

THEORIES OF UNIMOLECULAR GASEOUS REACTIONS

Though we have dealt at length with the two theories of reactions rates, *viz.*, the collision theory and the activated complex theory (ACT), which purport to find the theoretical basis for the Arrhenius equation, $k = A \exp(-E_a/RT)$, unimolecular gaseous reactions, which are the simplest reactions, have attracted considerable attention at the hands of theorists. There are at present five theories of the unimolecular gaseous reactions, *viz.*, Lindemann-Christiansen treatment, the Hinshelwood treatment, the Rice-Ramsberger-Kassel (RRK) treatment, N.B. Slater's treatment (which we shall not discuss here), and finally the most important of them all—the Marcus extension of the RRK treatment, known as the RRKM theory.

As we have shown earlier in this chapter, the unimolecular rate constant, as derived in the Lindemann-Christiansen theory, is given by Eq. 78, *viz.*,

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

For some purposes, it is convenient to write this equation as

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

According to Eq. 1, the plot of the first-order rate constant k^1 versus $[A]$ is a hyperbola (Fig. 1). The rate constant k^1 is a constant in the higher concentration range but falls off at lower concentrations. It can be shown that $k^1 = k_{\infty}^1/2$ when $k_{-1}[A] = k_2$ and we write the concentration at which this is true as $[A]_{1/2}$.

$$\text{Thus,} \quad [A]_{1/2} = \frac{k_2}{k_{-1}} = \frac{k_{\infty}^1}{k_1} \quad \dots(3)$$

Application of this relationship to experimental data raises some difficulties. The value of k_{∞}^1 is an experimental quantity; it was thought that, using the simple collision theory, it could be written as $z_1 \exp(-E_1/RT)$, where z_1 is the collision frequency factor and E_1 is the activation energy. Experimentally, however, it was found that the values of $[A]_{1/2}$ were always smaller than those estimated in this way. Thus, the error must lie in the estimation of k_1 rather than k_{∞}^1 (which is an experimental quantity). Thus, we must modify k_1 so that it is larger than $z_1 \exp(-E_1/kT)$.

Another difficulty with the Lindemann-Christiansen mechanism becomes evident when experimental results are plotted in another way. Rewriting Eq. 1 as

$$\frac{1}{k^1} = \frac{k_{-1}}{k_1 k_2} + \frac{1}{k_1[A]} \quad \dots(4)$$

and plotting $1/k^1$ versus $1/[A]$ should give a straight line. However, deviations from linearity have been found (Fig. 2).

1. The Hinshelwood Theory

The first difficulty with the Lindemann-Christiansen treatment that the first-order rates are maintained down to

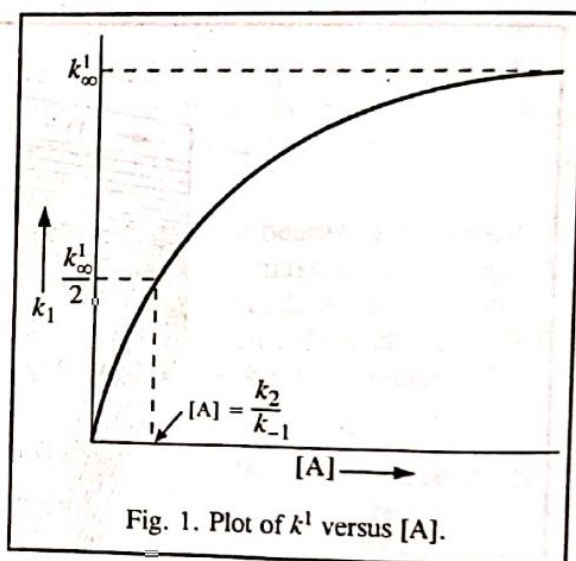


Fig. 1. Plot of k^1 versus $[A]$.

