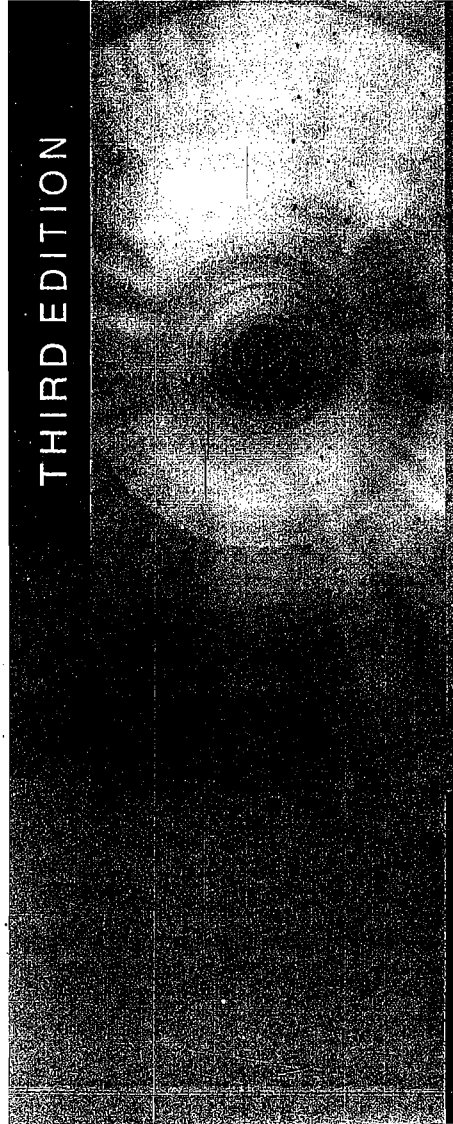


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Chemical Kinetics

THIRD EDITION



Keith J. Laidler

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TABLE 5.6 CALCULATED AND OBSERVED RATES FOR THE NITRIC OXIDE-CHLORINE REACTION

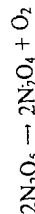
T/K	$k/\text{dm}^3 \text{ mol}^{-2} \text{ s}^{-1}$	
	Calculated	Observed
273	1.4	5.5
333	2.2	9.5
355	8.6	27.2
401	18.3	72.2
451	25.4	182
506	64.5	453
566	120.2	1130

The treatment of trimolecular gas reactions is one of the outstanding successes of conventional transition-state theory. Using very straightforward procedures, we can account for the unusual temperature dependences of these reactions in a simple way, and we can calculate reliable values for the pre-exponential factors. As was noted, a simple version of collision theory gave results in error by several orders of magnitude, and it gave no interpretation of the temperature dependence. Other theories can give satisfactory results only at the cost of considerable labor.

Kinetic data for some trimolecular reactions studied in the mass spectrometer have been compiled and discussed²⁷ and are listed in Table 5.7. All these reactions appear to occur with zero activation energy, so that the temperature dependence of the rates is attributed to that of the pre-exponential factors. The predicted temperature dependences for linear and nonlinear complexes are shown in the table (compare Table 5.4). In view of the simplicity of the model and the possible experimental error, the agreement between theory and experiment is very satisfactory. These trimolecular reactions occur much more slowly than bimolecular reactions having zero activation energy, because of the considerable entropy loss when the activated complex is formed.

5.3 UNIMOLECULAR REACTIONS

The early history of unimolecular gas reactions was one of considerable confusion, on both the experimental and theoretical sides. In the last century, van't Hoff was aware of two first-order gas reactions—the decompositions of arsine and of phosphine²⁸—but he realized that they occurred to a considerable extent on the surface of the reaction vessel. In 1921, Daniels and Johnston²⁹ investigated the decomposition of nitrogen pentoxide,



and believed it to be unimolecular. Much work was done subsequently on this reaction, but eventually it was realized that it occurs by a composite mechanism, to be considered in Section 8.5.

In 1922 Trautz and Winkler³⁰ discovered and investigated the first true unimolecular gas reaction, the isomerization of cyclopropane into propylene,

5.3 UNIMOLECULAR REACTIONS

TABLE 5.7 TEMPERATURE DEPENDENCES OF RATES OF TRIMOLECULAR ION-MOLECULE REACTIONS

Reaction	Experimental temperature dependence		Theoretical temperature dependence ^a		Reference to experimental work
	T^{-1}	$T^{-1.7}$	Linear complex	Nonlinear complex	
$\text{He}^+ + \text{He} \rightarrow \text{He}_2^+ + \text{He}$	T^{-1}		T^{-1}	$T^{-0.5}$	<i>b</i>
$\text{N}^+ + \text{N}_2 + \text{He} \rightarrow \text{N}_3^+ + \text{He}$	$T^{-1.7}$		T^{-2}	$T^{-1.5}$	<i>c</i>
$\text{N}_3^+ + \text{N}_2 + \text{He} \rightarrow \text{N}_4^+ + \text{He}$	$T^{-1.6}$		T^{-3}	$T^{-2.5}$	<i>c</i>
$\text{N}^+ + \text{N}_2 + \text{N}_2 \rightarrow \text{N}_3^+ + \text{N}_2$	$T^{-2.5}$		T^{-3}	$T^{-2.5}$	<i>d</i>
$\text{O}_2^+ + \text{O}_2 \rightarrow \text{O}_3^+ + \text{O}_2$	T^{-3}		T^{-4}	$T^{-3.5}$	<i>e</i>
$\text{N}_3^+ + \text{N}_2 + \text{N}_2 \rightarrow \text{N}_4^+ + \text{N}_2$	$T^{-4.4}$		T^{-4}	$T^{-3.5}$	<i>d</i>
$\text{H}_3^+ + \text{H}_2 + \text{H}_2 \rightarrow \text{H}_4^+ + \text{H}_2$	$T^{-4.6}$		$T^{-4.5}$	T^{-4}	<i>f</i>
$\text{H}_3\text{O}^+ + \text{H}_2\text{O} + \text{CH}_4 \rightarrow \text{H}_3\text{O}_2^+ + \text{CH}_4$	$T^{-6.2}$		$T^{-5.5}$	T^{-5}	<i>g</i>

^a M. Meot-Ner, J. J. Solomon, F. H. Field, and H. Gershinowitz, *J. Phys. Chem.*, **78**, 1773 (1974).

^b F. E. Niles and W. W. Robertson, *J. Chem. Phys.*, **42**, 3277 (1965).

^c D. K. Bohme, D. B. Dunkin, F. C. Fehsenfeld, and E. E. Ferguson, *J. Chem. Phys.*, **51**, 863 (1969).

^d A. Good, D. A. Durdan, and P. Kebarle, *J. Chem. Phys.*, **52**, 212 (1970).

^e D. A. Durdan, P. Kebarle, and A. Good, *J. Chem. Phys.*, **50**, 805 (1969).

^f R. C. Piatec and R. F. Porter, *Chem. Phys. Lett.*, **23**, 608 (1973).

