction (1) is in chemical equilibrium, then every process and its exact reverse occur at the same average rate and in terms of the mechanism of Figure 1, $R_1 = R_2$, $R_3 = R_4$, $R_5 = R_6$, $R_7 = R_8$. It is not necessary to measure or know these rates however to establish the existence of equilibrium; one uses the principle of approach from either side for the over-all reaction. The equilibrium state is given by the well-known relations (*2*)

$$K = \frac{[C][D]}{[A][B]} \qquad (5)$$

$$= e^{\Delta S^\circ/R} e^{-\Delta H^\circ/RT} \qquad (6)$$

$$= \frac{Q_C Q_D}{Q_A Q_B} e^{-\Delta H_0^\circ/RT} \qquad (7)$$

where brackets refer to activity or concentration for approximate considerations.

$$Q = \sum_i g_i e^{-\epsilon_i/kT} \qquad (8)$$

If all reactants and products are isolatable chemical species, the entropy of each may be evaluated by the measurement of heat capacities from 0°K. to the temperature of interest, and the enthalpy of each relative to the elements in their standard state may be evaluated by calorimetric studies. From the thermal properties of A, B, C, and D one may bypass all mechanistic considerations, such as Figure 1, and evaluate the equilibrium constant from Equation (6).

Also thermodynamic quantities can be related to the structures and mechanical properties of the reactants and products. For favorable cases the difference in standard enthalpy at absolute zero can be found from bond energies obtained by photochemical, electron-impact, and other

methods. The entropy of reactants and products can be calculated to various degrees of approximation from atomic weights, bond lengths, vibration frequencies, or force constants for stretching and bending of bonds, barriers hindering internal rotation, and electronic multiplicities. From these considerations, applied to each reactant and to each product molecule, one can calculate the equilibrium constant from Equations (7) and (8).

For certain species of interest, for example free radical reactants or products or high-temperature species, there may be no thermodynamic data and even no spectroscopic or structural data. Nevertheless approximate values of the entropy can be found if the structural and mechanical properties of the molecules of interest can be predicted theoretically or from empirical rules of molecular structure and molecular spectroscopy. By analogy with similar stable molecules one could for a particular species predict the molecular shape, the bond lengths, force constants, barriers to internal rotation, and electronic ground state. In this case the quality of the entropy factor in the computed equilibrium constant depends exclusively on the accuracy with which structural and mechanical properties are assigned. To predict ΔH°_0 in Equation (7) one must make an accurate estimate of all bond energies in the labile reactants or products; so far the prediction of enthalpies or bond energies has been much more difficult and less reliable than the prediction of entropies for such species.

REVIEW OF THE RATE EXPRESSION FOR ELEMENTARY BIMOLECULAR REACTION

For the initial rate of reaction (1) there are no products and no excited product pairs in terms of the mechanism in Figure 1. Even so the rate expression is particularly simple, provided that the reactants are essentially in equilibrium with excited reactant pairs. In terms of the mechanism of Figure 1 the requirement is that $R_1 \approx R_2$ or that $R_2 \gg R_3$. If this condition is met, the rate constant given by

$$\text{Rate} = -d[\text{A}]/dt = k[\text{A}][\text{B}] \qquad (9)$$

has the simple well-known form (*1*)

$$k = \kappa \frac{Q^\ddagger}{Q_A Q_B} \frac{\mathbf{k}T}{h} e^{-\Delta H_0^\ddagger/\mathbf{R}T} \qquad (10)$$

THE PROBLEM

The problem of computing a rate constant from Equation (10) is very nearly the same as that of computing an equilibrium constant from Equation (7), for the case where a product or a reactant is a free radical or other reactive species of unknown structure and unknown spectra. The structure, mechanical properties, and energy of the labile reactants and products must somehow be estimated. Similar information for the activated complex must be estimated for rate calculations.

Typically the kineticist reports his data in terms of the two parameters, **A** and **E**, of the Arrhenius equation

$$k = \mathbf{A}e^{-\mathbf{E}/\mathbf{R}T} \qquad (11)$$

Often the **E** term is regarded as purely empirical, and the **A** factor is related to the structural and mechanical properties of the activated complex. A small amount of numerical work with the rotational, vibrational, and internal rotational partition functions shows one that these functions are rather sensitive to bond distances, force constants, and barriers to internal rotation. If the kineticist takes the structure of the activated complex to be his adjustable parameter, then the theory is infinitely flexible; it can explain anything and predict nothing. If however one holds to the principle used in the derivation of Equation (10) that the activated complex is like a normal molecule aside from the single separable reaction coordinate, then one can appeal to the results of molecular theory, structure, and spectroscopy to determine the structure and properties of the activated complex. If these properties of the activated complex are fixed by considerations external to kinetics, then the predictions of **A** by means of the theory are precise to perhaps a factor of four and quite useful under certain circumstances. To predict **E** by theoretical methods or with empirical methods (with the empiricism in fields external to kinetics itself), one must make very accurate estimates of all bond energies in the activated complex; so far the prediction of **E** has been much more difficult and less reliable than the prediction of **A** in Equation (11).

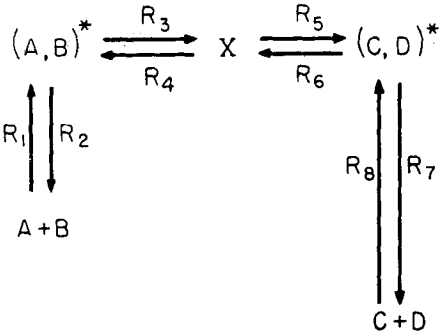


Fig. 1. A mechanism for attainment of chemical equilibrium for the reaction A + B = C + D. A + B represents the bulk normal state of the reactants; (A, B)* represents an excited, high-energy state for a pair of reactants; *X* represents an activated complex, the critical intermediate state between reactants and products; (C, D)* represents a pair of excited product molecules; and C + D represents normal product molecules. The vertical distance in the figures corresponds to an increase in energy; the transition between (A, B)* and (C, D)* is a constant energy path for the molecule pairs as a whole. R refers to rate.