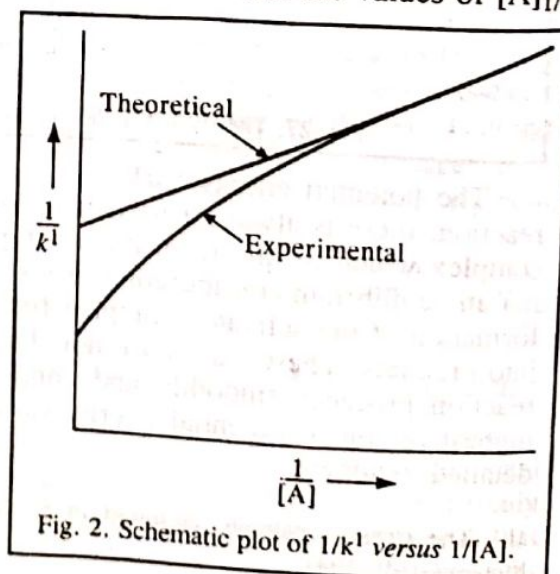


Fig. 2. Schematic plot of $1/k^1$ versus $1/[A]$.

lower concentrations than the theory appeared to permit, was overcome by Hinshelwood's suggestion that the expression $z_1 \exp(-E/RT)$ applied only if the energy is distributed among two degrees of freedom. However, for some unimolecular reactions, the number of degrees of freedom, s , is very large. The activation energy is distributed initially among these degrees of freedom; this distribution can be affected in many ways. 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 large number — the energy may find its way into the appropriate degrees of freedom so that A^* can immediately pass into the products. Hinshelwood derived the following formula for the fraction of molecules having energy in excess of ϵ^* :

$$f^* = \frac{1}{(s-1)!} \left(\frac{\epsilon_0^*}{kT} \right)^{s-1} \exp(-\epsilon_0^*/kT) \quad \dots(5)$$

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

$$k_1 = z_1 \frac{1}{(s-1)!} \left(\frac{\epsilon_0^*}{kT} \right)^{s-1} \exp\left(-\frac{\epsilon_0^*}{kT}\right) \quad \dots(6)$$

instead of simply as $z_1 \exp(-\epsilon_0^*/kT)$. Thus, an additional factor $\frac{1}{(s-1)!} \left(\frac{\epsilon_0^*}{kT} \right)^{s-1}$ has appeared and if s is sufficiently large, this may be greater than unity by many powers of 10. Eq. 5 can give much higher rates of activation and, therefore, much higher k_1/k_{-1} values than those given by the simple collision theory. It can be shown that the experimental activation energy per molecule ϵ_a is related to ϵ_0^* as

$$\epsilon_0^* = \epsilon_a + \left(s - \frac{3}{2}\right)kT$$

Thus, if $\epsilon_a = 170 \text{ kJ mol}^{-1}$ and $s=12$, then Eq. 5 gives a value of k_1/k_{-1} that is larger by more than 10^6 than that given by the older theory.

The following objections may be raised to the Hinshelwood theory:

(1) The number s of the degrees of freedom required to give agreement with experiment on the basis of the Hinshelwood theory is about one-half of the total number of vibrational modes. There is no satisfactory explanation for this.

(2) According to the Hinshelwood theory,

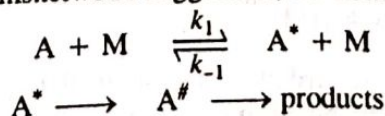
$$k_\infty^1 = \frac{k_1 k_2}{k_{-1}} = k_2 \frac{1}{(s-1)!} \left(\frac{\epsilon_0^*}{kT} \right)^{s-1} \exp\left(-\frac{\epsilon_0^*}{kT}\right) \quad \dots(7)$$

Thus, one would expect a strong temperature-dependence of the pre-exponential factor, especially for large values of s . No experimental evidence exists for this.

(3.) The Hinshelwood treatment cannot account for the lack of linearity found experimentally for the plot of $1/k^1$ versus $1/[A]$.

2. The RRK Theory

With a slight modification of the Lindemann-Christiansen mechanism, the theory of unimolecular reactions can, following the Hinshelwood suggestion, be written as



where M is any molecule, including another A , that can transfer energy to A when a collision occurs; A^* is the energized molecule and $A^\#$ is the activated molecule. To become an activated molecule, the molecule A must acquire at least the energy ϵ_0^* . The energy scheme for the Lindemann, Hinshelwood and

RRK, mechanisms is shown in Fig. 3. Hinshelwood's modification allowed A to acquire an amount of energy ϵ_0^* at an enhanced rate but regarded the rate at which A^* becomes A^\ddagger to be independent of that