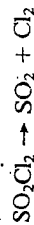
^g A. J. Cunningham, J. D. Poyant, and P. Kebarle, *J. Am. Chem. Soc.*, **94**, 7627 (1972).



Subsequent work on this reaction has given no evidence that it is other than elementary, and it appears to occur entirely in the gas phase and not at all on the surface of the vessel. Other truly unimolecular reactions discovered in the 1920s are the dissociation of molecular bromine³¹



the decomposition of sulfonyl chloride,³²



and the conversion of pinene into *dl*-limonene.³³

In 1919 Perrin³⁴ concluded that unimolecular gas reactions could be understood only on the basis of the radiation hypothesis,³⁵ according to which the energy required for reaction to occur is provided by radiation from the walls of the vessel. In 1919, however, there was no known unimolecular reaction, and there was not even any real reason to believe that such reactions existed. Perrin did not mention any example of a unimolecular reaction; he took it for granted that they existed and, most important, that they were first-order reactions at all pressures. His argument was that one could imagine expanding the reaction vessel to an infinite volume, when the molecules would be so far apart that no collisions took place. First-order kinetics implies that the probability that a given molecule A reacts, which is proportional

to $(-d[A]/dt)/[A]$, is independent of $[A]$. According to Perrin, this probability remains the same even if $[A]$ approaches zero, when there are no collisions. He therefore concluded that collisions could play no part in unimolecular processes, and the radiation hypothesis appeared to offer the only plausible alternative. The argument can be expressed in another way by saying that the frequency of collisions depends on the square of the pressure; dependence of the rate on the first power therefore appeared to be impossible.

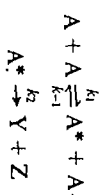
To some³⁶ this argument appeared compelling, while others³⁷ were skeptical. The controversy raged for a number of years until finally an alternative explanation for unimolecular reactions was accepted. It is now easy to see the fallacy in Perrin's argument: there were no known experimental examples and Perrin assumed behavior that eventually turned out to be incorrect. Unimolecular reactions do not remain first order at very low pressures.

5.3.1 Lindemann-Christiansen Hypothesis

In 1921 the Faraday Society held a discussion on "The Radiation Theory of Chemical Action." At this meeting, the whole problem, including that of unimolecular reactions, was hotly debated. One who expressed strong opposition to the radiation hypothesis was Lindemann (later Lord Cherwell). Realizing that if he destroyed the hypothesis he should suggest an alternative explanation for unimolecular reactions, he did so in a very brief communication which was later published.³⁸ A few days after Lindemann made his oral presentation, Christiansen³⁹ published his Ph.D. thesis in which the same treatment was included, in a more detailed and explicit form than appeared in Lindemann's written submission. This Lindemann-Christiansen hypothesis is the basis of all modern theories of unimolecular reactions, although a number of important modifications had to be made to it later.

The hypothesis provided a way in which, under some conditions, activation by collisions can give rise to first-order kinetics. It also led to the important prediction that at sufficiently low pressures all unimolecular reactions must become second order. Much later work has shown this to be the case.

The Lindemann-Christiansen hypothesis, as later interpreted and expanded by Hinshelwood⁴⁰ and others, can be formulated as follows. The process of forming a molecule A^* having sufficient energy to undergo reaction, the energization process, involves collision between two molecules of A . The energized molecule A^* may undergo de-energization by collision with a normal molecule, or it may undergo a unimolecular reaction to form products. These three processes are quite distinct, and the situation may be represented as



The rate of energization is $k_1[A]^2$. The energized species can be de-energized, at a rate $k_{-1}[A^*][A]$, or it can undergo conversion into products $Y + Z$ at a rate $k_2[A^*]$.

If the pressure is high enough, the rate $k_{-1}[A^*][A]$ with which A^* is de-energized will be greater than the rate of product formation, $k_2[A^*]$. When this is the case, the

energized molecules A^* are essentially in equilibrium with normal molecules, and the concentration $[A^*]$ is thus proportional to the first power of $[A]$, being given by

$$[A^*] = \frac{k_1}{k_{-1}} [A] \quad (5.12)$$

Thus, the rate of reaction, equal to $k_2[A^*]$, is also proportional to $[A]$:

$$v = k_2[A^*] = k_2 \frac{k_1}{k_{-1}} [A] \quad (5.13)$$

The kinetics are first order.

The situation, however, is different if the concentration of A is so small that de-energization is much less rapid than the rate at which A is converted into products. There is no longer an equilibrium involving A^* . Instead, the rate of product formation is almost equal to the rate at which A^* molecules are formed, since now these molecules, nearly always become products. The rate of reaction therefore equals the rate of energization, which is $k_1[A]^2$; the kinetics are second order.

After Lindemann and Christiansen put forward these suggestions, some experiments were done with the object of seeing whether the kinetics did become second order at sufficiently low pressures. At first there was considerable confusion, since many of the reactions studied were not truly unimolecular; some were composite reactions and others occurred on the surface of the vessel. Much early work was done on the nitrogen pentoxide decomposition (see Section 8.4.6), which did not show the change of kinetics, but which eventually turned out to occur by a composite mechanism.

An important aspect of the Lindemann-Christiansen hypothesis is the concentration of A at which there should be an observable transition from first-order towards second-order kinetics. According to the hypothesis, the kinetics are first order only when the rate of de-energization, $k_{-1}[A^*][A]$, is considerably greater than the rate of conversion of A^* into products, $k_2[A^*]$. When this is so, the rate of reaction is given by Eq. (5.13). A first-order rate constant under these conditions can be defined by

$$v = k_{\infty}^1 [A] \quad (5.14)$$

and thus is given by

$$k_{\infty}^1 = \frac{k_1 k_2}{k_{-1}} \quad (5.15)$$

We now consider in particular the situation when the rates of de-energization and of product formation are equal: the condition is

$$k_{-1}[A^*][A]_{1/2} = k_2[A^*] \quad (5.16)$$

where $[A]_{1/2}$ is the concentration at which this is satisfied. Now A^* has only a 50% chance of becoming products, and the rate is just half of the rate given by Eq. (5.13).

Thus,

$$v_{1/2} = \frac{1}{2} k_2 \frac{k_1}{k_{-1}} [A]_{1/2} \quad (5.17)$$

$$= \frac{1}{2} k_{\infty}^1 [A]_{1/2} \quad (5.18)$$

The first-order rate coefficient k^1 , defined under any condition by

$$v = k^1[A] \quad (5.19)$$

has fallen to one-half of its limiting (high-pressure) value k_∞ .