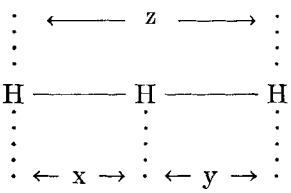
METHODS OF FIXING STRUCTURE AND PROPERTIES OF ACTIVITATED COMPLEXES

Theoretical Methods

Purely theoretical methods have been limited to the simplest of all chemical reactions with the H_3 activated complex, reaction (2) for example, or ortho-para hydrogen conversion represented by

$$\text{H} + \text{H}_2 = \text{H}_2 + \text{H} \qquad (12)$$

London (*3*), discussing this problem in terms of quantum mechanics, showed that a linear complex was the one of lowest energy. Such a complex may be regarded as a superposition of three diatomic molecules



(13)

To a rather gross approximation the energies of these diatomic molecules are

$$E_x = A + \alpha$$
$$E_y = B + \beta \qquad (14)$$
$$E_z = C + \gamma$$

To the same rough approximation the energy of the complex in (13) is

$$E = A + B + C \pm \{\tfrac{1}{2}[(\alpha - \beta)^2 + (\beta - \gamma)^2 + (\gamma - \alpha)^2]\}^{1/2} \qquad (15)$$

As in (14), each integral is a function of interatomic distance. Upon evaluation of the integrals one finds from Equation (14) for the dissociation energy of H_2: calculated, 53 kcal.; observed, 103 kcal.; for activation energy based on (15) calculated, 19 kcal.; observed, 6 kcal.

Some of the crude approximations of this theory can be modified by the addition of extra terms to the functions used. Hirschfelder (*4*) made an extensive study of this type; however the accurately convergent method which gives the correct properties (*5*) for hydrogen is so complicated that it has not yet been applied to the H_3 complex. By the most advanced method which he used Hirschfelder concluded that the activated complex was symmetrical, $r_x = r_y$, and there is no tendency toward the formation of a stable or metastable H_3 complex; that is, there is no potential energy well in the top of the pass. From the value of the

distance which gives the maximum energy along the reaction coordinate, the size and thus moments of inertia of the complex are obtained. By variation of both distances around the value which gives the lowest maximum energy along the reaction coordinate, the force constant for the symmetrical stretching vibration is obtained. By repeating the calculation for slight bending of the linear complex, one can obtain the force constant for bending. From vibration frequencies of the complex and of H_2, zero-point energy corrections and therefore activation energy are calculated. Thus a completely theoretical evaluation of all parameters (aside from κ, which is about unity) in Equation (10) is carried out. Results are about as good or as poor as those for H_2 itself by the same method: dissociation of H_2, 67 calculated, 103 observed; activation energy, 25 calculated, 6 observed. Other calculated quantities are given in Table 2. These computations are highly instructive; the structural and mechanical quantities are presumably quite good; and the energies are far too inaccurate to be useful.

Recently Barker and Eyring (*6*) have been active in further refinements of the purely quantum mechanical treatment of H_3, but this work remains unfinished.

A somewhat different approach to the problem has been made by the molecular orbital-approximation method (*7*). A general qualitative conclusion based on considerations of H_3 and H_4 is that the activation energy for radical-radical reactions should be low, for radical-molecule reactions medium, and for molecule-molecule reactions relatively high, where unsaturated molecules are excluded. For H_3 it is concluded that the activated complex is symmetrical. A very tedious single computation gives 8 kcal. for the activation energy, 6 observed. These computations are too complicated to permit, so far, variation of distances to give vibration frequencies. An attempt to produce a simple, tractable molecular-orbital method of computation gave highly inaccurate energies.

Semiempirical Method

Eyring and coworkers (*1, 8*) have developed and extensively used a method of computing the energies of H_3 and H_4 as a function of distances which is relatively simple to apply and gives results which are qualitatively instructive and quantitatively useful in certain cases. The method is based on Equations (14) and (15). In Equation (14) A is assumed at all distances to be a constant fraction of E_x; the fraction is taken to be something between about 0.10 and 0.20. For H_2 the fraction varies slowly, 0.10 to 0.14, with distance (at large distances, 1.5 to 5Å.), but it changes very rapidly, 0.10 to 0, at distances between 1.5 and about 0.8 Å. Since E_x as a function of distance can be observed spectroscopically and expressed conveniently as the Morse function, one can thus evaluate A and α as a function of distance; similarly B and β, C and γ can be found. These values are substituted into Equation (15) to give the total energy of H_3. A three-dimensional plot of potential energy against r_x and r_y reveals the reaction coordinate as a conspicuous canyon (Figure 2). The floor of the canyon goes through a maximum energy at easily determined distances in terms of r_x and r_y; thus activation energy and the size of the activated complex are given. Variations of distances around the saddle point of the complex give force constants and thus vibration

$$E = [2E_x + E_z] - (1 - f)[E_x + 2E_z] \quad (16)$$

The first term in brackets in Equation (16) is sum of the energy of three diatomic molecules, and the second term is an additive correction based on the London theory with its order of magnitude held strictly in check by spectroscopic parameters. Upon purely theoretical evaluation of terms in (15) itself, extremely large errors can accumulate within a minor range of permissible assumptions (*9*).