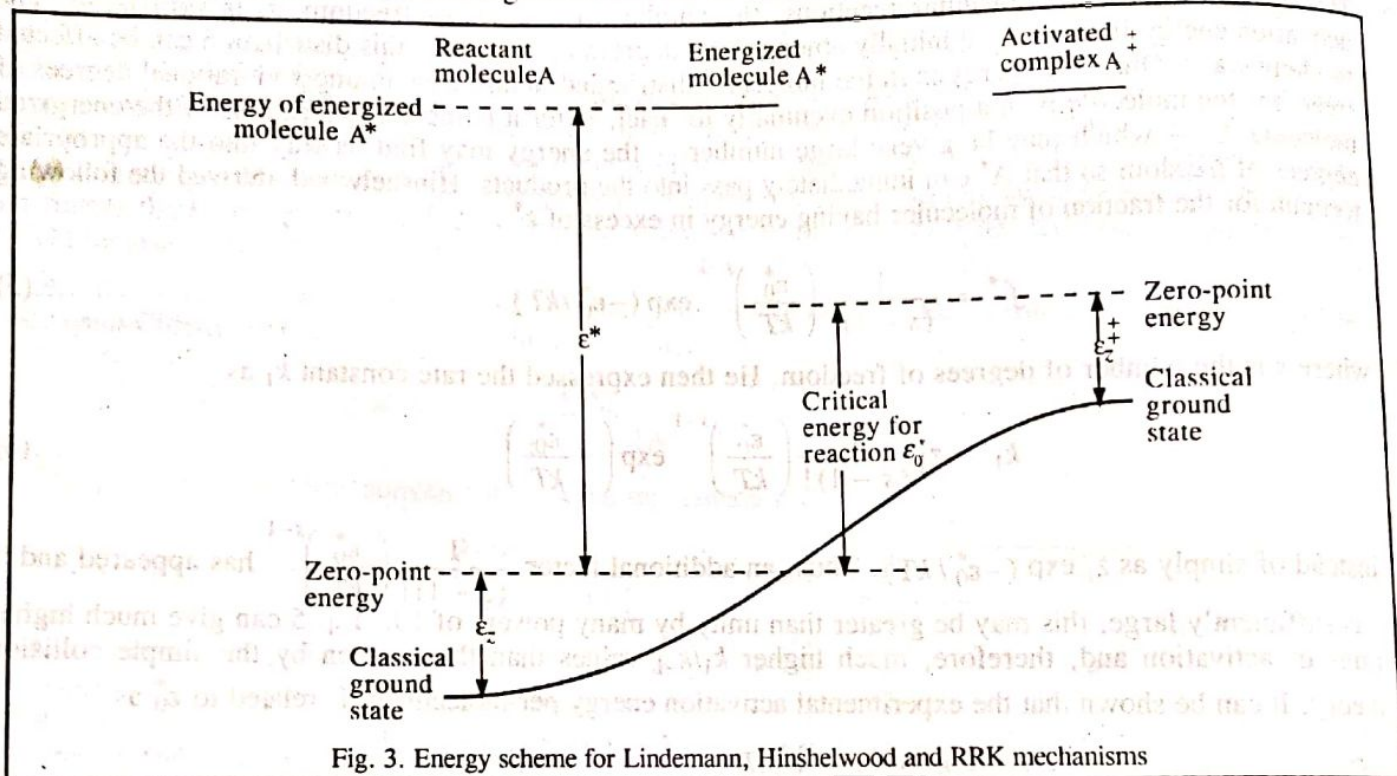


Fig. 3. Energy scheme for Lindemann, Hinshelwood and RRK mechanisms

energy. In the subsequent theoretical treatment, the rate constant k_2 was not treated as a constant but was considered to be larger the greater the value of ϵ^* . Eq. 2 can now be written in the more general form :

