

FOR REFERENCE

NOT TO BE TAKEN FROM THIS ROOM

To the memory of my mother Ester T. BARUH
and to my father Şalom BARUH

178686



**AN INVESTIGATION OF THE CARBON-CARBON
BOND RUPTURE IN FLUOROETHANES BY
RRKM THEORY**

by

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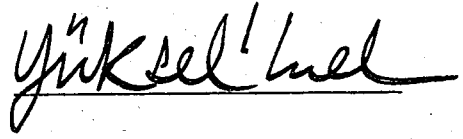
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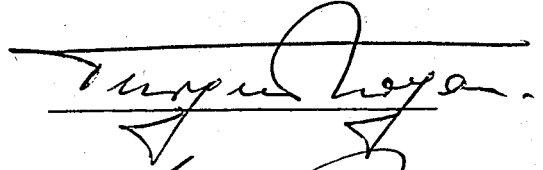
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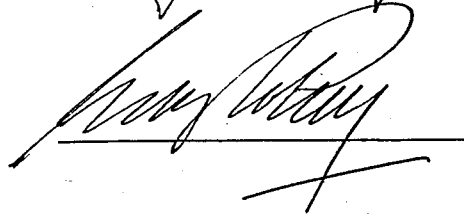
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ABSTRACT

In this dissertation, the thermal decompositions of ethane, 1,1,2,2-tetrafluoroethane, pentafluoroethane and hexafluoroethane have been subjected to a theoretical treatment in terms of the quantum statistical RRKM theory. The RRKM theory assumes that the activated molecule has a certain amount of vibrational energy spread among the various vibrational degrees of freedom of the molecule. Then the probability of one particular mode of vibration acquiring so much of this energy that the vibration leads to dissociation into fragments is calculated.

The experimental results have shown that the first order rate constant for unimolecular reactions is not a true constant but declines at low pressures. The decline or "fall-off" in the first order rate constant with pressure is an important criterion of unimolecular reactions. The rate constants in this fall-off region as well as the rate constants at the experimental pressures and temperatures for the carbon-carbon bond rupture for the above molecules have been evaluated.

As already known, the major difficulty in this field is the determination of the configuration of the transition state. This is done in two different ways where two different models are suggested:

In the first one, the complex is considered as a decomposing diatomic molecule in which the atoms have the masses of the actual fragments. From this assumption follows the derivation of the length of the critical bond (Gorin Model).

In the second one, the critical configuration has a value of the reaction coordinate such that the number of accessible internal states of the molecule is minimized. The R^\ddagger value given by the criterion of minimum state density is less than the value given by the Gorin Model at the rotational barrier. Choosing the critical configuration at the rotational barrier gives an overestimate of the unimolecular rate. In fact, the k_{uni} values calculated for the first model are higher than those obtained for the second one.

In the evaluation of the rate constants, the centrifugal effects which reduce the activation energy for the reaction and the anharmonicity, resulting in a decreasing spacing between successive vibrational levels, are considered.

As a result, the pressure at which the rate constant reaches one half its limiting high pressure value increases with the number of fluorine atoms. This behaviour is in harmony with activation energies for the carbon-carbon bond scission, increasing with the number of fluorine atoms in the hydrocarbon.

Ö Z E T

Bu çalışma, etan, 1,1,2,2-tetrafloroetan, pentafloroetan ve hegzafloeroetan'ın ısısız ayrışmalarını RRKM kuramı ile açıklamayı amaçlamıştır. RRKM kuramı, etkinleşmiş molekülün bir miktar titreşimsel erkeye sahip olduğunu ve bu erkenin molekülün çeşitli titreşim dereceleri arasında yayıldığını farzeder. Sonradan belirli bir titreşim derecesinin fazladan erke akışının sonucu olarak molekülün parçacıklara ayrışmasının ihtimali hesaplanır.

Deneyisel sonuçlar, tek molekülü tepkimelerin birinci derecedeki hız sabitinin gerçekten sabit bir sayı olmadığını ve alçak basınçlara doğru bir düşüş gösterdiğini göstermektedir. Hız sabitinin basınca bağlı olarak gösterdiği bu düşüş tek molekülü tepkimelerin önemli bir özelliğidir. Karbon-karbon bağının kırılma tepkimesinin hız sabiti düşüş gösterdiği bölgede ve deneyisel çalışmaların yapıldığı basınç ve sıcaklıkta değerlendirilmiştir.

Bilindiği gibi bu alanda en önemli sorun geçiş konumunun şeklinin saptanmasıdır. Bunun için iki ayrı modelin önerildiği iki ayrı yol kullanılmıştır.

İlk model olarak geçiş konumunun ayrışmakta olan iki atomlu bir molekül gibi kabul edildiği Gorin Modeli seçilmiştir. Bu modelde atomların kütlelerinin ayrışmakta olan parçaların kütleleri ile aynı olduğu kabul edilmiştir. Hesaplamalarda bu varsayıma dayanan kritik bağ uzunluğu kullanılmıştır.

İkinci model geçiş konumunda molekülün iç enerji seviyelerinin sayısının minimum olduğu varsayımına dayanmaktadır. Bu modelin hesaplama yönteminde elde edilen etkinleşmiş kompleksin kritik bağ uzunluğu, R^+ , nın değeri birinci modelle elde edilenden daha küçüktür. Bu durumda birinci model geçiş konumuna uygulandığında, tek moleküllü tepkimenin hız sabitinin değeri gerçek değerinden daha büyük olacağı düşünülmektedir. Bu çalışmada da ilk modelden elde edilen hız sabitlerinin ikinci modelden elde edilenlerden daha büyük olduğu görülmüştür.

Hız sabitlerinin hesaplanmasında, aktivasyon erkesini azaltan adyabatik dönüşümlerle, birbirini takip eden titreşim seviyelerinin arasındaki uzaklığı azalmasına neden olan anharmonisite etkileri de dahil edilmiştir.

Sonuç olarak, hız sabiti yüksek basınçtaki değerinin yarısına eşit olduğu basınç, flor atomlarının sayısı ile bir artış göstermektedir. Hidrokarbondaki flor atomlarının sayısına bağlı olarak artan karbon-karbon bağının kırılması için gerekli olan aktivasyon erkesi de belirtilen özellikle uyum halindedir.

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LIST OF SYMBOLS

A^*	Energized molecule
A^+	Activated complex
$E^*(\equiv E_{vr}^*)$	Total non-fixed energy in the active degrees of freedom of a given energized molecule A^*
E_v^*, E_r^*	Vibrational and rotational parts of E^*
E^+	Total non-fixed energy in the active degrees of freedom of a given activated complex A^+
E_v^+, E_r^+	Vibrational and rotational contributions to E^+
E_{vr}^+	$E_v^+ + E_r^+$
x	Translational energy of A^+ in the reaction coordinate
E_J, E_J^+	Energy of adiabatic rotations in their J^{th} energy level in A^* and A^+ respectively. $\Delta E_J = E_J^+ - E_J$
$N^*(E^*)$	Density of quantum states of A^* at energy E^*
$N^+(E_{vr}^+, x)$	Density of quantum states of A^+ having energy E_{vr}^+ in the active degrees of freedom and energy x in the reaction coordinate.
$N_{rc}^+(x)$	Density of quantum states for the translational motion of A^+ in the reaction coordinate with energy x .
$P(E_{vr}^+)$	Number of vibrational-rotational quantum states of A^+ at the quantized energy level E_{vr}^+ .
$\sum_{E_{vr}^+=0}^{E^+} P(E_{vr}^+)$	Number of quantum states of A^+ at all energies up to and including E^+ .
or $\Sigma P(E_{vr}^+)$	
E_z	Zero point energy of a molecule.
$P(E_n)$	Number of quantum states of a given system at the quantized energy level E_n .

$W(E) \equiv \sum_{E_n=0}^E P(E_n)$	Number of quantum states of a system at all energies up to and including E.
ΔE^\ddagger	Step length in the integration procedure.
ΔH_0^0	Bond dissociation energy at 0 ⁰ K.
E_Z^m	Zero point energy of the reactant molecule.
E_Z^p	Zero point energy of the produced radicals.
k	Rate constant in general.
k_{uni}	First-order rate constant.
k_∞	Limiting high pressure value of k_{uni}
k_{bim}	Second-order rate constant.
k_1, k_2	Rate constants for energization and de-energization respectively.
k_3	Rate constant for conversion of energized molecules to products when this is independent of energy.
$k_a(E)$	Same as k_3 when it is energy dependent.
E_0	Critical energy for a reaction.
A_∞	Limiting high pressure value of A.
E_∞	Limiting high pressure value of E_{Arr} .
E'	Reduced energy ($E' = E/E_Z$)
P 1/2	Pressure at which $k_{uni} = (1/2)k_\infty$
L^\ddagger	Statistical factor or reaction path degeneracy.
ΔS^\ddagger	Entropy of activation; $\Delta S^\ddagger = S(A^\ddagger) - S(A)$.
$\Gamma(n)$	The gamma function of argument n (See Appendix 1).
h	Planck constant
k	Boltzmann constant
N_A	Avogadro constant
R	Gas constant

P	Pressure
T	Temperature
Q	Partition function
F_a	Attractive force
F_c	Centrifugal force
σ	Symmetry number
S(A)	Entropy of species A
s	Number of vibrational degrees of freedom of a molecule.
s^+	Number of vibrational degrees of freedom of a complex.
ν	Vibrational frequency (fundamental)
ν, n	Vibrational quantum number
p	Number of rotations of a molecule, i.e. the number of different moments of inertia.
d_i	Degeneracy of the i^{th} rotation.
r	Number of rotational degrees of freedom, $r = \sum_{i=1}^p d_i$
r^*	Number of rotational degrees of freedom of the complex.
I	Moment of inertia
J	Rotational quantum number
τ	Lifetime of a molecule
$\omega(\tau)$	Probability that a molecule avoids a collision for τ seconds
$\langle R_c \rangle$	Average value of the critical bond length used in the Gorin Model.
R^+	Value of the critical bond length used in the second model.
Q_1, Q_1^+	Partition functions for adiabatic rotations in A and A^+ respectively.
Q_2, Q_2^+	Partition functions for active degrees of freedom in A and A^+ respectively.

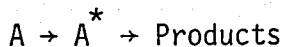
$\bar{\mu}$	Dipole of a molecule
α	Polarizability of a molecule
$V(r)$	Potential function
M	Total angular momentum
a	The constant in the attractive potential energy expression $V = -a/R^6$ in Section 4.2.1.
a_{es}	Electrostatic contribution to the constant in the attractive potential.
a_{ind}	Inductive contribution to the constant in the attractive potential.
a_{dis}	Dispersion contribution to the constant in the attractive potential.
e	Charge of an electron.
m	Mass of an electron.
N	Number of outer shell electrons.
r_m	Apparent distance between the centers of masses.
r_e	Equilibrium distance between the centers of masses.
D	Harmonic mean of the dissociation energies.
ω	Normal frequency of a vibration.
x	Parameter related to the spectroscopic normal frequency ω and the fundamental frequency ν . (Anharmonicity corrections)
f, k	Force constant.
a_{xy}, b_{xy}	Tabulated semi-empirical constants used to calculate D_e .
δ	Arbitrary length of region at top of potential energy barrier.
μ	Reduced mass.
F	Correction factor for centrifugal effects.

λ	Collisional energy transfer efficiency.
$a, \beta, w(E')$	Whitten-Rabinovitch functions.
Z	Second-order collision rate constant.
σ_d	Collision diameter.
t	Time.
β	Laplace transform parameter in Section 3.5.6.

I. INTRODUCTION

In a dilute gas, a completely isolated energetically activated chemical species may undergo a unimolecular reaction. This process may correspond to an internal rearrangement of atoms, the breaking of a bond, or the rotation of a group.

Suppose a reactant species A under appropriate conditions decomposes according to:



In order for the above unimolecular reaction to occur, the reacting molecule must have sufficient internal energy to break the necessary bonds or undergo the internal rearrangement. This activation energy is accumulated in a sequence of collisions with other molecules in the gas or with the vessel walls. Molecules which have sufficient energy to react are termed "energized molecules". These molecules do not necessarily react; the molecule attains a critical configuration which is structurally intermediate between reactant and products, and is called a transition state.

In the (relatively) long intervals between collisions, the energy redistributes itself over the various parts of the molecule. At STP there is about $10^{-9.3}$ sec between gas collisions, whereas a 600 cm^{-1} vibration

corresponds to $600 \times 3 \times 10^{10} = 1.8 \times 10^{13}$ oscillations/sec or about 10000 oscillations between successive collisions [1]. As a result, the energized molecule takes many different configurations. If any one of them corresponds to the localization of enough energy to break a bond or to isomerize, chemical reaction occurs.

A characteristic of the rate of a gaseous unimolecular reaction is that at sufficiently high pressures a unimolecular reaction is of the first order and the activated complex theory can be applied to the reaction. At lower pressures, the first order proportionality constant tends to decrease and at very small concentrations the kinetics become second order.

The purpose of this work is to subject the thermal decompositions of C_2H_6 , $C_2H_2F_4$, C_2HF_5 , C_2F_6 to a theoretical treatment in terms of the quantum statistical RRKM theory of unimolecular reactions with the intent to predict the pressure dependence of the rate in the fall-off region and to test plausible models for the transition state, which would explain the experimentally observed high-pressure limiting rates.

II. HISTORICAL

The theories of unimolecular reactions differ in their descriptions of the transition state. At the beginning of the twentieth century, a lot of gas phase reactions were known to be first-order processes and unimolecular, on the other hand unimolecular reactions were thought to be first order. The problem was to know how the reacting molecule acquires the activation energy needed for the reaction to take place.

2.1 BASIC THEORIES OF UNIMOLECULAR REACTIONS

2.1.1 First Theories of Unimolecular Reactions

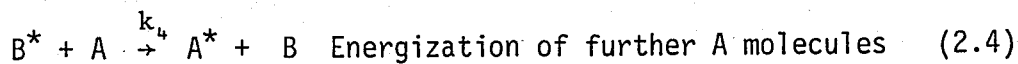
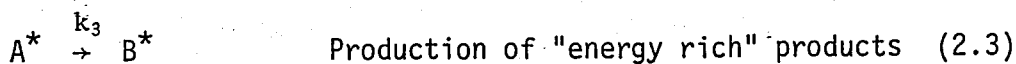
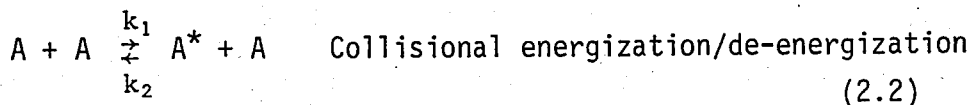
In 1919, Perrin [2] proposed molecules to acquire energy by the absorption of infrared radiation from the walls of the reaction vessel. The rate constant k was given by (2.1) in which ν is the frequency of the radiation absorbed.

$$k = \text{Constant} \times \exp(-h\nu/KT) \quad (2.1)$$

In 1920 Langmuir [3] showed that the density of the infrared radiation available from the walls was not sufficient to explain the observed

reaction rates. From then on, radiation theory was replaced by theories in which molecular collisions provided the activation energy.

In 1923 Christiansen and Kramers [4] postulated an overall first-order rate by supposing that product molecules had an excess of energy which could be used to re-energize reactant molecules. The process is described in the following form:



Stationary states are assumed for $[A^*]$ and $[B^*]$. The overall rate v is then:

$$v = \frac{-d[A]}{dt} = k_3 [A^*] = \left(\frac{k_3 k_1}{k_2} \right) [A] \quad (2.5)$$

This theory was found to be later unsatisfactory. First, product molecules don't have enough internal energy to energize more reactant molecules, since most unimolecular reactions are endothermic. Secondly, inert gases would be expected to remove the excess energy of the product molecules B^* and to reduce the overall rate of the reaction. In practice inert gases increase the rates of unimolecular reactions.

2.1.2 The Lindemann Theory

Finally Lindemann [5] recognized the importance of molecular collisions in the energization process and found that the first order rate-constant

for unimolecular reactions is not a constant but declines at low pressures. This theory forms the basis of all modern theories of unimolecular reactions. When a collision occurs between two molecules, one of them may get a critical amount of energy to enable it to become a product molecule.



M can represent a product molecule, an added "inert" gas molecule or a second molecule of reactant. k_1 is energy independent and is calculated from the collision theory equation. An energized molecule A^* may be de-energized by collision with a normal molecule.



k_2 is energy independent and equals the collision number Z_2 . The assumption is that every collision of A^* deenergizes it. A^* molecules which don't collide dissociate or isomerize



This process occurs with a rate constant independent of the energy content of A^* .

When the steady-state approximation is applied to the energized molecule A^* ,

$$-\frac{d[A^*]}{dt} = k_1[A][M] - k_2[A^*][M] - k_3[A^*] = 0 \quad (2.9)$$

Then

$$[A^*] = \frac{k_1[A][M]}{k_2[M] + k_3} = \frac{k_1[A]}{k_2 + k_3(1/[M])} \quad (2.10)$$

and the overall rate of the reaction is given by

$$-\frac{d[A]}{dt} = k_3[A^*] = \frac{(k_3 k_1 / k_2)[A]}{1 + \frac{k_3}{k_2[M]}} \quad (2.11)$$

At high pressures, when $k_2[A] \gg k_3$

$$-\frac{d[A]}{dt} = \frac{k_1 k_3}{k_2} [A] = k_\infty [A] \quad (2.12)$$

and k_∞ is the first order constant at high pressures.

At low pressures, when $k_2[A] \ll k_3$

$$-\frac{d[A]}{dt} = k_1[A][M] = k_{bim} [A][M] \quad (2.13)$$

and the rate of the reaction is equal to the second order rate of energization.

Thus, it is shown that at sufficiently high pressures, the rate of a gaseous unimolecular reaction will be first order, while in the limit of very low concentrations, a second-order rate law will be obeyed. The relative magnitudes of the rate constants k_1 , k_2 and k_3 determine the pressure range in which the transition will occur.

2.1.3 The Hinshelwood Theory

The failure of Lindemann theory in its simple form has been shown by the calculation of transition pressures $P^{1/2}$ which are much too high to agree with experiment. On the other hand the rate of energization

is too low to account for the observed rate of reaction.

$$k_1 = Z_1 \exp(-E_0/kT) \quad (2.14)$$

Both inconveniences are remedied by an increase in the rate constant k_1 . Hinshelwood [6] developed Lindemann's theory by assuming that the required energy could be drawn in part from mainly the vibrational degrees of freedom of the reactant molecule. The rate-constant k_1 , in the modified Hinshelwood-Lindemann theory is given by

$$k_1 = \frac{Z_1}{(s-1)!} \left(\frac{E_0}{kT}\right)^{s-1} \exp(-E_0/kT) \quad (2.15)$$

Equation (2.15) gives much bigger values of k_1 than does (2.14). k_2 is approximated by

$$k_2 = Z_2 \approx Z_1 \quad (2.16)$$

The high-pressure rate-constant given by Hinshelwood-Lindemann theory is

$$k_\infty = \frac{k_1 k_3}{k_2} = \frac{k_3}{(s-1)!} \left(\frac{E_0}{kT}\right)^{s-1} \exp(-E_0/kT) \quad (2.17)$$

Thus the overall rate at high pressures is

$$-\frac{d[A]}{dt} = \frac{k_3}{(s-1)!} \left(\frac{E_0}{kT}\right)^{s-1} \exp(-E_0/kT)[A] \quad (2.18)$$

At low pressures the overall rate is

$$-\frac{d[A]}{dt} = \frac{Z_1}{(s-1)!} \left(\frac{E_0}{kT}\right)^{s-1} \exp(-E_0/kT)[A][M] \quad (2.19)$$

(2.11) can be rearranged as

$$k_{\text{uni}} = - \frac{1}{[A]} \left(\frac{d[A]}{dt} \right) = \frac{k_1 [M]}{1 + k_2 [M]/k_3} \quad (2.20)$$

where k_{uni} is the pseudo-first-order rate constant.

The linear form of (2.20) relates the first-order high-pressure rate-constant k_{∞} to the general constant

$$\frac{1}{k_{\text{uni}}} = \frac{1}{k_1} \frac{1}{p} + \frac{1}{k_{\infty}} \quad (2.21)$$

For a fixed temperature, if (2.21) is valid a plot of $1/k_{\text{uni}}$ vs $1/p$ should be a straight line. This linear relation is not generally obeyed by accurate experimental measurements. The assumption of Hinshelwood theory that all critically energized molecules react at the same rate is a simplification. It is more logic that k_3 increases with the energy possessed by the molecule in excess of the critical energy. The more elaborate theories consider both the rate constants k_1 and k_3 energy dependent.

2.1.4 The RRK Theory

In the theories of Kassel [7,8], Rice and Ramsperger [9,10] the model of the reactant molecule is a group of simple harmonic oscillators. These theories assume that for a reaction to occur a critical amount of energy E_0 flows into one particular oscillator. The total energy E of the molecule is assumed to be rapidly redistributed so that for any energized molecule there is a finite probability that E_0 will be found in

the relevant part of the molecule. The rate constant k_3 or $k_a(E)$ for conversion of energized molecules to products is proportional to this probability.

There are two main differences between the Rice-Ramsperger and the Kassel theories. First, Rice and Ramsperger used classical statistical mechanics, whereas Kassel also developed a quantum treatment. Secondly, Kassel assumed that the energy was concentrated into one oscillator (i.e. two squared terms in the energy expression) Rice and Ramsperger assumed only one squared term. Kassel's classical expression for k_{uni}/k_∞ is given in (2.22)

$$\frac{k_{uni}}{k_\infty} = \frac{1}{(s-1)!} \int_0^\infty \frac{x^{s-1} \exp(-x) dx}{1 + \frac{A}{k_2[M]} \left(\frac{x}{x + E_0/kT} \right)^{s-1}} \quad (2.22)$$

where $x = (E - E_0)/kT$, k is the Boltzmann constant, A is a proportionality constant (equated to the experimental high-pressure Arrhenius frequency factor), and s is the number of "effective" oscillators of the molecule. "s" is chosen by fitting the theoretical with the experimental decline of the rate constant with concentration. It is usually much smaller than the number of molecular vibrations of the reactant.

The Rice and Ramsperger theory on the one hand and the Kassel theory on the other are based on the same model and are often referred to collectively as the RRK theory. The quantum statistical (mechanical) treatment gives results in good agreement with experiment. The classical statistical mechanical treatment gives agreement only with a reduced number of reactions.

2.1.5 The Slater Theory

The model of the classical Slater [11] theory, put forward in 1939, is a group of oscillators which are classical and harmonic and which have independent frequencies. The reaction takes place when a specified coordinate attains a critical distance or angle. The rate-constant k_3 is replaced by a "specific dissociation probability" L which is the frequency with which the specified coordinate attains the critical value necessary for the reaction. The resulting expression for $k_{\text{uni}}/k_{\infty}$ is given by (2.23)

$$\frac{k_{\text{uni}}}{k_{\infty}} = \frac{1}{\left(\frac{1}{2}n - \frac{1}{2}\right)!} \int_0^{\infty} \frac{x^{\frac{1}{2}(n-1)} e^{-x} dx}{1 + x^{\frac{1}{2}(n-1)} \theta^{-1}} \quad (2.23)$$

where $x = (E - E_0)/kT$, n is the number of normal modes that contribute to the reaction and θ is a complicated function of pressure, temperature, the critical energy and the molecular parameters.

The work of Laidler and Gill [12], shows that, when the number of vibrational modes of the reactant is small, the values predicted by the Slater formulation are too low. These workers suggest that at low concentrations transfers of energy between the vibrational modes do take place, the effect being less important for complex molecules.

Thiele and Wilson [13] compared the high pressure experimental data with the Slater theory; they concluded that the theory should include the possibility of the existence of more than one reaction coordinate, and the theory has since been extended [14,15].

The two major disadvantages of this theory are that the model consists of classical oscillators and it is assumed that the critical state resembles that of the reactant. In some cases, passage to the critical state is associated with large entropy changes and the approximation of the similarity between the critical and initial states may not be exact.

2.1.6 The Absolute Rate Theory

This theory is also known as Transition-State Theory or Activated Complex Theory and applies thermodynamic and statistical-mechanical arguments to a system in which activated complexes are at equilibrium with the reactant molecules. For a general reaction $A + B \rightarrow \text{Products}$, the reaction scheme is (2.24)



The equilibrium concentration of activated complexes evaluated from statistical-mechanical equations with expressions for k^{\ddagger} , leads to the equation (2.25) [19]

$$k = - \frac{d[A]/dt}{[A][B]} = \frac{kT}{h} \frac{Q^{\ddagger}}{Q_A Q_B} \exp(-E_0/kT) \quad (2.25)$$

for the overall rate constant.

In this equation E_0 is the critical energy, Q_A and Q_B are the complete partition functions for the reactants and Q^{\ddagger} is the partition function for all the degrees of freedom of the activated complex except the reaction coordinate. The motion in the reaction coordinate has its partition function included in the factor kT/h .

For a unimolecular reaction the ART expression becomes (2.26); it gives the limiting high-pressure rate constant

$$k_{\infty} = \frac{kT}{h} \frac{Q^{\ddagger}}{Q} \exp(-E_0/kT) \quad (2.26)$$

The translational contributions to Q and Q^{\ddagger} are identical. Assuming that rotational contributions also cancel, the approximation (2.27) results, in which there are n frequencies for the molecule and $(n-1)$ frequencies for the activated complex.

$$k_{\infty} = \frac{\nu_1 \nu_2 \dots \nu_n}{\nu_1^{\ddagger} \nu_2^{\ddagger} \dots \nu_{n-1}^{\ddagger}} \exp(-E_0/kT) \quad (2.27)$$

The pre-exponential factor at high pressures is expected to be of the order of a vibration frequency, about 10^{13} sec^{-1} . If the geometry of the activated complex is very different from that of the reactant molecule the rate constant is multiplied by a factor $(I_A^{\ddagger} I_B^{\ddagger} I_C^{\ddagger} / I_A I_B I_C)$ which involves the principal moments of inertia of the reactant and activated complex. When loose activated complexes are formed, vibrational degrees of freedom in the reactant molecule are replaced by rotational degrees of freedom in the activated complex, and this factor contributes to much higher pre-exponential factors.

Marcus and Rice [16,17] have developed a quantum mechanical transition state formulation of the RRK theory. This theory takes into account the possibility of a large increase in entropy while forming the activated complex. It also takes into consideration the participation of the rotational degrees of freedom in intramolecular energy transfer. The present work being mainly concerned with the RRKM (Rice, Ramsperger, Kassel and Marcus) theory, it will be discussed in more detail in Chapter III.

2.2 BASIC QUESTIONS IN UNIMOLECULAR REACTIONS

Two different points of view exist in the description of a unimolecular reaction in terms of molecular properties. Based on the statistical point of view, the rate constant is assumed to depend on the internal energy of the molecule [20]. In the 1950's Marcus [17] developed the RRKM theory whereas Rosenstock, Wallenstein, Wahrhaftig and Eyring [21] developed the (quasi-equilibrium theory) QET.

In the other model, representing the quantum point of view, the distribution of energy is considered to depend on which modes are excited. The rate constant is a function of electronic, vibrational and rotational quantum numbers $\{v, v_1, v_2, \dots, v_{3N-6}, J, K, \dots\}$. A chemical reaction is then defined in terms of two such states: the initial and the final state. This method is called state-to-state chemistry [22], and it has been made necessary by the advent of lasers.

2.2.1 Comparison of the Basic Theories of Unimolecular Reactions

Recent research has shown that the different theories are not mutually exclusive, but relationships exist among them.

RRKM/QET

Both are based on the assumption that all the ways into which the energy E is distributed among the different molecular oscillators are equally probable.

The RRKM theory was designed for studying thermal reactions: it only considers dissociations involving a single electronic state and assumes that the system has reached a state of microcanonical equilibrium before it reacts.

QET assumes that fast radiationless transitions will degrade electronic excitation energy into vibrational energy of the ground state. Both theories are based on the concept of transition state.

Klots [23]

The dissociation of a transition state and the process by which two fragments associate to form a loose transition state are two time-inverted motions.

Klots' theory and QET are complementary, the first one deals with the last part of the reaction path, part which is disregarded in RRKM theory. As a result Klots' theory is good for studying problems of kinetic energy release, whereas QET is designed for calculating rate constants.

Klots' theory is a special version of Light's phase space theory [24-26]. Marcus [24] compares RRKM/QET with phase space theory as follows: 'When the transition state is loose, RRKM and phase space theory become similar. When it is not loose, phase space theory no longer applies'.

Slater [27]

Slater's theory does not take into account the anharmonicity of molecular vibrations and assumes normal-mode behaviour in a system undergoing dissociation.

RRKM and Slater's

'When theories are applied to the same model, they both lead to the same mathematical expression for the rate constant' says Lorquet [28]. What differs in the two theories is the interpretation to be given to the different parameters which enter the equation (e.g. ν , n and E_0).

Quack and Troe [29]

They propose to correlate each vibrational and rotational energy level from the reactant molecule to its dissociation products. Their work applies in particular to simple bond fission reactions and the reverse radical association reactions. Each vibrational-rotational level is called a channel. A channel is declared open or closed at a particular energy E , according to whether its maximum energy is below or above energy E . The theory requires a knowledge of the different electronic-vibrational-rotational energy levels along the reaction path. The transition state is not localized at any position along the reaction coordinate.

They developed a simple and useful model using a maximum number of known molecular parameters, containing a minimum number (one) of adjustable parameters. The model gives a connection between this parameter and features of the potential properties. It allows for an empirical evaluation of unimolecular rate constants and may be related to more complete theories of unimolecular reactions.

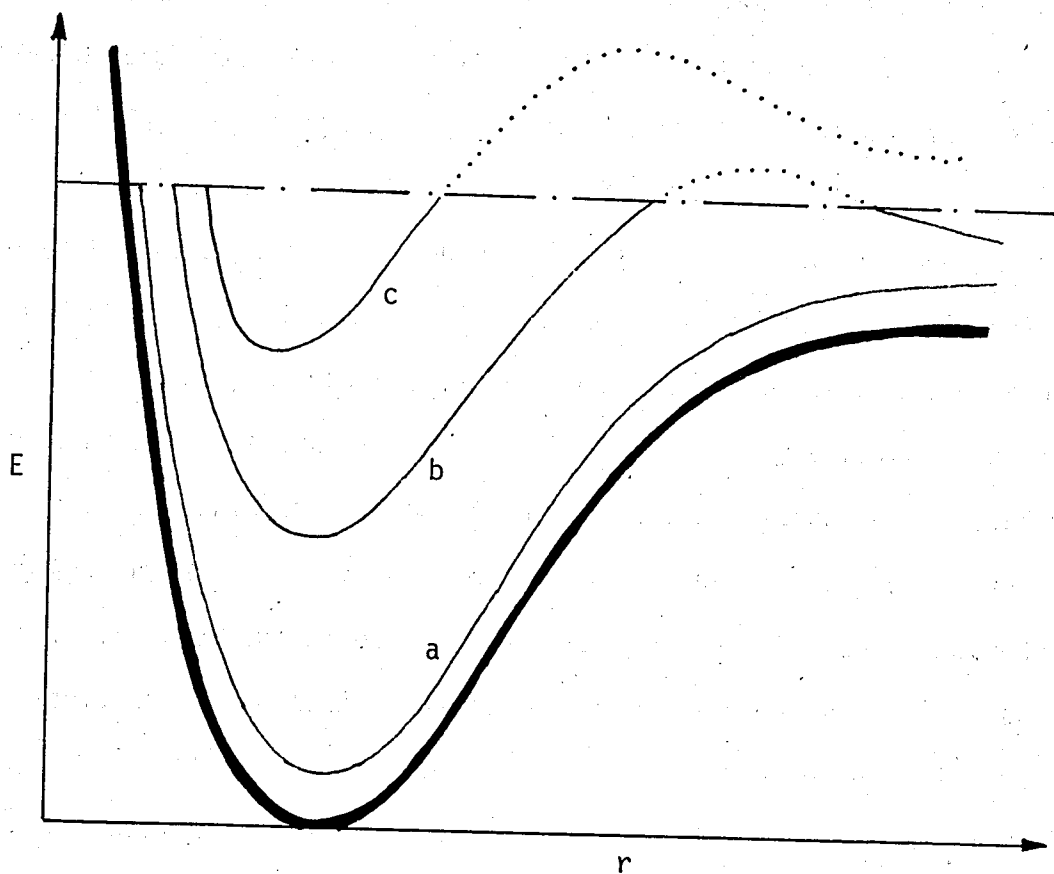


Figure 2.1 - Adiabatic channel theory

— Potential energy curve as a function of the reaction coordinate r

a Open channel at energy E

b Closed channel at energy E

c Closed channel at energy E

2.2.2 The Transition State

Eyring and Polanyi [30] suggested the presence of a little well at the top of the potential barrier. This led to the existence of a short lived activated complex. When it became apparent that this well didn't exist in real life, the energy barrier along the reaction coordinate was proposed. This was termed as saddle point. Ab initio calculations [31, 32,33] denied the existence of the hump. The third extension of the theory was done by Wigner [34]. The transition state is presented as a critical surface in phase space [20] which divides the stable molecule and its fragments. It turns out that even when there exists an energy barrier, the best location of the critical surface is not at the saddle point. According to Wigner [34], there is a surface which divides phase space into two regions: one is the reactant side, the other is the product side. The rate constant calculated by the transition state theory is greater than the true rate constant $k^{\text{TS}} \geq k^{\text{real}}$. A principle has been proposed to determine the position of the surface: the surface is shifted until the rate constant is a minimum [35,36-39]. The rate constant calculated by transition state theory provides an upper bound to the real rate constant. A bottleneck determines the rate of flux in phase space. Bunker and Pattengill [40,41], have proposed a method of finding the location of the critical surface which minimizes the reactive flux. According to these authors the transition state should be located at that particular position.