On the other hand the semiempirical method seems to be subject to a major qualitative error. Hirschfelder's (*4*) improved theoretical treatment showed no well in the top of the energy maximum, that is, no tendency toward metastable H_3. The semiempirical method does find such a shallow well for H_3 and much deeper wells for certain other cases. In terms of the London theory itself $f = A/E_x$ is roughly constant at large distances for H_2 but decreases rapidly at small distances. The assumption about constancy of f is worst at short distances corresponding to the activated complex itself. In view of this one should distrust detailed shapes and curvatures (and thus force constants) of the potential-energy surface in the close vicinity of the activated complex itself. One can vary f to give the observed activation energy; the resultant potential-energy surface identifies the reaction coordinate and establishes the essential geometry of the activated complex. It probably fails to give good values of vibration frequencies,

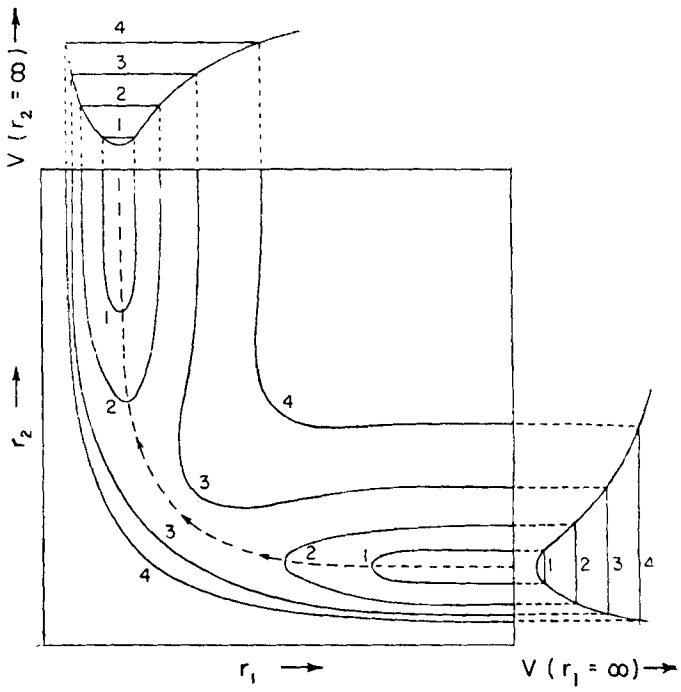


Fig. 2 Potential-energy surface for the reaction $H + H_2 = H_2 + H$, represented by contours of constant potential energy.

frequencies. The application of this method to chemical problems and to cases much more complicated than hydrogen systems has been given in detail by Glasstone, Laidler, and Eyring (*1*).

This method gives results which are surprisingly good (*9*) in view of the crudeness of Equations (14) and (15). To some extent success is due to the sensitivity of the calculated activation energy to the fitted parameter, $f = A/E_x$, which becomes three fitted parameters if the atoms X–Y–Z are different. To a greater extent success arises from the fact that use of spectroscopic values of E_x, E_y, and E_z automatically keeps dominant quantities to the correct order of magnitude, and the crude London theory gives in essence a correction term to the simple sum of energies from the three diatomic molecules. For the symmetric activated complex shown in (13) the energy is

and thus the semiempirical method is not necessarily a very good way to test or use Equation (10).

Empirical Methods

In view of the considerable body of knowledge and techniques accumulated in the fields of molecular structure and molecular spectroscopy, it has seemed worthwhile to try completely different methods of fixing the structure and mechanics of the activated complex (*10* to *13*). These data would determine the **A** factor in Equation (11); the activation energy is then taken from measured rates. There are several different approaches to this problem, some being simpler than others, some more precise (that is less dependent on the investigator's judgment). In view of the uncertainties in experimental **A** factors, an order of magnitude or more in many cases, it is not necessary for the model used to be particularly refined. Several recent approaches of this type will be reviewed.

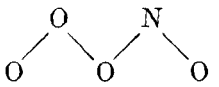
These methods will be illustrated with reference to three examples

$$H + H_2 = H_2 + H \qquad (17)$$

$$O_3 + NO = O_2 + NO_2 \qquad (18)$$

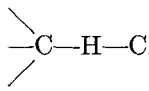
$$(CH_3)_3CH + Cl = (CH_3)_3C + HCl \qquad (19)$$

The general shape of the activated complex is determined by the rule of equivalence with respect to reactants and products and by use of the principle that the purely *s* type of bond has no directional properties, and *p* or *sp* hydrides are directional in character. Thus reaction (17) has a linear symmetrical activated complex; that for reaction (18) may be taken as planar (for molecules or complexes with free internal rotations the simplest structure may be taken as reference model)



(20)

and the complex for (19) is

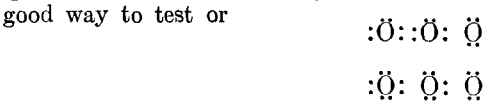


(21)

The bond orders are fixed by assigning reasonable valence-bond structures to the complexes. The H_3 complex is given the structures

$$H{:}H\dot{H} \qquad \dot{H}H{:}H \qquad (22)$$

which means that each bond is to be regarded as half order. For the complex of reaction (18) (when one ignores angles for the sake of more clearly showing electron-dot structures) the following structures are approximately equal in energy:



(23)

indicating that the bonds may be regarded as of the order 3/2, 1, 1, 3/2. Other electron-dot structures could be considered; the single electron could be permuted among the atoms, and no-bond structures adjacent to the transferred atoms could be invoked. Orders such as 13/8, 7/8, 7/8, 13/8, or other sequences could be justified. Differences of this magnitude have negligible effect on the computed **A** factors; the important point here is to utilize some consideration of molecular structure to avoid gross errors in assigning bond distances. For reaction (19) the bonds in the activated complex may be regarded as the same as those in the reactant except for those adjacent to the transferred hydrogen atom. The C–H and H–Cl bonds there may be taken as half order in each case; considerations of electronegativity and bond strength might lead to slightly different orders, say 0.4, 0.6, but again such differences are inconsequential to this discussion.