$$k^1 = \frac{k_2(k_1/k_{-1})}{1 + k_2/k_{-1}[M]} \quad \dots(8)$$

In the Hinshelwood version, both k_2 and k_1/k_{-1} are treated as independent of ϵ^* , the amount of energy in the energized molecule. Hinshelwood's result (Eq. 6) involves the critical energy ϵ_0^* , rather than ϵ^* . After the derivation of the Hinshelwood formula (in 1927), O.K. Rice and H.C. Rampsberger, and independently L.S. Kassel, proposed theories (in 1928) wherein both k_2 and k_1/k_{-1} were treated as dependent on ϵ^* . These theories are referred to jointly as the RRK theory. In this theory, k_2 is replaced by $k_2(\epsilon^*)$ and k_1/k_{-1} by $f(\epsilon^*)$, which is a distribution function, so that Eq. 8 is written as

$$dk^1 = \frac{k_2(\epsilon^*)f(\epsilon^*)}{1 + k_2(\epsilon^*)/k_{-1}[M]} d\epsilon^* \quad \dots(9)$$

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

$$k^1 = \int_{\epsilon_0^*}^{\infty} \frac{k_2(\epsilon^*)f(\epsilon^*)}{1 + k_2(\epsilon^*)/k_{-1}[M]} d\epsilon^* \quad \dots(10)$$

In the RRK formatism, a molecule is regarded as a system of loosely coupled oscillators. In the energized molecule A^* , the 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^* may be in a particular normal mode and reaction can occur. Thus, for example, energy in an energized ethane molecule, $C_2H_6^*$, may pass into a normal vibrational

mode which corresponds to an extension of the C—C bond and if the energy is sufficiently great, the bond will break leading to the formation of two $\cdot\text{CH}_3$ radicals. In the RRK theory, the oscillators are all assumed to have the same vibrational frequency.

An important feature of the RRK theory is that the energized molecules A^* have random lifetimes, which means that the energy is distributed randomly among the various normal modes so that the process $A^* \rightarrow A^\ddagger$ depends entirely on statistical factors. Another important feature of the theory is that the collisions that produce A^* molecules and also those that deactivate them are strong collisions. This means that during collisions large amounts of energy ($\gg kT$) are transferred. This implies that activation more often occurs in a single collision than as a result of successive collisions. When an energized molecule A^* undergoes a collision it is assumed that it inevitably gets de-energized.

According to the RRK theory, 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 of objects. The number of such ways is given by

$$w = \frac{(j + s - 1)!}{j!(s - 1)!} \quad \dots(11)$$

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

$$w' = \frac{(j - m + s - 1)!}{(j - m)!(s - 1)!} \quad \dots(12)$$

The probability that a particular oscillator has m quanta and all s oscillators have j quanta is given by the ratio

$$r = \frac{w'}{w} = \frac{(j - m + s - 1)! j!}{(j - m)!(j + s - 1)!} \quad \dots(13)$$

Applying the Stirling approximation ($n! = n^n/e^n$), the terms in e^n cancel out, giving

$$r = \frac{(j - m + s - 1)^{j-m+s-1} j^j}{(j - m)^{j-m} (j + s - 1)^{j+s-1}} \quad \dots(14)$$

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

$$r = \frac{(j - m)^{j-m+s-1} j^j}{(j - m)^{j-m} j^{j+s-1}} = \left(\frac{j - m}{j}\right)^{s-1} \quad \dots(15)$$

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^* , the minimum energy that a molecule must have for decomposition to take place. Eq.15, thus, becomes

$$r = \left(\frac{\epsilon^* - \epsilon_0^*}{\epsilon^*}\right)^{s-1} \quad \dots(16)$$

The rate at which the energy ϵ_0^* passes into this particular oscillator is proportional to this quantity so that

$$k_2 = k^\ddagger \left(\frac{\epsilon^* - \epsilon_0^*}{\epsilon^*}\right)^{s-1} \quad \dots(17)$$

We next turn our attention to the distribution function $f(\epsilon^*)$ which, according to the RRK theory, is given by

$$f(\epsilon^*) = \frac{1}{(s - 1)!} \left(\frac{\epsilon^*}{kT}\right)^{s-1} \frac{1}{kT} \exp(-\epsilon^*/kT) \quad \dots(18)$$

It is assumed here that the energy ε^* is distributed among s normal modes of vibration.