At one extreme there is the transition state methods which express the rate constant in terms of molecular frequencies corresponding to a

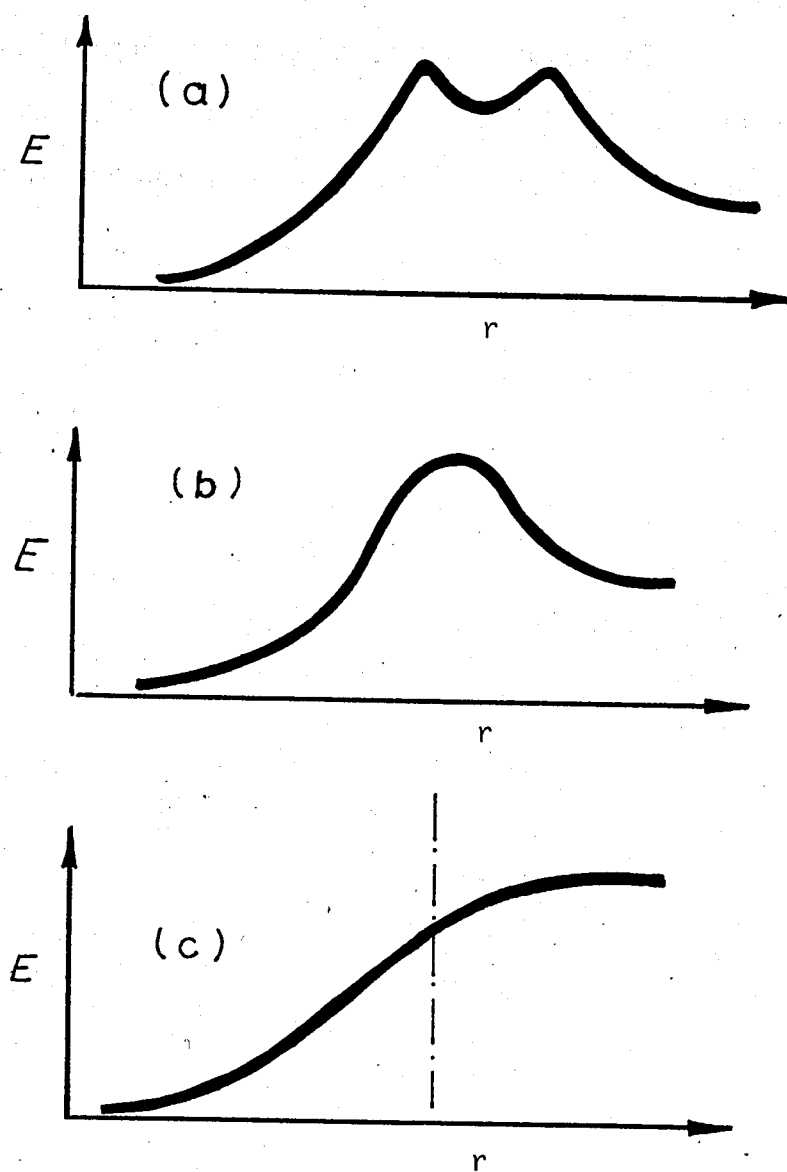


Figure 2.2 - The concept of transition state

- (a) activated complex
- (b) saddle point
- (c) critical surface.

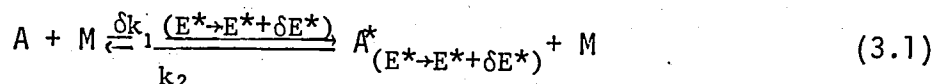
certain point on the potential energy surface and needs guesswork. At the other extreme, there are dynamical treatments [42] which require a knowledge of the entire potential energy surface. At the intermediate there is the Bunker and Pattengill method which requires knowledge of the molecular frequencies and moments of inertia along the reaction path. Another method related to this one, for which no transition state is defined, is the adiabatic channel method developed by Quack and Troe [29].

III. RRKM THEORY

3.1 THE DERIVATION OF THE RRKM EXPRESSION FOR k_{uni}

The unimolecular reaction rate drops with decreasing pressure when the lifetime of the active molecules becomes comparable to the time between successive collisions.

The following reaction sequence is considered,



A^* and A^+ denote the active molecule and activated complex respectively, M is any third body deactivating A^* . Steady state treatment for A^* and A^+ gives a relation between the unimolecular rate constant, k_{uni} , and the pressure, p .

$$\delta k_{uni} = k_a(E^*) (\delta k_1(E^* \rightarrow E^* + \delta E^*) / k_2) / (1 + k_a(E^*) / k_2 p) \quad (3.4)$$

The k 's, functions of the energy of the initial A^* molecule, are evaluated for a small energy range. k_{uni} is then obtained by integration over all possible energies

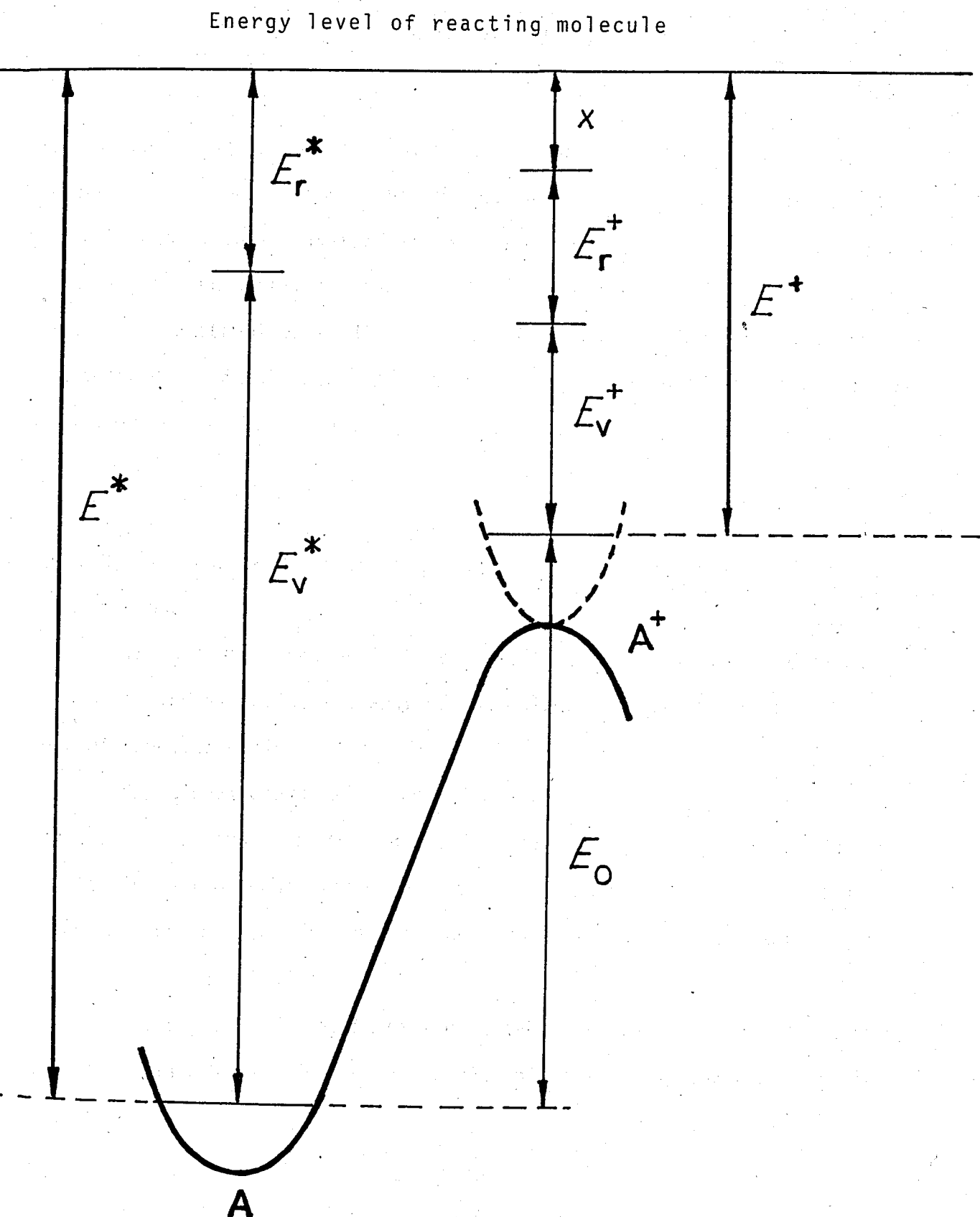


Figure 3.1 - Energy terminology for a unimolecular reaction; adiabatic and inactive degrees of freedom are excluded.

$$k_{\text{uni}} = \int_{E^* = E_0}^{\infty} \frac{k_a(E^*) dk_1(E^* \rightarrow E^* + dE^*) / k_2}{1 + k_a(E^*) / k_2 [M]} \quad (3.5)$$

Evaluation of the integrand involves a calculation of the number of ways of distributing energy among the various degrees of freedom of the active molecule and of the activated complex. The vibrational zero point energy of A^* and A^+ and also the potential energy of the broken bond of the activated complex cannot be so distributed and are called "fixed energy". The remaining "non-fixed" energy of the active molecule and of its corresponding activated complex are denoted by E^* and E^+ respectively.

$$E^* - E^+ = E_0$$

where E_0 is a constant approximately equal to the bond strength of the breaking bond.

The non-fixed energy is considered to be free to move around the molecule. The vibrational energy of the molecule is assumed to be subject to rapid redistribution.

Rotational energy might contribute to a reaction (centrifugal force might assist a bond breaking reaction). There are some limitations due to the requirement of conservation of the angular momentum. If a rotational degree of freedom stays in the same quantum state during the reaction, there is no exchange of energy.

The degrees of freedom of the active molecule are "active", "adiabatic" or "inactive". The active degrees of freedom can contribute their

energy to the breaking bond. The adiabatic ones remain in the same quantum state during the decomposition of the molecule and contribute little energy to the breaking bond. When the molecule has become an activated complex the energy transfer between the "inactive" degrees of freedom and this bond takes place rapidly. Inactive degrees of freedom exchange energy between themselves but cannot contribute it toward the energy required for surmounting the potential energy barrier.

The quantity $\delta k_1(E^* \rightarrow E^* + \delta E^*)/k_2$, which is the equilibrium constant for the reaction (3.1) is given as the partition ratio $Q(A^*_{(E^* \rightarrow E^* + \delta E^*)})/Q(A)$. The function $Q(A)$ denoted as Q_2 , is the molecular partition function for all the active modes of A. The function $Q(A^*_{(E^* \rightarrow E^* + \delta E^*)})$ is the partition function for A^* having non-fixed energy in the range E^* to $E^* + \delta E^*$. If δE^* is small the exponential terms in the expression $Q = \sum g_i \exp(-E_i/kT)$ are all the same, $\exp(-E^*/kT)$ and the partition function is expressed as:

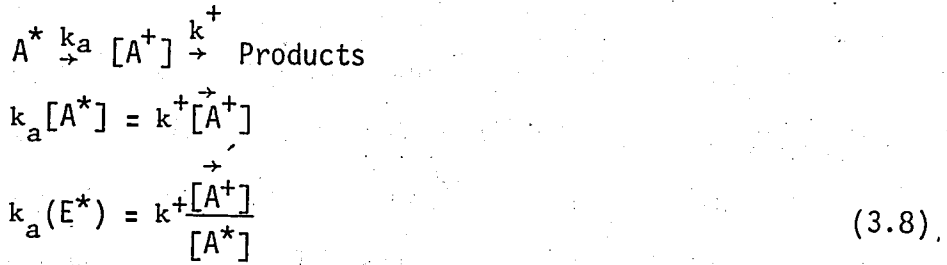
$$\begin{aligned} Q(A^*_{(E^* \rightarrow E^* + \delta E^*)}) &= \left(\sum_{E^* \rightarrow E^* + \delta E^*} g_i \right) \exp(-E^*/kT) \\ &= N^*(E^*) \delta E^* \exp(-E^*/kT) \end{aligned} \quad (3.6)$$

Division by $Q(A) \equiv Q_2$ gives then the required result

$$\frac{\delta k_1(E^* \rightarrow E^* + \delta E^*)}{k_2} = \frac{N^*(E^*) \exp(-E^*/kT) \delta E^*}{Q_2} \quad (3.7)$$

where $N^*(E^*)$ is the density of quantum states.

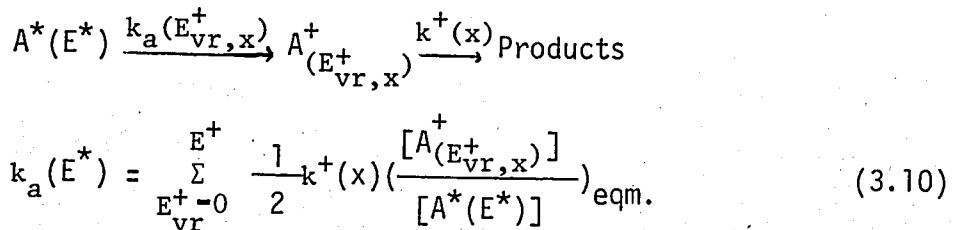
$k_a(E^*)$ is the rate constant for the formation of activated complexes from energized molecules with non-fixed energy E^* . The steady state treatment is applied to A^+



At equilibrium the concentration of forward crossing complexes is half the total concentration of complexes

$$k_a (E^*) = \frac{1}{2} k^+ \left(\frac{[A^+]}{[A^*]} \right)_{\text{eqm.}} \tag{3.9}$$

The overall reaction can be written in the form



where

$$E^* = E_0 + E^+ \quad \text{and} \quad x = E^+ - E_{vr}^+ .$$

The decomposition of the activated complex into products is treated as the translation of a particle of mass μ in a one dimensional box of length δ .

If the energy in the reaction coordinate is x , then $x = \frac{1}{2} \mu v^2$ and the speed of translation is $v = (2x/\mu)^{1/2}$.

The time taken for the mass μ to cross the box is $t = \delta / (2x/\mu)^{1/2}$.

The rate constant for crossing the barrier is therefore

$$k^+(x) = \left(\frac{2x}{\mu} \right)^{1/2} / \delta = \left(\frac{2x}{\mu \delta^2} \right)^{1/2} \tag{3.11}$$

The equilibrium ratio of concentrations of A^+ and A^* is calculated from statistical mechanics as the ratio $Q(A^+)/Q(A^*)$ of the partition functions of the activated complex and energized molecule. The two species under consideration have a total energy in the range $E^* \rightarrow E^* + \delta E$. Each partition function is of the form $(\Sigma g_i) \exp(-E^*/kT)$, where Σg_i is the number of quantum states in the small energy range, and $Q(A^+)/Q(A^*)$ reduces to $\Sigma g_i^+ / \Sigma g_i^*$. A^+ having less non-fixed energy than A^* , $[A^+]/[A^*]$ will be small.

Σg_i^* can be replaced by a continuous distribution function $N^*(E^*)\delta E^*$.

At this point, the activated complex contains a translational degree of freedom and Σg_i^* can be replaced by a continuous distribution function $N^*(E^*)\delta E^*$.

The number of quantum states of the activated complex in the range of total energy $E^* \rightarrow E^* + \delta E^*$ can be denoted by $N^+(E^*)\delta E^*$ but is written as $N^+(E^+)\delta E^+$. Thus the concentration ratio for the small energy range becomes

$$([A^+]/[A^*])_{eqm} = \Sigma g_i^+ / \Sigma g_i^* = N^+(E^+) / N^*(E^*) \quad (3.12)$$

The density of states $N^+(E^+)$ for a specified division of E^+ into the vibrational-rotational energy E_{vr}^+ and the translational energy x is needed. This density is denoted by $N^+(E_{vr}^+, x)$. In order to split $N^+(E_{vr}^+, x)$ into contributions from E_{vr}^+ and x , $P(E_{vr}^+)$ and $N_{rc}^+(x)\delta x$ are defined.

$P(E_{vr}^+) \rightarrow$ Number of vibrational-rotational quantum states of A^+ with vibrational-rotational non-fixed energy equal to E_{vr}^+ .

$N_{rc}^+(x)\delta x \rightarrow$ Number of translational quantum states of A^+ with energy in the reaction coordinate in the range $x \rightarrow x + \delta x$.

The overall number of states in an energy range δx is given by the product

of these two quantities

$$N^+(E_{vr}^+, x) = P(E_{vr}^+) N_{rc}^+(x) \quad (3.13)$$

The required concentration ratio is

$$\left(\frac{[A^+(E_{vr}^+, x)]}{[A^*(E^*)]} \right)_{eqm} = \frac{P(E_{vr}^+) N_{rc}^+(x)}{N^*(E^*)} \quad (3.14)$$

To evaluate $N_{rc}^+(x)$ one has to use the wave-mechanical treatment of a particle of mass μ in a box of length δ . The energy x of the n^{th} level is

$$x = n^2 h^2 / 8\mu\delta^2 \quad (3.15)$$

where h is Planck's constant. The number of quantum states with energy up to and including x is $n = (8\mu\delta^2 x / h^2)^{1/2}$. The number of states in the energy range $x \rightarrow x + \delta x$ is $\delta n = (dn/dx)\delta x$ and this number of states is equal to $N_{rc}^+(x)\delta x$

$$N_{rc}^+(x) = \frac{dn}{dx} = \left(\frac{2\mu\delta^2}{h^2 x} \right)^{1/2} \quad (3.16)$$

The expression for $k_a(E^*)$ can be evaluated using (3.10), (3.11), (3.14) and (3.16)

$$\begin{aligned} k_a(E^*) &= \sum_{E_{vr}^+=0}^{E^+} \frac{1}{2} \left(\frac{2x}{\mu\delta^2} \right)^{1/2} \frac{P(E_{vr}^+) (2\mu\delta^2 / h^2 x)^{1/2}}{N^*(E^*)} \\ &= \sum_{E_{vr}^+=0}^{E^+} \frac{P(E_{vr}^+)}{hN^*(E^*)} \end{aligned} \quad (3.17)$$

$$= \frac{1}{hN^*(E^*)} \sum_{E_{vr}^+=0}^{E^+} P(E_{vr}^+) \quad (3.18)$$

The sum in (3.18) is the total number of vibrational-rotational quantum states of the activated complex with energies $\leq E^+$.

Two final modifications are introduced.

The ART treatment at high pressures shows that the correct k_∞ is obtained if the expression (3.18) for $k_a(E^*)$ is multiplied by Q_1^+/Q_1 where Q_1^+ and Q_1 are the partition functions for the adiabatic rotations in the activated complex and A molecule.

The second modification concerns the possibility that a reaction can proceed by several paths which are kinetically equivalent. The correct rate-constant $k_a(E^*)$ is obtained by including a factor L^\ddagger , the statistical factor in (3.18)

$$k_a(E^*) = L^\ddagger \frac{Q_1^+}{Q_1} \frac{\sum_{E^+} \sum_{vr=0}^{E^+} P(E^+_{vr})}{hN^*(E^*)} \quad (3.19)$$

Provided that the complex is chosen so that it can form products or return to reactants by only one route, the statistical factor is given by $L^\ddagger = \alpha(\sigma^+/\sigma)$ where α is the number (1 or 2) of optical isomers of the complex and σ and σ^+ are the symmetry numbers for the molecule and the complex respectively ($\sigma^+ = 1$ for asymmetric species) [43,44].

The overall first-order rate-constant k_{uni} is obtained by substituting (3.7) and (3.19) into (3.5)

$$k_{uni} = \frac{L^\ddagger Q_1^+}{hQ_1 Q_2} \int_{E^*=E_0}^{\infty} \frac{\sum_{E^+} \sum_{vr=0}^{E^+} P(E^+_{vr}) \exp(-E^*/kT) dE^*}{1 + k_a(E^*)/k_2[M]} \quad (3.20)$$

But $E^* = E_0 + E^+$ and $dE^* = dE^+$, the final result is then:

$$k_{\text{uni}} = \frac{L^\ddagger Q_1^\ddagger \exp(-E_0/kT)}{hQ_1 Q_2} \int_{E^\ddagger=0}^{\infty} \frac{\sum_{E_{\text{vr}}^\ddagger=0}^{E^\ddagger} \{P(E_{\text{vr}}^\ddagger)\} \exp(-E^\ddagger/kT) dE^\ddagger}{1 + k_a(E_0 + E^\ddagger)/k_2[M]} \quad (3.21)$$

3.2 THE HIGH PRESSURE LIMIT

The high pressure limit is obtained from (3.21) by putting $[M] \rightarrow \infty$

$$k_\infty = \frac{L^\ddagger Q_1^\ddagger}{hQ_1 Q_2} \exp(-E_0/kT) \int_{E^\ddagger=0}^{\infty} \left\{ \exp(-E^\ddagger/kT) \sum_{E_{\text{vr}}^\ddagger=0}^{E^\ddagger} P(E_{\text{vr}}^\ddagger) \right\} dE^\ddagger \quad (3.22)$$

The above expression is reversed

$$k_\infty = \frac{L^\ddagger Q_1^\ddagger}{hQ_1 Q_2} \exp(-E_0/kT) \sum_{E_{\text{vr}}^\ddagger=0}^{\infty} \left\{ P(E_{\text{vr}}^\ddagger) \int_{E^\ddagger=E_{\text{vr}}^\ddagger}^{\infty} \exp(-E^\ddagger/kT) dE^\ddagger \right\} \quad (3.23)$$

The evaluation of the integral gives

$$\int_{E^\ddagger=E_{\text{vr}}^\ddagger}^{\infty} \exp(-E^\ddagger/kT) dE^\ddagger = [-kT \exp(-E^\ddagger/kT)]_{E^\ddagger=E_{\text{vr}}^\ddagger}^{\infty} = kT \exp(-E_{\text{vr}}^\ddagger/kT)$$

The value of k_∞ becomes

$$k_\infty = \frac{L^\ddagger Q_1^\ddagger}{hQ_1 Q_2} kT \exp(-E_0/kT) \sum_{E_{\text{vr}}^\ddagger=0}^{\infty} [P(E_{\text{vr}}^\ddagger) \exp(-E_{\text{vr}}^\ddagger/kT)]$$

The sum is the partition function Q_2^\ddagger for the active vibrations and rotations in the activated complex. The final expression for the high pressure rate constant is given by (3.24)

$$k_\infty = L^\ddagger \frac{kT}{h} \frac{Q_1^\ddagger Q_2^\ddagger}{Q_1 Q_2} \exp(-E_0/kT) \quad (3.24)$$

3.3 THE LOW-PRESSURE LIMIT

At very low pressures the first-order rate-constant becomes proportional to the pressure. The second order rate constant k_{bim} is given by (3.25)

$$\begin{aligned}
 k_{\text{bim}} &= \lim_{[M] \rightarrow 0} \left(\frac{k_{\text{uni}}}{[M]} \right) \\
 &= \frac{k_2}{Q_2} \exp(-E_0/kT) \int_{E^+=0}^{\infty} N^*(E_0 + E^+) \exp(-E^+/kT) dE^+ \\
 &= \frac{k_2}{Q_2} \int_{E^*=E_0}^{\infty} N^*(E^*) \exp(-E^*/kT) dE^* = k_2 \frac{Q_2^*}{Q_2} \quad (3.25)
 \end{aligned}$$

where Q_2^* is the partition function for energized molecules.

3.4 TREATMENT OF ADIABATIC ROTATIONS IN RRKM THEORY

The term "adiabatic rotations" describes rotations that are constrained to remain in the same quantum state when the activated complex is formed from the active molecule because of restrictions imposed by angular momentum conservation.

The energy of the rotation is given by $E_J = (h^2/8\pi^2 I)J(J+1)$. When $I^+ > I$ so that $E_J > E_J^+$ the adiabatic rotations release energy into the active degrees of freedom of the molecule. The multiplicity of available quantum states of the complex is increased, in this way the specific rate-constant k_a is increased. In bond fission reactions, investigated in this study, the moments of inertia change and there is a reduction of E_0 . In

this case there is a single doubly degenerate adiabatic rotational degree of freedom [43-45]. These reactions have a "loose" transition state in which the two largest moments of inertia of the reactant molecule are appreciably larger than they are in the "ground" state. One consequence of this, is that the rate constants for such reactions tend to be faster, both at the high and low-pressure limits, than those for tight transition states.

The energy diagram of Figure 3.2 shows that the energy in the active degrees of freedom of A^* is

$$E_{\text{active}}^* = E_0 + E^+ + E_J^+ - E_J = E_0 + E^+ + \Delta E_J$$

where $\Delta E_J = E_J^+ - E_J$.

Equations (3.7) and (3.19) should be modified

$$\left(\frac{\delta k_1}{k_2}\right)_J = \frac{N^*(E_{\text{active}}^*) \exp[-(E_0 + E^+ + E_J^+)/kT] \delta E_{\text{active}}^*}{Q} \quad (3.26)$$

$$k_{E_J}(E_{\text{active}}^*) = \frac{L^\ddagger}{hN^*(E_{\text{active}}^*)} \sum_{E_{vr}^+=0}^{E^+} P(E_{vr}^+) \quad (3.27)$$

The right expression for k_{uni} is given by (3.28)

$$k_{\text{uni}} = \frac{L^\ddagger \exp(-E_0/kT)}{hQ} \times \sum_{J=0}^{\infty} (2J+1) \exp(-E_J^+/kT) \int_{E^+=0}^{\infty} \frac{\{\sum P(E_{vr}^+)\} \exp(-E^+/kT) dE^+}{1 + k_{E_J}(E_0 + E^+ + \Delta E_J)/k_2} \quad (3.28)$$

The expression is simplified by replacing ΔE_J by its mean value $\langle \Delta E_J \rangle$.

$$\frac{E_J}{E_J^+} = \frac{I^+}{I} \quad \text{whence} \quad \langle \Delta E_J \rangle = E_J^+ - E_J = \left(1 - \frac{I^+}{I}\right) \langle E_J^+ \rangle \quad (3.29)$$

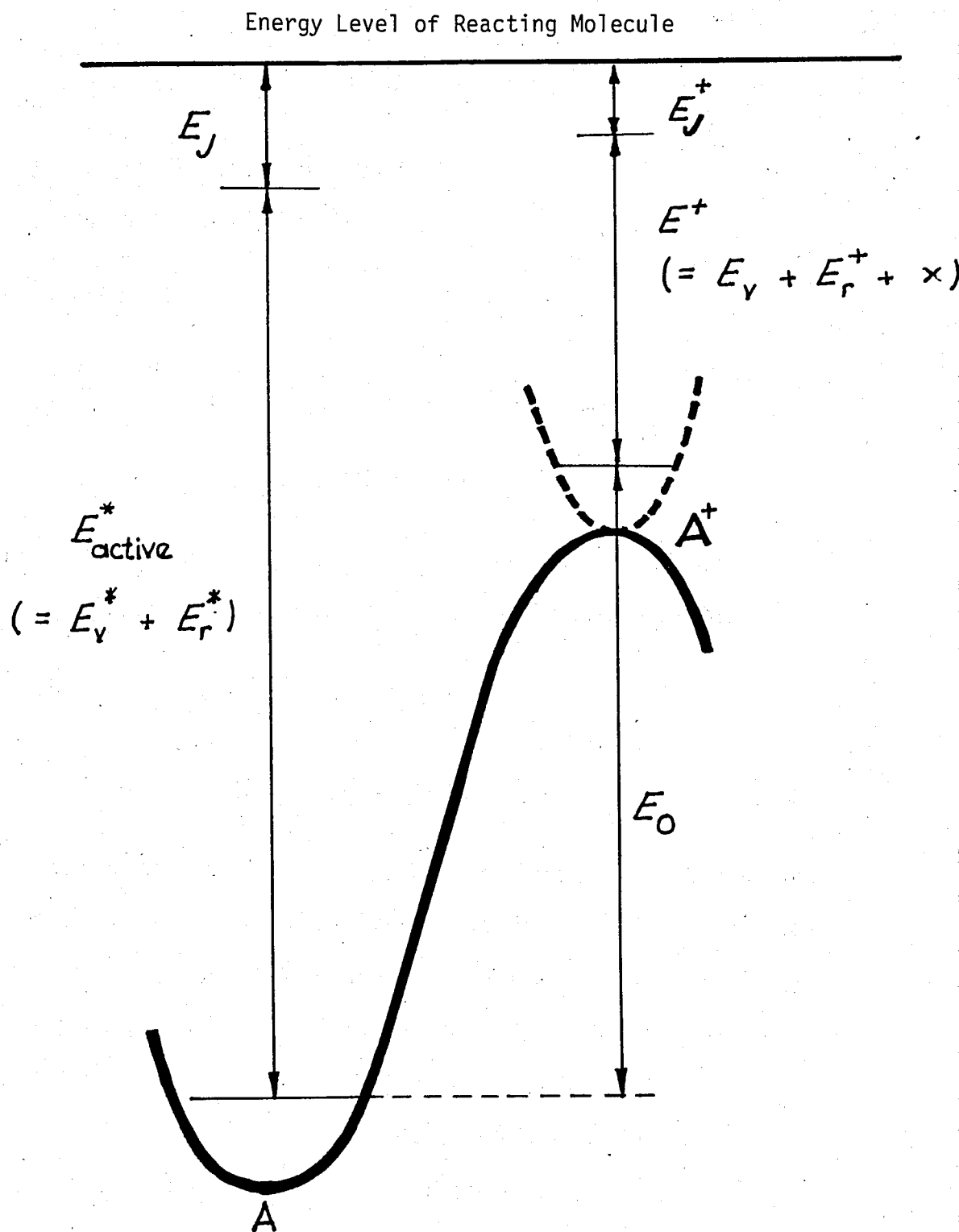


Figure 3.2 - Energy diagram for a unimolecular reaction with adiabatic rotations included.

There are $(2J+1)$ rotational states for each value of J .

$$\langle E_J^+ \rangle = \frac{\int_0^\infty E_J^+ (2J+1) \exp(-E_J^+/kT) dJ}{\int_0^\infty (2J+1) \exp(-E_J^+/kT) dJ}$$

$$x = (E_J^+)/kT = h^2 J(J+1)/8\pi^2 I^+ kT$$

$$dx = (h^2/8\pi^2 I^+ kT)(2J+1)dJ$$

The result for $\langle E_J^+ \rangle$ is

$$\langle E_J^+ \rangle = kT \frac{\int_0^\infty x \exp(-x) dx}{\int_0^\infty \exp(-x) dx} = kT \quad (3.30)$$

and

$$\langle \Delta E_J \rangle = \langle E_J^+ \rangle - \langle E_J \rangle = (1 - I^+/I)kT \quad (3.31)$$

When ΔE_J in (3.28) has been replaced by $\langle \Delta E_J \rangle$ the only function of J remaining is $(2J+1)\exp(-E_J^+/kT)$. The equation can be rewritten as

$$\begin{aligned} k_{\text{uni}} &= C \sum_{J=0}^{\infty} [(2J+1)\exp(-E_J^+/kT)] \\ &= C \int_0^\infty (2J+1)\exp(-E_J^+/kT) dJ = CQ_1^+ \end{aligned} \quad (3.32)$$

in which C includes the remaining terms in (3.28) and Q_1^+ is the classical partition function for the two dimensional rotation. The final equations for k_{uni} and $k_a(E_{\text{active}}^*)$ are (3.33) and (3.34) which differ from (3.21) and (3.19) only in the omission of the factor Q_1^+/Q_1 in the expression for k_a and in the modified energy at which k_a is evaluated.

$$k_{\text{uni}} = \frac{L^{\ddagger} Q_1^+ \exp(-E_0/kT)}{hQ} \int_{E^+=0}^{\infty} \frac{\{ \sum_{\text{vr}=0}^{E^+} P(E_{\text{vr}}^+) \} \exp(-E^+/kT) dE^+}{1 + k_a(E_0 + E^+ + \langle \Delta E_J \rangle) / k_2 [M]} \quad (3.33)$$

$$k_a(E_0 + E^+ + \langle \Delta E_J \rangle) = \frac{L^\ddagger}{h N^*(E_0 + E^+ - (I^+/I-1)kT)} \sum_{E_{vr}^+} P(E_{vr}^+) \quad (3.34)$$

The high pressure limit which includes the factor Q_1^+/Q_1 agrees with the Absolute Rate Theory expression

$$k_\infty = L^\ddagger \frac{kT}{h} \frac{Q^+}{Q} \exp(-E_0/kT) \quad (3.35)$$

where $Q^+ = Q_1^+ Q_2^+$ and $Q = Q_1 Q_2$.

A simplification for $k_a(E^*)$ may be obtained in the form

$$k_a(E_0 + E^+ + \langle \Delta E_J \rangle) = \frac{1}{F} k_a(E_0 + E^+) \quad (3.36)$$

where

$$F = N^*(E_0 + E^+ + \langle \Delta E_J \rangle) / N^*(E_0 + E^+) \quad (3.37)$$

The factor F is less than unity and may be considered constant. Numerical values for F can be obtained using various expressions for the state densities. Hay and Belford [46] derived (3.38), Waage and Rabinovitch [47] derived (3.39). The Whitten Rabinovitch [48] expression for $N^*(E^*)$ leads to (3.40) as expressions for F .

$$F_{HB} = \exp[-(s-1)(I^+/I-1)kT/(E_0 + E_z + kT)] \quad (3.38)$$

$$F_{WR} = [1 + (s-1)(I^+/I-1)kT/(E_0 + aE_z)]^{-1} \quad (3.39)$$

$$F_{Wh-R} = [1 - (I^+/I-1)kT/(E_0 + aE_z)]^{s-1} \quad (3.40)$$

In these equations s is the number of active vibrational degrees of freedom ($+1/2r$ if there are in addition r active rotational degrees of freedom), E_z

is the zero point energy of the molecule and a is a parameter having a value between 0 and 1 which can be calculated from the properties of the molecule. The high pressure limit is still given by (3.35) and the low pressure rate constant is given by (3.41)

$$k_{\text{bim}} = \left(F \frac{Q_1^+}{Q_1}\right) \left(k_2 \frac{Q_2^*}{Q_2}\right) \quad (3.41)$$

From these equations expressions for f_∞ and f_0 can be derived

$$f_\infty = Q_1^+/Q_1 \quad (3.42)$$

$$f_0 = FQ_1^+/Q_1 \quad (3.43)$$

The effect on k_{uni} is to increase k_∞ by the factor Q_1^+/Q_1 and to shift the fall-off curve of $\log k_{\text{uni}}/k_\infty$ v.s. $\log P$ to higher pressures by $-\log F$ along the $\log p$ axis.

$$k_{\text{uni}} = \frac{L^\ddagger Q_1^+ \exp(-E_0/kT)}{hQ} \int_{E^+=0}^{\infty} \frac{P(E_{\text{vr}}^+) \exp(-E^+/kT) dE^+}{1 + k_a(E_0 + E^+)/Fk_2[M]} \quad (3.44)$$

F_{WR} gives good results even for high values of I^+/I .

3.5 THE EVALUATION OF SUMS AND DENSITIES OF MOLECULAR QUANTUM STATES IN RRKM THEORY [18]

The quantities $\sum_{E_{\text{vr}}^+=0}^{E^+} P(E_{\text{vr}}^+)$ and $N^*(E^*)$ are fundamental to any application of the RRKM theory. An illustration and clarification of their significance is necessary.

3.5.1 Sum of Quantum States, $\sum_{E_v=0}^E P(E_v)$

The degeneracy $P(E_v)$ is the number of vibrational quantum states with a vibrational energy E_v , $\sum_{E_v=0}^E P(E_v)$ is the total number of states with energy not exceeding E .

In the case of a single simple harmonic oscillator of frequency ν , it has one quantum state at each energy level. The sum $\sum P(E_v)$ is obtained by counting the number of quantum states up to and including energy E .

For $E/h\nu = 0$ to 0.9 there is one state $\nu = 0$

For $E/h\nu = 0.9$ to 1.9 the total is two, $\nu = 0$ and $\nu = 1$.