There are empirical rules, based on the structure of molecules, which give bond lengths in terms of bond order. Pauling (*14*) gives a table of normal covalent radii for single, double, and triple bonds. Also Pauling (*15*) has given an empirical formula for correcting integral-order bond lengths to lengths for fractional bonds; for example half-order bonds are 0.18 Å. longer than single bonds, and three-halves-order bonds are the geometric mean of single and double bond lengths. For these examples the bond lengths in Angstroms in the activated complex would be 0.92, 0.92 for (17); 1.20, 1.32, 1.36, 1.25 for (18); and 1.25, 1.47 for (19).

The assignment of bond angles is more arbitrary than that of bond lengths. The important decision is between linear or bent configurations, and considerations of *s* or *p* orbitals usually gives the clue here. For bent bonds it is convenient to assume 120-deg. angles, in the absence of any definite information.

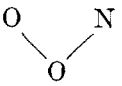
Badger (*16*) has proposed an empirical rule which relates the stretching-force constant to bond distance:

$$k_r = 1.86 \times 10^5/(r - d_{ij})^3 \text{ dynes/cm.} \qquad (24)$$

For the bond between hydrogen and an atom of the first row of the periodic table, $d_{H_1} = 0.34$. Other values are $d_{H_2} = 0.59$, $d_{H_3} = 0.65$, $d_{11} = 0.68$, $d_{12} = 0.90$, and $d_{22} = 1.18$. Stretching-force constants for H–H and C–H half bonds happen to be equal and are, for example, 2.6×10^5 dynes/cm.

Bending-force constants may be assigned by comparison with roughly equivalent stable molecules. For bending about X–H–X half bonds the force constant derived from hydrogen-bonded systems was assigned (*11*) as 0.16×10^{-11} erg./radian.^{2} By the fitting of force constants to the kinetic data for the reaction $H_2 + Cl = H + HCl$, the value for bending of H–H–Cl was assigned (*13*) the value 0.046×10^{-11} erg./radian^2. Angular force constants are often divided by the product of the two included bond lengths to give force constants in units of dynes/cm. A few values of this sort taken from more extensive tables (*17*, *18*) include H–O–H, 0.69×10^5; H–C–H in CH_4, 0.30×10^5; F–C–F in CF_4, 0.71×10^5.

For exact partition-function calculations one needs vibration frequencies, not force constants, for the activated complex. However the force constants suffice for the classical partition function, which is discussed in a later section and yields a satisfactory approximation in some cases. For the activated complex of reaction (17) it is easy to carry out a complete vibrational analysis (*11*), including the introduction of a cross-product potential-energy term which reduces to zero the vibration frequency of the antisymmetric stretching mode and thus converts it very naturally to the reaction coordinate. By modifying the activated complex of reaction (18) in the direction of greater symmetry, that is, treating the nitrogen atom as if it were an oxygen atom, one can easily solve the vibrational problem here, finding six in-plane normal-mode frequencies plus one reaction coordinate (*10*, *12*). Alternatively the frequencies for this complex may be transferred directly from corresponding motions in similar stable molecules, NO_2, N_2O_4, and O_3, after they are classified as three stretching modes, one reaction coordinate, and three bending modes. This classification could be arrived at from general symmetry considerations (*10*), or more simply the complex may be regarded as a bent triatomic molecule



with one stretching mode, one bending mode, and one reaction coordinate, with the addition of the end atoms giving rise to four vibrations, symmetric and antisymmetric stretching and bending. Thus reaction (18) can be subjected to a relatively rigorous vibrational analysis or treated by the more empirical methods used for more complicated activated complexes. For reaction (19) the activated complex is so large that a detailed vibrational analysis is hopelessly complicated and unnecessary. For the activated complex in (19) there will be extensive duplication of frequencies between the complex and the hydrocarbon reactant. In Equation (10) these identical vibration frequencies give rise to identical

terms in the numerator and denominator and hence cancel. It is preferable to cancel in advance all equivalent vibration frequencies (and methyl-group internal rotations) rather than to evaluate each set for reactant and complex and then to cancel them in the calculations. All vibrations and methyl-group internal rotations of the $(CH_3)_3C$ group may be taken as the same in reactant and activated complex; these may be canceled without being evaluated, and in subsequent considerations the $(CH_3)_3C$ group is to be regarded as a rigid body, not as a mass point. Thus the vibration problem for the reactant is reduced to the three vibrations (one stretch, two bends) of the hydrogen atom against the massive rigid body. The vibration problem for the activated complex is reduced to that of a linear triatomic molecule (symmetric stretch, reaction coordinate, and two bends which are largely motions of hydrogen) plus two wagging motions of the rigid body against the rest of the molecule. For the vibration frequencies of the three-body problem one may make use of the convenient formulas collected by Herzberg (*19*); for the wagging vibrations one may use the approximate relation

$$\nu = 4.1 \times 10^8 (k_\theta/I)^{1/2} \text{ cm.}^{-1} \qquad (25)$$

A corresponding expression holds for bending at right angles to this axis.