Substituting Eqs. 17 and 18 into Eq. 10, we obtain

$$k^1 = \int_{\varepsilon_0}^{\infty} \frac{k^{\#} \left(\frac{\varepsilon^* - \varepsilon_0}{\varepsilon^*} \right)^{s-1} \frac{1}{(s-1)!} \left(\frac{\varepsilon^*}{kT} \right)^{s-1} \frac{1}{kT} \exp(-\varepsilon^*/kT) d\varepsilon^*}{1 + \frac{k^{\#}}{k_{-1}[M]} \left(\frac{\varepsilon^* - \varepsilon_0}{\varepsilon^*} \right)^{s-1}} \quad \dots(19)$$

This equation may be reduced using the following substitutions: $x = (\varepsilon^* - \varepsilon_0)/kT$; $b = \varepsilon_0/kT$. Changing $d\varepsilon^*/kT$ to dx and thereby the limits of integration, we obtain

$$k^1 = \int_0^{\infty} \frac{[(s-1)!] e^{-(x+b)} k^{\#} x^{s-1} dx}{1 + (k^{\#}/k_{-1}[M])[x(x+b)]^{s-1}} \quad \dots(20)$$

$$= \frac{k^{\#} e^{-b}}{(s-1)!} \int_0^{\infty} \frac{x^{s-1} e^{-x} dx}{1 + (k^{\#}/k_{-1}[M])[x(x+b)]^{s-1}} \quad \dots(21)$$

or
$$k^1 = \frac{k^{\#} \exp(-\varepsilon_0/kT)}{(s-1)!} \int_0^{\infty} \frac{x^{s-1} e^{-x} dx}{1 + (k^{\#}/k_{-1}[M])[x/(x+b)]^{s-1}} \quad \dots(22)$$

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

$$k_{\infty}^1 = k^{\#} \exp(-\varepsilon_0/kT) \quad \dots(23)$$

For given values of $[M]$, ε_0^* and s , the integral in Eq. 22 can be evaluated numerically. Eq. 22 generally gives a reasonable agreement with experiment, if s is taken to be about one-half of the total number of normal vibrational 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.

In this expression, the rate constant $k^{\#}$ corresponds 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 to the final state. The variation of k_2 with $\varepsilon^*/\varepsilon_0^*$, given by Eq. 17, is shown in Fig. 4.

The significance of $k^{\#}$ in RRK theory is also rather 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. 23) would be the average of the various normal-mode frequencies. It would, therefore, 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. The RRK theory provides no explanation for such high values. According to Laidler and Steel (1961), the interpretation is provided by CTST (conventional transition state theory), which gives the following expression for $k^{\#}$:

$$k^{\#} = (kT/h) (q_{\#}/q_r) \quad \dots(24)$$

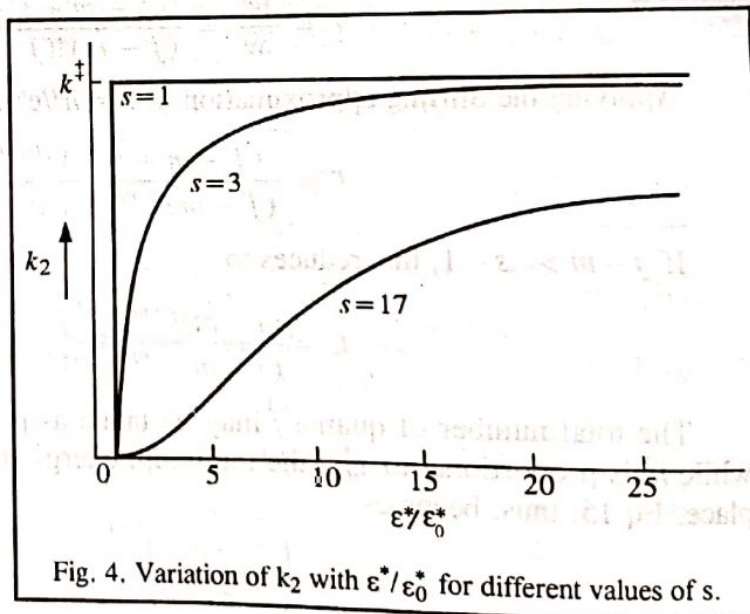


Fig. 4. Variation of k_2 with $\varepsilon^*/\varepsilon_0^*$ for different values of s .

where $q_{\#}$ is the partition function for the activated complexes and q_r for the reactants. If it is reasonably assumed that the activated complexes have much looser structures than the reactants, $q_{\#} \gg q_r$ and the large pre-exponential factors are accounted for.