Subsequent discussions of this problem, beginning with that of Hinshelwood,⁴⁰ have made use of the steady-state hypothesis, which we consider later (Section 8.2.2). The arguments so far are independent of that hypothesis, which provides a useful general equation for the rate. According to the steady-state hypothesis, the concentration $[A^*]$ can be regarded as essentially constant with time, so that $d[A^*]/dt = 0$. It follows from the mechanism that

$$\frac{d[A^*]}{dt} = k_1[A]^2 - k_{-1}[A^*][A] - k_2[A^*] = 0 \quad (5.20)$$

and therefore that

$$[A^*] = \frac{k_1[A]^2}{k_{-1}[A] + k_2} \quad (5.21)$$

The rate of formation of products is

$$v = k_2[A^*] = \frac{k_1 k_2 [A]^2}{k_{-1}[A] + k_2} \quad (5.22)$$

At sufficiently high concentrations $k_{-1}[A] \gg k_2$, and the rate is

$$v = \frac{k_1 k_2}{k_{-1}} [A] = k_\infty^1 [A] \quad (5.23)$$

as found previously [Eq. (5.13)]. At low concentrations, on the other hand, $k_2 \gg k_{-1}[A]$ and

$$v = k_1[A]^2 \quad (5.24)$$

It follows from Eq. (5.22) that the first-order rate coefficient, defined by Eq. (5.19), is given by

$$k^1 = \frac{k_1 k_2 [A]}{k_{-1}[A] + k_2} \quad (5.25)$$

which for some purposes is written more conveniently as

$$k^1 = \frac{k_2(k_1/k_{-1})}{1 + k_2/k_{-1}[A]} \quad (5.26)$$

According to these equations, a plot of k^1 versus $[A]$ is a hyperbola, as shown in Fig. 5.5. The first-order coefficient k^1 is constant in the higher concentration range but falls off at lower concentrations. As previously shown, $k^1 = k_\infty^1/2$ when $k_{-1}[A] = k_2$, and we write the concentration at which this is true as $[A]_{1/2}$. Thus,

$$[A]_{1/2} = \frac{k_2}{k_{-1}} = \frac{k_\infty^1}{k_1} \quad (5.27)$$

using Eq. (5.23).

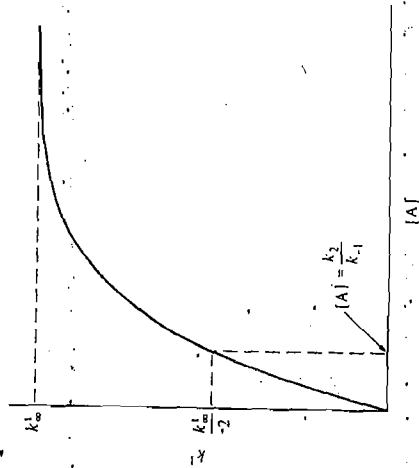


Figure 5.5 Plot of k^1 versus $[A]$, according to Eq. (5.26).

However, when this relationship was applied to experimental data, some difficulties arose. The value of k_∞^1 is an experimental quantity, and it was thought that k_1 could be estimated easily on the basis of simple collision theory; it was originally set as $z_1 e^{-E_1/RT}$, where z_1 is the collision frequency factor and E_1 is the activation energy. However, the experimental values of $[A]_{1/2}$ were always much smaller than those estimated in this way. Since there can be no doubt about k_∞^1 , which is an experimental quantity, the error must be in the estimation of k_1 . Thus, a modification must be made to allow k_1 to be much larger than $z_1 e^{-E_1/RT}$.

A second difficulty with the Lindemann-Christiansen hypothesis becomes apparent when experimental results are plotted in another way. Equation (5.25) may be written as

$$\frac{1}{k^1} = \frac{k_{-1}}{k_1 k_2} + \frac{1}{k_1 [A]} \quad (5.28)$$

and a plot of $1/k^1$ against the reciprocal of the concentration should give a straight line. However, deviations from linearity have been found of the kind shown schematically in Fig. 5.6.

5.3.2 Hinshelwood's Treatment

The first difficulty with the original Lindemann-Christiansen hypothesis, that the first-order rates are maintained down to lower concentrations than the theory appeared to permit, was overcome successfully by Hinshelwood.⁴¹ He pointed out that the expression $z e^{-E/RT}$ only applies if the energy is distributed among two degrees of freedom (see Section 3.1 and the appendix to Chapter 3). For some unimolecular reactions, however, the number of degrees of freedom s is considerable. The activation energy is distributed initially among these degrees of freedom, and there are many ways in

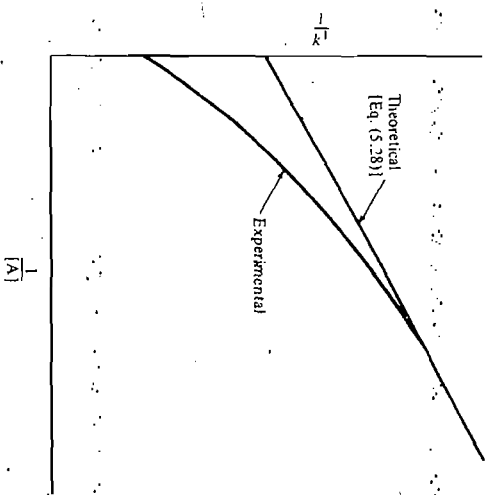


Figure 5.6 Schematic plots of $1/k^1$ versus $1/[A]$.

which this distribution may be effected. Once the energy is in the molecule, distributed in any way among s vibrational degrees of freedom, the molecule is in a position eventually to react. After a number of vibrations of the energized molecule A^* —which may be a very considerable number—the energy may find its way into appropriate degrees of freedom so that A^* can pass at once into products.

Hinshelwood derived the statistical expression (3.41) that was given in the appendix to Chapter 3. This formula gives the fraction of molecules having energy in excess of e_0^{\ddagger} as

$$f^* = \frac{1}{(s-1)!} \left(\frac{e_0^{\ddagger}}{kT} \right)^{s-1} e^{-e_0^{\ddagger}/kT} \quad (5.29)$$

where s is the number of degrees of freedom. He then expressed the rate constant k_1 as

$$k_1 = z_1 \frac{1}{(s-1)!} \left(\frac{e_0^{\ddagger}}{kT} \right)^{s-1} e^{-e_0^{\ddagger}/kT} \quad (5.30)$$

instead of simply as $z_1 e^{-e_0^{\ddagger}/kT}$. Thus, an additional factor has appeared,

$$\frac{1}{(s-1)!} \left(\frac{e_0^{\ddagger}}{kT} \right)^{s-1}$$

and if s is sufficiently great this may be greater than unity by many powers of 10.

The activation energy for k_1 predicted in the Hinshelwood formulation differs from that predicted by the simple collision theory. Equation (5.30) can be written

$$k_1 \propto T^{1/2} \left(\frac{1}{T} \right)^{s-1} e^{-e_0^{\ddagger}/kT} \quad (5.31)$$

This equation leads to

$$\frac{d \ln k_1}{dT} = \frac{(\frac{1}{2} - s)kT + e_0^{\ddagger}}{kT^2} \quad (5.32)$$

Since by the definition of the experimental activation energy [Eq. (2.81)]

$$\frac{d \ln k_1}{dT} \equiv \frac{E_a}{RT^2} = \frac{e_a}{kT^2} \quad (5.33)$$

where e_a is the experimental activation energy per molecule, it follows that

$$e_0^{\ddagger} = e_a + (s - \frac{1}{2})kT \quad (5.34)$$

Equation (5.30) can give much higher rates of activation and therefore much higher k_1/k_{-1} values than simple collision theory. For example, if the experimental activation energy is 170 kJ mol^{-1} and s is 12, Eq. (5.30) gives a value of k_1/k_{-1} that is larger by more than 10^6 than that given by the older theory.