$\sum P(E_v)$ is a stepwise function having a constant value throughout the energy range between any two of the quantized energy levels (Figure 3.3).

3.5.2 Density of Quantum States, $N(E)$

The density of quantum states or the number of quantum states per unit energy is the gradient of the plot of $\sum P(E_v)$ against E_v .

$$N(E) = \lim_{\delta E \rightarrow 0} \left(\frac{W(E + \delta E) - W(E)}{\delta E} \right) \quad (3.45)$$

$$= \frac{d}{dE} W(E) = \frac{d}{dE} \sum_{E_v=0}^E P(E_v) \quad (3.46)$$

3.5.3 Separation of Vibrational and Rotational Degrees of Freedom

The total number of vibrational-rotational states corresponding to a given vibrational level of energy E_v is the number of $P(E_v)$ of vibrational states of this energy multiplied by the number of possible

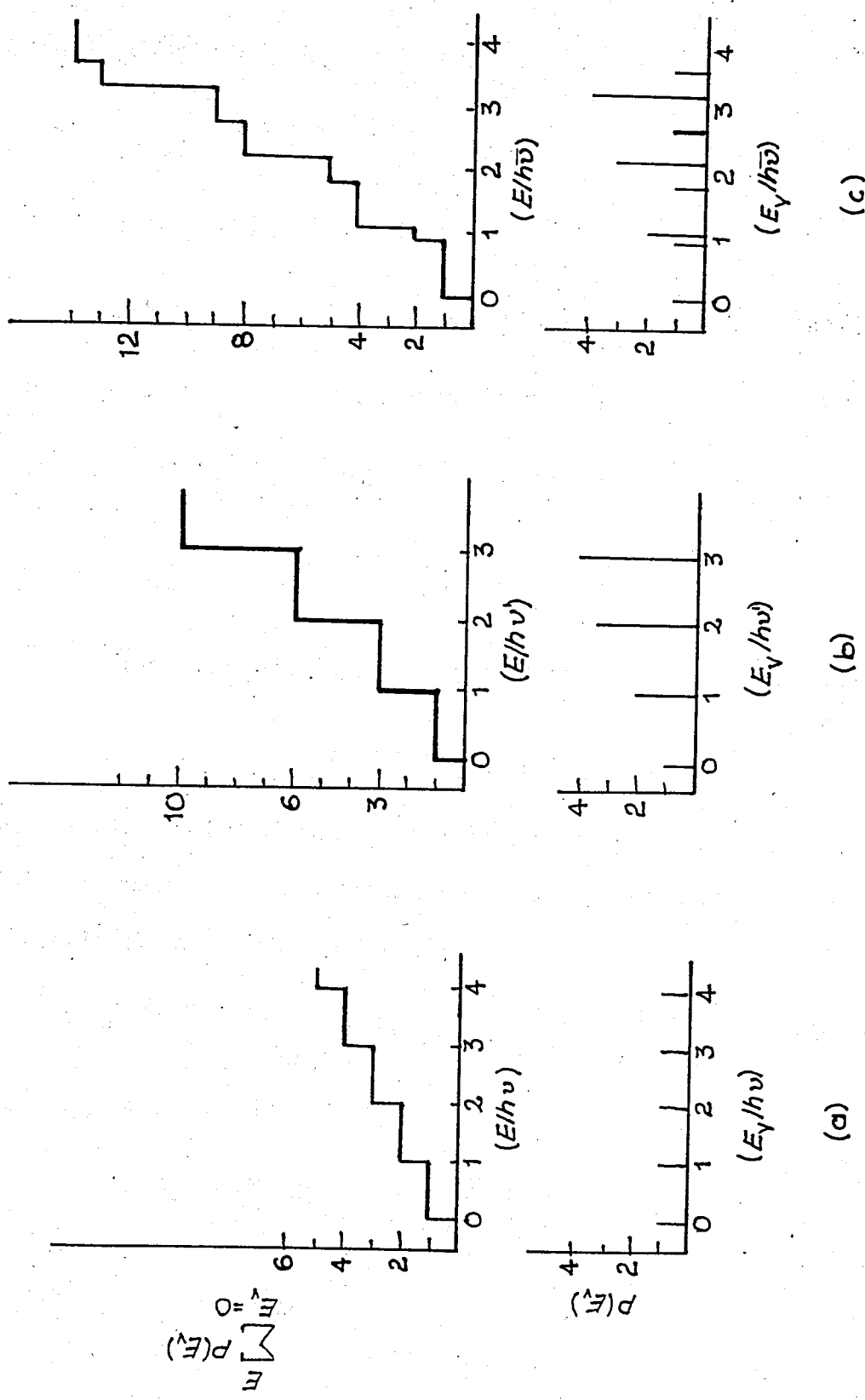


Figure 3.3 - Distribution of vibrational quantum states for (a) a single oscillator of frequency ν , (b) a doubly degenerate oscillator of frequency ν' , and (c) a system of three oscillators comprising (a) and (b).

rotational states with energy $E_r \leq E_{vr} - E_v$ denoted by

$$\sum_{E_r=0}^{E_{vr}-E_v} P(E_r) \equiv W_r(E_{vr} - E_v) \quad (3.47)$$

The total number of states is given by

$$W(E_{vr}) = \sum_{E_v=0}^{E_{vr}} P(E_v) W_r(E_{vr} - E_v) \quad (3.48)$$

The density of vibrational rotational states is

$$N(E_{vr}) = \sum_{E_v=0}^{E_{vr}} P(E_v) N_r(E_{vr} - E_v) \quad (3.49)$$

$$N(E_{vr}) = \int_{E_v=0}^{E_{vr}} N_v(E_v) N_r(E_{vr} - E_v) dE_v \quad (3.50)$$

For classical rotations the sum of states is given by (3.51)

$$W(E_r) \equiv \sum_{E_r=0}^{\infty} P(E_r) = \frac{Q_r}{\Gamma(1 + \frac{r}{2})} \left(\frac{E_r}{kT}\right)^{\frac{1}{2}r} \quad (3.51)$$

where $r = \sum_{i=1}^p d_i$. r is the sum of degeneracies of p rotors. In this equation $\Gamma(x)$ is the gamma function, properties of which are discussed in Appendix 1.

The rotational partition function is

$$Q_r = \left(\frac{8\pi^2 kT}{h^2}\right)^{\frac{1}{2}r} \prod_{i=1}^p \{I_i^{\frac{1}{2}d_i} \Gamma(\frac{1}{2}d_i)\} \equiv \prod_{i=1}^p \left(\frac{8\pi^2 I_i kT}{h^2}\right)^{\frac{1}{2}d_i} \Gamma(\frac{1}{2}d_i) \quad (3.52)$$

The density of states is

$$N(E_r) = \frac{d}{dE_r} W(E_r) = \frac{Q_r}{(kT)^{\frac{1}{2}r} \Gamma(\frac{1}{2}r)} E_r^{\frac{1}{2}r-1} \quad (3.53)$$

since $\Gamma(1 + \frac{1}{2}r) = \frac{1}{2}r \Gamma(\frac{1}{2}r)$.

The results for the RRKM theory are obtained by substitution of equations (3.53) and (3.51) into (3.50) and (3.48).

$$N^*(E^*) = \frac{Q_r^*}{(kT)^{\frac{1}{2}r} \Gamma(\frac{1}{2}r)} \int_{E_V^*=0}^{E^*} (E^* - E_V^*)^{\frac{1}{2}r-1} N_V^*(E_V^*) dE_V^* \quad (3.54)$$

$$\sum_{E_{VR}^+=0}^{E^+} P(E_{VR}^+) = \frac{Q_r^+}{(kT)^{\frac{1}{2}r^*} \Gamma(1 + \frac{1}{2}r^*)} \sum_{E_V^+=0}^{E^+} [(E^+ - E_V^+)^{\frac{1}{2}r^*} P(E_V^+)] \quad (3.55)$$

The expression for k_{uni} assuming classical active rotations is obtained by substituting (3.54) and (3.55) in (3.21).

$$k_{uni} = \frac{L^{\ddagger} Q_1^{\ddagger} Q_r^{\ddagger} \exp(-E_0/kT)}{h Q_1 Q_2 (kT)^{\frac{1}{2}r^*} \Gamma(1 + \frac{1}{2}r^*)} \int_{E^+=0}^{\infty} \frac{\sum_{E_V^+=0}^{E^+} (E^+ - E_V^+)^{\frac{1}{2}r^*} P(E_V^+) \exp(-E^+/kT) dE^+}{1 + k_a(E_0 + E^+)/k_2[M]} \quad (3.56)$$

$$k_a(E_0 + E^+) = L^{\ddagger} \frac{Q_1^{\ddagger}}{Q_1} \frac{Q_r^{\ddagger}}{(kT)^{\frac{1}{2}r^*} \Gamma(1 + \frac{1}{2}r^*)} \frac{\sum_{E_V^+=0}^{E^+} (E^+ - E_V^+)^{\frac{1}{2}r^*} P(E_V^+)}{h N^*(E_0 + E^+)} \quad (3.57)$$

3.5.4 Direct Count of Vibrational States

3.5.4.1 The Method

The working is done in two stages. The first stage is a listing of all possible combination of quantum numbers for which the total vibrational energy is below the required energy limit. The second table is constructed in which the given energy range is split up into as many small increments as required.

In general, the number of ways of distributing j quanta in p oscillators is given by the permutation theory as $(j+p-1)!/j!(p-1)! [49]$.

Even with a fast computer, the direct count is very time consuming and expensive at high energies.

3.5.4.2 Grouped-Frequency Models [50]

For large molecules, the vibration frequencies can be grouped into five or six groups of degenerate vibrations, chosen such that the geometric mean of all the frequencies is not changed. The use of five or seven groups of vibrations give results close to those calculated from the actual molecular vibration frequencies.

3.5.4.3 Commensurable Frequency Models [51]

In this method all frequencies are multiples of the lowest frequency. All the energy levels of the molecule are multiples of the energy corresponding to the lowest frequency and the number of states is worked out by inspection. Then the number of states corresponding to each combination can be evaluated from the combinatorial expression.

3.5.5 Approximate Calculations

3.5.5.1 Classical Approximation [52]

The molecule is treated as a set of classical harmonic oscillators. In this approximation s quantum oscillators of frequency ν_i ($i = 1$ to s) give rise to the following sum of states

$$W(E_V) \equiv \sum_{E_V=0}^{E_V} P(E_V) \approx \frac{E_V^S}{s! \prod_{i=1}^s h\nu_i} \quad (3.58)$$

The density of quantum states is obtained by differentiation

$$N(E_V) = \frac{d}{dE_V} \Sigma P(E_V) = \frac{E_V^{s-1}}{(s-1)! \prod_{i=1}^s h\nu_i} \quad (3.59)$$

The classical approximation is poor at low energies, the results are more reliable at high energies.

3.5.5.2 Semi Classical Approximation [16]

The classical expressions (3.58) and (3.59) were modified by Marcus and Rice to give semiclassical expressions (3.60) and (3.61)

$$W(E_V) \equiv \sum_{E_V=0}^{E_V} P(E_V) = \frac{(E_V + E_Z)^s}{s! \prod_{i=1}^s h\nu_i} \quad (3.60)$$

$$N(E_V) = \frac{(E_V + E_Z)^{s-1}}{(s-1)! \prod_{i=1}^s h\nu_i} \quad (3.61)$$

where

$$E_Z = \sum_{i=1}^s \left(\frac{1}{2} h\nu_i \right) \quad (3.62)$$

This approach gives a better approximation than the classical expressions (3.58) and (3.59), however the number of states at any level is over-estimated.

3.5.5.3 The Whitten-Rabinovitch Approximation [50]

The energy levels in RRKM calculations are too low to admit classical or semiclassical approximations, but are high enough so that the direct sum is difficult. Rabinovitch and Diesen [53] suggested that

an appropriate fraction of the zero point energy should be added to E_V , they introduced a correction factor a to get the following expressions

$$W(E_V) = \frac{(E_V + aE_Z)^S}{s! \prod_{i=1}^S h\nu_i} \quad (3.63)$$

$$N(E_V) = \frac{(E_V + aE_Z)^{S-1}}{(s-1)! \prod_{i=1}^{S-1} h\nu_i} \quad (3.64)$$

Whitten and Rabinovitch [50] characterized the correction factor a , the dependence on the energy involved, the nature of the molecular frequency pattern concerned (Figure 3.4).

The values increase with increasing energy, approaching unity at high energies. Whitten and Rabinovitch have defined a frequency dispersion parameter β

$$\beta = \frac{s-1}{s} \times \frac{\langle \nu^2 \rangle}{\langle \nu \rangle^2} \quad (3.65)$$

where $\langle \nu \rangle$ is the mean frequency and $\langle \nu^2 \rangle$ is the mean square frequency of the molecule. The value of β vary from unity for molecules with similar frequencies to two for molecules with different frequencies.

$$w(E') = \frac{1-a}{\beta} = \frac{\Delta}{\beta} \quad (3.66)$$

$w(E')$ is a function of E' and is described by the equations (3.67) and (3.68)

$$0.1 < E' < 1.0 \quad w = (5.00E' + 2.73E'^{0.5} + 3.51)^{-1} \quad (3.67)$$

$$1.0 < E' < 8.0 \quad w = \exp(-2.419 E'^{0.25}) \quad (3.68)$$

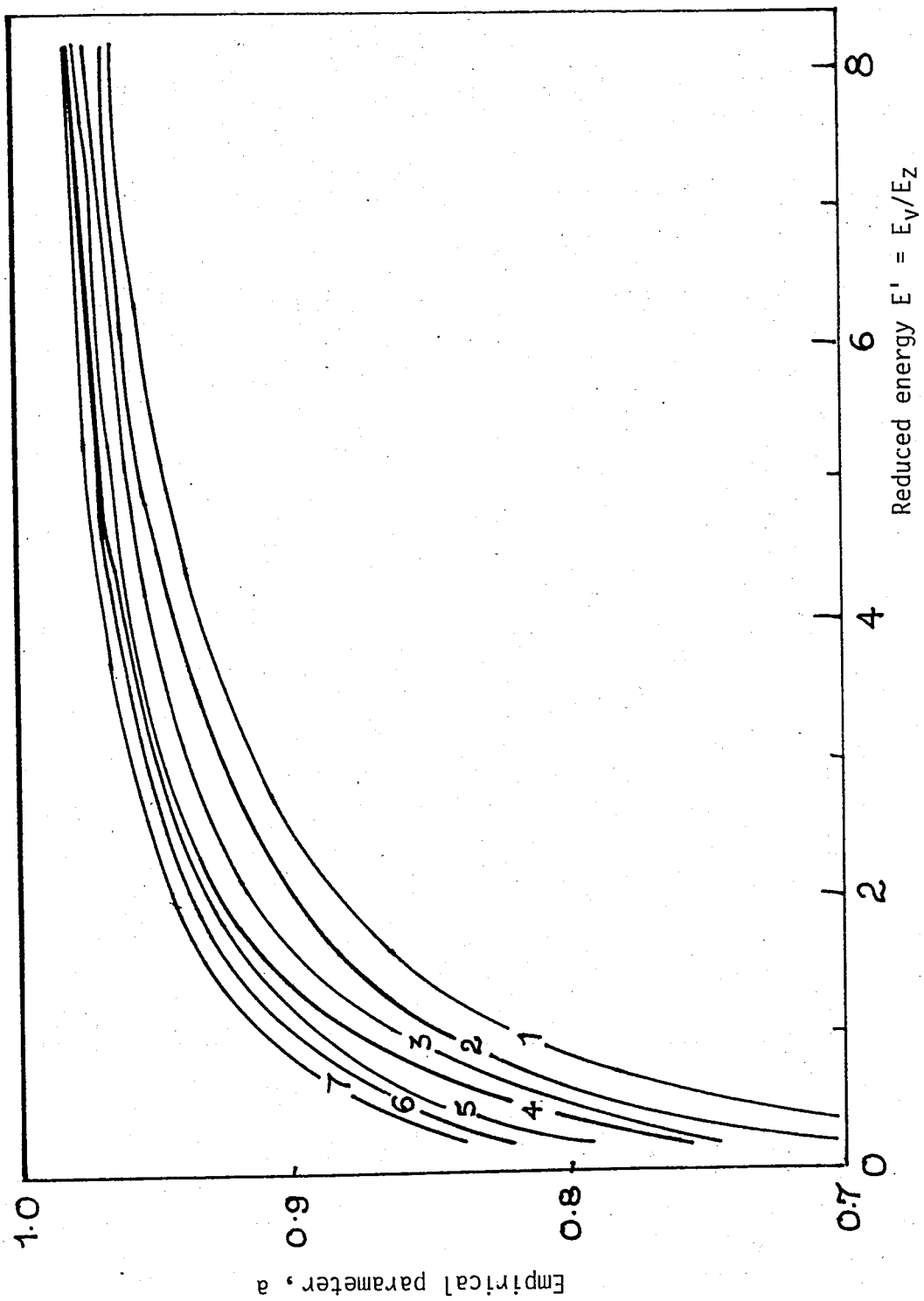


Figure 3.4 - Values of a for various molecules at various energies.

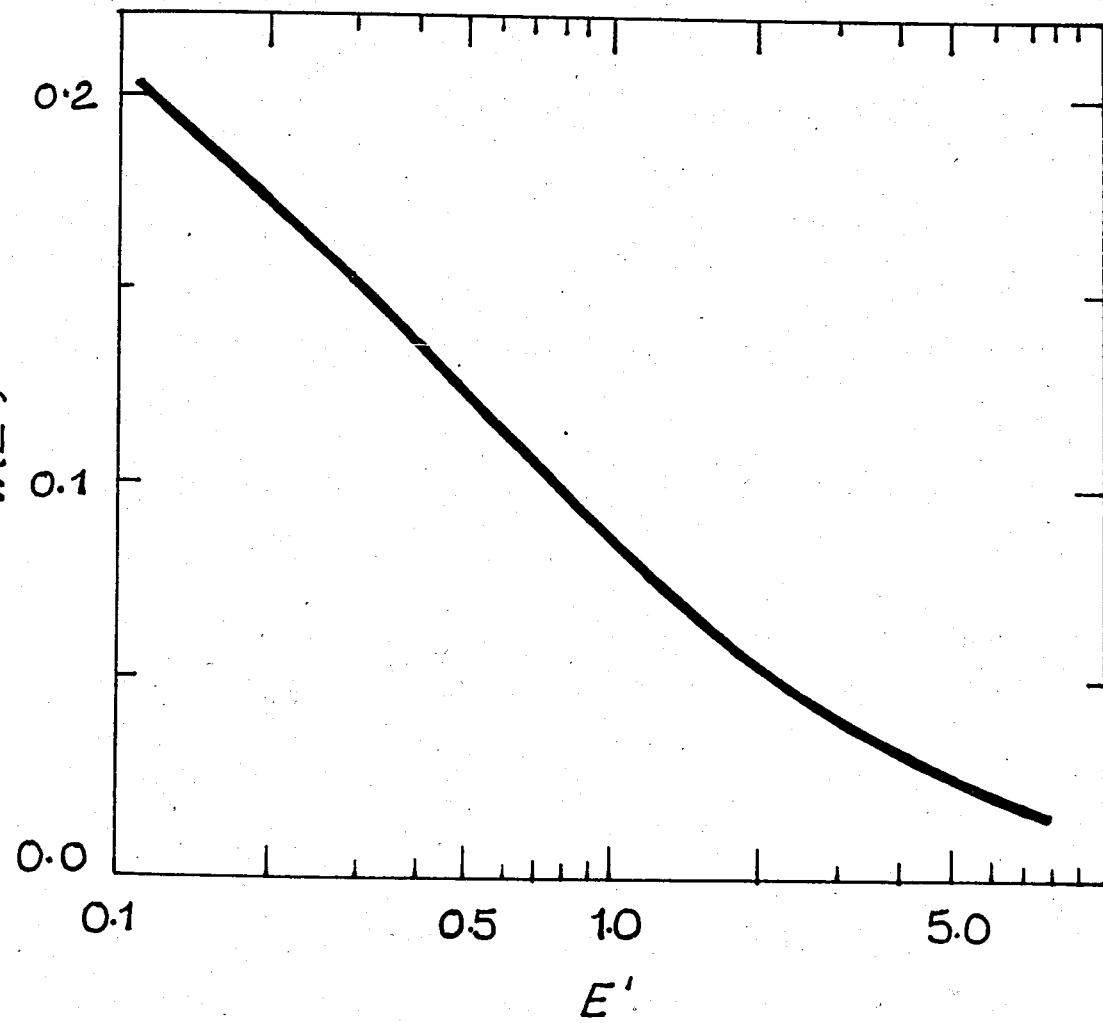


Figure 3.5 - The function $w(E')$.

The modified approximation expression is

$$\sum_{E_V=0}^E P(E_V) = [E_V + (1 - \beta w)E_Z]^S / \Gamma(s + 1) \prod_{i=1}^s h\nu_i \quad (3.69)$$

The density $N(E_V)$ is then

$$N(E_V) = \frac{(E_V + aE_Z)^{s-1}}{(s-1)! \prod h\nu_i} \left[1 - \beta \left(\frac{dw}{dE'} \right) \right] \quad (3.70)$$

where dw/dE' is given by

$$0.1 < E' < 1.0 \quad \frac{dw}{dE'} = -(5.00 + 1.365E'^{-0.5})w^2 \quad (3.71)$$

$$1.0 < E' < 8.0 \quad \frac{dw}{dE'} = -(0.60478E'^{-0.75})w \quad (3.72)$$

The different problems encountered while using this approximation are the following:

1. For simple molecules the error is small because of relatively small values of s
2. For big molecules, the large value of s can cause large errors
3. The calculation in the region $0 < E' < 0.25$ requires further consideration.

The Whitten-Rabinovitch approximation is simple and easy to apply.

Its accuracy is good and compares with those of other approaches.

3.5.5.4 Whitten-Rabinovitch Treatment of Vibrational - Rotational

Spectra

When there are active rotations to be taken into account, Whitten and Rabinovitch have suggested (3.74), in which $a = 1 - \beta w(E_{vr}/E_z)$ and β now becomes

$$\beta = \frac{s-1}{s} \frac{s+\frac{1}{2}r}{s} \frac{\langle v^2 \rangle}{\langle v \rangle^2} \quad (3.73)$$

$$W(E_{vr}) \equiv \sum_{E_{vr}=0}^{E_{vr}} P(E_{vr}) = \frac{Q_r}{(kT)^{\frac{1}{2}r} \Gamma(1+s+\frac{1}{2}r) \prod_{i=1}^s h\nu_i} (E_{vr} + aE_z)^{s+\frac{1}{2}r} \quad (3.74)$$

where $r = \sum_{i=1}^p d_i$.

The density of vibrational-rotational states is obtained by differentiation of (3.74)

$$N(E_{vr}) = \frac{Q_r (E_{vr} + aE_z)^{s+\frac{1}{2}r-1}}{(kT)^{\frac{1}{2}r} \Gamma(s+\frac{1}{2}r) \prod_{i=1}^s h\nu_i} \left[1 - \beta \left(\frac{dw}{dE'} \right) \right] \quad (3.75)$$

Forst and Prasil found a modified version of (3.75) which is also satisfactory [54].

3.5.6 Inverse Laplace Transformation of the Partition Function

This treatment is based on the observation that the partition function Q for any system can be considered as the Laplace transform of the energy level density $N(E)$.

$$Q(\beta) = L\{N(E)\} = \int_0^{\infty} N(E) \exp(-\beta E) dE \quad (3.76)$$

where $\beta = 1/kT$

so

$$N(E) = L^{-1}\{Q(\beta)\} \quad (3.77)$$

$$W(E) = \sum_{E_n=0}^E P(E_n) = L^{-1}\{Q(\beta)/\beta\} \quad (3.78)$$

3.5.6.1 Direct Inversion of an Approximate Partition Function

Haarhoff [55] applied this technique in 1963. The partition function for the system is given by the following expression

$$Q(\beta) = \prod_{i=1}^s \left\{ \frac{\exp(-\frac{1}{2}h\nu_i)}{1 - \exp(-h\nu_i\beta)} \right\} \quad (3.79)$$

This expression can be expressed as a power series in β .

$$\frac{Q(\beta)}{\beta} = \left(\prod_{i=1}^s h\nu_i \right)^{-1} \left(\frac{1}{\beta^{s+1}} - \frac{a_2}{\beta^{s-1}} + \frac{a_4}{\beta^{s-3}} - \frac{a_6}{\beta^{s-5}} + \dots \right) \quad (3.80)$$

The a_n are constants involving the frequencies ν_i .

$$a_2 = (\langle v^2 \rangle / \langle v \rangle^2) E_z^2 / 6s \quad (3.81)$$

According to the equation

$$L^{-1}(\beta^{-m}) = E^{m-1} / (m-1)! \quad (m = \text{positive integer}) \quad (3.82)$$

one can write

$$\begin{aligned} W(E_V) &= L^{-1}\{Q(\beta)/\beta\} = (\pi h \nu_i)^{-1} \left[\frac{(E_V + E_Z)^s}{s!} - \frac{a_2 (E_V + E_Z)^{s-2}}{(s-2)!} + \dots \right] \\ &= \frac{(E_V + E_Z)^s}{s! \pi h \nu_i} \left[1 - \frac{a_2'}{(E_V + E_Z)^2} + \frac{a_4'}{(E_V + E_Z)^4} - \dots \right] \end{aligned} \quad (3.83)$$

There are $\frac{1}{2}s+1$ or $\frac{1}{2}(s+1)$ terms according to whether s is even or odd. The terms represent a smooth curve on which the stepped functions are superimposed.

Haarhoff also derived the equation (3.84) as an approximation to the series expression for the density of states and extended the same treatment to vibrational-rotational systems.

$$N(E_V) = \left(\frac{2}{\pi s}\right)^{\frac{1}{2}} \frac{(1 - 1/12s)\lambda}{h\langle v \rangle(1 + \eta)} [(1 + \frac{1}{2}\eta)(1 + 2/\eta)^{\frac{1}{2}}\eta]^s [1 - 1/(1 + \eta)^2]^{\beta_0} \quad (3.84)$$

where

$$\eta = 1 + E_V/E_Z$$

$$\lambda = \prod_{i=1}^s (\langle v \rangle / v_i)$$

$$\beta_0 = \frac{(s - 1)(s - 2)}{6s} \frac{\langle v^2 \rangle}{\langle v \rangle^2} - \frac{s}{6}$$

Forst [56] and his coworkers have also extended the series treatment to vibrational-rotational systems.

3.5.6.2 Inversion by Complex Integration: Method of Residues [57]

Another method of carrying out the inverse Laplace transformation is by means of the complex integration formula.

$$L^{-1}\{f(\beta)\} = \frac{1}{2\pi i} \int_{\gamma - i_{\infty}}^{\gamma + i_{\infty}} f(\beta) \exp(\beta E) d\beta = \frac{1}{2\pi i} \int_{\gamma - i_{\infty}}^{\gamma + i_{\infty}} \phi(\beta) d\beta \quad (3.85)$$

where β is a complex variable.

The integration can be done by using the method of residues. The integral of a function $\phi(\beta)$ along a line is equal to $2\pi i$ times the sum of

the residues of $\phi(\beta)$ at all its poles.

For $s = 1$ $W(E_V)$ is given by (3.86)

$$W(E_V) = \text{sum of residues at poles of } \frac{\exp(\frac{1}{2}h\nu\beta)\exp[\beta(E_V + E_Z)]}{[1 - \exp(-\beta h\nu)]\beta} \quad (3.86)$$

$\beta = (2\pi n_i/h\nu)$ ($n = 0, \pm 1, \pm 2, \dots$) and substitution of these values gives
(3.87)

$$W(E_V) = \frac{(E_V + E_Z)}{h\nu} + \sum_{n=1}^{\infty} \frac{(-1)^n}{\pi n} \sin\left[\frac{2\pi n(E_V + E_Z)}{h\nu}\right] \quad (3.87)$$

This expression is illustrated in Figure 3.6.

3.5.6.3 Evaluation of Complex Inversion by Method of Steepest Descent [58]

The energy level density $N(E)$ is given by (3.87) in which β^* is the value of β which satisfies (3.89)

$$N(E) \approx Q(\beta^*) \exp(\beta^* E) [2\pi(\partial^2 \ln Q / \partial \beta^2)_{\beta=\beta^*}]^{-1/2} \quad (3.88)$$

where

$$(\partial \ln Q / \partial \beta)_{\beta=\beta^*} = -E \quad (3.89)$$

$W(E)$ may be obtained by integration of $N(E)$. But in the first order approximation it is given more simply by:

$$W(E) \approx N(E) / \beta^* \quad (3.90)$$

For a system of s quantized harmonic oscillators with frequencies ν_i , the partition function is given by:

$$Q(\beta) = \prod_{i=1}^s \left\{ \frac{\exp(\frac{1}{2}h\nu_i)}{1 - \exp(-h\nu_i\beta)} \right\} \quad (3.91)$$

$$\frac{\partial \ln Q}{\partial \beta} = \sum_{i=1}^s \left[\frac{1}{2}h\nu_i - \frac{h\nu_i}{\exp(h\nu_i\beta) - 1} \right] \quad (3.92)$$

$$\frac{\partial^2 \ln Q}{\partial \beta^2} = \sum_{i=1}^s \frac{(h\nu_i)^2 \exp(h\nu_i\beta)}{[\exp(h\nu_i\beta) - 1]^2} \quad (3.93)$$

$$N(E_V) = Q(\beta^*) \exp[\beta^*(E_V + E_Z)] \left\{ 2 \prod_{i=1}^s \frac{(h\nu_i)^2 \exp(h\nu_i\beta^*)}{[\exp(h\nu_i\beta^*) - 1]^2} \right\}^{-1/2} \quad (3.94)$$

$$\sum_{i=1}^s \frac{h\nu_i}{\exp(h\nu_i\beta^*) - 1} = E_V - \sum_{i=1}^s \frac{1}{2}h\nu_i \quad (3.95)$$

The method has been applied to harmonic oscillators [59], to vibrational-rotational systems and to anharmonic oscillators [60]. A generalization of the method as seen in Eqs. (3.88) to (3.95) has been developed by Forst and Prasil [54,61] and by Hoare and Ruijgrok [62,63].

3.5.7 Comparisons

In the case of a small molecule (5-7 vibrations) and a medium sized molecule (15-21 vibrations) good results are obtained by the methods of Haarhoff [32], Whitten and Rabinovitch [27], by the inverse transformation as a series [33,34] and by the generalized steepest descent method [38,39,40]. The expressions of Wahrhaftig [29] and coworkers are less accurate. The Whitten-Rabinovitch expressions [27] are the simplest to program and use the least computer time. The steepest descent method is simple to program but requires more computer time.

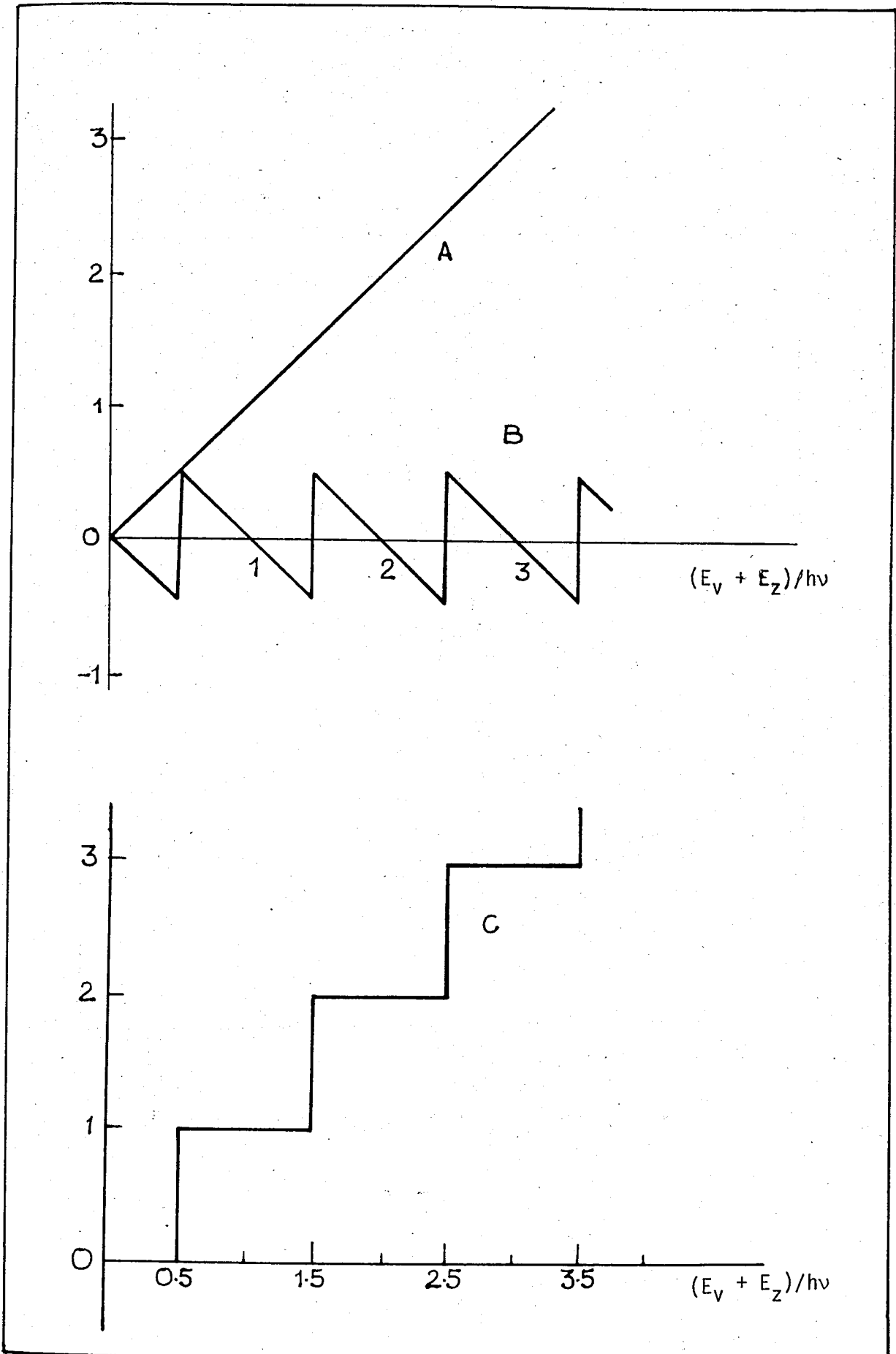


Figure 3.6 - Illustration of equation (3.87).