Equation (25) is a valid approximation only if the moment of inertia of the wagging group is small as compared with the molecule about a parallel axis. If the two moments are of comparable size, a better approximation is obtained by use of the reduced moment in Equation (25)

$$I = I_1 I_2/(I_1 + I_2) \qquad (26)$$

This treatment for reaction (19) can be extended to any type of atom transfer process

$$X - y + Z \rightarrow X + yZ \qquad (27)$$

where the complex may be linear or bent. Considerable cancellation can be expected between X in the reactant and in the complex when these are complicated groups. After the exploitation (without computation) of this cancellation the group so treated is regarded as rigid. The degrees of freedom which must be considered in a partition-function calculation for various cases are listed in Table 1. In all cases vibration frequencies for the three-atom problem can be found from Herzberg's relations (*19*), the wagging vibrations can be treated as simple separate problems depending on moments of inertia of the wagging groups and bending force constants, and the internal rotations can be treated by the following simple method.

Internal rotations are characterized by reduced moments of inertia and barriers to internal rotation. The reduced moment of inertia is given by Equation (26), which was introduced above for wagging motions. I_1 and I_2 are moments of inertia of the two groups about axes parallel to the axis of internal rotation and passing through the center of gravity of each group. For coaxial symmetric tops this treatment is exact; I_1 is simply the moment of inertia of one group about the common axis, and I_2 is the moment of inertia of the second group about the axis. For less symmetrical internal rotations the exact treatment of internal rotation becomes more complex (*20a*). However a simple approximate method (*10*) may be used in connection with Equation (26). If an internal rotation is about some bond, one should imagine the bond to be cut, thus separating the molecule into two pieces; find the center of mass of one piece; pass a line through this point parallel to the severed bond; and compute I_1 as the moment of inertia about this line. Next one should find the center of mass of the second piece, pass a line through this point parallel to the severed bond, and compute I_2 as the moment of inertia about this second line.

Unless there is conspicuous steric hindrance, internal rotation about fractional bonds in the activated complex is usually regarded as essentially free. In case there is conspicuous evidence for a barrier, each case must be considered separately (*20b*).

The electronic multiplicity of the activated complex can be predicted, subject to some uncertainty, from the rules for stable molecules. If there are an even number of electrons, the multiplicity is usually one. The molecule O_2 is anomalous in having a multiplicity of three. This sort of anomaly, which is understood in terms of advanced quantum theories of valence, is possible only for certain highly symmetrical systems. It is usually safe to predict an electronic multiplicity of one for activated complexes.

If there are an odd number of electrons, the electronic multiplicity must be at least two, and it usually is two for systems of low symmetry. However in highly symmetrical systems orbital degeneracy may be present in addition to the spin degeneracy of two. Thus the Cl atom has a $^2P_{3/2}$ ground state with a multiplicity of four, and NO has a ground state ($^2\pi_{1/2}$) of multiplicity two but a low energy-excited state ($^2\pi_{3/2}$) of multiplicity four. The less symmetrical molecule NO_2 has multiplicity two. Thus one can usually predict the correct multiplicity, but in exceptional cases there may be an uncertainty of not more than a factor of three.

These considerations (all outside the field of kinetics itself) establish, with the uncertainties as pointed out, all the structural and mechanical features of the activated complex.

Table 1. Degrees of Freedom in Atom Transfer Reactions Which Do Not Cancel and Must Be Considered in Partition-Function Calculations for $Xy + Z = X + yZ$

			Noncanceling degrees of freedom					
			Vibrations					
Model*	T,	R I.R.	Sym. str.	Antisym. str.	Bend	wag	Total number External	Internal
z	3						3	
X	3	3					6	
x − y	3	2	1				5	1
X − y	3	3	1		2‡		6	3
x − y − z linear	3	2	1	1†	2		5	4
x − y − z bent	3	3	1	1†	1		6	3
X − y − z linear	3	3	1	1†	2‡	2	6	6
X − y − z bent	3	3	1	1	1†	1	2	6	6
X − y − Z linear	3	3	1	1	1†	2‡	4	6	9
X − y − Z bent	3	3	2	1	1†	1	4	6	9

*Lower case x, y, or z stands for atoms; upper case X or Z stands for complex groups regarded as rigid bodies.
†The reaction coordinate.
‡To a fair approximation, especially for light y, these bending frequencies are the same in reactant and complex.

Comparisons of the Methods in Establishing the Properties of the Complex H_3.

It is only for reaction (17) with the H_3 complex that fairly detailed, even though still highly approximate, quantum mechanical computations have been carried out. This complex also has been extensively examined by the semiempirical method. It is one of the cases treated by the empirical method described above. Also recent, carefully obtained kinetic data (*21*) on this reaction have been so extensive and so precise that the activation energy and vibration frequencies could be found solely as a best fit to

TABLE 2. STRUCTURE AND PROPERTIES OF THE H_3 COMPLEX AS OBTAINED BY THEORETICAL SEMIEMPIRICAL, AND EMPIRICAL METHODS

	Bond distance, Å	Vibration frequencies, sec.$^{-1}$ × 10^{-13} Stretch	Bend	Ref.
Theoretical	0.96	9.5	3.3	*4*
Semiempirical (f = 0.14)	0.88	*	2.7	*1*
Empirical	0.92	8.8	3.6	*11*
Kinetic	†	9.6	3.6	*21*

*The approximation of constant f breaks down badly at small distances. The shape of the potential energy function at the top of the pass is too uncertain to justify evaluation of the stretching frequencies.