A number of difficulties still remain, however, particularly the following:

1. The number s of degrees of freedom required to give agreement with experiment on the basis of Hinshelwood's proposal usually turns out to be only about one-half of the total number of vibrational modes. No satisfactory explanation has been given for this.
2. According to Hinshelwood's treatment, k_{∞} is given by

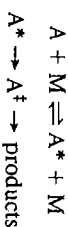
$$k_{\infty}^1 = \frac{k_1 k_2}{k_{-1}} = k_2 \frac{1}{(s-1)!} \left(\frac{e_0^{\ddagger}}{kT} \right)^{s-1} e^{-e_0^{\ddagger}/kT} \quad (5.35)$$

Therefore, one would expect a strong temperature dependence of the pre-exponential factor, especially for large values of s . There is no experimental evidence for this.

3. Hinshelwood's treatment does not affect the argument that a plot of $1/k^1$ versus $1/[A]$ should be linear (Fig. 5.6). The lack of linearity found experimentally still calls for an explanation.

5.3.3 Rice-Ramsperger-Kassel (RRK) Treatment

The treatment of Hinshelwood and the further developments of the theory of unimolecular reactions are considered best in terms of the following scheme:



Here M is any molecule, including another A , that can transfer energy to A when a collision occurs. A distinction is made between an *activated* molecule, represented by the symbol A^{\ddagger} , and an *energized* molecule, represented as A^* . An *activated* molecule A^{\ddagger} is by definition one that is passing directly through the dividing surface of the potential-energy surface. An *energized* molecule A^* , on the other hand, is one that

has acquired all the energy it needs to become an activated molecule A^\ddagger ; however, it must undergo vibrations before it does so. Figure 5.7 shows an energy diagram that relates to the Hinshelwood modification and also to the RRK mechanism now to be considered. To become an activated molecule A^\ddagger , the molecule A must acquire at least the energy ϵ_0^\ddagger . Hinshelwood's modification allowed A to acquire an amount of energy ϵ_0^\ddagger at an enhanced rate but regarded the rate at which A^* becomes A^\ddagger to be independent of that energy. In the further developments of the theory, the rate constant k_2 was not treated as constant but was considered to be larger the greater the value of ϵ^* .

We may approach this problem by starting with Eq. (5.26), which now can be written in a more general form:

$$k^1 = \frac{k_2(k_1/k_{-1})}{1 + k_2/k_{-1}[M]} \quad (5.36)$$

In Hinshelwood's modification both k_2 and k_1/k_{-1} are treated as independent of ϵ^* , the amount of energy in the energized molecule. Hinshelwood's formula, Eq. (5.30), involves the critical energy ϵ_0^\ddagger but not ϵ^* , the amount of energy in an individual energized molecule.

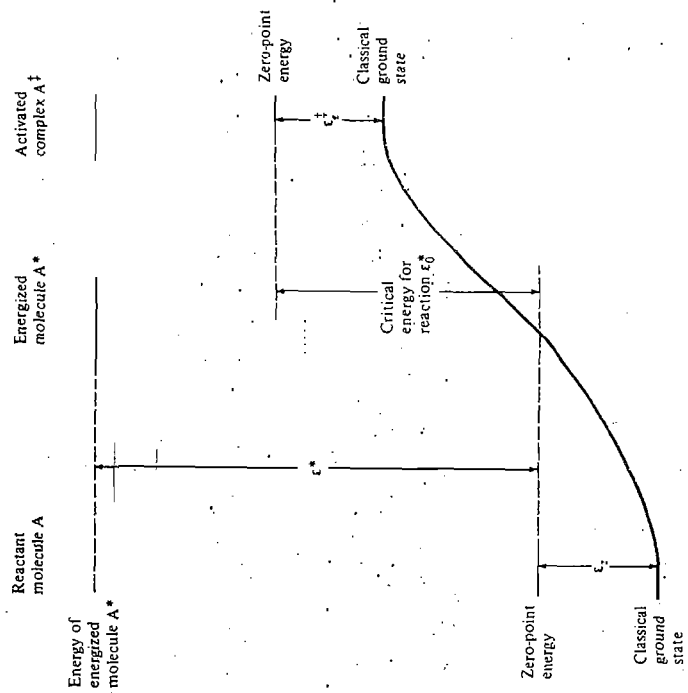


Figure 5.7 Energy scheme for Lindemann, Hinshelwood, and RRK mechanisms.

Very shortly after Hinshelwood suggested his modified formula, O. K. Rice and Ramsperger⁴² and independently Kassel⁴³ proposed theories in which both k_2 and k_1/k_{-1} were treated as dependent on the energy ϵ^* contained within an individual energized molecule. These theories are referred to jointly as RRRK theory. Equation (5.36) must now be modified: k_2 must be replaced by $k_2(\epsilon^*)$ and k_1/k_{-1} (now written as f) by $f(\epsilon^*)$, which is a distribution function. The expression

$$dk^1 = \frac{k_2(\epsilon^*)f(\epsilon^*)}{1 + k_2(\epsilon^*)/k_{-1}[M]} d\epsilon^* \quad (5.37)$$

is a *microcanonical* rate constant, relating to energized molecules having energy between ϵ^* and $\epsilon^* + d\epsilon^*$. To obtain the ordinary rate coefficient k^1 , the expression must be integrated from ϵ_0^\ddagger —the minimum energy that can lead to reaction—to infinity:

$$k^1 = \int_{\epsilon_0^\ddagger}^{\infty} \frac{k_2(\epsilon^*)f(\epsilon^*)}{1 + k_2(\epsilon^*)/k_{-1}[M]} d\epsilon^* \quad (5.38)$$

Figure 5.8 summarizes the way in which the theories arise from this general equation.