3. The RRKM (Rice-Rampsberger-Kassel-Marcus) Theory

During 1951-52, R.A. Marcus extended the RRK treatment to bring it in line with the TST (transition state theory). In the RRKM theory, 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 zero-point energies. Fig. 5. shows the energy scheme for the RRKM mechanism.

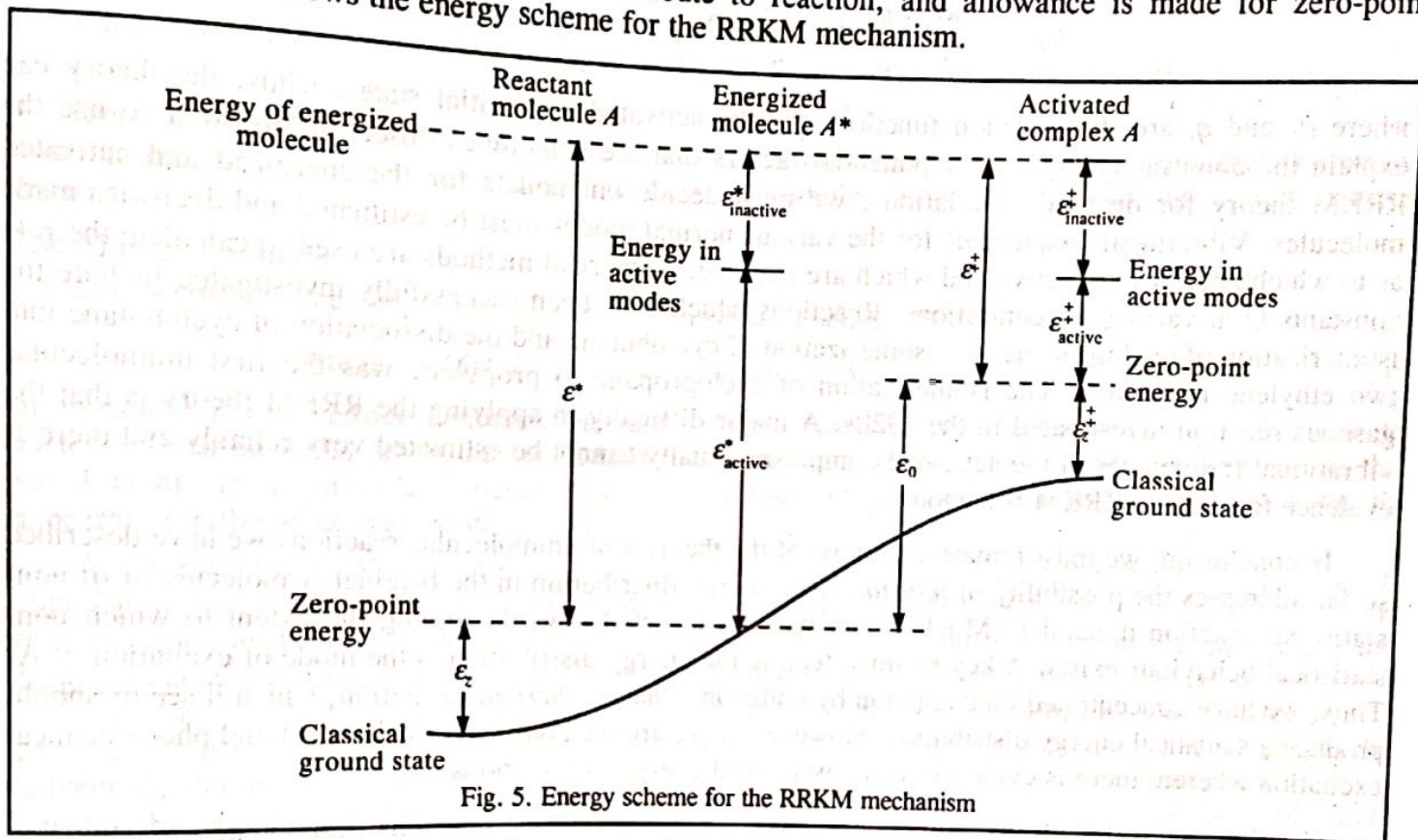


Fig. 5. Energy scheme for the RRKM mechanism

The total energy contained in the energized molecule is classified as either active or inactive (also referred to as adiabatic). The inactive energy is the energy that remains in the same quantum state during the course of the reaction and, 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 $A^{\#}$ is formed. Vibrational energy and the energy of internal rotations are active. In the RRKM theory, the distribution function $\int (\epsilon^*) d\epsilon^*$ is calculated using quantum statistics and is given by