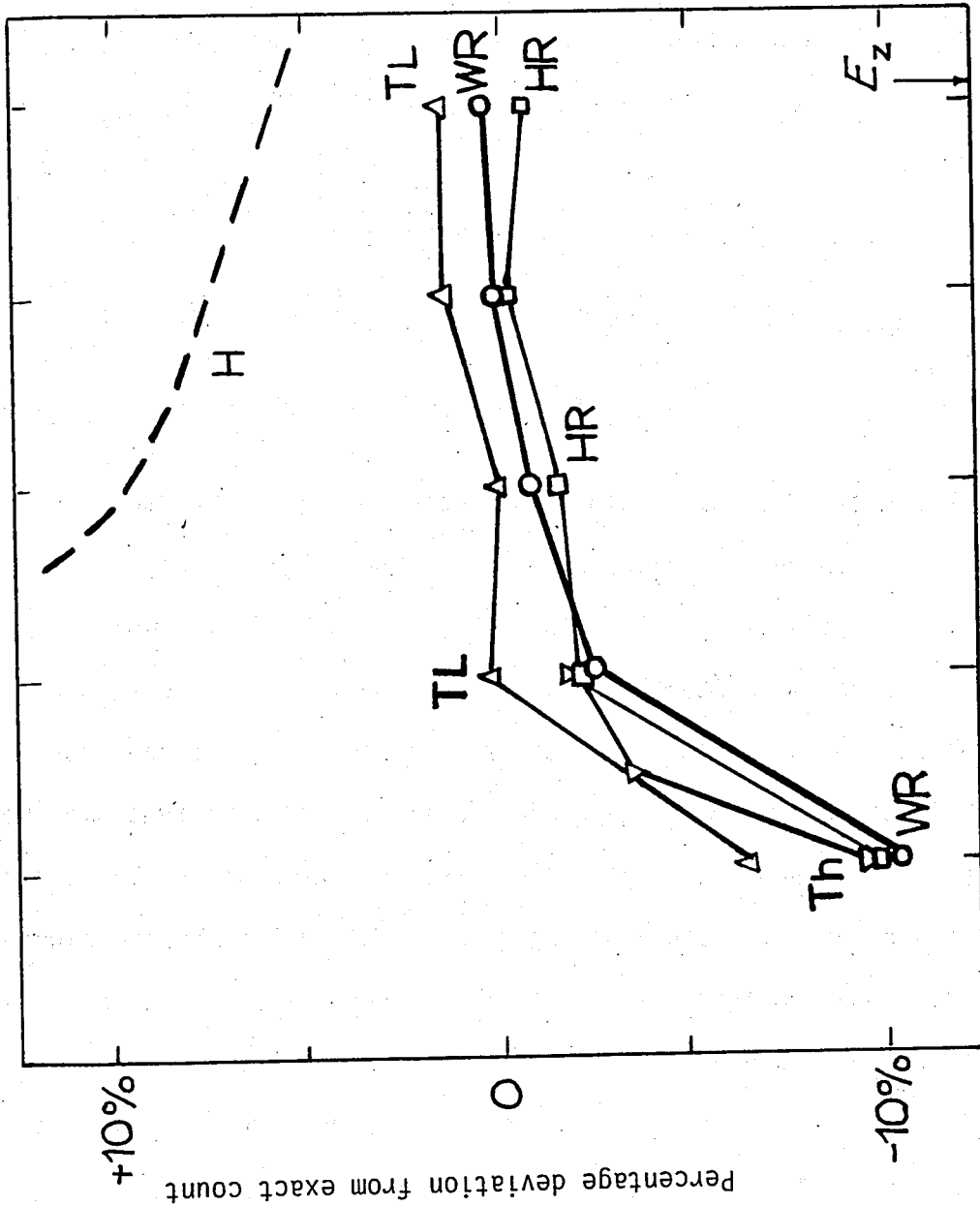


Figure 3.7 - Percentage deviation from exact count [64] $W(E_v)$ for cyclopropane [3221(6), 1478(3), 1118(7), 879(3), 750(2) cm⁻¹] WR = Whitten-Rabinovitch expression [18]; TL = Tou and Lin steepest descent [60]; HR = Hoare and Ruijgrok steepest descent [62]; H = Haarhoff's five term series [65].

The Whitten-Rabinovitch treatment is preferable, being checked by exact count data if the energies of interest are very low. The steepest-descent method offers the greatest scope for development of models containing anharmonic vibrations and hindered or non rigid rotations.

3.6 ASSUMPTIONS OF THE RRKM THEORY [18]

There are five fundamental assumptions of the RRKM theory [18].

3.6.1 Free Exchange of Energy Between Oscillators

If we consider the phase space of the energized molecule A^* , for each point in it, there are uniquely determined paths representing the past and the future of the dynamical state of the molecule [66]. The paths lie on a hypersurface of constant energy and angular momentum. The RRKM theory assumes that the phase-space of the molecules cannot be subdivided into smaller regions. If the phase-space were decomposable, not all states of the same energy would be freely interchangeable. Figure 3.8 represents schematically the phase-space for a dissociating polyatomic molecule. Thus the non-fixed energy of the active vibrations and rotations redistributes itself rapidly. The energetic molecule is converted into products or deactivated by collision.

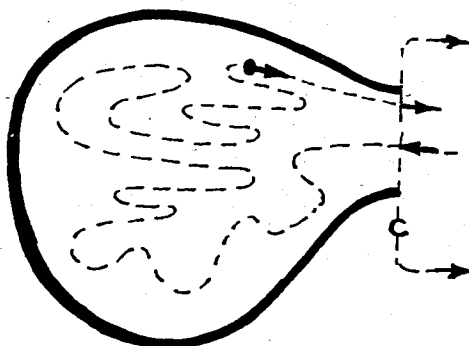


Figure 3.8 - Schematic representation of the phase space for a dissociating polyatomic molecule [66].

3.6.2 Strong Collisions

This assumption means that the states of the molecule before and after the collision are totally unrelated and relatively large amounts of energy ($\gg kT$) are transferred in collisions. The processes of activation and deactivation are treated as single-step processes. In thermal unimolecular reactions the reacting molecules have average energies which are less than $10 \text{ kcal mole}^{-1}$ above the critical energy. Many colliding molecules are able to remove this amount of energy on a single collision, so that this assumption will often be a good approximation. On the other hand, in chemically activated reactions, energized molecules may be formed with much higher excess energies and this assumption is more likely to collapse. For this latter case the reaction is considered from each energy level, together with all the collisional processes which transfer molecules from one energy level to another.

3.6.3 The Equilibrium Hypothesis

This assumption sustains that the concentration of the complexes crossing forward is the same in the steady-state as it would be at total equilibrium where no net reaction occurs.

3.6.4 Random Lifetimes

This assumption means that the process $A^* \rightarrow A^+$ is governed by statistical considerations and there is no tendency for all A^* to decompose after their formation or to exist for some length of time before decomposing.

The lifetime τ associated with a phase point is the time before it reaches the boundary C in the absence of collisions (Figure 3.8). The gap length t is the total time interval between boundary crossings. Molecules with a particular energy have a random distribution.

$$P(\tau) = k_a \exp(-k_a \tau) \quad \text{or} \quad P(t) = k_a \exp(-k_a t) \quad (3.96)$$

This equation means that the probability of any phase point reaching the boundary is uniform for any equal time interval. If the lifetime distributions are not random, then the passage of A^* to A^+ is no longer the rate determining step for dissociation. Instead some slow redistribution of energy within the species A^* , in the absence of collisions, may become rate determining. The RRKM theory, in assuming rapid intramolecular energy transfer, assumes implicitly the notion of random lifetime.

Theoretical [67,68] and experimental evidence has indicated that the random lifetime assumption may not always be true, especially for some

diatomic or triatomic molecules or for cases where E_0/kT is very low.

3.6.5 Continuous Distribution Function $N^*(E^*)$

The energized molecule is treated in terms of a continuously variable energy. A different treatment would be required for the case where the energy levels of A were separated.

3.7 ON NON- RRKM UNIMOLECULAR KINETICS [70-72]

As mentioned before the main assumption of RRKM theory is that activated molecules behave as if all their accessible states are occupied in random order (Figure 3.9a)

$$P(\tau) = k_a \exp(-k_a \tau)$$

For thermal reactions the most usual procedure is the detailed strong collision assumption which says that after an activating collision any energy is likely in proportion to its equilibrium probability and that the states at that energy are all equally probable (Figures 3.9a and 3.9b).

In experiments based on chemical activation detailed strong collision conditions are intentionally avoided. The RRKM assumption would render the pattern of initial energization equivalent to a random one in a negligibly short time as shown in Figure 3.9d. The initial energy distribution of the energized molecules is quite different between thermal reactions and chemical activation. Figure 3.10 is a diagram of the two types of distributions, where $E^* - E_0$ signifies energy in excess of the

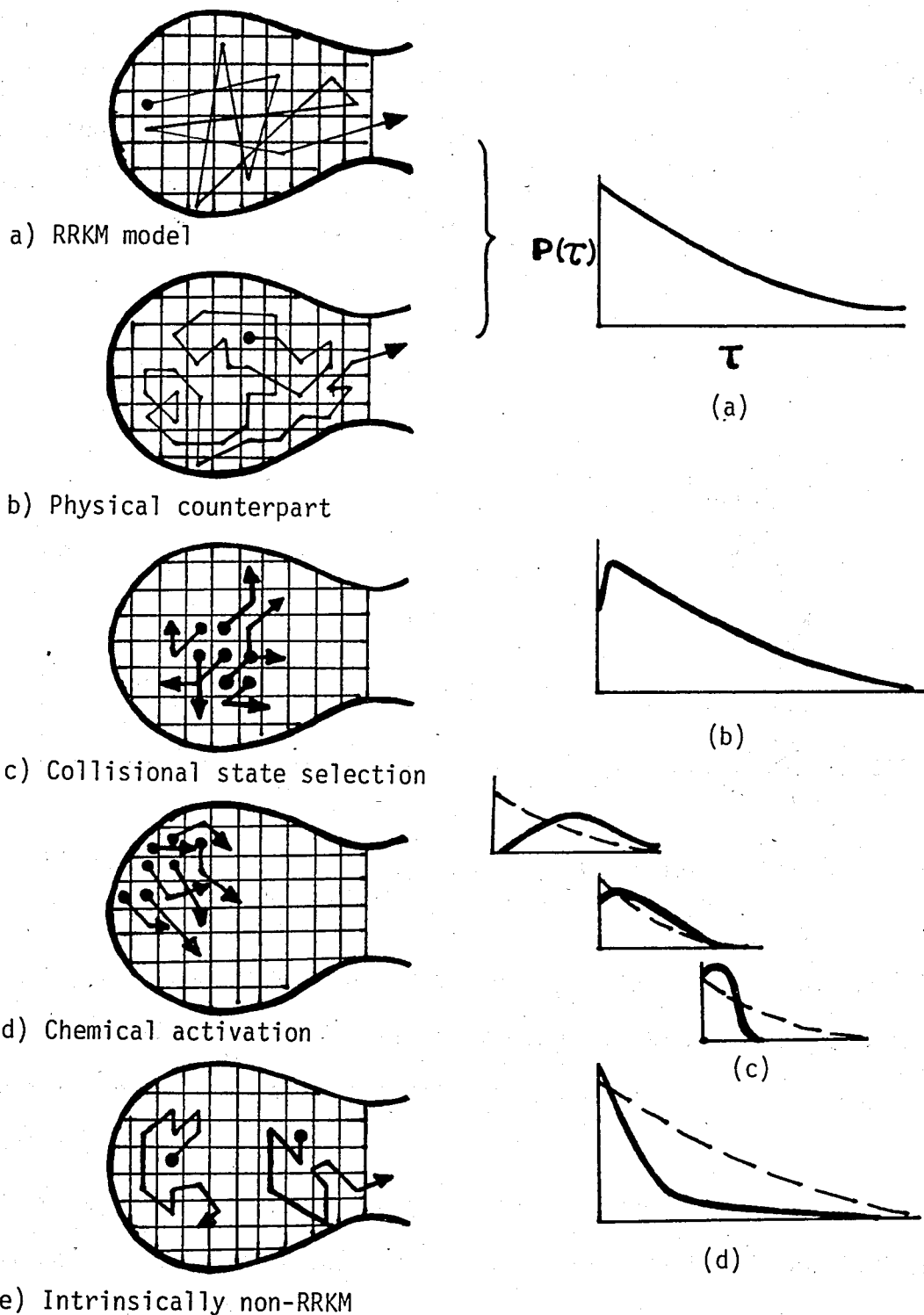


Figure 3.9 - Relation of state occupation (schematically shown at constant energy) to lifetime distribution for the RRKM theory and for various actual situations. Dashed lines in lifetime distributions indicate RRKM behaviour.

critical energy E_0 . The thermal experiment creates a broad distribution of energized molecular species. In contrast, a rather narrow band of initial energies is created using chemical activation.

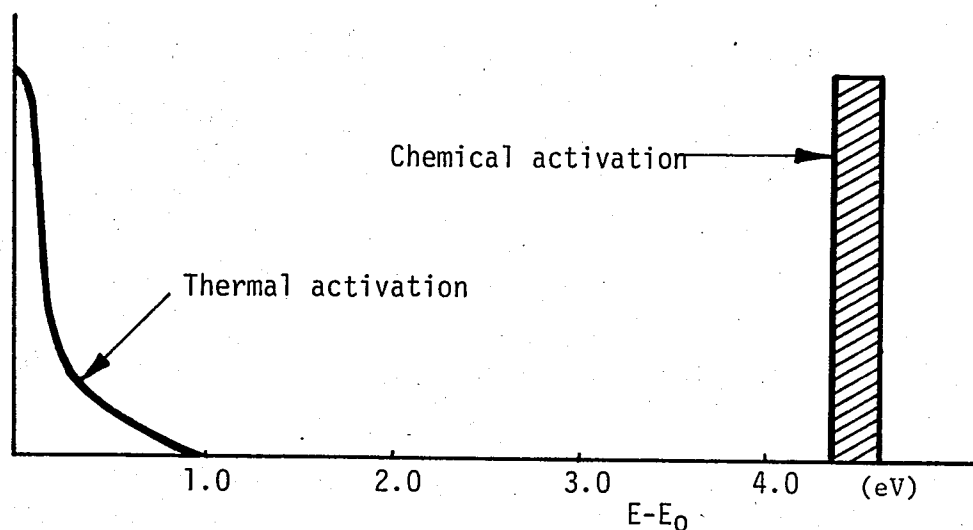


Figure 3.10 - Comparison of energized molecular distributions for thermal and chemical activation.

Apparent non-RRKM behaviour arises from state selection. Deposition of the energy in favorable or unfavorable locations in the molecule may depress or enhance the probability of a short lifetime with respect to reaction.

Another possibility is an intrinsically non-RRKM molecule. If transitions between two or more groups of states were less probable than those leading to products, this could arise. Even if the detailed strong collision assumption were exactly true, $P(\tau)$ would be non random.

The possible ways in which reaction rates might be found to depend on the frequency of molecular collisions are the following:

1. No significant deviations from the RRKM assumption under the experimental conditions 3.9b, 3.9c and the middle point $P(\tau)$ of 3.9d.
2. Apparent non-RRKM features arising only from state selection—the $P(\tau)$ of 3.9d.
3. Intrinsically non-RRKM.
4. Both (2) and (3).

The probability that a molecule avoids a collision for τ seconds is

$$\omega(\tau) = \exp(-k_2[M]\tau) \quad (3.97)$$

in which k_2 is a bimolecular rate constant for deactivation of reactant molecules by any collider M.

The rate of collisional preparation is $k_1[M]$. The overall rate for a particular energy is then:

$$k_{\text{uni}} = k_1[M] \int_0^{\infty} \omega(\tau)P(\tau)d\tau \quad (3.98)$$

For RRKM kinetics, substitution of Eqs. (3.96) and (3.97) in (3.98) yields the form

$$k_{\text{uni}} = \frac{k_1[M]}{1 + k_2[M]/k_a} \quad (3.99)$$

The RRKM theory is a mathematical idealization and does not correspond to any actual molecular mechanics. In the case of non-RRKM features arising from state selection, this is a matter of degree not of kind. A molecule may be free of non-RRKM character. If we know the molecule's critical configuration the RRKM statistical procedures will give k_a correctly; if we have to guess the critical configuration, unreasonable guesses will not be required. It is difficult in a single experiment to establish non-RRKM kinetics. When the basic RRKM is to be examined, the molecule should be subjected to every feasible tests - thermal studies, chemical activation of all possible kinds, high pressure measurements and any other procedure that seem relevant.

IV. GENERAL THEORETICAL PROCEDURE

To carry out the calculation of k_{uni} as a function of pressure one should set up models of the molecule A and the activated complex A^\ddagger . The parameters needed for A are the vibrations and internal rotations as well as its overall moments of inertia and its collision diameter. These informations can be obtained from experimental measurements or can be estimated by empirical methods. The same data must be specified for the activated complex, but it is not possible to determine it experimentally. The information might be obtained by a solution of the Schrödinger equation for the system. Such calculations not being practicable, empirical methods have to be employed.

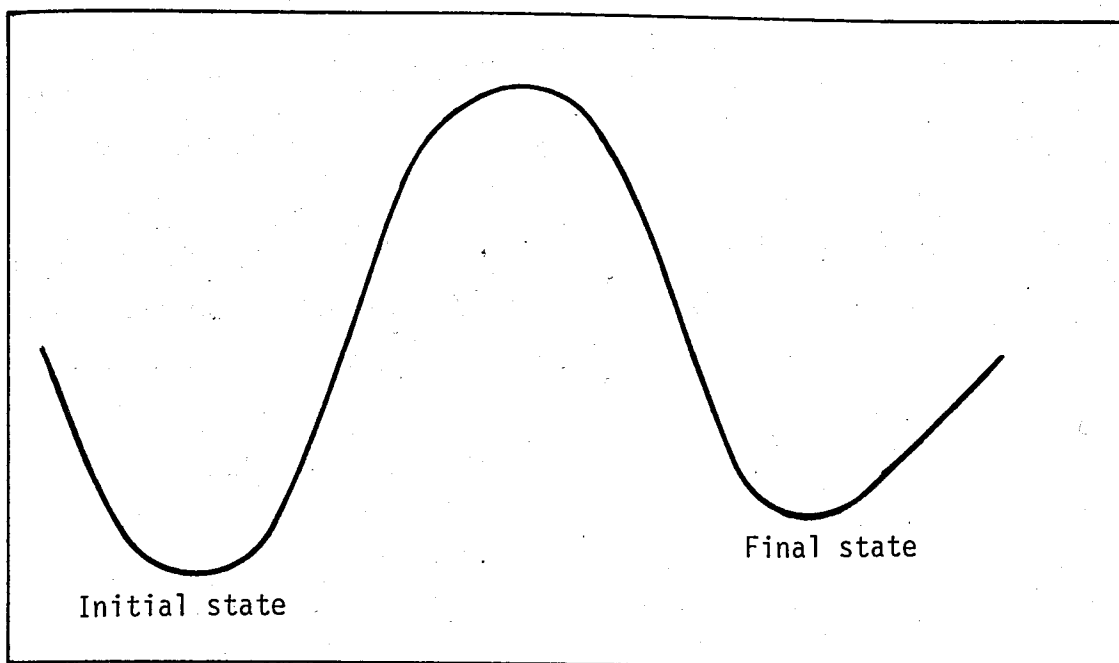
4.1 SELECTION OF A MODEL

In the selection of a model for a reaction the first thing to do is to decide how many rotational degrees of freedom will be included in the models of A and A^\ddagger , and which of these degrees are active. A change in the number of internal rotational degrees of freedom produces a model with a high or low A-factor. The activated complex can be classified as "rigid" or "loose". In a "loose" complex, there is some degree of free internal

rotation which was not present in the reactant molecule. The loose complex is associated with bond-fission reactions. The rigid complex has no internal rotations which were not present in the reactant molecule. The nature of the complex can be determined by examination of the potential curve for the reaction coordinate. If the barrier is high for both the forward and the reverse reaction, as shown in the potential energy profile in Figure 4.1a, there are relatively strong chemical interactions in the transition region. This type of barrier occurs when there is considerable activation energy for both the forward and reverse reaction. Figure 4.1b shows a potential energy profile of a reaction path in which the energy of activation of the reverse reaction is close to zero, as in the dissociation of ethane and fluoroethanes to form two methyl or fluoromethyl radicals. Here the forces at the peak of the barrier may be weak enough to permit the rotational motions of a loose complex.

After a structure has been proposed for the activated complex, values must be assigned to the vibration frequencies and moments of inertia of the complex. This could be done accurately if the geometry of the complex was known and if a complete set of force constants for the complex could be constructed. It is difficult to realize these aims in practice. Analogous structures in normal molecules and free radicals as well as semi-empirical correlations of bond lengths and force constants with bond order can be considered.

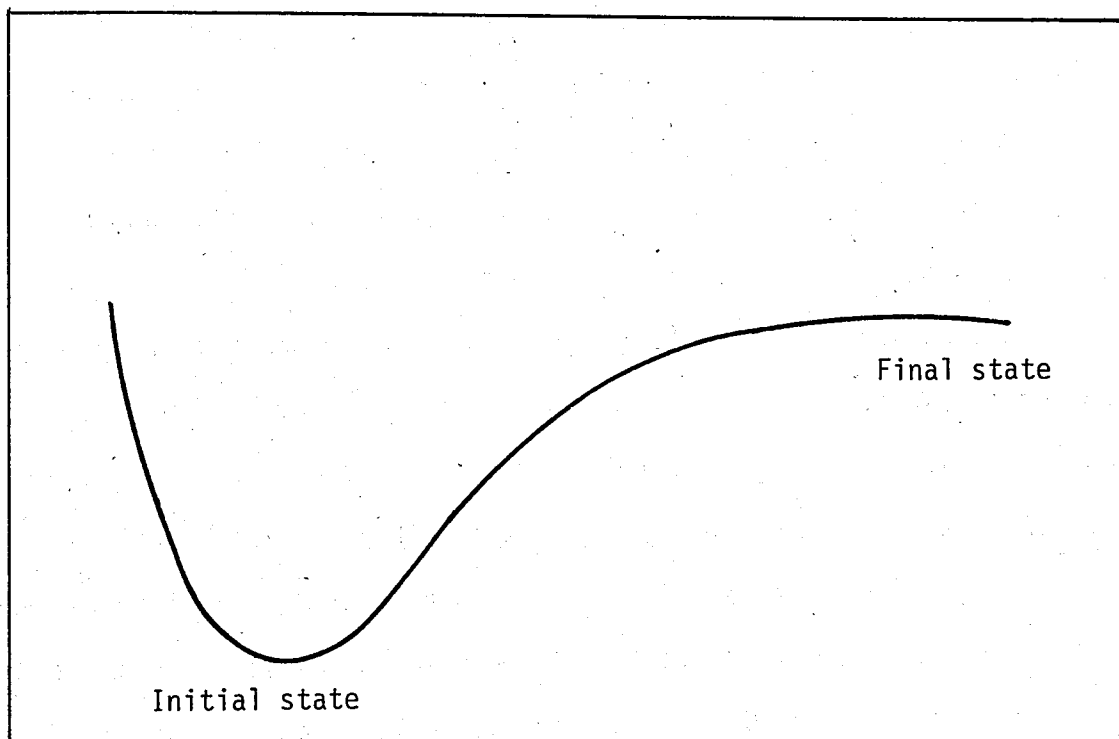
Potential energy



(a)

Reaction coordinate

Potential energy



(b)

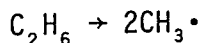
Reaction coordinate

Figure 4.1 - Typical potential energy profiles

- a) Rigid activated complex
- b) Loose activated complex.

4.2 DETERMINATION OF THE LENGTH OF THE CRITICAL BOND

Two procedures have been used for determining the length of the critical bond in the loose activated complex for the dissociation of a molecule into two fragments, e.g.,



4.2.1 The Gorin Model (Model I)

The fragments formed by the dissociation of a molecule are assumed to have the same geometry and vibration frequencies as the free radicals and to have a large degree of rotational freedom. The reaction coordinate is treated by considering the complex as a decomposing diatomic molecule in which the atoms have the masses of the actual fragments. The distance R_c is large enough to make the assumption mentioned above, which is a basic assumption in the Gorin theory [73,74]. It is assumed that the radicals are attracted by a force F_a , due to the intermolecular attractive potential $V_a = -a/R^6$ and this force is opposed by a centrifugal force arising from the rotation of the two radicals about a common center of mass. The centrifugal force is $F_c = M^2/\mu R^3$ where μ is the reduced mass, M is the total angular momentum of the complex equal to $[J(J+1)]^{1/2}\hbar$ and J is the angular momentum quantum number. The activated complex is defined to exist at a critical separation R_c , at which the centrifugal force is equal and opposite to the attractive force $F_a = -6a/R^7$. R_c is given by

$$R_c = [6a\mu/J(J+1)\hbar^2]^{1/4} \quad (4.1)$$

where a is the constant in attractive potential energy expression $V = -a/R^6$. The average value of R_c for dissociating molecules was given by Tschuikow-Roux [75] by (4.2),

$$\langle R_c \rangle_{av} = \frac{\pi^{1/2}}{\Gamma(2/3)} \left(\frac{2a}{kT} \right)^{1/6} \text{erf} \left[\left(\frac{2a}{kT} \right)^{1/2} / R_m^3 \right] \quad (4.2)$$

For practical cases $(2a/kT)^{1/2}/R_m^3 > 2$ so that the error function is equal to unity, hence

$$\langle R_c \rangle_{av} = 1.3092 (2a/kT)^{1/6} \quad (4.3)$$

For reactants having permanent dipole $\bar{\mu}$, polarizability α , and are in thermal equilibrium, the attractive potential is given by [76]

$$\begin{aligned} V_a &= -a/R^6 \\ &= -(a_{es} + a_{ind} + a_{dis})/R^6 \end{aligned} \quad (4.4)$$

where $a_{es} = 2\bar{\mu}_1^2\bar{\mu}_2^2/3kT$ is the electrostatic contribution due to dipole-dipole interaction, $a_{ind} = \alpha_1\mu_2^2 + \alpha_2\mu_1^2$ is the inductive contribution due to dipole induced dipole interaction, a_{dis} is the dispersion contribution due to instantaneous induced dipole moments interaction between R_1 and R_2 . Slater and Kirkwood [77,78] have given an estimation for a_{dis} .

$$a_{dis} = (3/2)(e\hbar/m_e^{1/2})\alpha_1\alpha_2 / [(\alpha_1/N_1)^{1/2} + (\alpha_2/N_2)^{1/2}] \quad (4.5)$$

where e and m_e are the charge and mass of an electron and N is the number of outer shell electrons. The dipole moments for the fluorohydrocarbon radicals are taken as 90% of the values for the corresponding fluorohydrocarbon molecules. Polarizabilities are based on known atom polarizabilities [79].

Thus in this approach the critical configuration is located at the maximum of the potential energy surface separating reactants and products and the average value of the critical bond length is given by (4.3). However when the ratio of the adiabatic rotational partition functions of the activated complex to the molecule Q_1^+/Q_1 is expressed as the ratio of the square of the appropriate distances

$$Q_1^+/Q_1 = \langle\langle r_m^2 \rangle\rangle / r_e^2 \quad (4.6)$$

the square of the apparent distance between the centers of masses $\langle\langle r_m^2 \rangle\rangle$ is used. Waage and Rabinovitch [22] have evaluated $\langle\langle r_m^2 \rangle\rangle$ for a London dispersion force between particles as

$$\langle\langle r_m^2 \rangle\rangle = 1.354(2a/kT)^{1/3} \quad (4.7)$$

4.2.2 The Criterion of Minimum State Density (Model II)

Bunker and Pattengill [41] proposed to ask the RRKM theory to prescribe its own critical value of the reaction coordinate. They required that the critical configuration have a value of the reaction coordinate such that the number of accessible internal states of the molecule is minimized. The proposal is that this "bottleneck" should represent the critical configuration or dividing surface of the RRKM theory. In studies where the potential energy of the reaction coordinate is represented by a Morse function, the criterion of minimum state density gives a value of r^+ at the critical configuration less than the value of r^+ at the rotational barrier [42]. The rotational barrier is located in the product region

and choosing the critical configuration at this point (Gorin model) would give an overestimate of the unimolecular rate. The critical configurations required to fit the experimental rate constants are much "tighter" than those of the Gorin model. The minimum state density criterion can be expressed as

$$\partial N(E^+) / \partial r^+ = 0 \quad (4.8)$$

r^+ is the value of the reaction coordinate where (4.8) is satisfied. The internal energy of the critical configuration E^+ is

$$E^+ = E^* - V(r^+) + E_J(1.0 - I/I^+) \quad (4.9)$$

where E^* is the internal energy of the energized molecule, $V(r^+)$ is the potential energy associated with the reaction coordinate, E_J is the external rotational energy of the energized molecule, and the I 's are the moments of inertia. The internal energy of the energized molecule and critical configuration is the vibrational-internal rotational energy. Equation (4.9) applies to the situation where the unimolecular reaction can be described by the bond rupture of a diatomic molecule. The density $N(E^+)$ can be written as a summation of the product of sum of vibrational-internal rotational states, $P(E^+ - E_t^+)$ times the density of translational states in the reaction coordinate, $N(E_t^+)$,

$$N(E^+) = \sum_{E_t^+=0}^{E^+} P(E^+ - E_t^+) N(E_t^+) ; \quad E_t^+ = 0 \quad (4.10)$$

$$N(E_t^+) = (2\mu\delta^2/h^2 E_t^+)^{1/2} \quad (4.11)$$

E_t^+ is the translational energy associated with the reaction coordinate and μ is the reduced mass of the separating fragments.

If $P(E^+ - E_t^+)$ can be represented by a continuous function, (4.10)

becomes

$$N(E^+) = \int_0^{E^+} N(E^+ - E_t^+) N(E_t^+) dE_t^+ \quad (4.12)$$

where $N(E^+ - E_t^+)$ is the density of vibrational-internal rotational states in the critical configuration. To find an approximation for $N(E^+)$, it is assumed that $N(E^+ - E_t^+)$ can be represented by the vibrational-internal rotational density expression

$$N(E^+ - E_t^+) = \frac{Q_{ir}^+(E^+ - E_t^+)^{s+r^*/2-2}}{\Gamma(s + r^*/2 - 1) \pi h \nu_i^+} \quad (4.13)$$

Q_{ir}^+ is the internal rotational partition function, $s-1$ and r^* are the number of vibrations and internal rotations in the critical configuration, and the ν_i^+ 's are the vibrational frequencies. Combining (4.9)-(4.13) and integrating one gets,

$$N(E^+) \propto \frac{Q_{ir}^+ [E^* - V(r^+) + E_J(1.0 - I/I^+)]^{s+r^*/2-(3/2)}}{\Gamma(s + r^*/2 - 1) \pi h \nu_i^+} \quad (4.14)$$

When a semiempirical correction is made for the zero-point energy of the critical configuration E_Z^+ one gets,

$$N(E^+) \propto \frac{Q_{ir}^+ [E^* - V(r^+) + E_J(1.0 - I/I^+) + a E_Z^+]^{s+r^*/2-(3/2)}}{\Gamma(s + r^*/2 - 1) \pi h \nu_i^+} \quad (4.15)$$

where a is the empirical constant used in the Whitten-Rabinovitch approximation [50].

As shown by (4.15) the position of the critical configuration along r^+ depends on changes in the molecular structure. The terms in (4.15) dependent on the molecular structure are I^+ , the ν_i^+ 's, Q_{ir}^+ , E_z^+ and the number of vibrational frequencies s and internal rotors r^* . In the absence of any structural effects, the minimum state density criterion will depend only on $V(r^+)$ and the critical configuration will be located at the top of the potential energy barrier.

Since in this study only the rate constants for thermal unimolecular reactions will be calculated, the effect of external rotational energy can be approximately accounted for by calculating the difference in average energies between reacting molecules and critical configurations as shown by Marcus [43]. For the thermal situation a very good approximation of the average rotational energy of critical configurations is $\langle E_J^+ \rangle = RT$ [80]. The appropriate expression for $E_J^+ - E_J$ is obtained by noting that the rotational energies of A^* and A^+ in a given level J are related by $E_J/E_J^+ = I^+/I$ whence $E_J^+ - E_J = (1 - I^+/I)\langle E_J^+ \rangle$ and

$$\langle E_J^+ \rangle - \langle E_J \rangle = (1 - I^+/I)RT \quad (4.16)$$

Thus the expression for $N(E^+)$ used in this work is

$$N(E^+) \propto \frac{Q_{ir}^+ [E^* - V(r^+) - RT(1 - I^+/I) + aE_z^+]^{s+r^*/2-(3/2)}}{\Gamma(s + r^*/2 - 1) \pi h \nu_i^+} \quad (4.17)$$

The expression used for external rotations in (4.17) is modified according to the suggestion of Marcus [43] and the proposal of Hase and coworkers [81] as shown in (4.18)

$$N(E^+) \propto \frac{Q_{ir}^+ [E^* - V(r^*) - RT(1 - (\frac{I_{xx}^+ I_{yy}^+ I_{zz}^+}{I_{xx} I_{yy} I_{zz}})^{1/2})] \frac{\ell}{2} + aE_z^+ s + r^*/2 - (3/2)}{\Gamma(s + r^*/2 - 1) \pi h \nu_i^+} \quad (4.18)$$

where ℓ is the number of adiabatic rotational degrees of freedom. This final expression for counting the number of states (4.18) is minimized using the computer program prepared by W. L. Hase and D.L. Bunker [82] with my further modifications (Appendix II).

4.3 CALCULATION OF THE ACTIVATION PARAMETERS

The high pressure A factor is significant, and in fact the Gorin model is chosen so that the calculated A factor agrees with the experimental value. The experimental high pressure Arrhenius parameters are defined by (4.19)

$$A_\infty = k_\infty e^{E_\infty/kT} \quad (4.19)$$

The critical energy E_0 is determined from the limiting high pressure activation energy E_∞ by equating (3.24) to the Arrhenius expression (4.19) and logarithmically differentiating both sides with respect to $(1/RT)$ [28].

$$k_\infty = L^{\ddagger} \frac{kT}{h} \frac{Q_1^+ Q_2^+}{Q_1 Q_2} \exp(-E_0/RT) \quad (3.24)$$

The result is

$$E_0 = E_\infty - \frac{1}{2}(r^* - r + 2)RT + \langle E_V \rangle - \langle E_V^+ \rangle \quad (4.20)$$

where $\langle E_V \rangle$ and $\langle E_V^+ \rangle$ are the mean vibrational energies (above the ground state) of the active molecule and the activated complex.

After the determination of the E_0 parameter from (4.20) it is possible to compute the value of k_∞ from (3.24) and compare this value with the experimentally determined high pressure rate constant.