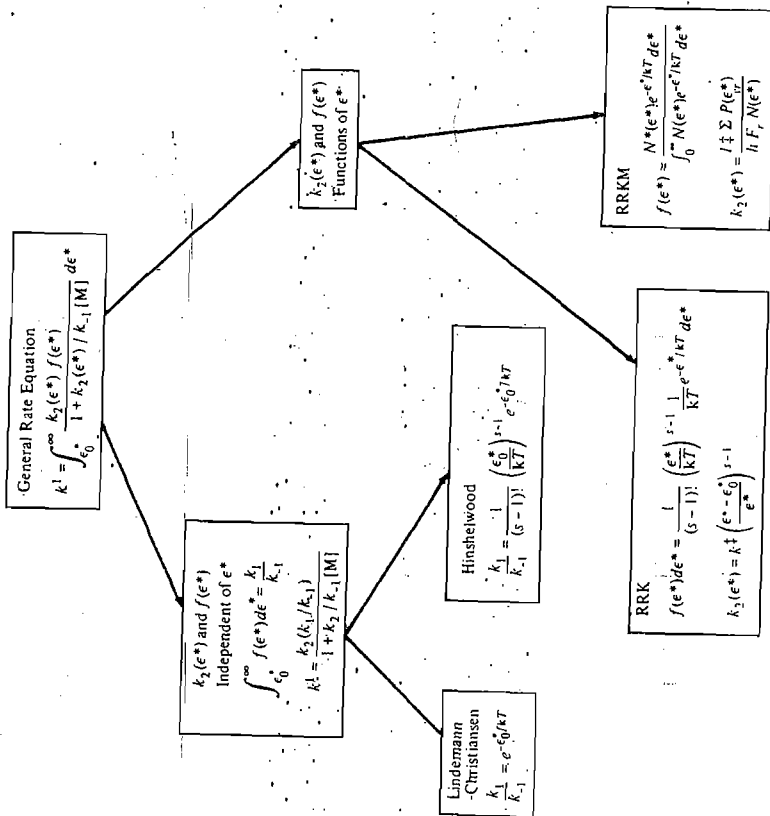


Figure 5.8 Diagram showing the relationship between some of the theories of unimolecular gas reactions. The symbols are defined in the text.

Although it is convenient to consider the Rice-Rampersperger and Kassel theories together as RRRK theory, there are two important differences between them. First, Rice and Rampersperger used classical statistical mechanics, whereas Kassel introduced a quantum treatment as well as a statistical one. Second, Kassel proposed that reactions occur only when the critical energy ϵ_0^\ddagger is concentrated in one normal mode of vibration, that is, in two "square terms." In the Rice-Rampersperger treatment, the energy goes into one "square term," which is not realistic. Most later RRRK treatments are essentially Kassel treatments, and the present account relates more closely to the Kassel version.

In RRRK theory a molecule is regarded as a system of loosely coupled oscillators. In the energized molecule A^* an amount of energy ϵ^* is distributed among the normal modes of vibration. Because the normal modes are coupled loosely, the energy can flow between them, and after a sufficient number of vibrations the critical amount of energy ϵ_0^\ddagger may be in a particular normal mode and reaction can occur. For example, energy in an energized molecule of ethane, C_2H_6 , may pass into a normal mode which corresponds to an extension of the C—C bond. If the energy is sufficiently great the bond will break with the formation of two methyl radicals. In RRRK theory, the oscillators are regarded as all having the same frequency of vibration.

An essential feature of RRRK theory is that the energized molecules A^* have *random lifetimes*. By this is meant that the energy is distributed randomly among the various normal modes, so that the process $A^* \rightarrow A^\ddagger$ depends entirely on statistical factors. In other words, the process by which A^* is formed does not lead to a species in which the energy is more likely to be in certain normal modes, in which case there might be a higher or lower probability of forming A^\ddagger .

Another important feature of the theory is that the collisions that produce A^* molecules and also those that deactivate them are *strong collisions*. By this is meant that in the collision processes large amounts ($\gg kT$) of energy are transferred. In other words, activation more often occurs in a single collision than as a result of a number of successive collisions. When an energized molecule A^* undergoes a collision, it is assumed in the strong-collision theories that de-energization is almost inevitable.

The way in which RRRK theory treats the dependence of k_2 on ϵ^* is as follows. The statistical weight of a system of s degrees of vibrational freedom containing j quanta of vibrational energy is equal to the number of ways in which j objects can be divided among s boxes, each of which can contain any number; the number of such ways is

$$w = \frac{(j+s-1)!}{j!(s-1)!} \quad (5.39)$$

The statistical weight for states in which the s oscillators have j quanta among them, and one particular one has m quanta, is similarly

$$w' = \frac{(j-m+s-1)!}{(j-m)!(s-1)!} \quad (5.40)$$

The probability that a particular oscillator has m quanta and all s oscillators have j quanta is the ratio of these:

$$\frac{w'}{w} = r = \frac{(j-m+s-1)j!}{(j-m)!(j+s-1)!} \quad (5.41)$$

If the Sterling approximation ($n! = n^n/e^n$) is applied to this expression, the terms in e^n cancel out, and the result is

$$r = \frac{(j-m+s-1)^{j-m+1} j!}{(j-m)^{j-m} (j+s-1)^{j+s-1}} \quad (5.42)$$

Provided that $j-m \gg s-1$, this reduces to

$$r = \frac{(j-m)^{j-m+s-1} j!}{(j-m)^{j-m} j^{j+s-1}} \quad (5.43)$$

$$= \left(\frac{j-m}{j}\right)^{s-1} \quad (5.44)$$

The total number of quanta j may be taken as proportional to ϵ^* , the total energy of the molecule, while m is proportional to ϵ_0^\ddagger , the minimum energy that a molecule must have for decomposition to take place. § The expression given above therefore is equal to

$$r = \left(\frac{\epsilon^* - \epsilon_0^\ddagger}{\epsilon^*}\right)^{s-1} \quad (5.45)$$

The rate with which the required energy ϵ_0^\ddagger passes into this particular oscillator is proportional to this quantity, so that

$$k_2 = k_2^\ddagger \left(\frac{\epsilon^* - \epsilon_0^\ddagger}{\epsilon^*}\right)^{s-1} \quad (5.46)$$

In this expression k_2^\ddagger is the rate constant corresponding to the free passage of the system through the dividing surface; when ϵ^* is sufficiently large, the energized molecule is essentially an activated molecule and therefore can pass immediately into the final state. The variation of k_2 with $\epsilon^*/\epsilon_0^\ddagger$, according to Eq. (5.46), is shown in Fig. 5.9.

RRK theory also treats the distribution function $f(\epsilon^*)$ as dependent on ϵ^* . If the energy ϵ^* is distributed among s normal modes of vibration we have from Eq. (3.37) that

$$f(\epsilon^*) = \frac{1}{(s-1)!} \left(\frac{\epsilon^*}{kT}\right)^{s-1} \frac{1}{kT} e^{-\epsilon^*/kT} d\epsilon^* \quad (5.47)$$

Introduction of this expression and Eq. (5.46) into the general rate equation (5.38) gives

$$k^{\ddagger} = \int_0^{\infty} \frac{k_2^\ddagger \left(\frac{\epsilon^* - \epsilon_0^\ddagger}{\epsilon^*}\right)^{s-1} \frac{1}{(s-1)!} \left(\frac{\epsilon^*}{kT}\right)^{s-1} \frac{1}{kT} e^{-\epsilon^*/kT}}{1 + \frac{k_2^\ddagger}{k_{-1}[M]} \left(\frac{\epsilon^* - \epsilon_0^\ddagger}{\epsilon^*}\right)^{s-1}} d\epsilon^* \quad (5.48)$$

This equation may be reduced by making the following substitutions:

$$x = \frac{\epsilon^* - \epsilon_0^\ddagger}{kT} \quad b = \frac{\epsilon_0^\ddagger}{kT} \quad (5.49)$$

§ This depends on the assumption that the oscillators all have the same frequency, so that all the quanta are equal in size.