†An unsymmetrical complex was taken from the potential energy surface which shows a small, false (*4*) well in the top of the pass. Distances of 0.85 and 1.25 Å. were used in the computation of vibration frequencies.

the experimental data, within the framework of the general activated-complex theory. In Table 2 there is a comparison of bond distance, frequency of symmetric stretching vibration, and frequency of the bending vibrations for the four methods mentioned above: theoretical, semiempirical, empirical, and kinetic. All these methods for this reaction agree as to the structure and mechanical properties of the activated complex.

CALCULATION OF A FACTORS FOR BIMOLECULAR REACTIONS

Evaluation of Separated Partition Functions

Experimental rate data are usually reported in terms of the Arrhenius equation

$$k = \mathbf{A} \exp(-\mathbf{E}/\mathbf{R}T) \qquad (11)$$

whereas theoretical rate expressions take the form

$$k = \mathbf{B}(T) \exp(-\mathbf{W}/\mathbf{R}T) \qquad (28)$$

The relations between these two quantities are

$$\mathbf{E} = \mathbf{W} + \theta\mathbf{R}T \qquad (29)$$

$$\mathbf{A} = \mathbf{B} \exp \theta \qquad (30)$$

where the quantity θ is given by

$$\Theta = Td \ln \mathbf{B}/dT \qquad (31)$$

In terms of the activated complex theory discussed here the rate factor **A** in units of cc.(mole^{-1})(sec.$^{-1}$) is

$$\mathbf{A} = 3.41 \times 10^{34} \kappa T \pi_p \mathbf{A}_p \qquad (32)$$

where κ is the transmission coefficient taken as unity in the absence of more detailed information (*22*), and $\pi_p\mathbf{A}_p$ is the product of partition functions for all kinds of energy, each of the form

$$\mathbf{A}_p = \exp(\theta_p) Q^\ddagger / Q_A Q_B \qquad (33)$$

The product includes translational, rotational vibrational, internal rotational, and electronic degrees of freedom.

In c.g.s. units translational partition functions per cc. are given by

$$Q_{tr} = 1.88 \times 10^{20} (MT)^{3/2} \qquad (34)$$

$$\theta_{tr} = 3/2 \qquad (35)$$

The translational **A** factor, including the term in θ, is

$$\mathbf{A}_{tr} = 1.18 \times 10^{-21} (M^\ddagger / M_A M_B T)^{3/2} \qquad (36)$$

Rotational partition functions for linear (gram-molecular weight and Angstrom units) molecules of moment of inertia are given by

$$Q_r^L = 0.0412\, IT/\sigma \qquad (37)$$

$$\theta_r^L = 1 \qquad (38)$$

and for a nonlinear molecule with three principal moments of inertia, I_1, I_2, I_3, are

$$Q_r^N = 0.0148 (I_1 I_2 I_3)^{1/2} T^{3/2} / \sigma \qquad (39)$$

$$\theta_r^N = 3/2 \qquad (40)$$

It is not necessary to evaluate the individual moments of inertia; their product can be found much more simply (*23*) by means of any Cartesian coordinate system with the center of mass as the origin by means of

$$I_1 I_2 I_3 = \begin{vmatrix} +I_{xx} & -I_{xy} & -I_{xz} \\ -I_{xy} & +I_{yy} & -I_{yz} \\ -I_{xz} & -I_{yz} & +I_{zz} \end{vmatrix} \qquad (41)$$

where $I_{xx} = \sum m_i(y_i^2 + z_i^2)$, $I_{xy} = \sum m_i x_i y_i$, etc.

For each free internal rotation the partition function is

$$Q_{fir} = 0.360\, (IT)^{1/2}/\sigma \qquad (42)$$

The effect of symmetry numbers may be evaluated in either of two ways: (1) the rotational symmetry number may be found for each reactant, for the activated complex, and for each internal rotation of both reactants and complex and (2) on the other hand, one may forget about symmetry numbers; omit them from Equations (37), (39), and (42); and find the integral value of the product

$$\pi\sigma_A\sigma_B/\sigma^\ddagger \qquad (43)$$

simply by inspection. The product in Equation (43) is the number of equivalent reaction coordinates, if one permutes both reactants about all equivalent modes of attack. For example for the reaction

$$CH_4 + Cl \rightarrow H_3C - H - Cl \rightarrow CH_3 + HCl \qquad (44)$$

the symmetry number of methane is twelve, Cl is one, and the complex is three. The ratio (12)(1)/3 is equal to four, the number of equivalent hydrogen atoms in methane. For calculations based on one structure the symmetry numbers in the rotational and internal rotational partition functions automatically account for this multiplicity of identical reaction sites. One must be careful not to apply this factor twice or to be inconsistent between reactants and complex.

Vibrational partition functions in terms of normal mode frequencies in cm.$^{-1}$ are given by

$$Q_v = 1 - \exp(-1.44\nu/T)^{-1} \qquad (45)$$

$$\theta_v = \frac{1.44\nu/T}{\exp(1.44\nu/T) - 1} \qquad (46)$$

When $1.44\nu \ll T$, the vibrational partition functions take on their classical value

$$Q_v' = T/1.44\nu, \qquad \theta_v = 1 \qquad (47)$$

Electronic partition functions are based simply on the fundamental definition

$$Q_e = \sum_i g_i \exp(-\epsilon_i/\mathbf{k}T) \qquad (48)$$

$$\theta_e = T\, d \ln Q_e/dT \qquad (49)$$

Often the sum in (48) is only the single term, the ground-state multiplicity. For nitric oxide at ordinary temperatures it is a sum of two terms. For reactions at high temperatures, say above 2,000°K., the higher terms in the sum over electronic states may become very important.