On the other hand, to test the validity of the model, the entropy of activation obtained from the experimental, high pressure pre-exponential factor (4.21)

$$\Delta S^\ddagger = R[\ln(A_\infty h/kT) - 1] \quad (4.21)$$

can be compared with that calculated from statistical thermodynamics based on the choice of models,

$$\Delta S^\ddagger = S^+ - S \quad (4.22)$$

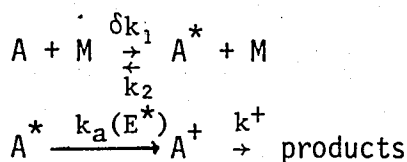
where S^+ and S are, respectively, the entropy of the activated complex and molecule.

There are an infinite number of models reproducing a given set of Arrhenius parameters, thus the Arrhenius parameters don't specify uniquely the model to be used.

4.4 CALCULATION OF THE FALL-OFF PRESSURE

4.4.1 Neglecting Centrifugal Effects

The thermal decomposition of A, as shown in section 3.1, may be represented by



where A^* denotes an active molecule with an energy greater than some critical minimum, and A^+ is the activated complex. M is any colliding molecule capable of deactivating A^* . The detailed form of the fractional rate, k_{uni}/k_∞ , in the pressure dependent region is derived from (2.20) and (3.24).

Equation (3.20)

$$k_{uni} = \frac{L^\ddagger Q_1^+ \exp(-E_0/kT)}{h Q_1 Q_2} \int_{E^+=0}^{\infty} \frac{\left\{ \sum_{E_{vr}^+=0}^{E^+} P(E_{vr}^+) \right\} \exp(-E^+/kT) dE^+}{1 + k_a(E_0 + E^+)/k_2[M]}$$

in which $k_a(E^+ + E_0)$ is given by

$$k_a(E^+ + E_0) = \frac{L^\ddagger Q_1^+}{h Q_1 N^*(E_0 + E^+)} \sum_{E_{vr}^+=0}^{E^+} P(E_{vr}^+)$$

is divided by (3.24), the high pressure rate constant

$$k_\infty = \frac{L^\ddagger Q^+}{Q} \frac{kT}{h} \exp(-E_0/kT)$$

where $Q^+ = Q_1^+ Q_2^+$ and $Q = Q_1 Q_2$.

$$\frac{k_{uni}}{k_\infty} = \frac{1}{kT} \frac{1}{Q_2^+} \int_{E^+=0}^{\infty} \frac{\left\{ \sum_{E_{vr}^+=0}^{E^+} P(E_{vr}^+) \right\} \exp(-E^+/kT) dE^+}{1 + k_a(E_0 + E^+)/k_2[M]} \quad (4.23)$$

where Q_2^+ is the partition function of the active degrees of freedom of the complex A^+ ; E_0 is critical energy; and E^+ is the energy of the active modes of A^+ less the zero point energy E_z^+ . The total sum of the degeneracies of all possible energy eigenstates of the active degrees of freedom of the activated complex at energy E^+ is shown by (3.55)

$$\sum_{E_{vr}^+=0}^{E^+} P(E_{vr}^+) = \frac{Q_r^+}{(kT) r^{*/2} \Gamma(1 + \frac{1}{2}r^*)} \sum_{E_V^+=0}^{E^+} [(E^+ - E_V^+)^{\frac{1}{2}r^*} P(E_V^+)]$$

where Q_r^+ is the rotational partition function of the activated complex and E_V^+ is the energy of the v^{th} vibrational level of A^+ less E_Z^+ . The exact evaluation of $\sum P(E_V^+) (E^+ - E_V^+)^{\frac{1}{2}r^*}$ is impractical. The accurate semi-empirical technique of Whitten and Rabinovitch has been used in these calculations [50].

$$\sum_{E_V^+=0}^{E^+} P(E_V^+) (E^+ - E_V^+)^{\frac{1}{2}r^*} \approx \frac{\Gamma(1 + \frac{1}{2}r^*) (E^+ + a^+ E_Z^+)^{s^+ + (\frac{1}{2})r^*}}{\Gamma(s^+ + 1 + \frac{1}{2}r^*) \prod_{i=1}^{s^+} \nu_i^+} \quad (4.24)$$

Thus

$$\sum_{E_{vr}^+=0}^{E^+} P(E_{vr}^+) = \frac{Q_r^+ (E^+ + a^+ E_Z^+)^{s^+ + \frac{1}{2}r^*}}{(kT) r^{*/2} \Gamma(s^+ + 1 + \frac{1}{2}r^*) \prod_{i=1}^{s^+} \nu_i^+} \quad (4.25)$$

The modified expression for $N^*(E^*)$, the density of energy eigenstates of the active degrees of freedom of A^* at a total energy E_{vr}^* is,

$$N^*(E^*) = Q_r(E^+ + E_0 + aE_Z)^{s + \frac{1}{2}r - 1} / (kT)^{\frac{1}{2}r} \Gamma(s + \frac{1}{2}r) \prod_{i=1}^s \nu_i \quad (4.26)$$

where Q_r is the rotational partition of the active molecule; a is the correction factor in the Whitten-Rabinovitch approximation; s is the total number of vibrational frequencies ν_i ; and r is the number of active rotations. The same definitions hold for the daggered quantities.

The expression for $k_{\text{uni}}/k_{\infty}$ becomes

$$\frac{k_{\text{uni}}}{k_{\infty}} = \frac{Q_r^+}{(kT)^{\frac{1}{2}r^*+1} Q_2^+} \frac{(E^+ + a^+ E_Z^+)^{s^+ + \frac{1}{2}r^*} \int_0^{\infty} \exp(-E^+/kT) dE^+}{\Gamma(s^+ + 1 + \frac{1}{2}r^*) \prod_{i=1}^{s^+} v_i^+} \frac{1}{1 + k_a(E_0^+ + E^+)/k_2[M]} \quad (4.27)$$

For low values of Q_1^+/Q_1 a better result is obtained by including this factor in the expression for k_{uni} and not in the expression for $k_a(E^*)$ [83]. The centrifugal effects will be considered in the next section, and further modifications will be made. Replacing $\sum_{E_{\text{vr}}^+} P(E_{\text{vr}}^+)$ by (4.25) and $N^*(E_0^+ + E^+)$ by (4.26) the expression for $k_a(E_0^+ + E^+)$ becomes

$$k_a(E_0^+ + E^+) = \frac{L^{\ddagger}}{h} \frac{Q_r^+(E^+ + a^+ E_Z^+)^{s^+ + \frac{1}{2}r^*} \Gamma(s^+ + \frac{1}{2}r^*) (kT)^{\frac{1}{2}r^*} \prod_{i=1}^s v_i^+}{Q_r^+(E_0^+ + E^+ + a E_Z^+)^{s^+ + \frac{1}{2}r^* - 1} \Gamma(s^+ + \frac{1}{2}r^* + 1) (kT)^{\frac{1}{2}r^*} \prod_{i=1}^{s^+} v_i^+} \quad (4.28)$$

Since $k_2[M] = \lambda ZP$ and $L^{\ddagger} = \sigma/\sigma^+$ in these reactions the terms in $k_{\text{uni}}/k_{\infty}$ can be rearranged to give

$$\frac{k_{\text{uni}}}{k_{\infty}} = \frac{1}{(RT)^{1 + \frac{1}{2}r^*}} \frac{1}{Q_V^+} \frac{\int_0^{\infty} (E^+ + a^+ E_Z^+)^{s^+ + \frac{1}{2}r^*} \exp(-E^+/RT) dE^+}{\Gamma(s^+ + 1 + \frac{1}{2}r^*) \prod_{i=1}^{s^+} v_i^+} \bigg/ \left[1 + \left(\frac{L^{\ddagger}}{h} \frac{Q_r^+(E^+ + a^+ E_Z^+)^{s^+ + \frac{1}{2}r^*} \Gamma(s^+ + \frac{1}{2}r^*) (RT)^{\frac{1}{2}r^*} \prod_{i=1}^s v_i^+}{Q_r^+(E_0^+ + E^+ + a E_Z^+)^{s^+ + \frac{1}{2}r^* - 1} \Gamma(s^+ + \frac{1}{2}r^* + 1) (RT)^{\frac{1}{2}r^*} \prod_{i=1}^{s^+} v_i^+} \right) / \lambda ZP \right] \quad (4.29)$$

The factor a (or a^+) is a function of the reduced energy $x (E^+ = E^+/E_Z^+)$ and approaches unity as x becomes large. It is defined as shown in (3.66) by

$$a = 1 - \beta w(x)$$

where β is a constant and $w(x)$ is an expression which depends on the energy range.

$$a^+ = 1 - \beta^+ / (5.00x + 2.73x^{0.5} + 3.51) \quad \theta \leq x < 1.0 \quad (4.30)$$

$$a^+ = 1 - \beta^+ \exp(-2.419x^{0.25}) \quad 1.0 \leq x \leq 8.0 \quad (4.31)$$

θ is defined to be equal to the ratio of $v_{i,\min}^+$ to E_Z^+ .

For the active molecule

$$E^* = E_0 + E^+$$

Since $E_0 > E_Z$, $E^*/E_Z > 1$ and the expression for a becomes

$$a = 1 - \beta \exp[-2.419(E_Z^+/E_Z)^{0.25}(E_0 + E^+/E_Z^+)^{0.25}] \quad (4.32)$$

$$1.0 \leq x \leq 8.0$$

$$a = 1 - \beta \exp[-2.419(E_Z^+/E_Z)^{0.25}(E_0/E_Z^+ + x)^{0.25}] \quad (4.33)$$

$$\approx 1$$

As shown in (3.73) the value of β is

$$\beta = [(s-1)(s + \frac{1}{2}r)/s] \Sigma v^2 / (\Sigma v)^2$$

At low energies in the range $0 \leq x < \theta$ the rotation vibration energy level sum is

$$\Sigma P(E_V^+) (E^+ - E_V)^{\frac{1}{2}r^+} = (E^+)^{\frac{1}{2}r^+} \quad 0 \leq x < \theta \quad (4.34)$$

The contribution to $(k_{\text{uni}}/k_{\infty})$ at energies $x > 8.0$ is completely negligible.

Finally with the aid of equations (4.24)-(4.34) and upon the change of E^+/E_Z^+ to x (4.23) becomes

$$\frac{k_{uni}}{k_{\infty}} = C_1 \sum_{n=1}^s \int \frac{G_n(x) \exp(-C_0 x) dx}{1 + C_2/p [G_n(x)/H(x)]} \quad (4.35)$$

where

$$G_1(x) = [\Gamma(\alpha^+ + 1) \frac{\pi v_i^+}{\Gamma(1 + \frac{1}{2}r^*)} (E_Z^+)^{s^+}] x^{r^*/2} \quad 0 \leq x < \theta \quad (4.36)$$

$$G_2(x) = [x + 1 - \beta^+ / (5.00x + 2.73x^{0.5} + 3.51)]^{\alpha^+} \quad \theta \leq x \leq 1.0 \quad (4.37)$$

$$G_3(x) = [x + 1 - \beta^+ \exp(-2.419x^{0.25})]^{\alpha^+} \quad 1.0 \leq x \leq 8.0 \quad (4.38)$$

$$H(x) = [x + \frac{E_0}{E_Z^+} + \frac{E_Z}{E_Z^+} (1 - \beta \exp(-2.419(E_Z^+/E_Z)^{0.25} (E_0/E_Z^+ + x)^{0.25}))]^{\alpha} \quad (4.39)$$

The quantity $[1 - \beta \exp[-2.419(E_Z^+/E_Z)^{0.25} (E_0/E_Z^+ + x)^{0.25}]$ being very small the final expression for $H(x)$ will be

$$H(x) = [x + \frac{E_0 + E_Z}{E_Z^+}]^{\alpha} \quad (4.40)$$

where

$$\alpha = s + \frac{1}{2}r - 1 \quad (4.41)$$

$$\alpha^* = s^+ + \frac{1}{2}r^* \quad (4.42)$$

At a fixed temperature C_1 and C_2/p are dimensionless constants and are defined as

$$C_0 = E_Z^+ / RT \quad (4.43)$$

$$C_1 = (E_Z^+)^{\alpha^+ + 1} / Q_V^+ (RT)^{1 + \frac{1}{2} r^*} \Gamma(\alpha^+ + 1) \prod_{i=1}^s v_i^+ \quad (4.44)$$

$$C_2 / P = [(E_Z^+)^{\alpha^+ - \alpha} / \lambda Z P h (RT)^{\frac{1}{2}(r^* - r)}] (\sigma_1 / \sigma_1^+) (Q_{ir}^+ / Q_{ir}) [\Gamma(\alpha + 1) / \Gamma(\alpha^+ + 1)] \cdot \left(\prod_{i=1}^s v_i / \prod_{i=1}^s v_i^+ \right) \quad (4.45)$$

where R is the gas constant and h is Planck's constant. The evaluation of the integral in (4.35) using Simpson's rule was carried out with a UNIVAC 1106 for several pressures. The fall-off behaviour of all the four molecules was studied using Models I and II.

4.4.2 Including Centrifugal Effects

When centrifugal effects are included the quantity $\langle \Delta E_J \rangle$ is included in $N^*(E^*)$ and consequently in $H(x)$. (4.40) becomes

$$H(x) = \left[x + \frac{E_0 + \langle \Delta E_J \rangle + E_Z}{E_Z^+} \right]^\alpha \quad (4.46)$$

$\langle \Delta E_J \rangle$ for Model I is given by

$$\langle \Delta E_J \rangle = -RT[(I^+ / I) - 1] \ell / 2 \quad (4.47)$$

where I^+ / I is the ratio of the moments of inertia of the adiabatic rotations in the complex and molecule, in which the resulting fragments are treated as "atoms" of a diatomic molecule, and ℓ is the number of such rotations.

For model II the expression used for $\langle \Delta E_J \rangle$ is

$$\langle \Delta E_J \rangle = -RT \left[\left(\frac{I_{xx}^+ I_{yy}^+ I_{zz}^+}{I_{xx}^- I_{yy}^- I_{zz}^-} \right)^{1/2} - 1 \right] \rho / 2 \quad (4.48)$$

4.5 CALCULATION OF $k_a(E^*)$ and k_{uni}

$k_a(E^*)$ and k_{uni} are evaluated by the computer program according to (3.19) and (3.21).

$$k_a(E^*) = \frac{L^\ddagger \sum_{E_{vr}^+=0}^{E^+} P(E_{vr}^+)}{hN^*(E^*)}$$

$$k_{uni} = \frac{L^\ddagger Q_1^+ \exp(-E_0/kT)}{hQ} \int_{E^+=0}^{\infty} \frac{\sum_{E_{vr}^+=0}^{E^+} P(E_{vr}^+) \exp(-E^+/kT) dE^+}{1 + k_a(E^*)/k_2[M]}$$

The non-fixed energy is given by

$$E^* = E_0 + E^+$$

or

$$E^* = E_0 + E^+ + \langle \Delta E_J \rangle$$

according to whether centrifugal effects are neglected or not.

4.6 ANHARMONICITY CORRECTIONS FOR $W(E^+)$ and $N^*(E^*)$

The molecule undergoing decomposition is highly excited and during the time lag between activation and decomposition most of its vibrations will pass through high quantum states where the departure from a harmonic potential is considerable. Anharmonicity is responsible

for energy transfer among the vibrations. Anharmonicity results in a decreasing spacing between successive vibrational levels of an anharmonic oscillator. The effect of anharmonicity on $k_a(E^*)$ and k_{uni} is investigated for Models I and II.

Until the appropriate force constants are available for polyatomic molecules, it is difficult to make very accurate predictions on the effects of anharmonicity. For this purpose, the molecule is considered as an assembly of independent Morse oscillators.

The application of a Morse oscillator representation to an actual molecular system requires the assignment of x or D_e to each oscillator [84].

$$D_e = hv/2x \quad (4.49)$$

The parameter x is related to the spectroscopic normal frequency ω and the fundamental frequency ν by

$$x = (\omega - \nu)/\omega$$

If the vibration is a simple stretching vibration, D_e may be calculated from the quadratic (f_2) and cubic (f_3) force constants

$$D_e = (f_2)^3/2(f_3)^2 \quad (4.50)$$

These force constants can be obtained from Badger's rule as modified by Hershbach and Lawrie [85]

$$(-1)^j f_j = 10^{-(r_e - a_{xy})/b_{xy}} \quad j = 2 \text{ or } 3 \quad (4.51)$$

where r_e is the equilibrium bond length between atoms of rows x and y in the periodic table and a_{xy} and b_{xy} are tabulated semi-empirical constants.

Equations (4.50) and (4.51) can only be used for bond-stretching vibrations. Equation (4.49) is used for determining D_e of more complex motions. Haarhoff [86] has started with the Whitten-Rabinovitch approximation and modified the equations (3.63) and (3.64) to include anharmonicity.

The energy levels of a classical Morse oscillator with energy referred to potential minimum as zero are given by

$$\epsilon = (n + \frac{1}{2})h\nu - (n + \frac{1}{2})^2(h\nu)^2/4D_e \quad (4.52)$$

where D_e is the dissociation energy of the oscillator and

$$\epsilon = E + E_z$$

Solving for the quantum number n

$$(n + \frac{1}{2}) = (2D_e/h\nu)\{1 - [1 - (\epsilon/D_e)]^{1/2}\} \quad (4.53)$$

so that the density of levels at energy E is

$$\frac{dn}{dE} = \frac{1}{h\nu[1 - (\epsilon/D_e)]^{1/2}} = \frac{1}{h\nu} \left[1 + \frac{\epsilon}{2D_e} + \frac{3}{8} \left(\frac{\epsilon}{D_e} \right)^2 + \dots \right] \quad (4.54)$$

The Laplace transform of dn/dE gives

$$L\left\{\frac{dn}{dE}\right\} = \frac{1}{h\nu_i} \left[\frac{1}{s} + \frac{1}{2D_e s^2} + \frac{1}{4D_e^2 s^3} + \dots \right] = \ell_i(s) \quad (4.55)$$

For s oscillators

$$\ell(s) = \prod_{i=1}^s \ell_i(s) \quad (4.56)$$

and

$$N(E) = L^{-1}\{\ell(s)\} = L^{-1}\{\prod \ell_i(s)\} \quad (4.57)$$

Multiplication of (4.56) and term by term inversion in (4.57) yields

$$N(E) = \frac{\epsilon^{s-1}}{\Gamma(s) \prod_i h\nu_i} \left\{ 1 + \frac{\epsilon}{s} \sum \frac{1}{2D_e} + \frac{\epsilon^2}{s(s+1)} \left[\frac{5}{2} \sum \left(\frac{1}{2D_e}\right)^2 + \frac{1}{2} \left(\sum \frac{1}{2D_e}\right)^2 \right] + \dots \right\} \quad (4.58)$$

The series in (4.58) is a correction factor for anharmonicity. (4.58) can be generalized to include r rotations by writing $s+r/2$ for s and the corresponding correction factor for $W(E)$ can be obtained by writing $r+2$ for r . By various manipulations Haarhoff truncated the series in (4.58) to obtain

$$\begin{array}{l} k = 0 \quad \frac{N^*(E^*) \text{ (anharmonic)}}{N^*(E^*) \text{ (harmonic)}} \\ k = 1 \quad \frac{W(E^+) \text{ (anharmonic)}}{W(E^+) \text{ (harmonic)}} \end{array} \begin{array}{l} \searrow \\ \nearrow \end{array} C_k(E) \quad (4.59)$$

$$C_k(E) = \left\{ \left(1 + \frac{2}{E'}\right)^{(E'/2)(1+E'/2)} \exp - \frac{(\alpha - 1)}{3(1+E')} s E_Z / (n+1) D \right. \\ \left. \cdot \exp[M_2(1 + E')^2(E_Z/D)^2 + M_3(1 + E')^3(E_Z/D)^3] \right\} \quad (4.60)$$

where D is the harmonic mean of the dissociation energies defined by

$$D^{-1} = \langle D_e^{-1} \rangle$$

$$M_2 = s[4s + (5/2)(r + 2k)]/8(n + 1)^2(n + 2)$$

$$M_3 = s[24s^2 + (59/2)s(r + 2k) + (37/4)(r + 2k)^2]/24(n+1)^3(n+2)(n+3)$$

$$n = s + k - 1 + (r/2)$$

$$E' = E/E_Z$$

$$\alpha = \langle v^2 \rangle / \langle v \rangle^2$$

(4.60) is unreliable at energies which represent an appreciable fraction of E_d , the energy required to dissociate the entire molecule ($E_d = \sum D_e - E_Z$). The usefulness of formula (4.59) is limited to roughly $E < 0.1E_d$.

If the anharmonicity constraints are known for the molecule and the complex the dissociation energy for each oscillator is calculated from (4.49).

If the anharmonicity constants are not given in the literature, D_e is evaluated from (4.50) for bond stretching vibrations. The assignment of D_e to a bending, deformation or rocking frequency is little better than guesswork.

The mean of the dissociation energies is then evaluated. Finally the subroutine evaluates the anharmonic correction (4.50) for $W(E^+)$ and $W(E^*)$.

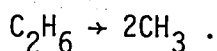
V. RESULTS AND DISCUSSION

As mentioned previously the purpose of this dissertation is to give a theoretical treatment of the thermal unimolecular C-C bond fission reactions in ethane and fluoroethanes with use of RRKM theory. Under the conditions of the experiments the mode of decomposition in the mono- [87], di- [88], and trifluoroethanes [89] consists exclusively of the unimolecular elimination of hydrogen fluoride. However, at high temperatures ($T > 1300^{\circ}\text{K}$), in the thermal decomposition of 1,1,2,2-tetrafluoroethane [90] and pentafluoroethane [91] performed by E. Tschuikow-Roux and coworkers, there is a significant contribution from the C-C bond rupture. The shock-tube studies provide evidence that the activation energy for dehydrofluorination reaction increases with additional fluoro substitution, while the preexponential factors change only in a minor way. Therefore, for any given temperature the values of the rate constants decrease with increasing n in the series $\text{C}_2\text{H}_{6-n}\text{F}_n$ ($n = 1,5$). Then, in relation to the HF elimination, the parallel reaction involving the C-C bond scission becomes progressively more important at the elevated temperatures used in shock-tube studies. This manifests itself by the appearance of products resulting from free-radical reactions.

In this chapter, the C-C bond fission in C_2H_6 , $C_2H_2F_4$, C_2HF_5 , C_2F_6 is investigated theoretically using a Gorin model (Model I) and a model using the criterion of minimum density (Model II). The calculated results are compared with the experimental ones and a conclusion is drawn.

5.1 ETHANE

The unimolecular dissociation of ethane has been widely studied [92]. Abnormally high A factors have been obtained for this unimolecular dissociation reaction



The high A factor is attributed to the conversion of low frequency vibrations or hindered rotations into free, or almost free rotations in the transition state. A review of the experimental data and of the theoretical models has been given by Waage and Rabinovitch [93]. There is wide disagreement on the magnitudes of the relevant reaction parameters and on their interpretation. Critical configurations have been presented that fit either the forward or reverse rates. In the temperature ranges at which these studies were carried out, the rate constants are all within a factor of 2 of one another. It seems probable that experimental uncertainties have led to the divergence in the Arrhenius parameters.

Lin and Back [94] obtained values of k_{uni} at temperatures between 550° and $726^{\circ}C$ and at pressures between 1 and 600 Torr. Their A factor of 10^{16} sec^{-1} is lower than that calculated by Rabinovitch and Setser [95].

Trenwith [96] studied the reaction at pressures between 0.5 and 280 torr and at temperatures of 566⁰ and 600⁰C. The fall-off curves obtained are steeper than those of Lin and Back [94], but the A factor is in good agreement with that of Lin and Back's work [94].

Quinn [97] has measured a larger A factor which is in good agreement with the theoretical value found by Rabinovitch and Setser [95], where a loose Gorin model is postulated.

Lin and Laidler [98] used four different activated complex models for RRKM calculations for the ethane decomposition. They found good agreement for their models I and IV with the data of Lin and Back [94] for the fall-off shape and the region of the fall-off.

Waage and Rabinovitch [93] have extended the calculations with the models I and IV of Lin and Laidler and found out that they don't get the Arrhenius parameters of Lin and Back [94]. They present a bending model for the activated complex in which four bending vibration frequencies are lowered until the calculated rate of recombination of the two methyl radicals agree with the observed rate. The results for this model are similar to those for the loose complex of Rabinovitch and Setser [95].

Hase [42], by minimization of the state density at the critical configuration required the measured decomposition and recombination rates to be interpreted in terms of a critical configuration with lowered H-C-C bending frequencies and a negative critical energy for recombination. He found good agreement between the calculated and measured rates.

Growcock, Hase and Simons [99] studied the kinetics of the chemically activated ethane. Their result agrees, via RRKM theory with most other chemically activated ethane data.

TABLE 5.1 - Experimental and Theoretical Thermal Parameters for Ethane Decomposition

	A factor (sec^{-1})	E_{∞} (kcal mole^{-1})	Temp. ($^{\circ}\text{C}$)	Reference
Experimental Studies				
	$10^{16.3}$	86.0	327	(100a)
	$10^{14.5}$	81.0	537	(100b)
	$10^{17.45}$	91.7	586	(97)
	10^{16}	86.0	638	(94)
	$10^{16.4}$	88.0	583	(96)
	$10^{16.3}$	88.0	583	(96)
Calculational Studies				
	$10^{17.5}$	87.2	600	(95)
	$10^{17.1}$	90.4	600	(98) I ^a
	$10^{16.9}$	89.4	600	(98) IV ^a
	$10^{18.6}$		600	(101)
	$10^{18.1}$	90.6	600	(93)
	$10^{18.09}$	90.6	600	(present work) I ^a
	$10^{16.6}$		327	(99)
	$10^{16.5}$	87.8	600	(present work) II ^a
	$10^{16.88}$	89.7	600	(present work) II ^a

^a Model number in the reference cited.

^b Centrifugal effects are neglected.

^c Centrifugal effects are included.

TABLE 5.2 - Summary of P 1/2 Values for Ethane Decomposition

	T ($^{\circ}$ C)	P 1/2 (Torr)	Reference
Experimental studies	566	5.1	(96)
	600	6.3	(96)
	685	54.0	(94)
Theoretical studies	25	0.21	(93)
	247	3.6	
	600	117.0	
	685	240.0	
	25	0.015	(98)
	247	0.43	
	600	22.0	
	685	47.0	
	25	1.06	(95)
	300	12.2	
	600	100.0	
	25	0.14	(101)
	247	3.8	
	600	200.0	
	600	6.6	(42a)
	685	15.0	
	600	5.5	(99)
	600	12.0	(Present work)I ^{a,b}
	600	43.0	(Present work)I ^{a,c}
600	0.65	(Present work)II ^{a,b}	
600	2.7	(Present work)II ^{a,c}	

^a Model I or II in the reference cited.

^b Centrifugal effects are neglected.

^c Centrifugal effects are included.

The first part of the theoretical calculations at 600°C involves a loose Gorin model for the critical configuration; in the second part the geometry of the critical configuration is determined by the minimization of the density of states.

5.1.1 Model I

5.1.1.1 Data

A. The Molecule

TABLE 5.3 - Vibrational Frequencies of C_2H_6 [105] (D_{3d})

	Wave number (cm^{-1})	Type of vibration	Species
ν_1	2915	C-H stretching	A_{1g}
ν_2	1388	CH_3 deformation	A_{1g}
ν_3	955	C-C stretching	A_{1g}
ν_4	260	CH_3 torsion (from specific heat)	A_{1u}
ν_5	2915	C-H stretching	A_{2u}
ν_6	1370	CH_3 deformation	A_{2u}
ν_7	2974	C-H stretching	E_u
ν_8	1460	CH_3 deformation	E_u
ν_9	822	CH_3 -C rocking (external deformation)	E_u
ν_{10}	2950	C-H stretching	E_g
ν_{11}	1469	CH_3 deformation	E_g
ν_{12}	1190	CH_3 -C rocking (external deformation)	E_g

TABLE 5.4 - Molecular Parameters of C_2H_6 [106]

$R(C-C)$ (A)	1.543
$R(C-H)$ (A)	1.102
$\angle CCH$	$109^{\circ}37'$
$\angle HCH$	$109^{\circ}19'$

* The energized molecule is assumed to have the geometry of the ground state C_2H_6 molecule, except that the torsional frequency along the figure axis is treated as an active free rotation.

B. The Activated Complex

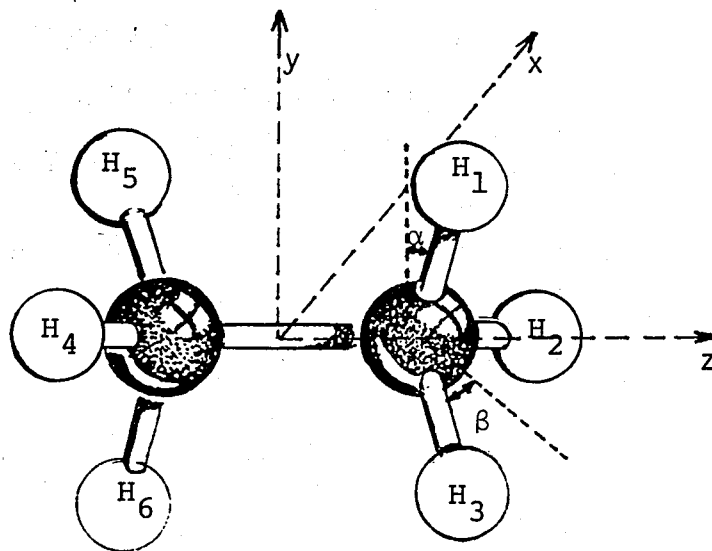
The observed high pre-exponential factor suggesting a loose transition state, the R_{C-C} distance is taken as the most probable internuclear distance $\langle R_C \rangle_{av}$ for a Gorin-model activated complex given by (4.3)

$$\langle R_C \rangle_{av} = 1.3092(2a/kT)^{1/6} \quad (4.3)$$

This model is identical to the "loose" model (Complex 3) for ethane used by Rabinovitch and Setser [95]. The CH_3 group is taken as planar. The three overall rotational degrees of freedom are adiabatic. There are five active internal rotational degrees of freedom which include the figure axis rotation plus two doubly degenerate tumblings of each CH_3 group about its own axis. The 12 vibrational frequencies of the complex are the frequencies of two planar CH_3 radicals. In fact the deviation of CH_3 from planarity is less than 10° [107]. The C-H bond length in the methyl group is taken to be the same as in the ethane molecule with $\angle HCH = 120^{\circ}$.

TABLE 5.5 - Vibrational Frequencies of CH_3 (D_{3h})

	Wave number (cm^{-1})	Type of vibration	Species
ν_1	3044	C-H stretching (calculated)	A_1'
ν_2	617	Out of plane bending	A_2''
ν_3	3161	Asymmetric stretching	E'
ν_4	1398	In plane bending	E'

5.1.1.2 The Moments of InertiaA. The Molecule (Table 5.4)I. *External Rotation*Figure 5.1 - Geometrical representation of C_2H_6 .