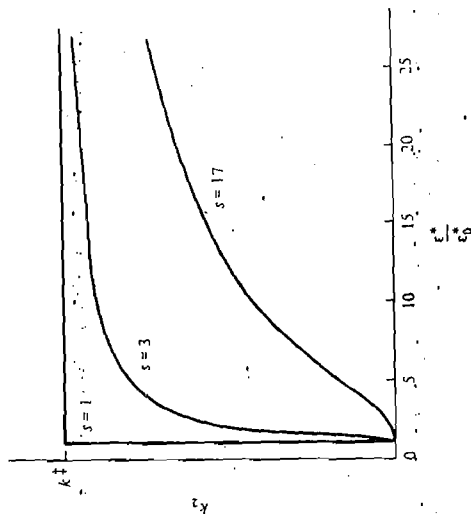


Figure 5.9 Variation of k^\ddagger with $\epsilon^\ddagger/\epsilon_0$, as given by Eq. (5.46), for different values of s , the number of degrees of freedom.

Changing $d\epsilon^\ddagger/kT$ to dx and consequently the limits of integration, we obtain

$$k^1 = \int_0^\infty \frac{1/[(s-1)!]e^{-(x+b)}k^\ddagger x^{s-1} dx}{1 + (k^\ddagger/k_0[M])x/(x+b)} \quad (5.50)$$

$$= \frac{k^\ddagger e^{-b}}{(s-1)!} \int_0^\infty \frac{x^{s-1} e^{-x} dx}{1 + (k^\ddagger/k_0[M])x/(x+b)} \quad (5.51)$$

$$\text{or } k^1 = \frac{k^\ddagger e^{-b/kT}}{(s-1)!} \int_0^\infty \frac{x^{s-1} e^{-x} dx}{1 + (k^\ddagger/k_0[M])x/(x+b)} \quad (5.52)$$

When $[M]$ is very large, that is, at the high-pressure first-order limit, this expression reduces approximately to

$$k_\infty^1 = k^\ddagger e^{-b/kT} \quad (5.53)$$

For given values of $[M]$, ϵ_0^\ddagger , and s , the integral in Eq. (5.52) can be obtained by numerical methods.⁴⁴ Usually, Eq. (5.52) gives reasonable agreement with experiment if s is taken to be about one-half the total number of normal modes in the molecule. This is one unsatisfactory feature of the theory; it is impossible to predict what value of s should be taken for a given reaction.

The significance of k^\ddagger in RRR theory is also somewhat unsatisfactory. If there were a complete redistribution of energy among the normal modes on every vibration, the theory would predict that the pre-exponential factor for the reaction in its high-pressure limit [Eq. (5.53)] would be the average of the various normal-mode frequencies. It therefore would predict a pre-exponential factor of about 10^{13} s^{-1} for all unimolecular reactions. This is true for some reactions, but for many the values are very much greater than this. RRR theory provides no explanation for such high values. An in-

terpretation⁴⁵ is provided by conventional transition-state theory, according to which k^\ddagger is given by

$$k^\ddagger = \frac{kT}{h} \frac{q^\ddagger}{q_r} \quad (5.54)$$

where q^\ddagger is the partition function for the activated complexes and q_r for the reactants. If, as is plausible, the activated complexes have much looser structures than the reactants, q^\ddagger may be much larger than q_r , and the large pre-exponential factors are explained.

5.3.4 Slater's Treatment

The RRR theory is a statistical theory, and brief mention should be made here of a very different approach, a dynamical one, which although ultimately unsuccessful did contribute considerably to the development of our understanding of unimolecular reactions. This was the theory of N. B. Slater, first proposed⁴⁶ in 1939 and elaborated by him in a book⁴⁷ and a number of subsequent papers.⁴⁸

As an example consider the dissociation of ethane into two methyl radicals:



When the ethane molecule is energized as a result of collisions, the energy is distributed among the 18 normal modes of vibration. As it vibrates the C—C bond expands and contracts in a somewhat complicated way, because many of the 18 normal modes contribute to the extension and contraction of that bond. The essence of Slater's theory was that the bond breaks when, as a result of a number of normal-mode vibrations coming into phase, the C—C bond becomes extended by a critical amount. In the earlier versions of his theory, it was assumed that energy remains trapped in normal modes; this is in contrast to RRR theory, which assumes free exchange of energy between oscillators that have random lifetimes.

Some of the earlier quantitative treatments of individual reactions on the basis of Slater's theory were very encouraging. In particular, the theory seemed to be successful in avoiding the difficulty with RRR theory that for unknown reasons not all normal modes contribute to reaction. For example, for the isomerization of cyclopropane (see also Section 5.3.5), Slater was able to obtain good agreement with experiment when all 21 normal modes of vibration were allowed to contribute to reaction; for agreement with RRR theory only 12 normal modes could be used.

However, serious difficulties arose for certain reactions, such as the dissociation of hydrogen peroxide⁴⁹ and the decomposition of cyclobutane.⁵⁰ For these reactions the Slater theory gave low-pressure second-order rate constants that were much lower than the experimental values. The problem arises from Slater's assumption of no energy flow between normal modes. On that basis, certain modes cannot contribute to reaction at all. For example, in the hydrogen peroxide dissociation, torsional motions about the O—O bond bring about no extension of that bond and cannot lead to its dissociation. Energy in such modes thus makes no contribution, and therefore Slater's condition for energization is more stringent than the RRR condition.

Further evidence that there is a rapid exchange of energy between normal modes

is provided by experiments with molecules that have been energized in different ways; this will be considered later (Section 5.3.8).

Attempts have been made⁵¹ to modify Slater's treatment with a view to permitting flow between normal modes. However, in the meantime, Marcus had proposed his extension of RRK theory, and since this proved successful little further work was done on the basis of the Slater treatment.

In spite of this ultimate failure of Slater's theory, his work played an important role in the development of the theories of unimolecular reactions, particularly by suggesting crucial experiments. Aside from this, in the course of his work Slater gave important classical treatments of molecular vibrations and also suggested a quantum-mechanical treatment of unimolecular reactions.⁵²

5.3.5 Marcus's Extension of the RRK Treatment (RRKM)

Marcus⁵³ has extended the Rice-Ramsperger-Kassel theory in a direction that brings it into line with transition-state theory. The essence of his theory, now generally known as the Rice-Ramsperger-Kassel-Marcus (RRKM) formulation, is that the individual vibrational frequencies of the energized species and activated complexes are considered explicitly; account is taken of the way the various normal-mode vibrations and rotations contribute to reaction, and allowance is made for the zero-point energies.

Since RRKM theory is described in detail in two excellent books⁵⁴ by Robinson and Holbrook and by Forst, only a brief general account of the main assumptions and procedures is given here. Figure 5.8 shows the relationship of RRKM theory to the other theories, and Fig. 5.10 shows the energy scheme. The total energy contained in the energized molecule is classified as either *active* or *inactive* (also referred to as *adiabatic*). The inactive energy is energy that remains in the same quantum state during the course of reaction and that therefore cannot contribute to the breaking of bonds. The zero-point energy is inactive, as is the energy of overall translation and rotation, since this energy is preserved as such when the activated molecule A^\ddagger is formed. Vibrational energy and the energy of internal rotations are active.