Evaluation of Partition Functions by Classical Mechanics (*13*)

Up to this point partition functions on the basis of the quantum energy levels of each system have been discussed. For many molecular motions however the separation of the energy levels is less than kT at temperatures of practical interest, and in such cases the partition function may be evaluated by classical mechanics. This method is advantageous because less detailed information is required. In particular one does not have to solve the dynamical-vibration problem; knowledge of the potential-energy function suffices.

Rotational and translational motions may always be treated classically; hence the criterion of validity of the classical

method lies in the treatment of vibration. If one arbitrarily selects 0.2 cal./deg. mole as a maximum error in the entropy of vibration (or 10% in the rate), then the classical method is valid for frequencies (in cm.$^{-1}$) such that $\nu \leq 1.1T$, where the temperature is in °K. While many vibrations in stable molecules lie above this boundary, most of these vibrations are essentially unchanged in the activated complex and hence may be canceled. The key decision concerns the new motions which arise in the activated complex but were not present in either reactant. If these motions are of low frequency, then the classical method is valid and useful.

The classical partition function (also called the *phase integral*) may be written

$$Q = \frac{q_e \mathbf{C}}{\sigma} \int \cdots \int e^{-V/\mathbf{k}T}\, dx_1 \cdots dz_n \qquad (50)$$

$$\mathbf{C} = \left(\frac{2\pi \mathbf{k}T}{h^2}\right)^{3n/2} \prod_{i=1}^{n} m_i^{3/2} \qquad (51)$$

One may of course transform from Cartesian coordinates to some other coordinate system. If a few vibrational motions have too high frequencies, one may correct this partition function by multiplication of the ratio ($Q_{q.m.}/Q_{class}$) of the quantum partition function to the classifical function for each high frequency. Also groups such as CH_2, CH_3, etc., may be regarded as single particles in the classical calculation and the quantum partition function for their internal motions introduced later.

One convenient method of integrating Equation (50) is a serial procedure in which the first atom is placed anywhere in the container, and the successive atoms are described by coordinates relative to the preceding atoms. In these calculations groups such as CH_3, CH_2, or CH are regarded as single atoms, and the hydrogen vibrations are treated separately by the quantum method or canceled out.

This method was applied (*13*) to the reaction of a chlorine atom with a hydrocarbon, but the calculations are equally applicable to any reaction of the type

$$X - H + z \rightarrow X + H - z \qquad (52)$$

The serial integration starts in an identical fashion for both the hydrocarbon reactant and the activated complex. Consequently all the earlier factors cancel in the desired ratio $Q\ddagger/Q_{R-H}$ of the partition functions of the activated complex and the reactant hydrocarbon. There remain just the additional factor introduced by the chlorine atom and the effect of released constraints on the reacting hydrogen. Only a single reaction site, a single C–H bond, is being considered.

It is easiest to consider the reacting hydrogen in a CH group, and a detailed model is given in Figure 3. The reacting hydrogen has a stretching motion and two bending motions in the CH group of the reactant hydrocarbon. The complete partition function contains the factor for these three quantized vibrations. In the activated complex the C–H stretching motion becomes the reaction coordinate and is omitted, but there are still the two C–H bending motions for which quantum mechanical partition-function factors must be included. The C–H stretching frequency in the reactant molecule is so high that it does not contribute significantly at moderate temperatures. Consequently it yields a partition-function factor of unity. The two hydrogen bending frequencies may be shifted somewhat by the formation of the complex. It is difficult to estimate how large this shift will be, but as the frequencies are so high that their contribution is small, this factor may also be neglected.

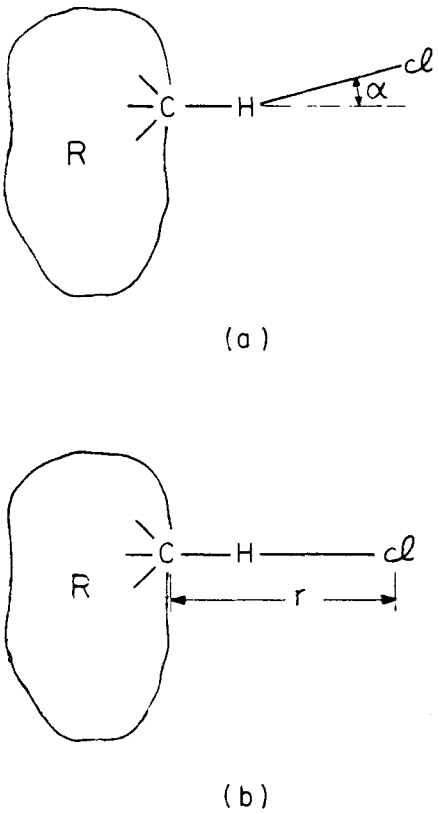


Fig. 3. The coordinates of a chlorine atom in an activated complex for reaction with the hydrocarbon R-H.

If the reacting hydrogen is in a CH_3 or CH_2 group (instead of a CH group), the situation is more complex. Nevertheless one C–H stretching mode becomes the reaction coordinate with the same resulting effect on the partition functions as described above. Also the same number of C–H bending modes will be present in the activated complex as in the reactant molecule, and the corresponding small quantum partition-function factors may be assumed to cancel one another in reasonable approximation.

The contribution to the partition function by the chlorine atom is not small, but now the frequencies are low and the classical method is appropriate. For the chlorine atom polar coordinates about the equilibrium position of the hydrogen atom at the reaction site (Figure 3) were chosen, and

$$\frac{Q}{Q_{R-H}} = q_e \left(\frac{2\pi \mathbf{k}T m_{Cl}}{h^2}\right)^{3/2} \cdot \iiint e^{-V(r,\theta,\phi)/\mathbf{k}T} \cdot r^2 \sin\theta\, dr\, d\theta\, d\phi \qquad (53)$$

was obtained.