Calculation of the coordinates

$$\alpha = 109^{\circ}37' - 90^{\circ} = 19^{\circ}37' = 19.62^{\circ}$$

$$\beta = 109^{\circ}19'/2 = 54^{\circ}40' = 54.66^{\circ}$$

$$x_{C_1, C_2} = 0$$

$$x_{H_1, H_6} = 0$$

$$x_{H_2, H_5} = \sin\beta r(C-H)$$

$$= \sin 54.66(1.102)$$

$$= 0.899$$

$$x_{H_3, H_4} = -0.899$$

$$z_{C_1} = 0.772$$

$$z_{C_2} = -0.772$$

$$z_{H_1, H_2, H_3} = \sin\alpha r(C-H) + 0.772$$

$$= \sin 19.62(1.102) + 0.772$$

$$= 1.142$$

$$z_{H_4, H_5, H_6} = -1.142$$

$$y_{C_1, C_2} = 0$$

$$y_{H_1} = \cos\alpha r(C-H)$$

$$= \cos 19.62(1.102)$$

$$= 1.038$$

$$y_{H_2, H_3} = -\sin 30 (1.038)$$

$$= -0.519$$

$$y_{H_4, H_5} = 0.519$$

$$y_{H_6} = -1.038$$

TABLE 5.6 - Parameters for Evaluation of Moment of Inertia Product of C_2H_6

Atom	m_i	x_i	y_i	z_i	$m_i x_i^2$	$m_i y_i^2$	$m_i z_i^2$
C_1	12.011	0	0	0.772	0	0	7.1583
C_2	12.011	0	0	-0.772	0	0	7.1583
H_1	1.0079	0	1.038	1.142	0	1.0860	1.3144
H_2	1.0079	0.899	-0.519	1.142	0.8146	0.2715	1.3144
H_3	1.0079	-0.899	-0.519	1.142	0.8146	0.2715	1.3144
H_4	1.0079	-0.899	0.519	-1.142	0.8146	0.2715	1.3144
H_5	1.0079	0.899	0.519	-1.142	0.8146	0.2715	1.3144
H_6	1.0079	0	-1.038	-1.142	0	1.0860	1.3144
					3.258	3.258	22.203

$$I_{xx} = \sum m_i y_i^2 + \sum m_i z_i^2 \quad (5.1)$$

$$I_{yy} = \sum m_i x_i^2 + \sum m_i z_i^2 \quad (5.2)$$

$$I_{zz} = \sum m_i x_i^2 + \sum m_i y_i^2 \quad (5.3)$$

$$I_{xx} = I_{yy} = 3.258 + 22.203 = 25.461 \text{ amu } \overset{0}{\text{Å}}^2 \quad 42.27 \times 10^{-40} \text{ g.cm}^2$$

$$I_{zz} = 3.258 + 3.258 = 6.516 \text{ amu } \overset{0}{\text{Å}}^2 \quad 10.82 \times 10^{-40} \text{ g.cm}^2$$

II. Internal Rotation

The moment of inertia for internal rotation is given by

$$I_{ir} = \frac{I_1 I_2}{I_1 + I_2} \quad (5.4)$$

In this case for a symmetrical top

$$I_{ir} = I_1/2 = (3/2)m_H \ell^2 \quad (5.5)$$

where

$$\ell = r_{C-H} \sin(180-\theta)$$

is the angle between the axis of rotation and the C-H bond. Thus

$$\begin{aligned} I_{ir} &= (3/2)(1.0079)(1.102)^2 \sin^2(180-109.62) \\ &= 1.629 \text{ amu } \text{\AA}^2 \\ &= 2.70 \times 10^{-40} \text{ g.cm}^2 \end{aligned}$$

B. The Complex

I. *External Rotation*

Calculation of $\langle R_C \rangle_{av}$

As shown by (4.3)

$$\begin{aligned} \langle R_C \rangle_{av} &= 1.3092(2a/kT)^{1/6} & a &= 1.09 \times 10^{-58} \text{ ergs cm}^6 \text{ [75]} \\ &= 1.3092(2 \times 1.09 \times 10^{-58} / 1.3805 \times 10^{-16} \times 873)^{1/6} \\ &= 4.57 \times 10^{-8} \text{ cm} \end{aligned}$$

Calculation of the coordinates

$$\begin{array}{ll} x_{C_1, C_2}^+ = 0 & y_{C_1, C_2}^+ = 0 \\ x_{H_1, H_6}^+ = 0 & y_{H_1}^+ = 1.102 \quad ; \quad y_{H_6}^+ = -1.102 \\ x_{H_2, H_5}^+ = \cos 30(1.102) = 0.954 & y_{H_4, H_5}^+ = \sin 30(1.102) = 0.551 \\ x_{H_3, H_4}^+ = -0.954 & y_{H_2, H_3}^+ = -0.551 \end{array}$$

$$z_{H_1, H_2, H_3}^+ = 2.285$$

$$z_{H_4, H_5, H_6}^+ = -2.285$$

TABLE 5.7 - Parameters for Evaluation of Moment of Inertia Product of $C_2H_6^+$ (Model I)

Atom	m_i	x_i^+	y_i^+	z_i^+	$m_i x_i^2$	$m_i y_i^2$	$m_i z_i^2$
C_1	12.011	0	0	2.285	0	0	62.7121
C_2	12.011	0	0	-2.285	0	0	62.7121
H_1	1.0079	0	1.102	2.285	0	1.2240	5.2625
H_2	1.0079	0.954	-0.551	2.285	0.9173	0.3060	5.2625
H_3	1.0079	-0.954	-0.551	2.285	0.9173	0.3060	5.2625
H_4	1.0079	-0.954	0.551	-2.285	0.9173	0.3060	5.2625
H_5	1.0079	0.954	0.551	-2.285	0.9173	0.3060	5.2625
H_6	1.0079	0	-1.102	-2.285	0	1.2240	5.2625
					3.672	3.670	156.999

$$I_{xx}^+ = I_{yy}^+ = 3.671 + 156.999 = 160.670 \text{ amu } \overset{0}{\text{A}^2} \quad 266.71 \times 10^{-40} \text{ g.cm}^2$$

$$I_{zz}^+ = 3.672 + 3.670 = 7.342 \text{ amu } \overset{0}{\text{A}^2} \quad 12.19 \times 10^{-40} \text{ g.cm}^2$$

II. Internal Rotation

$$\begin{aligned} I_{ir} &= (3/2)(1.0079)(1.102)^2 \\ &= 1.834 \text{ amu } \overset{0}{\text{A}^2} \\ &= 3.048 \times 10^{-40} \text{ g.cm}^2. \end{aligned}$$

5.1.1.3 Calculation of the Partition Functions

A. The Molecule

I. *Vibrational partition function*

$$Q_V = \prod_{i=1}^s [1 - \exp(-h\nu_i/kT)]^{-1} \quad (5.6)$$

where

$$\theta/T = hc\nu/kT = 1.4388\nu/T = 1.648 \times 10^{-3} \nu$$

TABLE 5.8 - Parameters for Evaluation of the Vibrational Partition Function of C_2H_6

ν_i	$1/1-e^{-\theta\nu_i/T}$
2915 (2)	1.0082
1388	1.1130
955	1.2614
1370	1.1168
2974 (2)	1.0075
1460 (2)	1.0991
822 (2)	1.3478
2950 (2)	1.0078
1469 (2)	1.0975
1190 (2)	1.1637

$$Q_V = (1.0075)^2(1.0078)^2(1.0082)^2(1.0975)^2(1.0991)^2(1.1130)(1.1168) \\ \cdot (1.1637)^2(1.2614)(1.3478)$$

$$= 5.8813$$

II. Rotational partition function

$$\begin{aligned}
 Q_r &= (\sqrt{\pi}/\sigma)(8\pi^2kT/h^2)^{3/2}(I_{xx}I_{yy}I_{zz})^{1/2} & (5.7) \\
 &= (\sqrt{\pi}/6)\left(\frac{(8)(3.14)^2(1.3805 \times 10^{-16})(873)}{(6.6262 \times 10^{-27})^2}\right)^{3/2}((42.27)^2(10.82 \times 10^{-120}))^{1/2} \\
 &= 4140.30
 \end{aligned}$$

III. Partition function for internal rotation

$$\begin{aligned}
 Q_{ir} &= (8\pi^3 I_{ir} kT)^{1/2} / hn & (5.8) \\
 &= \frac{((8)(3.14)^3(2.70 \times 10^{-40})(1.3805 \times 10^{-16})(873))^{1/2}}{(6.6262 \times 10^{-27})(3)} \\
 &= 4.5161
 \end{aligned}$$

B. The Activated Complex

I. Vibrational partition function

TABLE 5.9 - Parameters for Evaluation of the Vibrational Partition Function of $C_2H_6^+$ (Model I)

ν_i^+	$1/1 - e^{-\theta\nu_i^+/T}$
3044 (2)	1.0067
617 (2)	1.5668
3161 (4)	1.0055
1398 (4)	1.1109

According to (5.6)

$$Q_V^+ = (1.0067)^2(1.5668)^2(1.0055)^4(1398)^4 \\ = 3.8730$$

II. Rotational partition function

According to (5.7)

$$Q_r^+ = (\sqrt{3.14}/2) \left(\frac{(8)(\pi^2)(1.3805 \times 10^{-16})(873)}{(6.6262 \times 10^{-27})^2} \right)^{3/2} ((266.71)^2(12.19 \times 10^{-120}))^{1/2} \\ = 83089.86$$

III. Partition function for internal rotation

The complex, in addition to the figure axis rotation, has two doubly degenerate tumblings of each planar CH_3 group about its own axis [104].

Thus

$$Q_{ir}^+ = [(8\pi^3 I_{ir}^+ kT)^{1/2} / h\nu^+] [(8\pi^2 I_{ir}^+ kT)^{1/2} / h\sigma^+]^4 \quad (5.9) \\ = [((8)(3.14)^3(3.048 \times 10^{-40})(1.3805 \times 10^{-16})(873))^{1/2} / (6.6262 \times 10^{-27})(1)] \\ [((8)(3.14)^2(3.048 \times 10^{-40})(1.3805 \times 10^{-16})(873))^{1/2} / (6.6262 \times 10^{-27})(2)]^4 \\ = 3924.70$$

5.1.1.4 Calculation of $\langle E_v \rangle$, $\langle E_v^+ \rangle$, E_0 and E^+ A. Calculation of $\langle E_v \rangle$

$$\langle E_v \rangle = RT^2 d \ln Q_v / dT = RT \sum_{i=1}^s \{ (h\nu_i / kT) [\exp(h\nu_i / kT) - 1]^{-1} \} \quad (5.10)$$

TABLE 5.10 - Parameters for Evaluation of $\langle E_v \rangle$

ν_i	$\nu_i / e^{\theta\nu_i/T-1}$
2915 (2)	24.093
1388	156.844
955	249.664
1370	160.016
2974 (2)	22.286
1460 (2)	144.692
822 (2)	285.870
2950 (2)	23.005
1469 (2)	143.232
1190 (2)	194.849
	<hr/> 2242.578

$$\frac{T \partial \ln Q_v}{\partial T} = (1.648 \times 10^{-3})(2242.578) = 3.696$$

$$\begin{aligned} \langle E_v \rangle &= (3.696)(1.987 \times 10^{-3})(873) \\ &= 6.41 \text{ kcal mole}^{-1} \end{aligned}$$

B. Calculation of $\langle E_V^+ \rangle$ TABLE 5.11 - Parameters for Evaluation of $\langle E_V^+ \rangle$

v_i^+	$v_i^+ / e^{\theta v_i^+ / T - 1}$
3044 (2)	20.309
617 (2)	349.698
3161 (4)	17.371
1398 (4)	<u>155.106</u>
	1429.920

$$\frac{T \partial \ln Q_V^+}{\partial T} = (1.648 \times 10^{-3})(1429.920) = 2.356$$

$$\begin{aligned} \langle E_V^+ \rangle &= (2.356)(1.987 \times 10^{-3})(873) \\ &= 4.09 \text{ kcal mole}^{-1} \end{aligned}$$

C. Result for E_0

According to (4.20)

$$\begin{aligned} E_0 &= E_\infty - \frac{1}{2} (r^* - r + 2)RT + \langle E_V \rangle - \langle E_V^+ \rangle \\ &= 90.60^* - \frac{1}{2} (5 - 1 + 2)(1.987 \times 10^{-3})(873) + 6.41 - 4.09 \\ &= 87.72 \text{ kcal mole}^{-1} \end{aligned}$$

* Reference 93.

D. Calculation of E^+

In a thermal reaction the non-fixed energy E^+ has been calculated as follows [43]

$$E^+ = \left(1 + \frac{r^*}{2}\right)RT + \sum h\nu_i^+ [\exp(h\nu_i^+/kT) - 1]^{-1} \quad (5.11)$$

$$= (1 + 2.5)(1.987 \times 10^{-3})(873) + (2.859 \times 10^{-3})(1429.92)$$

$$= 10.16 \text{ kcal mole}^{-1}$$

5.1.1.5 Calculation of ΔS^\ddagger , k_∞ and A_∞

The experimental Arrhenius parameters chosen in this work are [93]

$$A_\infty = 10^{18.1}$$

$$E_\infty = 90.6 \text{ kcal mole}^{-1}$$

According to (4.21)

$$\Delta S^\ddagger = R(\ln A_\infty(h/kT) - 1)$$

$$= 1.987 \ln((10^{18.1})(6.6262 \times 10^{-27}) / (1.3805 \times 10^{-16})(873)) - 1)$$

$$= 20.15 \text{ cal mole}^{-1} \cdot \text{deg}^{-1}$$

From (3.24)

$$k_\infty = A_\infty e^{-E_\infty/RT} \quad (5.12)$$

$$= (10^{18.1}) e^{-90.6 / (1.987 \times 10^{-3} \times 873)}$$

$$= 2.62 \times 10^{-5} \text{ sec}^{-1}$$

The corresponding theoretical values are calculated below. ΔS_{th}^\ddagger is given by (3.22)

$$\Delta S_{th}^\ddagger = S_{th}^+ - S_{th}$$

The statistical-mechanical equation (5.13) is used to calculate S_{th}^\ddagger and S_{th}

$$S_{th} = R \ln Q + RT \frac{d}{dT} \ln Q \quad (5.13)$$

$$\begin{aligned} S_v &= 1.987(\ln 5.8813 + 3.696) \\ &= 10.68 \text{ cal mole}^{-1} \cdot \text{deg}^{-1} \end{aligned}$$

$$\begin{aligned} S_r &= 1.987(\ln 4140.30 + 1.5) && \text{since } T(d/dT) \ln Q_r = 3/2 \\ &= 19.53 \text{ cal mole}^{-1} \cdot \text{deg}^{-1} \end{aligned}$$

$$\begin{aligned} S_{ir} &= 1.987(\ln 4.5161 + 0.5) && \text{since } T(d/dT) \ln Q_{ir} = 1/2 \\ &= 3.99 \text{ cal mole}^{-1} \cdot \text{deg}^{-1} \end{aligned}$$

$$S_{th} = 34.20 \text{ cal mole}^{-1} \cdot \text{deg}^{-1}$$

$$\begin{aligned} S_v^+ &= 1.987(\ln 3.8730 + 2.3565) \\ &= 7.37 \text{ cal mole}^{-1} \cdot \text{deg}^{-1} \end{aligned}$$

$$\begin{aligned} S_r^+ &= 1.987(\ln 83089.86 + 1.5) \\ &= 25.49 \text{ cal mole}^{-1} \cdot \text{deg}^{-1} \end{aligned}$$

$$\begin{aligned} S_{ir}^+ &= 1.987(\ln 3924.70 + 2.5) && \text{since } T(d/dT) \ln Q_{ir} = 2.5 \\ &= 21.41 \text{ cal mole}^{-1} \cdot \text{deg}^{-1} \end{aligned}$$

$$S_{th}^+ = 54.27 \text{ cal mole}^{-1} \cdot \text{deg}^{-1}$$

$$\Delta S_{th}^\ddagger = 54.27 - 34.20 = 20.07 \text{ cal mole}^{-1} \cdot \text{deg}^{-1}$$

The value of $k_{\infty,th}$ is calculated using (3.24)

$$\begin{aligned}
 k_{\infty,th} &= L^{\ddagger} \frac{kT}{h} \frac{Q^{\ddagger}}{Q} \exp(-E_0/RT) & (3.24) \\
 &= \frac{(3)(1.3805 \times 10^{-16})(873)}{(6.6262 \times 10^{-27})} \times \frac{(3.8730)(2)(83089.86)(3924.70)}{(5.8813)(4140.30)(4.5161)} \\
 &\quad \times \exp(-87.720/(1.987 \times 10^{-3})(873)) \\
 &= 2.28 \times 10^{-5}
 \end{aligned}$$

Rearranging (4.21)

$$\begin{aligned}
 A_{\infty,th} &= \frac{ekT}{h} e^{\Delta S_{th}^{\ddagger}/R} & (5.14) \\
 &= \frac{(2.718)(1.3805 \times 10^{-16})(873)}{6.6262 \times 10^{-27}} e^{20.07/1.987} \\
 &= 10^{18.08}
 \end{aligned}$$

5.1.1.6 Calculation of the Anharmonicity Corrections

A. The Molecule

The anharmonicity correction factor derived by Haarhoff is given by (4.60)

$$\begin{aligned}
 C_k(E) &= \left\{ (1 + (2/E'))^{(E'/2)(1+(E'/2))} \exp\left[\frac{-(\alpha-1)}{3(1+E')}\right] \right\}^n \frac{E_z}{(n+1)D} \\
 &\quad \cdot \exp[M_2(1+E')^2(E_z/D)^2 + M_3(1+E')^3(E_z/D)^3]
 \end{aligned}$$

$$k = 0 \text{ for } N^*(E^*) ; \quad k = 1 \text{ for } W(E^+)$$

where D is the harmonic mean of the dissociation energies defined by

$$D^{-1} = \langle D_e^{-1} \rangle$$

$$E' = E/E_z$$

$$\alpha = \langle v^2 \rangle / \langle v \rangle^2$$

$$n = s + k - 1 + (r/2)$$

$$M_2 = s[4s + 5/2(r + 2k)]/8(n+1)^2(n+2)$$

$$M_3 = s[24s^2 + 59/2 s(r + 2k) + 37/4 (r + 2k)^2]/24(n+1)^3(n+2)(n+3)$$

The correction factor involves D , the mean Morse dissociation energy of the various oscillators, on the assumption that a molecule can be considered as a system of independent Morse oscillators.

One possible way of obtaining D is based on the observation that because of anharmonicity the (observed) fundamental frequency ν is related to the (zero order) normal frequency ω through the relation

$$\nu = (1 - x)\omega$$

where x is the anharmonicity constant of the vibration. For a Morse oscillator

$$D_e = h\nu/2x \quad (4.49)$$

so that the anharmonicity constant, when known provides a means of calculating D particularly for vibrations that are not simple stretching vibrations.

Based on the data given by Hansen and Dennison [106] the mean Morse dissociation energy is calculated.

TABLE 5.12 - Parameters for Evaluation of the Dissociation Energies for C_2H_6 [106]

Anharmonicity constants	Normal frequencies	D_e (kcal mole $^{-1}$)	D_e^{-1} (kcal mole $^{-1}$) $^{-1}$
$x_1 = 0.042$	$\omega_1 = 3042.8$	98.73	0.01013
$x_2 = 0.034$	$\omega_2 = 1449.3$	58.57	0.01707
$x_3 = 0.0225$	$\omega_3 = 1015.8$	62.78	0.01593
$x_4 = 0.0933$	$\omega_4 = 303.3$	4.19	0.23866
$x_5 = 0.0477$	$\omega_5 = 3061.0$	86.93	0.01150
$x_6 = 0.0405$	$\omega_6 = 1437.5$	48.44	0.02064
$x_7 = 0.046$	$\omega_7 = 3139.9$	92.63	0.01080
$x_8 = 0.035$	$\omega_8 = 1525.6$	59.83	0.01671
$x_9 = 0.0004$	$\omega_9 = 821.8$	2921.43	0.00034
$x_{10} = 0.0694$	$\omega_{10} = 3175.1$	60.57	0.01651
$x_{11} = 0.0690$	$\omega_{11} = 1551.6$	35.20	0.02841
$x_{12} = 0.045$	$\omega_{12} = 1246.0$	37.62	0.02658

$$D_e = \frac{(6.6262 \times 10^{-27})(3 \times 10^{10})(1.439 \times 10^{13})v}{2x}$$

D_e is calculated for all the oscillators.

$$\Sigma D_e^{-1} = 0.2739$$

$$\langle D_e^{-1} \rangle = 0.01611$$

$$D^* = 62.06 \text{ kcal mole}^{-1}$$

Another possible way of obtaining D for a simple stretching vibration, is by calculating the quadratic (f_2) and cubic (f_3) force constants. In a Morse oscillator they are related by

$$D_e = (f_2)^3 / 2(f_3)^2 \quad (4.50)$$

The two force constants can be obtained from Badger's rule modified by Hershbach and Laurie

$$(-1)^j f_j = 10^{-(r_e - a_{xy})/b_{xy}} \quad j = 2 \text{ or } 3 \quad (4.51)$$

where r_e is the equilibrium bond length between atoms of rows x and y in the periodic table and a_{xy} and b_{xy} are tabulated semiempirical constants.

For a C-H stretching vibration (6 fold degenerate)

	<u>a_{xy}</u>	<u>b_{xy}</u>
f_2	1.54	0.64
f_3	1.58	0.48
$f_2 = 4.8348 \times 10^5$		dynes cm^{-1}
$f_3 = 9.9045 \times 10^{13}$		dynes cm^{-2}
$D_e = 5.7602 \times 10^{-12}$		ergs molecule $^{-1}$ = 82.89 kcal mole $^{-1}$
$D_e^{-1} = 0.01206$		

For a C-C stretching vibration

	<u>a_{xy}</u>	<u>b_{xy}</u>
f_2	1.73	0.47
f_3	1.78	0.39

$$f_2 = 2.4996 \times 10^5 \text{ dynes cm}^{-1}$$

$$f_3 = 4.0522 \times 10^{13} \text{ dynes cm}^{-2}$$

$$D_e = 4.7555 \times 10^{-12} \text{ ergs molecule}^{-1} = 68.43 \text{ kcal mole}^{-1}$$

$$D_e^{-1} = 0.01461$$

For a C-H bending mode (10 fold degenerate)

To calculate D_e for bending modes, the following approach is used.

$$D_e = \frac{1}{2} kr^2$$

where k is an average value for a C-H bending force constant and r is an average distance for this bending motion [108].

$$D_e = \frac{1}{2} (0.46 \times 10^5) (10^{-16})$$

$$= 0.23 \times 10^{-11} \text{ ergs molecule}^{-1} = 33.10 \text{ kcal mole}^{-1}$$

$$D_e^{-1} = 0.03021$$

$$\langle D_e^{-1} \rangle = \frac{1}{17} ((6)(0.01206) + 0.01461 + (10)(0.03021))$$

$$= 0.02289$$

$$D = 43.69 \text{ kcal mole}^{-1}$$

B. The Complex

Since anharmonicity constants are not available, for the complex, the second way is chosen to calculate D .

For a C-H stretching vibration (6 fold degenerate)

$$D_e^{-1} = 0.01206$$

For a C-H bending vibration (6 fold degenerate)

An average value for the dissociation energy is taken by comparison with the dissociation energies for the bending motions in ethane.

$$D_e = 5.07 \times 10^{-12} \text{ ergs molecule}^{-1} = 72.99 \text{ kcal mole}^{-1}$$

$$D_e^{-1} = 0.01370$$

$$\langle D_e^{-1} \rangle = \frac{1}{12} ((6)(0.01206) + (6)(0.01370))$$

$$= 0.01285$$

$$D = 77.82 \text{ kcal mole}^{-1}$$

5.1.1.7 Evaluation of $k_{\text{uni}}/k_{\infty}$

A. Centrifugal Effects are Neglected

The parameters used in $k_{\text{uni}}/k_{\infty}$ are calculated below.

$$E_0 = 87.72 \text{ kcal mole}^{-1}$$

$$E_z = (1/2) \sum v_i$$

$$= (1/2) \{ (2)(2915) + 1388 + 955 + 1370 + (2)(2974) + (2)(1460) \\ + (2)(822) + (2)(2950) + (2)(1469) + (2)(1190) \}$$

$$= 15636.5 \text{ cm}^{-1} = 44.71 \text{ kcal mole}^{-1}$$

$$\begin{aligned}
 E_Z^+ &= \frac{1}{2} \sum v_i^+ \\
 &= \frac{1}{2} \{ (2)(3044) + (2)(617) + (4)(3161) + (4)(1398) \} \\
 &= 12779 \text{ cm}^{-1} = 36.54 \text{ kcal mole}^{-1}
 \end{aligned}$$

$$s = 17$$

$$s^+ = 12$$

$$r = 1$$

$$r^* = 5$$

$$\alpha = 16.5$$

$$\alpha^+ = 14.5$$

$$\Gamma(\alpha+1) = 8.563 \times 10^{13}$$

$$\Gamma(\alpha^++1) = 3.348 \times 10^{11}$$

$$\Gamma(1+r^*/2) = 3.2333$$

$$\begin{aligned}
 \prod_{i=1}^s v_i &= (2915)^2 (1388) (955) (1370) (2974)^2 (1460)^2 (822)^2 (2950)^2 \\
 &\quad \cdot (1469)^2 (1190)^2
 \end{aligned}$$

$$= 5.228 \times 10^{54} \text{ cm}^{-17}$$

$$\prod_{i=1}^{s^+} v_i^+ = (3044)^2 (617)^2 (3161)^4 (1398)^4$$

$$= 1.345 \times 10^{39} \text{ cm}^{-12}$$

$$(E_Z^+)^{\alpha^+-\alpha} = (12779)^{14.5-16.5} = 6.124 \times 10^{-9} \text{ cm}^2$$

$$(E_Z^+)^{\alpha^++1} = (12779)^{15.5} = 4.474 \times 10^{63} \text{ cm}^{-15.5}$$

$$(E_Z^+)^{s^+} = (12779)^{12} = 1.897 \times 10^{49} \text{ cm}^{-12}$$

$$(RT)^{1+r^*/2} = (1.987 \times 0.3498 \times 873)^{3.5} = 5.503 \times 10^9 \text{ cm}^{-3.5}$$

$$(RT)^{(r^*-1)/2} = (1.987 \times 0.3498 \times 873)^2 = 3.682 \times 10^5 \text{ cm}^{-2}$$

$$\begin{aligned} \langle v^2 \rangle &= [(2)(2915)^2 + (1388)^2 + (955)^2 + (1370)^2 + (2)(2974)^2 \\ &\quad + (2)(1460)^2 + (2)(822)^2 + (2)(2950)^2 + (2)(1469)^2 \\ &\quad + (2)(1190)^2]/17 \\ &= 4092174.2 \text{ cm}^{-2} \end{aligned}$$

$$\begin{aligned} \langle v \rangle &= [(2)(2915) + 1388 + 955 + 1370 + (2)(2974) + (2)(1460) \\ &\quad + (2)(822) + (2)(2950) + (2)(1469) + (2)(1190)]/17 \\ &= 1839.59 \text{ cm}^{-1} \end{aligned}$$

$$\langle v \rangle^2 = 3384084.9 \text{ cm}^{-2}$$

$$\beta = (16/17)(17.5/17)(4092174.2/3384084.9) = 1.1716$$

$$\begin{aligned} \langle v^{+2} \rangle &= ((4)(3161)^2 + (2)(3044)^2 + (4)(1398)^2 + (2)(617)^2)/12 \\ &= 5589879.2 \text{ cm}^{-2} \end{aligned}$$

$$\begin{aligned} \langle v^+ \rangle &= ((4)(3161) + (2)(3044) + (4)(1398) + (2)(617))/12 \\ &= 2129.83 \text{ cm}^{-1} \end{aligned}$$

$$\langle v^+ \rangle^2 = 4536190 \text{ cm}^{-2}$$

$$\beta^+ = (11/12)(14.5/12)(5589879.2/4536190) = 1.3649$$

$$\begin{aligned} Z &= (\sigma_d^2 N_A / R) (8\pi N_A k / \mu)^{1/2} (1/T)^{1/2} \\ &= 10.82 \times 10^6 \text{ Torr}^{-1} \text{ sec}^{-1} \end{aligned} \quad (5.15)$$

where $\sigma_d [93] = 5.3 \times 10^{-8} \text{ cm}$

$$N_A = 6.0225 \times 10^{23} \text{ mole}^{-1}$$

$$R = 6.2362 \times 10^4 \text{ cm}^3 \text{ Torr K}^{-1} \text{ mole}^{-1}$$

$$k = 1.3805 \times 10^{-16} \text{ erg K}^{-1}$$

$$\mu = ((1/30) + (1/30))^{-1} = 15 \text{ g mole}^{-1}$$

$$T = 873^{\circ} \text{K}$$

Since according to (4.23)

$$k_{\text{uni}}/k_{\infty} = C_1 \sum_{n=1}^3 \int_0^{\infty} \frac{G_n(x) \exp(-C_0 x) dx}{1 + C_2/P[G_n(x)/H(x)]}$$

$$C_0 = E_Z^+ / RT \quad (4.43)$$

$$= 12779 / (1.987)(0.3498)(873)$$

$$= 21.06$$

$$C_1 = (E_Z^+)^{\alpha^+ + 1} / Q_V^+ (RT)^{1+r^*/2} \Gamma(\alpha^+ + 1) \Pi v_i^+ \quad (4.44)$$

$$= (4.474 \times 10^{63}) / (3.8730)(5.503 \times 10^9)(3.348 \times 10^{11})(1.345 \times 10^{39})$$

$$= 466.17$$

$$\theta = v_{\text{min}}^+ / E_Z^+$$

$$= 617 / 12779 = 0.048$$

$$G_1(x) = [\Gamma(\alpha^+ + 1) \Pi v_i^+ / \Gamma(1+r^*/2) (E_Z^+)^{s^+}] x^{r^*/2} ; 0 \leq x < \theta \quad (4.36)$$

$$= [(3.348 \times 10^{11})(1.345 \times 10^{39}) / (3.2333)(1.897 \times 10^{49})] x^{5/2}$$

$$= 7.34 x^{2.5}$$

$$0 \leq x < 0.048$$

$$G_2(x) = [x + 1 - \beta^+ / (5.00x + 2.73x^{0.5} + 3.51)]^{\alpha^+} \theta \leq x < 1.0 \quad (4.37)$$

$$= [x + 1 - 1.3649 / (5.00x + 2.73x^{0.5} + 3.51)]^{14.5}$$

$$0.048 \leq x < 1.0$$

$$G_3(x) = [x + 1 - \beta^+ \exp(-2.419x^{0.25})]^{\alpha^+} \quad 1.0 \leq x \leq 8.0 \quad (4.38)$$

$$= [x + 1 - 1.3649 \exp(-2.419x^{0.25})]^{14.5}$$

$$H(x) = [x + (E_0 + E_Z) / E_Z^+]^{\alpha} \quad (4.40)$$

$$= [x + (87.72 + 44.71) / 36.54]^{16.5}$$

$$= (x + 3.624)^{16.5}$$

$$\begin{aligned}
 C_2/P &= [(E_z)^{\alpha^+ - \alpha} / \lambda Z P h (RT)^{1/2} (r^* - r)] (\sigma_1 / \sigma_1^+) (Q_{jr}^+ / Q_{ir}^+) [\Gamma(\alpha+1) / \Gamma(\alpha^++1)] \\
 &\quad (\bar{V}_i^s / \bar{V}_i^+) \quad (4.45) \\
 &= (6.124 \times 10^{-9}) / P (10.82 \times 10^6 \times 9.537 \times 10^{-11}) (0.3498) (3.682 \times 10^5) \\
 &\quad (3) (4033.69 / 4.825 \times 8.563 \times 10^{13}) / (3.348 \times 10^{11}) \\
 &\quad ((5.228 \times 10^{54}) / (1.345 \times 10^{39})) \\
 &= 1.1489 \times 10^{11} / P
 \end{aligned}$$

Thus when centrifugal effects are neglected.

$$\begin{aligned}
 k_{uni} / k_{\infty} &= 466.17 \left[\int_0^{0.048} \frac{7.34x^{2.5} \exp(-21.06x) dx}{1 + \frac{1.1489 \times 10^{11}}{P} [7.34x^{2.5} / (x + 3.624)^{16.5}]} \right. \\
 &\quad + \frac{1}{0.048} \frac{[x+1-1.3649 / (5.00x+2.73x^{0.5}+3.51)]^{14.5} \exp(-21.06x) dx}{1 + \frac{1.1489 \times 10^{11}}{P} [x+1-1.3649 / (5.00x+2.73x^{0.5}+3.51)]^{14.5} / (x+3.624)^{16.5}} \\
 &\quad \left. + \int_1^8 \frac{[x+1-1.3649 \exp(-2.419x^{0.25})]^{14.5} \exp(-21.06x) dx}{1 + \frac{1.1489 \times 10^{11}}{P} [x+1-1.3649 \exp(-2.419x^{0.25})]^{14.5} / (x+3.624)^{16.5}} \right]
 \end{aligned}$$

B. Centrifugal Effects are Included

I. *The Direct Method*

According to (4.47)

$$\langle \Delta \epsilon_j \rangle = RT(1 - (I^+ / I))$$

To calculate I^+ / I (4.6) and (4.7) are used.

$$I^+ / I = \langle \langle r_m^2 \rangle \rangle / r_e^2$$

and

$$\langle\langle r_m^2 \rangle\rangle = 1.354(2a/kT)^{1/3}$$

$$\begin{aligned} \langle\langle r_m^2 \rangle\rangle &= 1.354 \left(\frac{(2)(1.09 \times 10^{-58})}{(1.3805 \times 10^{-16})(873)} \right)^{1/3} \\ &= 16.498 \times 10^{-16} \text{ cm}^2 \end{aligned}$$

$$I^+/I = \frac{16.498 \times 10^{-16}}{(1.543)^2} = 6.929$$

$$\begin{aligned} \langle \Delta E_J \rangle &= -(1.987 \times 10^{-3})(873)(5.929) \\ &= -10.28 \text{ kcal mole}^{-1} \end{aligned}$$

$$\begin{aligned} H(x) &= [x + (E_0 + E_z + \langle \Delta E_J \rangle) / E_z^+]^\alpha & (4.46) \\ &= [x + (87.72 + 44.71 - 10.28) / 36.45]^{16.5} \\ &= (x + 3.35)^{16.5} \end{aligned}$$

TABLE 5.13 - Contribution of Centrifugal Effects to k_{uni}/k_∞ for $C_2H_6 \rightarrow 2CH_3\cdot$ at $873^\circ K$ (Model I)

P (torr)	$(k_{uni}/k_\infty)^a$	$(k_{uni}/k_\infty)^b$
10^{-1}	0.0236	0.0077
1	0.1365	0.0522
10	0.4658	0.2517
10^2	0.9082	0.6674
10^3	1.1936	1.0706
10^4	1.2781	1.2521
10^5	1.2945	1.2907
10^6	1.2961	1.2957
10^7	1.2962	1.2962
10^8	1.2962	1.2962
10^9	1.2962	1.2962

^a Neglecting the centrifugal effects ($\log(k_{uni}/k_\infty) = 0.5$ at $P = 12$ mm Hg)

^b Including the centrifugal effects ($\log(k_{uni}/k_\infty) = 0.5$ at $P = 43$ mm Hg)

$$\begin{aligned}
k_{\text{uni}}/k_{\infty} = & 466.17 \left[\int_0^{0.048} \frac{7.34x^{2.5} \exp(-21.06x) dx}{1 + \frac{1.1489 \times 10^{11}}{\rho} [7.34x^{2.5}/(x + 3.35)]^{16.5}} \right. \\
& + \frac{1}{0.048} \frac{\int [x+1-1.3649/(5x+2.73x^{0.5}+3.51)]^{14.5} \exp(-21.06x) dx}{1 + \frac{1.1489 \times 10^{11}}{\rho} [x+1-1.3649/(5x+2.73x^{0.5}+3.51)]^{14.5} / (x+3.35)^{16.5}} \\
& \left. + \frac{1}{1} \frac{\int_0^8 [x+1-1.3649 \exp(-2.419x^{0.25})]^{14.5} \exp(-21.06x) dx}{1 + \frac{1.1489 \times 10^{11}}{\rho} [x+1-1.3649 \exp(-2.419x^{0.25})]^{14.5} / (x+3.35)^{16.5}} \right]
\end{aligned}$$

II. The Waage-Rabinovitch approximation [45]

When centrifugal effects are taken into account the fall-off curve can also be located by using the Waage-Rabinovitch approximation.

$$k_a(E_0 + E^+ + \langle \Delta E_J \rangle) = \frac{1}{F} k_a(E_0 + E^+) \quad (3.36)$$

F is given by (3.39)

$$F^{-1} = 1 + \frac{(s + (r/2) - 1)(I^+/I - 1)RT}{E_0 + aE_z}$$

$$= 2.311$$

$$F = 0.433$$

where $I^+/I = 6.929$

$$a = 1 - \beta \exp -2.4191(E_0 + \langle \Delta E_J \rangle + E^+/E_z)^{0.25}$$

$$= 0.9331$$

Since $F < 1$ the fall-off curve is shifted to higher pressures by $-\log F$ along the $\log p$ axis. According to the Waage-Rabinovitch approximation the $k_{\text{uni}}/k_{\infty}$ ratio equals 0.5 at $P = 28$ Torr.

5.1.1.8 Calculation of $k_a(E^*)$

The computer program calculates $k_a(E^*)$ according to (3.19)

$$k_a(E^*) = \frac{L^{\ddagger} \sum_{E_{\text{vr}}^+ = 0}^{E^+} P(E_{\text{vr}}^+)}{hN^*(E^*)}$$

The input data is given in Table 5.14.

TABLE 5.14 - Properties of the Active Molecule and Activated Complex (C_2H_6 , Model I)

	Molecule	Complex
Frequencies (cm^{-1})	2915 (2) 1388 955 1370 2974 (2) 1460 (2) 822 (2) 2950 (2) 1469 (2) 1190 (2)	3044 (2) 617 (2) 3161 (4) 1398 (4)
E_0 (kcal mole $^{-1}$)		87.72
s	17	12
r	1	5
Moments of inertia, amu \AA^2		
I_{xx}, I_{yy}	25.461	160.67
I_{zz}	6.516	7.34
$I_{\text{i.r.}}$	1.629	1.834 (5)
		./...

Table 5.14 continued...