In RRKM theory, the distribution function $f(e^*)$ is expressed as

$$f(e^*)de^* = \frac{N(e^*)e^{-e^*/kT} de^*}{\int_0^\infty N(e^*)e^{-e^*/kT} de^*} \quad (5.55)$$

where $N(e^*)$ is the density of states having energy between e^* and $e^* + de^*$. (The *density of states* is defined as the number of states per unit energy range.) The denominator in Eq. (5.55) is the partition function relating to the active-energy contributions.

The expression for $k_2(e^*)$ in RRKM theory is

$$k_2(e^*) = \frac{kT \sum P(e_{\text{active}}^*)}{hN(e^*)F_r} \quad (5.56)$$

where kT is the statistical factor (Section 4.5) and $\sum P(e_{\text{active}}^*)$ is the number of vibrational-rotational quantum states of the activated molecule, corresponding to all energies up to and including e_{active}^* . The factor F_r is introduced to correct for the fact that the rotations may not be the same in the activated molecule as in the energized molecule.

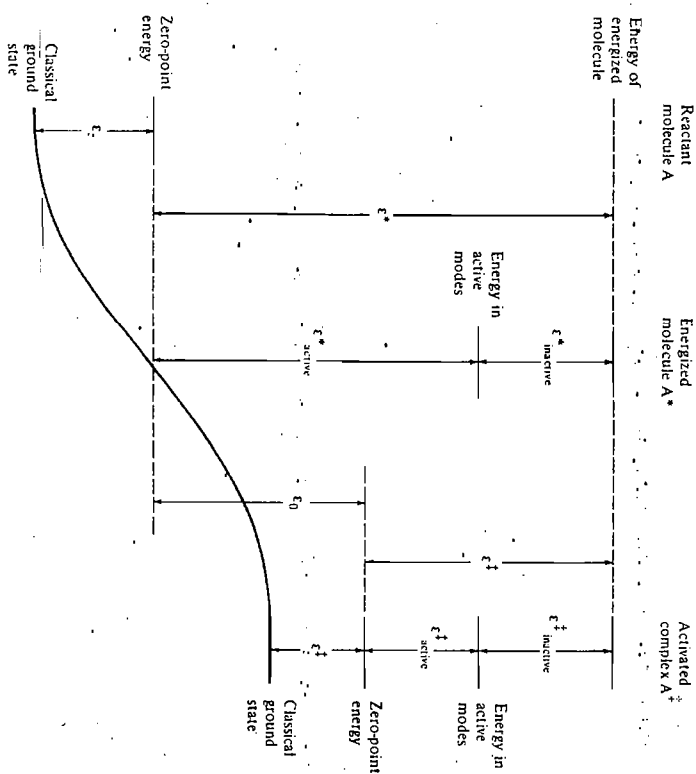


Figure 5.10 Energy scheme for the RRKM mechanism, in which (1) $f(e^*)de^*$ is calculated using quantum-statistical mechanics, and (2) $k_2(e^*)$ is expressed using CTST. The energy in A^* and A^\ddagger is either inactive (zero-point, overall translational, overall rotational) or active (all vibrations and free rotations).

A particularly satisfactory feature of RRKM theory is that it leads to the same expression for the limiting high-pressure first-order rate constant that is given by conventional transition-state theory:

$$k_{\infty}^1 = \frac{kT}{h} \frac{q_{\ddagger}}{q_r} e^{-e_0/kT} \quad (5.57)$$

where q_r and q_{\ddagger} are the partition functions for activated and initial states. Thus, the theory can explain the abnormally high pre-exponential factors that are sometimes obtained.

To make detailed calculations using RRKM theory it is necessary to decide on models for the energized and activated molecules. Vibrational frequencies for the various normal modes must be estimated and decisions made as to which energies are active and which inactive. Numerical methods are used to calculate rate coefficients k^1 at various reactant concentrations.

On the whole, the theory has been very successful in interpreting the experimental results. For a variety of reactions it has proved possible to formulate models for A^*

and A^* that lead to good agreement with experiment over a range of pressures. Detailed calculations, with very satisfactory results, have been carried out for the following reactions: the cyclopropane isomerization,⁵⁵ the dissociation of cyclobutane into two ethylene molecules,^{55,56} the isomerization of cyclobutane,⁵⁷ the dissociation of ethane,⁵⁸ and the decomposition of the ethyl radical into ethylene and a hydrogen atom.⁵⁸

The isomerization of cyclopropane into propylene has been studied very extensively from both experimental and theoretical points of view. As previously noted, it was the first true unimolecular reaction to be studied. In the 1920s it was used to test the radiation hypothesis, always with negative results.⁵⁹ A careful study of the reaction over a considerable pressure range was made by Pritchard and coworkers,⁶⁰ whose results are shown plotted in Fig. 5.11. Note that the Hinshelwood treatment accounts for the falling off of k' but it does this only very approximately. The RRK theory accounts for the falling off much better, but s has to be taken as 12 instead of 21, which is the number of degrees of vibrational freedom in the molecule. This was shown by Slater,⁶¹ who also applied his own treatment to the reaction. As seen from the figure, Slater was able to obtain equally good agreement by using all 21 modes. However, as previously discussed, Slater's theory is no longer considered to be satisfactory. A better interpretation of the results has been provided by the RRKM treatment.⁶²

There has been some discussion of whether the cyclopropane isomerization proceeds by a concerted mechanism, in which a C—C bond is broken and a hydrogen

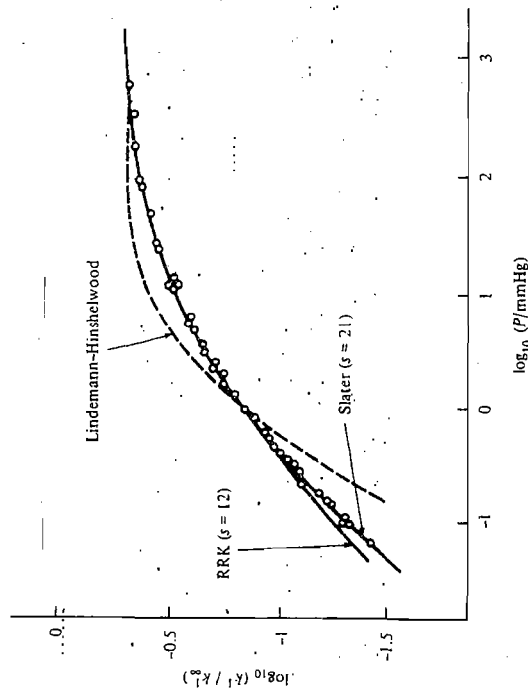
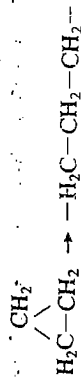


Figure 5.11 Plots of $\log_{10}(k'/k_0)$ versus $\log_{10}(P/\text{mmHg})$ for the thermal isomerization of cyclopropane. The points are experimental, while the curves are those calculated from the theories, as indicated. The experimental values are displaced 0.3 units to the right to lie in the same range as the theoretical curves.