The potential function has been estimated (*13*) in reasonable approximation, and the resulting integral yields agreement with the **A** factor observed in kinetic measurements. The potential function would be expected to be about the same for each exposed hydrogen atom in a hydrocarbon molecule. The total energy increase to the activated complex may vary somewhat from one reacting hydrogen to another, but this effect is in the activation energy for that particular reaction. The additional energy required for nonoptimal values of the coordinates in V should be nearly the same for each site. Consequently one sees that Equation (53) yields the same result for each site, and the kinetic **A** value is the same for each site. The experimental data (*24*) for several hydrocarbons follow this prediction approximately (within a factor of about two).

The preceding conclusion illustrates the power of the classical method. It sweeps away unimportant factors and emphasizes the essential features of the potential-energy function of the activated complex. At the present time this method is being extended to other types of reaction.

Evaluation and Summary

The application of theoretical and semiempirical methods to problems in reaction kinetics has been summarized by Glasstone, Laidler, and Eyring (*1*). By rather difficult computations results were found which were moderately successful quantitatively but very instructive qualitatively and which gave the thermodynamic formulation

$$k = (\mathbf{k}T/h) e^{\Delta S\ddagger/R}\, e^{-\Delta H\ddagger/RT} \qquad (54)$$

of rate constants. This relation has proved very valuable in the correlation of rate data, especially for organic reactions. One utilizes the rate constant and its temperature dependence to evaluate $\Delta H\ddagger$ and $\Delta S\ddagger$; as a check on the theory one looks

to the internal consistency for a class of reactions and to the reasonableness of entropy values obtained.

Recent efforts to apply theorems of molecular structure and molecular spectroscopy to these problems have sought to avoid the overwhelming complications of the theoretical approach and yet to provide predictions, not just correlations, at the level of accuracy of experimental kinetics. For the **A** factors in the Arrhenius equation there is relatively little (maybe a factor of 4) flexibility or spread in the values deduced from these considerations of molecular spectroscopy and structure. By these methods computations have been carried through for twenty-four bimolecular gas-phase reactions, involving a fairly diverse series of reactants and reaction types. In twenty-two of these cases there is agreement within the limit of experimental error between calculation and experimental result; in two cases the experimental A factors were much too high, a factor of 200 in one case and a factor of 10^5 in the other. In both cases the reaction was one of many occurring in a chain reaction, and it is easy to produce large errors in such a case by a wrong assignment in the mechanism, aside from errors in experimental technique. It is proposed that such an error in mechanism is involved in these cases.

Predictions of the energy of activation have not yet attained any comparable degree of accuracy, and at present it is usually best to regard the energy of activation as an empirical quantity to be obtained from experimental rate data or from general thermochemical correlations.

In some cases the activation energy of a dissociation reaction may be just the energy of dissociation; that is, the reverse reaction of recombination has no activation energy at all. Where this condition holds, the activation energy may be calculated from thermochemical data. In other cases this condition may not hold strictly, but a reasonable estimate may be made of the correction.

One may also note that the reaction rate becomes less sensitive to a given error in the activation energy as the temperature increases. Thus it becomes more feasible to predict reaction rates at high temperatures than at low.

In some experimental systems it is possible to measure the rate constant at only one temperature or over only a narrow range of temperature. With this method of calculating **A** in Equation (11) one can reliably estimate the activation energy **E** even from such meager data.

NOTATION

A, B, C, D = chemical species in a reaction

A, B, C = coulombic energy in London equation for energy of H_2 and H_3

A = preexponential factor in the Arrhenius equation

B = preexponential factor in general

C = term defined in Equation (51)

d_{ij} = constant depending on i and j

E = energy

E_x = energy for diatomic molecule with distance r_x

E_z = energy of diatomic molecule with distance $2r_x = r_z$

E = activation energy in the Arrhenius equation

f = fraction of coulombic energy in London theory

g = number of energy states with the same energy, the degeneracy factor

H = enthalpy

h = Planck's constant

i, j = rows of periodic table of two atoms

I = moment of inertia

K = equilibrium constant

k = rate constant

k_θ = angular-force constant for wagging, erg/radian^2

k = Boltzmann's constant, R/N

k_r = bond stretching-force constant

k_ϕ = bond bending-force constant

M = gram molecular weight

m = mass

m_i = mass of ith atom

P = product

Q = partition function or weighted sum over all energy states

$Q\ddagger$ = partition function for all motions of the activated complex except the reaction coordinate

q_e = electronic partition function (or multiplicity for a single state)

R = rate

R = gas constant

r = bond length

S = entropy

T = absolute temperature, °K.

V = potential energy

X = transition state or activated complex

X, Z = atom or groups of atoms

y = atom

Greek Letters

α, β, γ = exchange energy in London equation for energy of H_2 and H_3

ϵ = atomic or molecular energy level

κ = transmission coefficient, $R_5/(R_4 + R_5)$ in Figure 1

ν = vibration frequency

θ, ϕ = spherical polar coordinate

Θ = term defined in Equation (31)

σ = symmetry number, equivalent structures produced by real rotations

$\ddagger$ = symbol identifying the activated complex

ΔS^0 = difference in standard entropy between products and reactants

ΔH^0 = similar difference in standard enthalpy

ΔH_0^0 = ΔH^0 at absolute zero

$\Delta H_0^\ddagger$ = energy of activation at absolute zero

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