	Molecule	Complex
Symmetry number for internal rotation σ	3	2 (4) and 1 (1)
Average bond energy (kcal mole ⁻¹)		
D^*	62.06	77.82
D	43.69	77.82
Step length ΔE^\ddagger (kcal mole ⁻¹)		0.05
Number of rate constants to be calculated NEN		1200
L^\ddagger		3
Temperature (°K) T		873
Pressure (Torr) P		600
Collision number (Torr ⁻¹ sec ⁻¹) Z		10.82x10 ⁶

The results at $E^\ddagger = 10.16$ kcal mole⁻¹ are

$$k_a(E^\ddagger + E_0) = 0.7576 \times 10^9 \text{ sec}^{-1}$$

$$k_a(E^\ddagger + E_0 + \langle \Delta E_J \rangle) = 0.2740 \times 10^{10} \text{ sec}^{-1}$$

$$k_a(E^\ddagger + E_0)_{\text{anh}} = 0.2546 \times 10^9 \text{ sec}^{-1}$$

$$k_a^*(E^\ddagger + E_0)_{\text{anh}} = 0.1348 \times 10^9 \text{ sec}^{-1}$$

$$k_a(E^\ddagger + E_0 + \langle \Delta E_J \rangle)_{\text{anh}} = 0.1032 \times 10^{10} \text{ sec}^{-1}$$

$$k_a^*(E^\ddagger + E_0 + \langle \Delta E_J \rangle)_{\text{anh}} = 0.5854 \times 10^9 \text{ sec}^{-1}$$

5.1.1.9 Calculation k_{uni}

As shown in (3.20)

$$k_{\text{uni}} = \frac{L^\ddagger Q_1^+}{h Q_1 Q_2} \exp(-E_0/RT) \Delta E^\ddagger \sum_{i=1}^{i_{\text{max}}} \left[\frac{[\Sigma P(E_{\text{vr}}^+) \exp(-E^+/RT)]}{1 + k_a(E^*)/\lambda Z P} \right]$$

The input data for the computer program which evaluates k_{uni} is given in Table 5.14.

A. Neglecting Centrifugal Effects

$$k_{uni} = \frac{83089.86}{(9.537 \times 10^{-14})(4140.30)(5.8813)(4.5161)} \exp\left(\frac{-87.72}{(1.987 \times 10^{-3})(873)}\right)$$

$$(0.05)(0.6289 \times 10^6)$$

$$= 2.7194 \times 10^{-5} \text{ sec}^{-1}$$

$$k_{uni}(\text{anh}) = (4.3241 \times 10^{-11})(0.7005 \times 10^6)$$

$$= 3.0290 \times 10^{-5} \text{ sec}^{-1}$$

$$k_{uni}^*(\text{anh}) = (4.3241 \times 10^{-11})(0.6812 \times 10^6)$$

$$= 2.9455 \times 10^{-5} \text{ sec}^{-1}$$

B. Including Centrifugal Effects

$$k_{uni} = (4.3241 \times 10^{-11})(0.5306 \times 10^6)$$

$$= 2.2943 \times 10^{-5} \text{ sec}^{-1}$$

$$k_{uni}(\text{anh}) = (4.3241 \times 10^{-11})(0.6478 \times 10^6)$$

$$= 2.8011 \times 10^{-5} \text{ sec}^{-1}$$

$$k_{uni}^*(\text{anh}) = (4.3241 \times 10^{-11})(0.6113 \times 10^6)$$

$$= 2.6433 \times 10^{-5} \text{ sec}^{-1}$$

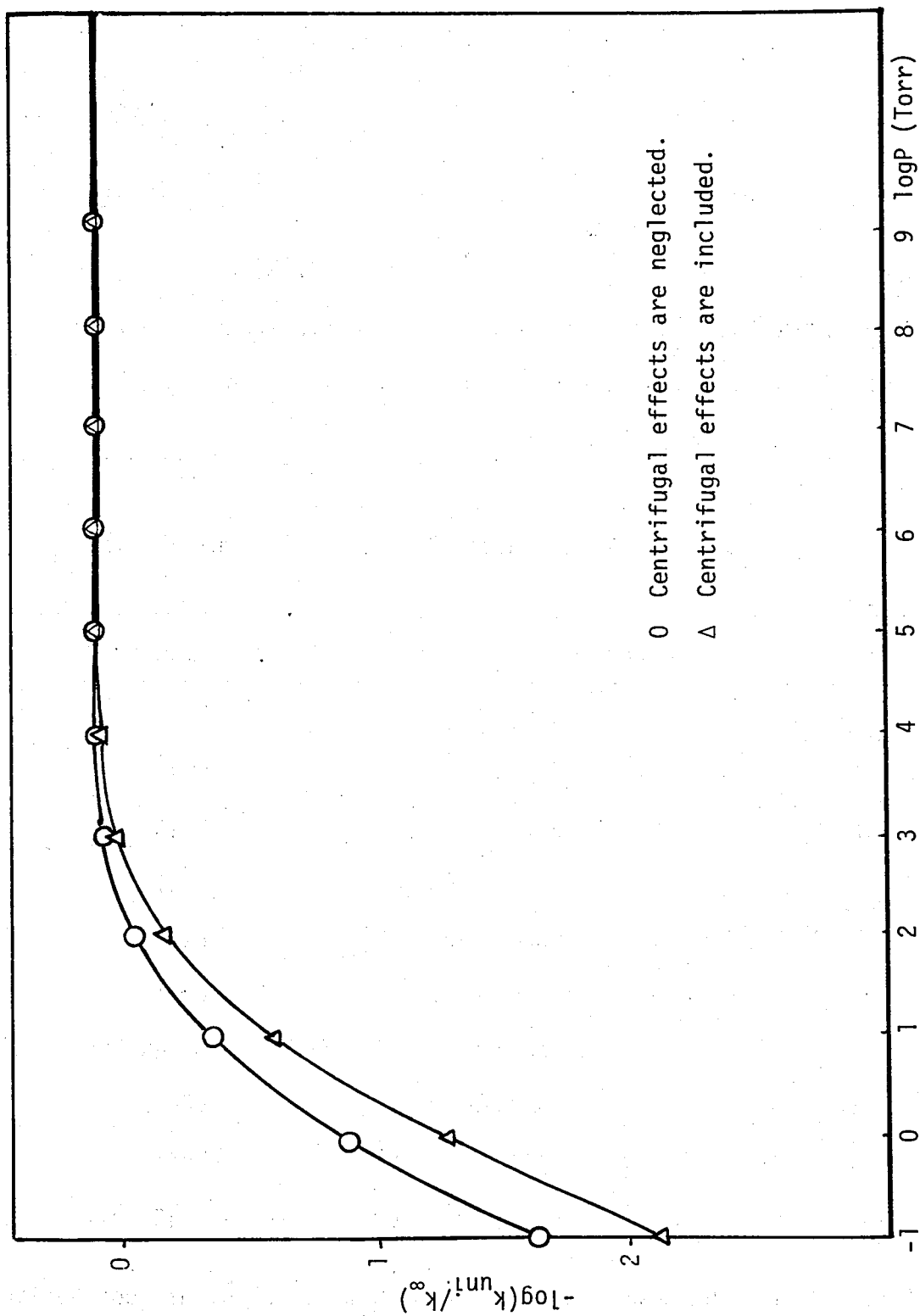


Figure 5.2 - Calculated fall-off curves for ethane decomposition at 873°K (Model I)

5.1.2 Model II

5.1.2.1 DataA. The Molecule

The energized molecule in this part is assumed to have the geometry and the vibrational frequencies of the ground state C_2H_6 molecule (Table 5.3 and Table 5.4). The torsional frequency is considered as a vibration.

B. The Activated ComplexTABLE 5.15 - The Vibrational Frequencies of $C_2H_6^\ddagger$ (Model II)

	Wave number (cm^{-1})	Type of vibration	Species
ν_1	2915	C-H stretching	A_{1g}
ν_2	1388	CH_3 deformation	A_{1g}
ν_3	2915	C-H stretching	A_{2u}
ν_4	1370	CH_3 deformation	A_{2u}
ν_5	2974	C-H stretching	E_u
ν_6	1460	CH_3 deformation	E_u
ν_7	$822\exp[-\alpha(r^+ - 1.543)]$	CH_3 -C rocking	E_u
ν_8	2950	C-H stretching	E_g
ν_9	1469	CH_3 deformation	E_g
ν_{10}	$1190\exp[-\alpha(r^+ - 1.543)]$	CH_3 -C rocking	E_g

The reaction coordinate is assumed to be the C-C bond extension and $V(r^+)$ is determined by representing the classical potential energy by a Morse function.

$$V(r^+) = D[1 - e^{-\beta(r^+ - r_e)}]^2 + E_Z^+ - E_Z^m \quad (5.16)$$

$$D = \Delta H_O^0 + E_Z^m - E_Z^p \quad (5.17)$$

and

$$\beta = (f/2D)^{1/2} \quad (5.18)$$

ΔH_O^0 = Bond dissociation energy at 0°K

E_Z^m = Zero point energy of the reactant molecule

E_Z^p = Zero point energy of the produced methyl radicals

f = C-C stretching force constant

The CH_3 rocking motions are the frequency lowerings in the molecule .

Values for the two degenerate CH_3 rocking frequencies are given as

$$\nu_a = 822 \exp[-\alpha(r^+ - 1.543)] \text{ cm}^{-1} \quad (2)$$

$$\nu_b = 1190 \exp[-\alpha(r^+ - 1.543)] \text{ cm}^{-1} \quad (2)$$

The known parameters for the calculation of $V(r^+)$ are:

$$\Delta H_O^0 = 87.2 \text{ kcal mole}^{-1} \quad [42b]$$

$$E_Z^m = 45.08 \text{ kcal mole}^{-1} \quad (\text{Model I})$$

$$E_Z^p = 36.54 \text{ kcal mole}^{-1} \quad (\text{Model I})$$

$$f = 5.1080 \times 10^5 \text{ dynes cm}^{-1} \quad [42b]$$

$$\alpha = 0.82 \quad [42b]$$

The calculated values of D and β are

$$D = 95.74 \text{ kcal mole}^{-1}$$

$$\beta = 1.96 \times 10^8 \text{ cm}^{-1}$$

$$\begin{aligned}
 E_Z^+ - E_Z^m &= \frac{1}{2} \{ (2)(1190)[\exp(-0.82(r^+ - 1.543)) - 1] \\
 &\quad + (2)(822)[\exp(-0.82(r^+ - 1.543)) - 1] - 955 - 260 \} (2.859 \times 10^{-3}) \\
 &= \{ 1190[\exp(-0.82(r^+ - 1.543)) - 1] + 822[\exp(-0.82(r^+ - 1.543)) - 1] \\
 &\quad - 607.5 \} (2.859 \times 10^{-3}) \\
 &= 5.752[\exp(0.82(r^+ - 1.543))] - 7.489 \text{ kcal mole}^{-1}
 \end{aligned}$$

Thus

$$V(r^+) = 95.74[1 - e^{-1.96(r^+ - 1.543)}]^2 + 5.752[\exp(-0.82(r^+ - 1.543))] - 7.489$$

The distance where the activated complex is supposed to be located is divided into smaller distances. The potential energy and the rocking frequencies are evaluated at each r^+ . The density of states is computed at every point and the minimum value is chosen by the computer program.

TABLE 5.16 - Potential Energy and Vibration Frequencies as a Function of r^+ for $C_2H_6^+$ (Model II)

r^+ (Å)	$V(r^+)$ (kcal mole ⁻¹)	ν_a (cm ⁻¹)	ν_b (cm ⁻¹)
3.000	79.30	249	360
3.250	83.04	203	294
3.500	85.32	165	239
3.750	86.68	135	195
4.000	87.47	110	159
4.250	87.93	89	129
4.500	88.18	73	105
4.750	88.31	59	86
5.000	88.37	48	70

5.1.2.2 The Moments of Inertia

A. The Molecule

The moments of inertia for the external rotation of the molecule are those calculated for Model I.

$$I_{xx} = I_{yy} = 25.461 \text{ amu } \overset{\circ}{\text{A}}^2 = 42.27 \times 10^{-40} \text{ g.cm}^2$$

$$I_{zz} = 6.516 \text{ amu } \overset{\circ}{\text{A}}^2 = 10.82 \times 10^{-40} \text{ g.cm}^2$$

B. The Complex

I. *External Rotation*

The moments of inertia are calculated at each value of r^+ , in the interval from $3 \overset{\circ}{\text{A}}$ to $5 \overset{\circ}{\text{A}}$.

The value of x^+ is supposed to change from $0.899 \overset{\circ}{\text{A}}$ in the molecule to $0.954 \overset{\circ}{\text{A}}$ in the complex.

In the same way the value of z^+ , the perpendicular distance from the hydrogens to the C atom, changes from $0.366 \overset{\circ}{\text{A}}$ in the molecule where $r_e = 1.543 \overset{\circ}{\text{A}}$ to 0. (The methyl groups are planar) in the Gorin model where $r_e^+ = 4.57 \overset{\circ}{\text{A}}$.

The change in z^+ and x^+ or y^+ is supposed to be proportional to the elongation of the distance r^+ .

TABLE 5.17 - Parameters for Evaluation of Moment of Inertia Product as a Function of r^+
for $C_2H_6^+$ (Model II)

r^+	Δr^+	Δx^+	x^+	Δz^+	z^+
	$(\Delta r^+ = r^+ - 1.543)$	$(\Delta x = \frac{\Delta r(0.954 - 0.899)}{(4.57 - 1.543)})$	$(x = 0.899 + \Delta x)$	$(\Delta z^+ = \frac{\Delta r^+(0.366)}{4.57 - 1.543})$	$(0.366 - \Delta z^+)$
3.000	1.457	0.026	0.925	0.176	0.189
3.250	1.707	0.031	0.930	0.206	0.160
3.500	1.957	0.036	0.935	0.237	0.129
3.750	2.207	0.040	0.939	0.270	0.099
4.000	2.457	0.045	0.944	0.297	0.069
4.250	2.707	0.049	0.948	0.327	0.039
4.500	2.957	0.054	0.953	0.358	0.008
4.750	-	-	0.954	-	0
5.000	-	-	0.954	-	0

TABLE 5.18 - Change in x^+ as a Function of r^+ for $C_2H_6^+$ (Model II)

	3.000	3.250	3.500	3.750	4.000	4.250	4.500	4.750	5.000
m_i	x	x	x	x	x	x	x	x	x
12.011	0	0	0	0	0	0	0		
12.011	0	0	0	0	0	0	0		
1.0079	0	0	0	0	0	0	0		
1.0079	0.925	0.930	0.935	0.939	0.944	0.948	0.953	0.954	0.954
1.0079	-0.925	-0.930	-0.935	-0.939	-0.944	-0.948	-0.953	-0.954	-0.954
1.0079	0	0	0	0	0	0	0	0	0
1.0079	0.925	0.930	0.935	0.939	0.944	0.948	0.953	0.954	0.954
1.0079	-0.925	-0.930	-0.935	-0.939	-0.944	-0.948	-0.953	-0.954	-0.954
	3.450	3.487	3.525	3.555	3.592	3.623	3.662	3.669	3.669

TABLE 5.19 - Change in z^+ as a Function of r^+ for $C_2H_6^+$ (Model II)

	3.000	3.250	3.500	3.750	4.000	4.250	4.500	4.750	5.000
m_i	z^+	z^+	z^+	z^+	z^+	z^+	z^+	z^+	z^+
12.011	1.5	1.625	1.75	1.875	2.00	2.125	2.25	2.375	2.5
12.011	-1.5	-1.625	-1.75	-1.875	-2.00	-2.125	-2.25	-2.375	-2.5
1.0079	1.689	1.785	1.879	1.974	2.069	2.164	2.25	2.375	2.5
1.0079	1.689	1.785	1.879	1.974	2.069	2.164	2.25	2.375	2.5
1.0079	1.689	1.785	1.879	1.974	2.069	2.164	2.25	2.375	2.5
1.0079	-1.689	-1.785	-1.879	-1.974	-2.069	-2.164	-2.25	-2.375	-2.5
1.0079	-1.689	-1.785	-1.879	-1.974	-2.069	-2.164	-2.25	-2.375	-2.5
1.0079	-1.689	-1.785	-1.879	-1.974	-2.069	-2.164	-2.25	-2.375	-2.5
	71.301	82.700	94.920	108.017	121.976	136.794	152.445	169.610	187.934

TABLE 5.20 - Moments of Inertia as a Function of r^+ for $C_2H_6^+$
(Model II)

r^+ (Å)	$I_{xx}^+ = I_{yy}^+$ (amu Å ²)	I_{zz}^+ (amu Å ²)
3.000	74.751	6.900
3.250	86.187	6.974
3.500	98.445	7.050
3.750	111.572	7.110
4.000	125.568	7.184
4.250	140.417	7.246
4.500	156.107	7.324
4.750	173.279	7.340
5.000	191.603	7.340

II. Internal Rotation

The moment of inertia for internal rotation is proportional to the value of ℓ which changes from 1.038 Å in the molecule to 1.102 Å in the complex.

TABLE 5.21 - Parameters for Evaluation of the Moment of Inertia for Internal Rotation as Function of r^+ for $C_2H_6^+$ (Model II)

r^+ (Å)	Δr^+ (Å) ($\Delta r^+ = r^+ - 1.543$)	$\Delta \ell^+$ (Å) $\Delta \ell^+ = \frac{\Delta r^+ (1.102 - 1.038)}{3.027}$	ℓ^+ (Å) $\ell^+ = 1.038 + \Delta \ell^+$
3.000	1.457	0.031	1.069
3.250	1.707	0.036	1.074
3.500	1.957	0.041	1.079
3.750	2.207	0.047	1.085
4.000	2.457	0.052	1.090
4.250	2.707	0.057	1.095
4.500	2.957	0.063	1.101
4.750	-	-	1.102
5.000	-	-	1.102

TABLE 5.22 - Moment of Inertia for Internal Rotation as a Function of r^+ for $C_2H_6^+$ (Model II)

r^+ (Å)	$I_{i.r}^+$ (amu Å ²)
3.000	1.731
3.250	1.744
3.500	1.760
3.750	1.780
4.000	1.796
4.250	1.813
4.500	1.829
4.750	1.834
5.000	1.834

5.1.2.3 Calculation of the Partition Functions

Neglecting Centrifugal Effects

A. The Molecule

I. *Vibrational Partition Function*

The vibrational partition function for the molecule is calculated in the same way as in Section 5.1.1.3 with the exception that the contribution of the torsional mode ($\nu = 250 \text{ cm}^{-1}$) is also considered.

$$Q_v = 16.8758$$

II. *Rotational Partition Function*

$$Q_r = 4140.30$$

B. The Activated Complex

I. *Vibrational Partition Function*

The minimization procedure carried out for the number of states located the activated complex at $r^+ = 3.375 \overset{0}{\text{Å}}$.

$$\nu_a = 1190 \exp(-0.82(3.375 - 1.543)) = 265 \text{ cm}^{-1}(2)$$

$$\nu_b = 822 \exp(-0.82(3.375 - 1.543)) = 183 \text{ cm}^{-1}(2)$$

TABLE 5.23 - Parameters for Evaluation of the Vibrational Partition Function for $C_2H_6^+$ (Model II, neglecting Centrifugal Effects)

v_i^+	$1/1-e^{-\theta v_i^+/T}$
2915 (2)	1.0082
1388	1.1130
1370	1.1168
2974 (2)	1.0075
1460 (2)	1.0991
183 (2)	3.8409
2950 (2)	1.0078
1469 (2)	1.0975
265 (2)	2.8261

$$\theta = 1.648 \times 10^{-3} v^+$$

$$Q_V^+ = (1.0082)^2 (1.1130)(1.1168)(1.0075)^2 (1.0991)^2 (3.8409)^2 (1.0078)^2 (1.0975)^2 (2.8261)^2$$

$$Q_V^+ = 223.3198$$

II. Rotational Partition Function

r^+	Δr^+	Δx^+	x^+	Δz^+	z^+
3.375	1.832	0.033	0.932	0.222	0.144

TABLE 5.24 - Parameters for Evaluation of Moment of Inertia Product of $C_2H_6^+$ (Model II, neglecting Centrifugal Effects)

Atom	m_i	z_i^+	x_i^+
C_1	12.011	1.6885	0
C_2	12.011	-1.6885	0
H_1	1.0079	1.8325	0
H_2	1.0079	1.8325	0.932
H_3	1.0079	1.8325	-0.932
H_4	1.0079	-1.8325	0
H_5	1.0079	-1.8325	0.932
H_6	1.0079	-1.8325	-0.932
	$\Sigma m_i z_i^2 = 88.743$		$3.502 = \Sigma m_i x_i^2$

$$I_{xx}^+ = I_{yy}^+ = 88.743 + 3.502 = 92.245 \text{ amu } \text{\AA}^2 \quad 153.13 \times 10^{-40} \text{ g.cm}^2$$

$$I_{zz}^+ = (2)(3.502) = 7.004 \text{ amu } \text{\AA}^2 \quad 11.63 \times 10^{-40} \text{ g.cm}^2$$

$$Q_r^+ = \frac{\sqrt{3.14} (8)(3.14)^2 (1.3805 \times 10^{-16})(873)}{6 (6.6262 \times 10^{-27})^2} \Bigg)^{3/2} \left((153.13)^2 (11.63 \times 10^{-120}) \right)^{1/2}$$

$$= 1.5537 \times 10^4$$

III. Partition Function for Internal Rotation

$r^+(A)$	$\Delta r^+(A)$	$\Delta \rho^+(A)$	$\rho^+(A)$	I_{ir}^+ (amu \AA^2)
3.375	1.832	0.039	1.077	1.753

$$Q_{ir}^+ = ((8)(3.14)^3(2.91 \times 10^{-40})(1.3805 \times 10^{-16})(873))^{1/2} / (6.6262 \times 10^{-27})(3)$$

$$= 4.667$$

Including Centrifugal Effects

A. The Molecule (See Section 5.1.2.3)

I. *Vibrational Partition Function*

$$Q_v = 16.8758$$

II. *Rotational Partition Function*

$$Q_r = 4140.30$$

B. The Activated Complex

I. *Vibrational Partition Function*

The minimization procedure carried out for the calculation of the number of states located the activated complex at $r^+ = 3.6 \overset{0}{\text{Å}}$.

$$v_a = 1190 \exp(-0.82(3.6 - 1.543)) = 220 \text{ cm}^{-1}$$

$$v_b = 822 \exp(-0.82(3.6 - 1.543)) = 152 \text{ cm}^{-1}$$

TABLE 5.25 - Parameters for Evaluation of the Vibrational Partition Function of $C_2H_6^+$ (Model II, including Centrifugal Effects)

ν_i^+	$1/1-e^{-\theta\nu_i/T}$
2915 (2)	1.0082
1388	1.1130
1370	1.1160
2974 (2)	1.0075
1460 (2)	1.0991
152 (2)	4.5189
2950 (2)	1.0078
1469 (2)	1.0975
220 (2)	3.2883

$$Q_V^+ = (1.0082)^2(1.1130)(1.1160)(1.0075)^2(1.0991)^2(4.5189)^2(1.0078)^2 \\ (1.0975)^2(3.2883)^2$$

$$Q_V^+ = 417.10$$

II. Rotational Partition Function

$r^+(\text{\AA})$	$\Delta r^+(\text{\AA})$	$\Delta x^+(\text{\AA})$	$x^+(\text{\AA})$	$\Delta z^+(\text{\AA})$	$z^+(\text{\AA})$
3.600	2.057	0.037	0.936	0.249	0.117

TABLE 5.26 - Parameters for Evaluation of Moment of Inertia Product of $C_2H_6^+$ (Model II, including Centrifugal Effects)

Atom	m_i	x_i^+	z_i^+
C ₁	12.011	0	1.800
C ₂	12.011	0	-1.800
H ₁	1.0079	0	1.917
H ₂	1.0079	0.936	1.917
H ₃	1.0079	-0.936	1.917
H ₄	1.0079	0	-1.917
H ₅	1.0079	0.936	-1.917
H ₆	1.0079	-0.936	-1.917
$\Sigma m_i x_i^2 =$		3.532	$\Sigma m_i z_i^2 = 100.055$

$$I_{xx}^+ = I_{yy}^+ = 100.055 + 3.532 = 103.587 \text{ amu } \overset{0}{\text{Å}}^2 \quad 171.95 \times 10^{-40} \text{ g.cm}^2$$

$$I_{zz}^+ = (2)(3.532) = 7.064 \text{ amu } \overset{0}{\text{Å}}^2 \quad 11.73 \times 10^{-40} \text{ g.cm}^2$$

$$Q_r^+ = \frac{\sqrt{3.14}}{6} \left(\frac{(8)(3.14)^2 (1.3805 \times 10^{-16})(873)}{(6.6262 \times 10^{-27})^2} \right)^{3/2} ((171.954)^2 (11.7266 \times 10^{-120}))$$

$$= 1.7499 \times 10^4$$

III. Partition Function for Internal Rotation

$r^+(\text{Å})$	$\Delta r^+(\text{Å})$	$\Delta \ell^+(\text{Å})$	$\ell^+(\text{Å})$	$I_{i,r}^+(\text{amu } \overset{0}{\text{Å}}^2)$
3.600	2.057	0.043	1.081	1.768

$$Q_{ir}^+ = ((8)(3.14)^3(2.93 \times 10^{-40})(1.3805 \times 10^{-16})(873))^{1/2} / (6.6262 \times 10^{-27})(3)$$

$$= 4.708$$

5.1.2.4 Calculation of $\langle E_v \rangle$, $\langle E_v^+ \rangle$ and E^+

A. Calculation of $\langle E_v \rangle$

$$T \partial \ln Q_v / \partial T = 4.497$$

$$\langle E_v \rangle = 7.80 \text{ kcal mole}^{-1}$$

B. Calculation of $\langle E_v^+ \rangle$

I. *Neglecting Centrifugal Effects*

$$T \partial \ln Q_v^+ / \partial T = 5.008$$

$$\langle E_v^+ \rangle = 8.69 \text{ kcal mole}^{-1}$$

II. *Including Centrifugal Effects*

$$T \partial \ln Q_v^+ / \partial T = 5.119$$

$$\langle E_v^+ \rangle = 8.88 \text{ kcal mole}^{-1}$$

C. Calculation of E^+

$$E^+ = (1 + 0.5)(1.987 \times 10^{-3})(873) + (2.859 \times 10^{-3})(3038.84)$$

$$= 11.29 \text{ kcal mole}^{-1}$$

5.1.2.5 Calculation of ΔS^\ddagger , k_∞ and A_∞

A. Neglecting Centrifugal Effects

The value of E_0 is $84.30 \text{ kcal mole}^{-1}$. The value of E_∞ which corresponds to E_0 is

$$\begin{aligned} E_\infty &= E_0 + \frac{1}{2}(r^* - r + 2)RT - \langle E_V \rangle + \langle E_V^+ \rangle \\ &= (84.30)^2 + (1.5)(1.987 \times 10^{-3})(873) - 7.8 + 8.69 \\ &= 87.79 \text{ kcal mole}^{-1} \end{aligned}$$

$$\Delta S_{th}^\ddagger = S_{th}^+ - S_{th}$$

$$\begin{aligned} S_V &= 1.987(\ln 16.8758 + 4.497) \\ &= 14.55 \text{ cal mole}^{-1} \text{ deg}^{-1} \end{aligned}$$

$$S_r = 19.53 \text{ cal mole}^{-1} \text{ deg}^{-1} \text{ (Model I)}$$

$$S_{th} = 34.10 \text{ cal mole}^{-1} \text{ deg}^{-1}$$

$$\begin{aligned} S_V^+ &= 1.987(\ln 223.3198 + 5.008) \\ &= 20.69 \text{ cal mole}^{-1} \text{ deg}^{-1} \end{aligned}$$

$$\begin{aligned} S_r^+ &= 1.987(\ln 1.5537 \times 10^4 + 1.5) \\ &= 22.16 \text{ cal mole}^{-1} \text{ deg}^{-1} \end{aligned}$$

$$\begin{aligned} S_{ir}^+ &= 1.987(\ln 4.667 + 0.5) \\ &= 4.05 \text{ cal mole}^{-1} \text{ deg}^{-1} \end{aligned}$$

$$S_{th}^+ = 46.90 \text{ cal mole}^{-1} \text{ deg}^{-1}$$

$$\Delta S_{th}^\ddagger = 12.80 \text{ cal mole}^{-1} \text{ deg}^{-1}$$

$$k_{\infty,th} = \frac{(1.3805 \times 10^{-16})(873)}{6.6262 \times 10^{-27}} \frac{(223.32)(1.5537 \times 10^4)(4.667)}{(16.8758)(4140.30)} \exp\left(\frac{-84.30}{1.987 \times 873 \times 10^{-3}}\right)$$

$$= 0.33 \times 10^{-5}$$

$$A_{\infty,th} = \frac{(2.718)(1.3805 \times 10^{-16})(873)}{(6.6262 \times 10^{-27})} e^{12.80/1.987}$$

$$= 10^{16.49}$$

B. Including Centrifugal Effects

The value of E_0 is $85.97 \text{ kcal mole}^{-1}$. The value of E_{∞} corresponding to E_0 is

$$E_{\infty} = E_0 + \frac{1}{2}(r^* - r + 2)RT - \langle E_V \rangle + \langle E_V^+ \rangle$$

$$= 89.65 \text{ kcal mole}^{-1}$$

$$S_{th} = 34.10 \text{ cal mole}^{-1}$$

$$S_V^+ = 1.987(\ln 417.10 + 5.119)$$

$$= 22.16 \text{ cal mole}^{-1} \text{ deg}^{-1}$$

$$S_r^+ = 1.987(\ln 1.7499 \times 10^4 + 1.5)$$

$$= 22.39 \text{ cal mole}^{-1} \text{ deg}^{-1}$$

$$S_{ir}^+ = 1.987(\ln 4.708 + 0.5)$$

$$= 4.07 \text{ cal mole}^{-1} \text{ deg}^{-1}$$

$$S_{th}^+ = 48.62 \text{ cal mole}^{-1} \text{ deg}^{-1}$$

$$\Delta S_{th}^{\ddagger} = 14.52 \text{ cal mole}^{-1} \text{ deg}^{-1}$$

$$k_{\infty,th} = \frac{(1.3805 \times 10^{-16})(873)}{(6.6262 \times 10^{-27})} \frac{(417.10)(1.7499 \times 10^4)(4.708)}{(16.8758)(4140.30)} \exp\left(\frac{-85.97}{1.987 \times 873 \times 10^{-3}}\right)$$

$$= 0.27 \times 10^{-5}$$

$$A_{\infty,th} = \frac{(2.718)(1.3805 \times 10^{-16})(873)}{6.6262 \times 10^{-27}} e^{14.52/1.987}$$

$$= 10^{16.87}$$

5.1.2.6 Calculation of the Anharmonicity Corrections

A. The Molecule

The molecule has 18 vibrational frequencies. The mean Morse dissociation energy is calculated as done in Section 5.1.1.6 for Model I, including the anharmonicity correction for the torsional vibration.

$$D = 35.11 \text{ kcal mole}^{-1}$$

B. The Activated Complex

The activated complex contains

6 C-H stretching vibrations (Model I)

10 C-H bending vibrations (Model I)

$$\langle D_e^{-1} \rangle = \frac{1}{16} ((6)(0.01206) + (10)(0.01370))$$

$$= 0.01309$$

$$D = 76.42 \text{ kcal mole}^{-1}$$

5.1.2.7. Evaluation of $k_{\text{uni}}/k_{\infty}$ TABLE 5.27 - Parameters for $k_{\text{uni}}/k_{\infty}$ for C_2H_6 (Model II)

	Centrifugal effects are neglected	Centrifugal effects are included
E_0	84.30 kcal mole ⁻¹	85.97 kcal mole ⁻¹
E_Z	15767 cm ⁻¹ = 45.08 kcal mole ⁻¹	15767 cm ⁻¹ = 45.08 kcal mole ⁻¹
E_Z^+	13595 cm ⁻¹ = 38.87 kcal mole ⁻¹	13519 cm ⁻¹ = 38.65 kcal mole ⁻¹
s	18	18
s^+	16	16
r	0	0
r^*	1	1
α	17	17
α^+	16.5	16.5
$\Gamma(\alpha+1)$	3.557×10^{14}	3.557×10^{14}
$\Gamma(\alpha^++1)$	8.563×10^{13}	8.563×10^{13}
$\Gamma(1+r^*/2)$	0.886	0.886
$\prod_{i=1}^s v_i$	$1.359 \times 10^{57} \text{ cm}^{-18}$	$1.359 \times 10^{57} \text{ cm}^{-18}$
$\prod_{i=1}^{s^+} v_i^+$	$1.345 \times 10^{49} \text{ cm}^{-16}$	$6.397 \times 10^{48} \text{ cm}^{-16}$
$(E_Z^+)^{\alpha^+-\alpha}$	$0.0086 \text{ cm}^{-0.5}$	$0.0086 \text{ cm}^{-0.5}$
$(E_Z^+)^{\alpha^++1}$	$2.1584 \times 10^{72} \text{ cm}^{-17.5}$	$1.9567 \times 10^{72} \text{ cm}^{-17.5}$
$(E_Z^+)^{s^+}$	$1.3617 \times 10^{66} \text{ cm}^{-16}$	$1.2448 \times 10^{66} \text{ cm}^{-16}$
$(RT)^{1+r^*/2}$	$14946.79 \text{ cm}^{-1.5}$	$14946.79 \text{ cm}^{-1.5}$
$(RT)^{(r^*-1)/2}$	$24.63 \text{ cm}^{-0.5}$	$24.63 \text{ cm}^{-0.5}$
$\langle v^{+2} \rangle$	$4042424.8 \text{ cm}^{-2}$	$4038398.5 \text{ cm}^{-2}$
		./...

Table 5.27 continued...