atom is transferred at the same time, or by a diradical mechanism. In the latter, a diradical is formed initially,



followed by a hydrogen atom transfer in a separate stage. The latter mechanism, however, can be excluded on the basis of symmetry arguments (Section 4.5) and with reference to a schematic potential-energy surface.⁶³

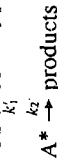
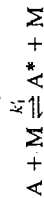
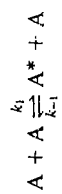
Work on the isomerization of methyl isocyanide, CH_3NC , into methyl cyanide, CH_3CN , has raised some interesting questions. The experimental results⁶⁴ on the fall-off at low pressures of the first-order rate coefficient could be interpreted satisfactorily by RRKM theory, and the same is true of other isocyanides, such as CD_3NC and $\text{C}_2\text{H}_5\text{NC}$.⁶⁵ However, dynamical calculations⁶⁶ have suggested that the results cannot be interpreted in terms of the hypothesis that energized molecules are converted randomly into activated complexes. When this is the case, one speaks of non-RRKM kinetics; the theoretical treatment of it is rather complicated.⁶⁷

On the whole, the RRKM theory has proved very satisfactory. A difficulty with applying it is that the vibrational frequencies for the activated complexes usually cannot be estimated very reliably. The fall-off behavior is not very sensitive to these frequencies, and this leads to the drawback that agreement with experiment can be obtained with various choices of activated complex frequencies, so that there is no way of knowing which choice is correct. The fall-off curves are more sensitive to the high-pressure Arrhenius parameters, which are sometimes not known accurately. The most stringent tests of RRKM theory are provided by chemical activation experiments, to be referred to later, and these provide good support for the theory in many cases. As will be seen, however, the chemical activation experiments do sometimes provide evidence for "non-RRKM-behavior."

5.3.6 Influence of Foreign Gases

The rate of a unimolecular gas reaction can be influenced by the addition of a non-reacting or "foreign" gas, which can contribute to energization. If the reaction is occurring in the low-pressure region where there is a fall-off in the first-order rate coefficient, the addition of a foreign gas may raise the rate coefficient to its high-pressure limiting value.

If a gas A is undergoing reaction and a foreign gas M is added, the reactions are



With the simple Lindemann-Christiansen-Hinshelwood assumptions, the steady-state treatment leads to

$$v = \frac{k_2 k_1 [A]^2 + k' [A] [M]}{k_{-1} [A] + k_{-1} [M] + k_2} \quad (5.58)$$

Corresponding but more complicated expressions are found for the RRK and RRRKM mechanisms.

By studying rates at various concentrations of A and M, it is possible to obtain k_1/k_2 and k_{-1}/k_2 . These ratios represent the relative effectiveness with which M and A transfer energy to A. This method is therefore a useful one for obtaining information about intermolecular energy transfer.

5.3.7 Intermolecular Energy Transfer

Much evidence has accumulated about the efficiencies of energy transfers between molecules and only a very brief summary is given here. The noble gases and other simple molecules tend to be ineffective in transferring energy; complex molecules are more effective. Molecules that are able to react chemically transfer more energy than nonreacting molecules. This result can be interpreted in terms of some distortion of potential-energy surfaces when there is chemical interaction. This is illustrated schematically in Fig. 5.12, which shows how relative translational energy may be converted into the vibrational energy of a molecule A—B when it collides with a molecule C with which it has some chemical affinity.

A rate constant k_{-1}^* can be defined for a process



on the assumption that deactivation occurs on every collision, that is, if the collisions are strong collisions. In the general case, a collision efficiency B_c can be defined by

$$k_{-1} = B_c k_{-1}^* \quad (5.59)$$

where k_{-1} is the rate constant for a particular substance. For large molecules B_c is approximately unity, while for small molecules it is much less than unity.

Another quantity of interest, which can be estimated from the experimental results, is $\langle \Delta E_d \rangle$, the average energy transferred per collision. There is a rough correlation between B_c and $\langle \Delta E_d \rangle$. Molecules having B_c values close to unity tend to have $\langle \Delta E_d \rangle$ values of 40–60 kJ mol⁻¹. Small molecules, having low B_c values, tend to transfer only about 2 kJ mol⁻¹ on each collision.

5.3.8 Intramolecular Energy Transfer

RRKM theory, now used almost exclusively for unimolecular gas reactions, is based on the assumption that when a molecule is energized the vibrational energy is exchanged rapidly between the normal modes. Specifically, it assumes that the rate of energy redistribution within a molecule A* is much greater than the rate with which A* is converted into products.

Two lines of evidence indicate that this assumption is usually valid. One is the success of conventional RRKM theory, which makes the assumption of rapid intramolecular energy transfer. As already discussed, the Slater theory, which assumed no

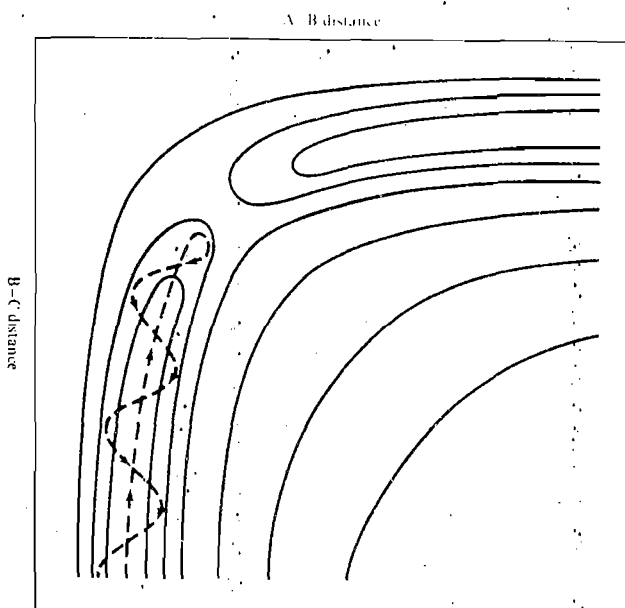
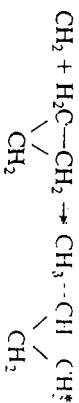


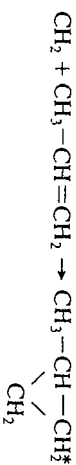
Figure 5.12 Conversion of translational energy into vibrational energy when a molecule A—B collides with C. Because there is the possibility of chemical reaction, there is a distortion of the energy valleys, and upon collision the A—B distance is altered, so that the molecule gains vibrational energy.

intramolecular energy distribution between collisions, was not satisfactory for a number of reactions.

The second line of evidence involves producing energized molecules in different ways and comparing their behavior. For example, Butler and Kistiakowsky⁶⁸ produced methylcyclopropane in two different ways and with different amounts of excess energy. They formed it by the addition of methylene to cyclopropane



and also by the process



The resulting methylcyclopropanes, although produced in different ways and having a range of energies, underwent decomposition in the same way, indicating that in spite of the different initial condition the energy is redistributed rapidly among the normal modes.