$$f(\epsilon^*) d\epsilon^* = \frac{\rho(\epsilon^*) \exp(-\epsilon^*/kT) d\epsilon^*}{\int_0^{\infty} \rho(\epsilon^*) \exp(-\epsilon^*/kT) d\epsilon^*} \quad (25)$$

where $\rho(\epsilon^*)$ is the density of states (DOS) having energy between ϵ^* and $\epsilon^* + d\epsilon^*$. (The DOS is defined as the number of states per unit energy range.) The denominator in Eq. 25 is the partition function relating to the active energy contributions.

According to the RRKM theory, the rate constant $k_2(\epsilon^*)$ is given by

$$k_2(\epsilon^*) = \frac{l^{\#} \Sigma P(\epsilon^*_{active})}{h \rho(\epsilon^*) F_r} \quad (26)$$

where $l^\#$ is the statistical factor and $\Sigma P(\epsilon_{\text{active}}^\#)$ is the number of vibration-rotation quantum states for the activated molecule corresponding to all energies upto and including $\epsilon_{\text{active}}^\#$. 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.

A noteworthy feature of the RRKM theory is that it leads to the same expression for the limiting high-pressure unimolecular (first-order) rate constant as is given by CTST :

$$k_\infty^1 = \left(\frac{kT}{h} \right) \frac{q_\#}{q_i} \exp(-\epsilon_0^*/kT) \quad \dots(27)$$

where $q_\#$ and q_i are the partition functions for the activated and initial states. Thus, the theory can explain the abnormally high pre-exponential factors that are sometimes observed. In order to use the RRKM theory for detailed calculations, we must 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 are inactive. Numerical methods are used to calculate the rate constants k^1 at various concentrations. Reactions which have been successfully investigated include the isomerization of cyclopropane, the isomerization of cyclobutane and the dissociation of cyclobutane into two ethylene molecules. The isomerization of cyclopropane to propylene was the first unimolecular gaseous reaction investigated in the 1920s. A major difficulty in applying the RRKM theory is that the vibrational frequencies of the activated complexes usually cannot be estimated very reliably and there is evidence for the non-RRKM behaviour.

In conclusion, we must remark that none of the theories of unimolecular reactions we have described so far addresses the possibility of *nonstatistical* energy distribution in the original A molecule or of non-statistical reaction dynamics. Much recent work is directed towards finding the extent to which non-statistical behaviour exists. A key factor affecting the energy distribution is the mode of excitation of A. Thus, we have concentrated on excitation by collisions, that is, *thermal* excitation, which it seems should produce a statistical energy distribution. However, there are methods such as chemical and photochemical excitation wherein there is evidence for nonstatistical energy distributions.

One potential method for obtaining information about unimolecular reactions with nonthermal activation is the use of molecular beams. (The reactions studied in this way are, of course, bimolecular but can be the activation steps of unimolecular mechanisms.) In such studies, it has been found that the translational energy distribution of reaction fragments is nonstatistical, contrary to the predictions of (say) the RRKM theory ; this implies that not all degrees of freedom participate in the fragmentation of the complex.

The reaction dynamics of molecules with many degrees of freedom is far from understood and is an area of intensive research. The issues we must analyze to construct a complete theory of unimolecular reactions are the process of acquisition of sufficient energy by a molecule for the breaking of a bond or bond rearrangement, the process of energy transfer within the molecule and the elementary chemical reaction steps. The last two processes compete with each other. The occurrence of chemical reaction requires the concentration of energy, say, within the bond that is to be broken, whereas energy transfer within the molecule tends to distribute the available energy among many, possibly all available degrees of freedom. There may occur the so-called bottlenecks to intramolecular energy transfer which restrict that transfer. These topics, including chaos in molecular dynamics, are being investigated by theorists and mathematical physicists.