	Centrifugal effects are neglected	Centrifugal effects are included
$\langle v^+ \rangle$	1699.375 cm ⁻¹	1689.875 cm ⁻¹
$\langle v^+ \rangle^2$	2887875.4 cm ⁻²	2855677.5 cm ⁻²
β^+	1.3533	1.3672
Z	10.82x10 ⁶ Torr ⁻¹ sec ⁻¹	10.82x10 ⁶ Torr ⁻¹ sec ⁻¹
C ₀	22.410	22.280
C ₁	561.28	572.95
θ	0.0135	0.0112
G ₁ (x)	9.55x10 ⁻⁴ x ^{0.5}	4.97x10 ⁻⁴ x ^{0.5}
G ₂ (x)	$\left[\frac{x+1-1.3533}{5.00x+2.73x^{0.5}+3.51} \right]^{16.5}$	$\left[\frac{x+1-1.3672}{5.00x+2.73x^{0.5}+3.51} \right]^{16.5}$
G ₃ (x)	$[x+1-1.3533\exp(-2.419x^{0.25})]^{16.5}$	$[x+1-1.3672\exp(-2.419x^{0.25})]^{16.5}$
H(x)	(x + 3.328) ¹⁷	(x + 3.173) ¹⁷ *
C ₂ /P	1.9048x10 ⁹ /P	4.0409x10 ⁹ /P

Thus when centrifugal effects are neglected

$$\begin{aligned}
 k_{\text{uni}}/k_{\infty} = & 561.28 \left[\int_0^{0.0135} \frac{9.55 \times 10^{-4} x^{0.5} \exp(-22.41x) dx}{1 + \frac{1.9048 \times 10^9}{P} \left[\frac{(9.55 \times 10^{-4} x^{0.5})}{(x+3.328)^{17}} \right]} \right. \\
 & + \frac{1}{0.0135} \frac{\int \left[\frac{x+1-1.3533}{5.00x+2.73x^{0.5}+3.51} \right]^{16.5} \exp(-22.41x) dx}{1 + \frac{1.9048 \times 10^9}{P} \left[\frac{x+1-1.3533}{5.00x+2.73x^{0.5}+3.51} \right]^{16.5} / (x+3.328)^{17}} \\
 & \left. + \frac{8}{1} \frac{\int \left[\frac{x+1-1.3533 \exp(-2.419x^{0.25})}{5.00x+2.73x^{0.5}+3.51} \right]^{16.5} \exp(-22.41x) dx}{1 + \frac{1.9048 \times 10^9}{P} \left[\frac{x+1-1.3533 \exp(-2.419x^{0.25})}{5.00x+2.73x^{0.5}+3.51} \right]^{16.5} / (x+3.328)^{17}} \right]
 \end{aligned}$$

When centrifugal effects are included

$$\frac{k_{\text{uni}}}{k_{\infty}} = 572.95 \left[\int_0^{0.0112} \frac{4.97 \times 10^{-4} x^{0.5} \exp(-22.28x) dx}{1 + \frac{4.0409 \times 10^9}{P} [(4.97 \times 10^{-4} x^{0.5}) / (x+3.173)]^{17}} \right. \\ \left. + \int_0^{0.0112} \frac{[x+1-1.3672/(5.00x+2.73x^{0.5}+3.51)]^{16.5} \exp(-22.28x) dx}{1 + \frac{4.0409 \times 10^9}{P} [x+1-1.3672/(5.00x+2.73x^{0.5}+3.51)]^{16.5} / (x+3.173)} \right. \\ \left. + \int_0^8 \frac{[x+1-1.3672 \exp(-2.4191x^{0.25})]^{16.5} \exp(-22.28x) dx}{1 + \frac{4.0409 \times 10^9}{P} [x+1-1.3672 \exp(-2.4191x^{0.25})]^{16.5} / (x+3.173)^{17}} \right]$$

$$\langle \Delta E_J \rangle = 1.5x \left(1 - \frac{(171.95)^2 (11.73)}{(42.27)^2 (10.83)} \right)^{1/2} (1.987 \times 10^{-3}) (873)$$

$$= 8.41 \text{ kcal mole}^{-1}$$

TABLE 5.28 - Contribution of Centrifugal Effects to $k_{\text{uni}}/k_{\infty}$ for $\text{C}_2\text{H}_6 \rightarrow 2\text{CH}_3\cdot$ at 873°K (Model II)

P (Torr)	$k_{\text{uni}}/k_{\infty}$ ^a	$(k_{\text{uni}}/k_{\infty})^b$
10 ⁻¹	0.2368	0.1075
1	0.5745	0.3482
10 ¹	0.9357	0.7278
10 ²	1.1374	1.0516
10 ³	1.1942	1.1912
10 ⁴	1.2031	1.2218
10 ⁵	1.2040	1.2258
10 ⁶	1.2041	1.2262
10 ⁷	1.2041	1.2262
10 ⁸	1.2041	1.2262
10 ⁹	1.2041	1.2262

^a Neglecting centrifugal effects ($k_{\text{uni}}/k_{\infty} = 0.5$ at $P = 0.65$ mm Hg)

^b Including centrifugal effects ($k_{\text{uni}}/k_{\infty} = 0.5$ at $P = 2.7$ mm Hg)

5.1.2.8 Calculation of $k_a(E^*)$ TABLE 5.29 - Properties of the Active Molecule and Activated Complex
(C_2H_6 , Model II)

	Molecule	Complex								
		Neglecting C.E.				Including C.E.				
Frequencies(cm^{-1})	2915 (2)									
	1388					2915 (2)				
	955					1388				
	260					1370				
	1370					2974 (2)				
	2974 (2)					1460 (2)				
	1460 (2)					2950 (2)				
	822 (2)					1469 (2)				
	2950 (2)									
	1469 (2)									
1190 (2)										
		r^+	3.00	3.25	3.50	3.75	4.00	4.25	4.50	4.75
			249	203	165	135	110	89	73	59
			360	294	239	195	159	129	105	86
E_0 (kcal mole $^{-1}$)			84.30				85.97			
s	18						16			
r	0						1			
Moments of inertia (amu \AA^2)		r^+	3.00	3.25	3.50	3.75	4.00	4.25	4.50	4.75
	$I_{xx} = I_{yy}$	25.46	74.151	86.187	98.445	111.572	125.568	140.47	156.117	173.279
I_{zz}	6.52	6.900	6.974	7.050	7.110	7.184	7.246	7.324	7.340	
Symmetry number for internal rotation							3			
σ	-									
Average bond energy (kcal mole $^{-1}$)							76.42			
D	35.11									
Increment for the summation (kcal mole $^{-1}$)										
ΔE^\ddagger	0.1									
Number of rate constants to be calculated										
NEN	1000									
Reaction path degeneracy										
L^\ddagger	1									

Table 5.29 continued...

	Molecule	Complex								
		<u>Neglecting C.E.</u>				<u>Including C.E.</u>				
Temperature ($^{\circ}\text{K}$) T	873									
Pressure (Torr) P	600									
Collision number (Torr $^{-1}$ sec $^{-1}$) Z	10.82×10^6									
Internal energy of energized molecule (kcal mole $^{-1}$) ECC					107.35			97.35		
Number of reaction coordinate intervals NN	8									
Potential energy of reaction coordinate (kcal mole $^{-1}$) $V(r^+)$		r^+	3.00	3.25	3.50	3.75	4.00	4.25	4.50	4.75
			79.30	83.04	85.32	86.68	87.47	87.93	88.18	88.31
Reduced moment of inertia changing with r^+ I_{ir}^+ (amu A^2)					r^+		I_{ir}^+			
					3.000		1.731			
					3.250		1.744			
					3.500		1.760			
					3.750		1.780			
					4.000		1.796			
					4.250		1.813			
					4.500		1.829			
					4.750		1.834			
					5.000		1.834			

The results at $E^+ = 11.29 \text{ kcal mole}^{-1}$ are

$$k_a(E^+ + E_0) = 0.3278 \times 10^8 \text{ sec}^{-1}$$

$$k_a(E^+ + E_0)_{\text{anh}} = 0.3405 \times 10^7 \text{ sec}^{-1}$$

$$k_a(E^+ + E_0 + \langle \Delta E_J \rangle) = 0.1433 \times 10^9 \text{ sec}^{-1}$$

$$k_a(E^+ + E_0 + \langle \Delta E_J \rangle)_{\text{anh}} = 0.1740 \times 10^8 \text{ sec}^{-1}$$

5.1.2.9 Calculation of k_{uni}

$$k_{\text{uni}} = \frac{L^\ddagger Q_1^+}{h Q_1 Q_2} \exp(-E_0/RT) \Delta E^+ \sum_{i=1}^{i_{\text{max}}} \left[\frac{[\Sigma P(E_{\text{vr}}^+)] \exp(-E^+/RT)}{1 + k_a(E^*)/\lambda ZP} \right]$$

The input data for the computer program which evaluates the summation for k_{uni} is given in Table 5.29.

A. Neglecting Centrifugal Effects

$$k_{\text{uni}} = \frac{1.5537 \times 10^4}{(9.537 \times 10^{-14})(4140.30)(16.8758)} \exp\left(\frac{-84.30}{(1.987 \times 10^{-3})(873)}\right) (0.1)(0.21)$$

$$= 4.0196 \times 10^{-6} \text{ sec}^{-1}$$

$$k_{\text{uni}}(\text{anh}) = (1.8279 \times 10^{-10})(0.2203 \times 10^5)$$

$$= 4.0269 \times 10^{-6} \text{ sec}^{-1}$$

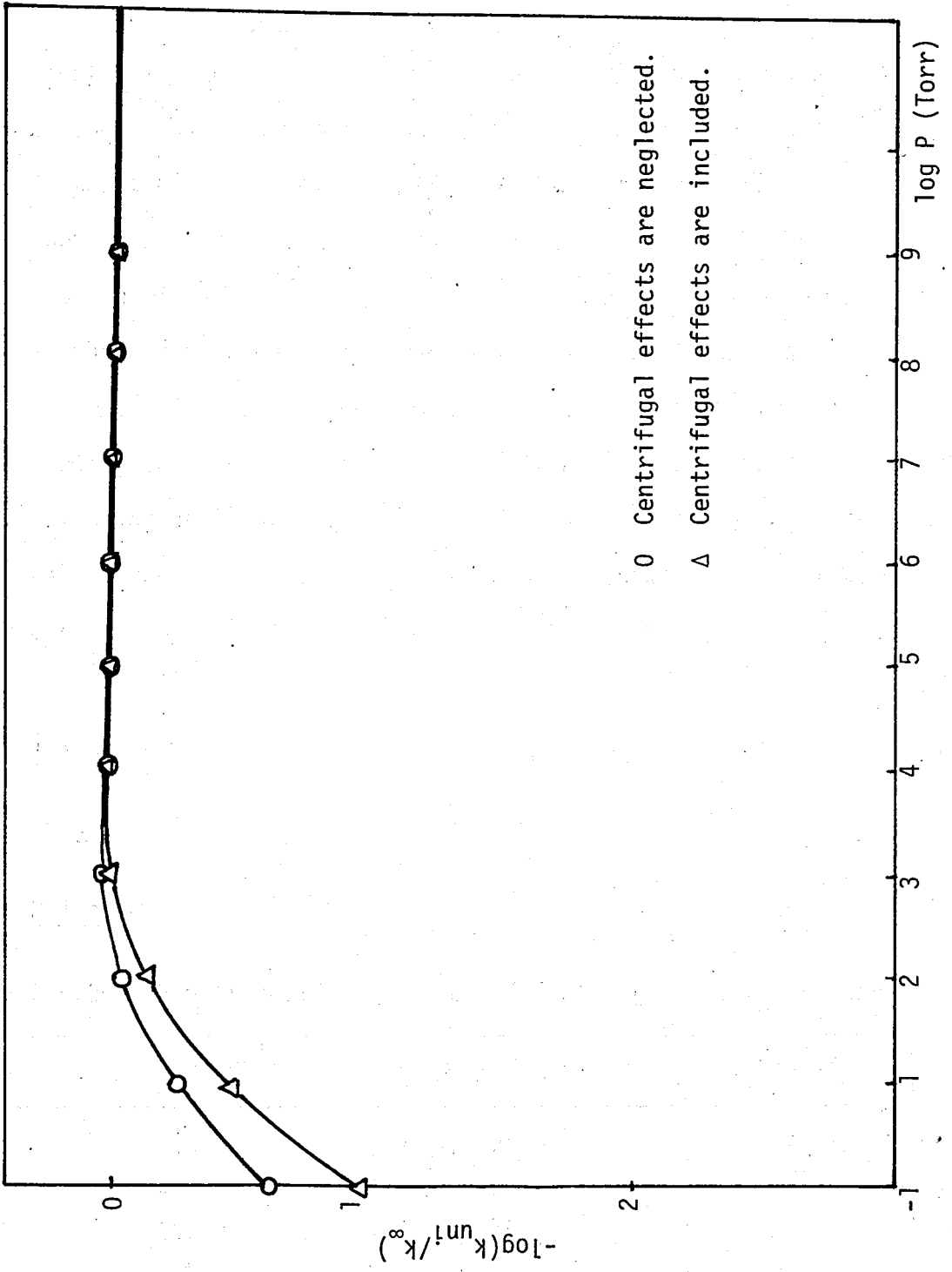
B. Including Centrifugal Effects

$$k_{\text{uni}} = (7.8613 \times 10^{-11})(0.4164 \times 10^5)$$

$$= 3.2735 \times 10^{-6} \text{ sec}^{-1}$$

$$k_{\text{uni}}(\text{anh}) = (7.8613 \times 10^{-11})(0.4193 \times 10^5)$$

$$= 3.2963 \times 10^{-6} \text{ sec}^{-1}$$



5.2 1,1,2,2-TETRAFLUOROETHANE

The kinetics of the thermal decomposition of a dilute mixture of 1,1,2,2-tetrafluoroethane in argon has been studied in a single pulse shock tube in the temperature range 1190-1450⁰K at total pressures of about 2900-4000 Torr [90].

Three of the vibrational frequencies of the CHF₂ radical have not been given in the literature. They have been determined in this work such that, their magnitudes fit the values required by the spectra and permit to obtain good agreement with the experimental results.

The following calculations evaluate the position of the fall-off region as well as the rate constant for the C-C bond scission in 1,1,2,2-tetrafluoroethane.

5.2.1 Model I

5.2.1.1 DataA. The Molecule*TABLE 5.30 - Vibrational Frequencies of C₂H₂F₄ [109] (C_{2h} symmetry)

	Wave number (cm ⁻¹)	Type of vibration	Species
v ₁	3015	C-H stretching	A _g
v ₂	1440	C-H bending	A _g
v ₃	1360	C-F stretching	A _g
v ₄	901	C-C stretching	A _g
v ₅	622	CHF ₂ deformation	A _g
v ₆	361	rocking	A _g

./...

* The energized C₂H₂F₄ molecule has the same configuration as the energized C₂H₆ molecule.

Table 5.30 continued...

	Wave number (cm^{-1})	Type of vibration	Species
ν_7	1440	C-H bending	B_g
ν_8	1080	C-F stretching	B_g
ν_9	478	rocking	B_g
ν_{10}	1322	C-H bending	A_u
ν_{11}	1125	C-F bending	A_u
ν_{12}	271	rocking (calculated)	A_u
ν_{13}	130	torsion	A_u
ν_{14}	3000	C-H stretching	B_u
ν_{15}	1336	C-F stretching	B_u
ν_{16}	1134	C-H bending	B_u
ν_{17}	539	CHF_2 deformation	B_u
ν_{18}	549	rocking (calculated)	B_u

TABLE 5.31 - Molecular Parameters of $\text{C}_2\text{H}_2\text{F}_4$ [110]
 (C_{2h} symmetry - the anti rotamer - 84%)

$\text{R}(\text{C}-\overset{\text{O}}{\text{C}})$ (Å)	1.518
$\text{R}(\text{C}-\overset{\text{O}}{\text{H}})$ (Å)	1.098
$\text{R}(\text{C}-\overset{\text{O}}{\text{F}})$ (Å)	1.350
Δ CCF	$108^{\circ}12'$
Δ FCF	$107^{\circ}18'$
Δ CCH	$110^{\circ}18'$

B. The Activated Complex

The activated complex is treated as in the ethane case.

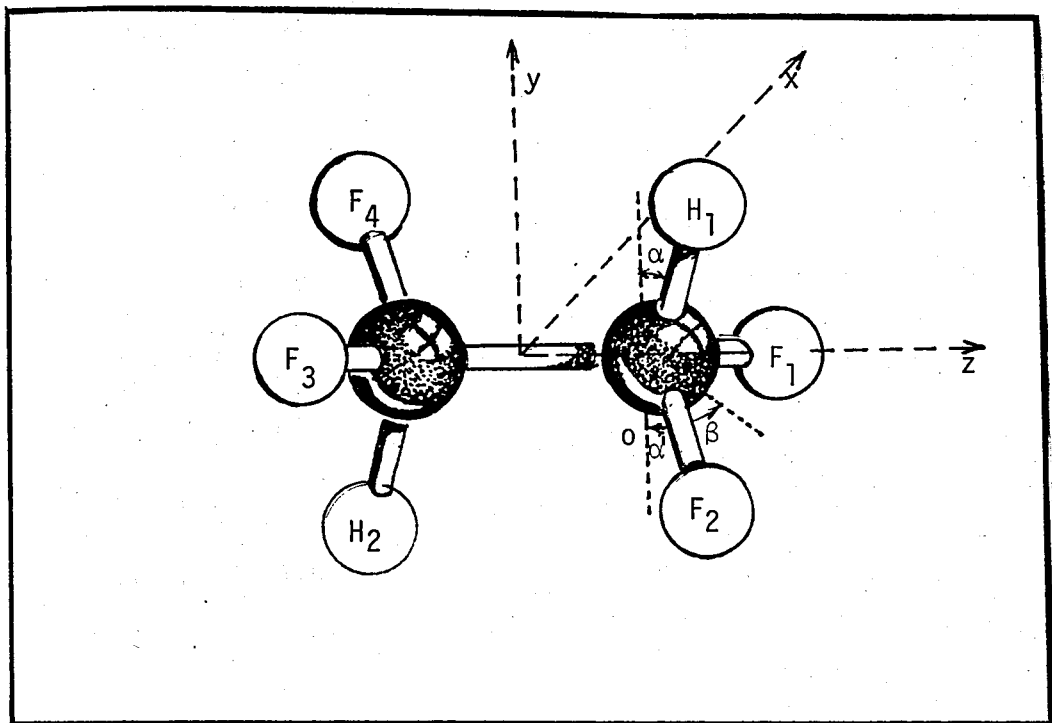
TABLE 5.32 - Vibrational Frequencies of CHF_2^{\cdot} [110] (C_s symmetry)

	Wave number (cm^{-1})	Type of vibration	Species
ν_1	3000 ^a	C-H stretching	A'
ν_2	1165.5	C-F stretching	A'
ν_3	700 ^a	C-F bending	A'
ν_4	650 ^a	C-F bending	A'
ν_5	1316.5	C-H bending	A''
ν_6	1175	C-F stretching	A''

^aThe values of the vibrational frequencies ν_1 , ν_3 , ν_4 have been estimated in this work. The estimation is based on the comparison of the entropy of activation to that calculated from statistical thermodynamics.

TABLE 5.33 - Molecular Parameters of CHF_2^{\cdot} [110] (C_s)

$R(\overset{\circ}{\text{C}}-\overset{\circ}{\text{F}})$ (Å)	1.350
$R(\overset{\circ}{\text{C}}-\overset{\circ}{\text{H}})$ (Å)	1.098
$\Delta\text{HCF} = \Delta\text{FCF}$	115°
Deviation from planarity	$12^{\circ}42'$

5.2.1.2 The Moments of InertiaA. The Molecule (Table 5.31)I. *External Rotation*Figure 5.4 - Geometrical representation of $C_2H_2F_4$.

Calculation of the coordinates

$$\alpha = 110^{\circ}18' - 90^{\circ} = 20^{\circ}18' = 20.3^{\circ}$$

$$\alpha' = 108^{\circ}12' - 90^{\circ} = 18^{\circ}12' = 18.2^{\circ}$$

$$\beta = 107^{\circ}18' / 2 = 53^{\circ}39' = 53.65^{\circ}$$

$$x_{C_1, C_2} = 0$$

$$x_{H_1, H_2} = 0$$

$$x_{F_1, F_4} = \sin(53.65^\circ)(1.35) \\ = 1.087$$

$$x_{F_2, F_3} = -1.087$$

$$z_{C_1} = 0.759$$

$$z_{C_2} = -0.759$$

$$z_{H_1} = (\sin 20.3^\circ \times 1.098) + 0.759 \\ = 1.140$$

$$z_{H_2} = -1.140$$

$$z_{F_1, F_2} = (\sin 18.2^\circ \times 1.35) + 0.759 \\ = 1.181$$

$$z_{F_3, F_4} = -1.181$$

$$y_{C_1, C_2} = 0$$

$$y_{H_1} = \cos(20.3^\circ)(1.098) \\ = 1.030$$

$$y_{H_2} = -1.030$$

$$y_{F_1, F_2} = -(\sin 30^\circ)(1.283) \\ = -0.641$$

$$y_{F_3, F_4} = 0.641$$

where

$$OC = \cos(18.2^\circ)(1.35) \\ = 1.283$$

TABLE 5.34 - Parameters for Evaluation of Moment of Inertia Product of $C_2H_2F_4$

Atom	m_i	x_i	y_i	z_i	$m_i x_i^2$	$m_i y_i^2$	$m_i z_i^2$	$m_i x_i y_i$	$m_i x_i z_i$	$m_i y_i z_i$
C ₁	12.011	0	0	0.759	0	0	6.919	0	0	0
C ₂	12.011	0	0	-0.759	0	0	6.919	0	0	0
H ₁	1.0079	0	1.030	1.140	0	1.069	1.310	0	0	1.184
F ₁	18.998	1.087	-0.641	1.181	22.447	7.806	26.498	-13.237	24.389	-14.382
F ₂	18.998	-1.087	-0.641	1.181	22.447	7.806	26.598	13.237	-24.389	-14.382
H ₂	1.0079	0	-1.030	-1.140	0	1.069	1.310	0	0	1.184
F ₃	18.998	-1.087	0.641	-1.181	22.447	7.806	26.498	-13.237	24.389	-14.382
F ₄	18.998	1.087	0.641	-1.181	22.447	7.806	26.498	13.237	-24.389	-14.382
					89.790	33.362	122.450	0	0	55.160

$$I_{xx} = 155.812 \text{ amu } \overset{O}{A}^2 = 258.65 \times 10^{-40} \text{ g} \cdot \text{cm}^2$$

$$I_{yy} = 212.240 \text{ amu } \overset{O}{A}^2 = 352.32 \times 10^{-40} \text{ g} \cdot \text{cm}^2$$

$$I_{zz} = 123.152 \text{ amu } \overset{O}{A}^2 = 204.43 \times 10^{-40} \text{ g} \cdot \text{cm}^2$$

$$ABC = I_{xx}(I_{yy}I_{zz} - I_{yz}^2)$$

$$= 3.559 \times 10^6 \text{ amu}^3 \overset{O}{A}^6$$

$$= 16.45 \times 10^{-114} \text{ g}^3 \cdot \text{cm}^6$$

II. Internal Rotation

$$\begin{aligned}
 I_{ir} &= \frac{1}{2}(2 \times 18.998 \times (1.283)^2 + 1.008 \times (1.030)^2) \\
 &= 31.80 \text{ amu } \overset{\circ}{\text{A}}^2 \\
 &= 52.80 \times 10^{-40} \text{ g.cm}^2
 \end{aligned}$$

$$\begin{aligned}
 \rho_{F_1, F_2} &= (1.350)(\sin 71.8^\circ) \\
 &= 1.283 \overset{\circ}{\text{A}}
 \end{aligned}$$

$$\begin{aligned}
 \rho_H &= (1.098)(\sin 69.7^\circ) \\
 &= 1.030 \overset{\circ}{\text{A}}
 \end{aligned}$$

B. The Complex

I. External Rotation

Calculation of $\langle R_c \rangle_{av}$ at $T = 1350^\circ\text{K}$

$$\langle R_c \rangle_{av} = 1.3092(2a/kT)^{1/6} \quad (4.3)$$

The a value to evaluate (4.3) is calculated below

$$\begin{aligned}
 a_{es} &= 2\mu_1^2\mu_2^2/3kT \quad (5.20) \\
 &= 2(1.77 \times 10^{-18})^4 / (3)(1.3805 \times 10^{-16})(1350) \\
 &= 0.35 \times 10^{-58} \text{ erg cm}^6
 \end{aligned}$$

where

$$\mu_{\text{CH}_2\text{F}_2} = 1.97\text{D} \quad [111]$$

$$\begin{aligned}
 \mu_{\text{CHF}_2} &= (1.97)(0.90) \\
 &= 1.77\text{D}
 \end{aligned}$$

$$= 1.77 \times 10^{-18} \text{ esu.cm}$$

$$\begin{aligned}
 a_{\text{ind}} &= \alpha_1 \bar{\mu}_2^2 + \alpha_2 \bar{\mu}_1^2 & (5.21) \\
 &= 2(2.008 \times 10^{-24})(1.77 \times 10^{-18})^2 \\
 &= 0.13 \times 10^{-58} \text{ ergs cm}^6
 \end{aligned}$$

where

$$\alpha(\text{C-H}) = 6.425 \times 10^{-25} \text{ cm}^3 \quad [79]$$

$$\alpha(\text{C-F}) = 6.825 \times 10^{-25} \text{ cm}^3 \quad [79]$$

$$\begin{aligned}
 \alpha(\text{CHF}_2) &= (2 \times 6.825 + 6.425) \times 10^{-25} \\
 &= 2.008 \times 10^{-24} \text{ cm}^3
 \end{aligned}$$

$$a_{\text{dis}} = (3/2)(\text{etr}/m_e^{1/2})\alpha_1\alpha_2/[(\alpha_1/N_1)^{1/2} + (\alpha_2/N_2)^{1/2}] \quad (5.22)$$

$$= \frac{3}{2} \left(\frac{(4.8033 \times 10^{-10})(6.6262 \times 10^{-27})}{(2)(3.14)(9.1096 \times 10^{-28})^{1/2}} \right) (2.008 \times 10^{-24})^2 / 2 \left(\frac{2.008 \times 10^{-24}}{19} \right)$$

$$= 1.56 \times 10^{-58} \text{ ergs cm}^6$$

$$a = 2.04 \times 10^{-58} \text{ ergs cm}^6$$

$$\langle R_c \rangle_{\text{av}} = 4.72 \times 10^{-8} \text{ cm}$$

Calculation of the coordinates

$$x_{\text{C}_1, \text{C}_2} = 0$$

$$y_{\text{C}_1, \text{C}_2} = 0$$

$$x_{\text{H}_1, \text{H}_2} = 0$$

$$\begin{aligned}
 y_{\text{H}_1} &= \cos 12.7^\circ (1.098) \\
 &= 1.071
 \end{aligned}$$

$$\begin{aligned}
 x_{\text{F}_1, \text{F}_4} &= \sin 57.5^\circ (1.35) \\
 &= 1.139
 \end{aligned}$$

$$y_{\text{H}_2} = -1.071$$

$$x_{\text{F}_2, \text{F}_3} = -1.139$$

$$\begin{aligned}
 y_{\text{F}_1, \text{F}_2} &= -(\sin 30^\circ)(\cos 12.7^\circ \times 1.35) \\
 &= -0.659
 \end{aligned}$$

$$y_{\text{F}_3, \text{F}_4} = 0.659$$

$$z_{C_1} = 2.36$$

$$z_{F_1, F_2} = (\sin 12.7^\circ \times 1.35) + 2.36 \\ = 2.657$$

$$z_{C_2} = -2.36$$

$$z_{F_3, F_4} = -2.657$$

$$z_{H_1} = (\sin 12.7^\circ \times 1.098) + 2.36 \\ = 2.601$$

$$z_{H_2} = -2.601$$

II. Internal Rotation

$$I_{ir}^+ = \frac{1}{2}((2)(18.998)(1.317)^2 + (1.008)(1.071)^2) \\ = 33.53 \text{ amu } \text{\AA}^2 \\ = 55.60 \times 10^{-40} \text{ g.cm}^2$$

$$r_{F_1, F_2} = (1.35)(\sin 77.3^\circ) \\ = 1.317 \text{ \AA}$$

$$r_H = (1.098)(\sin 77.3^\circ) \\ = 1.071 \text{ \AA}$$

5.2.1.3 Calculation of the Partition Functions

A. The Molecule

I. *Vibrational Partition Function*

$$Q_v = 6472.55$$

II. *Rotational Partition Function*

$$Q_r = \frac{\sqrt{3.14} (8)(3.14)^2 (1.3805 \times 10^{-16})(1350)}{2 (6.6262 \times 10^{-27})^2}^{3/2} (16.45 \times 10^{-11})^{1/2} \\ = 6.9712 \times 10^5$$

TABLE 5.35 - Parameters for Evaluation of Moment of Inertia Product of $C_2H_2F_4^+$ (Model I)

Atom	m_i	x_i^+	y_i^+	z_i^+	$m_i x_i^{+2}$	$m_i y_i^{+2}$	$m_i z_i^{+2}$	$m_i x_i^+ y_i^+$	$m_i x_i^+ z_i^+$	$m_i y_i^+ z_i^+$
C ₁	12.011	0	0	2.36	0	0	66.897	0	0	0
C ₂	12.011	0	0	-2.36	0	0	66.897	0	0	0
H ₁	1.0079	0	1.071	2.601	0	1.156	6.819	0	0	2.808
F ₁	18.998	1.139	-0.659	2.657	24.647	8.251	134.119	-14.260	57.494	-33.265
F ₂	18.998	-1.139	-0.659	2.657	24.647	8.251	134.119	14.260	-57.494	-33.265
H ₂	1.0079	0	-1.071	-2.601	0	1.156	6.819	0	0	2.808
F ₃	18.998	-1.139	0.659	-2.657	24.647	8.251	134.119	-14.260	57.494	-33.265
F ₄	18.998	1.139	0.659	-2.657	24.647	8.251	134.119	14.260	-57.494	-33.265
					98.588	35.316	683.908	0	0	-127.444

$$I_{xx}^+ = 719.22 \text{ amu } \overset{O_2}{A^2} = 1193.91 \times 10^{-40} \text{ g.cm}^2$$

$$I_{yy}^+ = 782.496 \text{ amu } \overset{O_2}{A^2} = 1298.94 \times 10^{-40} \text{ g.cm}^2$$

$$I_{zz}^+ = 133.904 \text{ amu } \overset{O_2}{A^2} = 222.28 \times 10^{-40} \text{ g.cm}^2$$

$$ABC^+ = 6.368 \times 10^7 \text{ amu } \overset{O_2}{A^2}$$

$$= 2.92 \times 10^{-112} \text{ g.cm}^2$$

III. Partition Function for Internal Rotation

$$Q_{ir} = \frac{((8)(30.96)(52.80 \times 10^{-40})(1.3805 \times 10^{-16})(1350))^{1/2}}{(6.6262 \times 10^{-27})(1)}$$

$$= 74.51$$

B. The Activated Complex

I. Vibrational Partition Function

$$Q_v^+ = 107.1316$$

II. Rotational Partition Function

$$Q_r^+ = \frac{\sqrt{3.14} ((8)(3.14)^2 (1.3805 \times 10^{-16})(1350))^{3/2} (2.92 \times 10^{-112})^{1/2}}{2 (6.6262 \times 10^{-27})^2}$$

$$= 2.9373 \times 10^6$$

III. Partition Function for Internal Rotations

$$Q_{ir}^+ = [((8)(3.14)^3 (55.60 \times 10^{-40})(1.3805 \times 10^{-16})(1350))^{1/2} / (6.6262 \times 10^{-27})] \times [((8)(3.14)^2 (55.60 \times 10^{-40})(1.3805 \times 10^{-16})(1350))^{1/2} / (6.6262 \times 10^{-27})]$$

$$= 16.72 \times 10^6$$

5.2.1.4 Calculation of $\langle E_v \rangle$, $\langle E_v^+ \rangle$, E_0 and E^+

A. Calculation of $\langle E_v \rangle$

$$T \partial \ln Q_v / \partial T = 8.833$$

$$\langle E_v \rangle = 23.69 \text{ kcal mole}^{-1}$$

B. Calculation of $\langle E_V^+ \rangle$

$$T \partial \ln Q_V^+ / \partial T = 5.93$$

$$\langle E_V^+ \rangle = 15.91 \text{ kcal mole}^{-1}$$

C. Result for E_0

$$\begin{aligned} E_0 &= 91.4 - \frac{1}{2}(5 - 1 + 2)(1.987 \times 10^{-3})(1350) + 23.69 - 15.91 \\ &= 91.14 \text{ kcal mole}^{-1} \end{aligned}$$

D. Calculation of E^+

$$\begin{aligned} E^+ &= (3.5)(1.987 \times 10^{-3})(1350) + (2.859 \times 10^{-3})(5562.82) \\ &= 25.29 \text{ kcal mole}^{-1} \end{aligned}$$

5.2.1.5 Calculation of ΔS^\ddagger , k_∞ and A_∞

The experimental [90] Arrhenius parameters are

$$A_\infty = 10^{17.4} \text{ sec}^{-1}$$

$$E_\infty = 91.4 \text{ kcal mole}^{-1}$$

According to (4.21) and (3.24)

$$\Delta S^\ddagger = 16.08 \text{ cal mole}^{-1} \text{ deg}^{-1}$$

$$k_\infty = 4.00 \times 10^2 \text{ sec}^{-1}$$

The corresponding theoretical values are given below

$$\begin{aligned} S_V &= 1.987(\ln(6472.55) + 8.833) \\ &= 34.99 \text{ cal mole}^{-1} \text{ deg}^{-1} \end{aligned}$$

$$S_r = 1.987(\ln(6.9712 \times 10^5) + 1.5) \\ = 29.72 \text{ cal mole}^{-1} \text{ deg}^{-1}$$

$$S_{ir} = 1.987(\ln 74.52 + 0.5) \\ = 9.56 \text{ cal mole}^{-1} \text{ deg}^{-1}$$

$$S_{th} = 74.27 \text{ cal mole}^{-1} \text{ deg}^{-1}$$

$$S_v^+ = 1.987(\ln 107.1316 + 5.93) \\ = 21.07 \text{ cal mole}^{-1} \text{ deg}^{-1}$$

$$S_r^+ = 1.987(\ln(2.9373 \times 10^6) + 1.5) \\ = 32.57 \text{ cal mole}^{-1} \text{ deg}^{-1}$$

$$S_{ir}^+ = 1.987(\ln(16.72 \times 10^6) + 2.5) \\ = 38.02 \text{ cal mole}^{-1} \text{ deg}^{-1}$$

$$S_{th}^+ = 91.66 \text{ cal mole}^{-1} \text{ deg}^{-1}$$

$$\Delta S_{th}^\ddagger = 17.39 \text{ cal mole}^{-1} \text{ deg}^{-1}$$

$$k_{\infty, th} = \frac{(1)(1.3805 \times 10^{-16})(1350)}{6.6262 \times 10^{-27}} \frac{5.2614 \times 10^{15}}{3.3620 \times 10^{11}} \exp\left(\frac{-91.14}{(1.987 \times 10^{-3})(1350)}\right) \\ = 7.72 \times 10^2 \text{ sec}^{-1}$$

$$A_{\infty, th} = \frac{(2.718)(1.3805 \times 10^{-16})(1350)}{6.6262 \times 10^{-27}} e^{17.39/1.987} \\ = 10^{17.68} \text{ sec}^{-1}$$

5.2.1.6 Calculation of the Anharmonicity Corrections

The anharmonicity constants for $C_2H_2F_4$ have not been encountered in the literature. The average dissociation energies have been calculated using the relationship given by Hershbach and Lawrie [85].

A. The Molecule

From the tables [85], for C-H stretching

	$\frac{a_{xy}}{}$	$\frac{b_{xy}}{}$
f_2	1.54	0.64
f_3	1.58	0.48

for a C-F and C-C stretching

	$\frac{a_{xy}}{}$	$\frac{b_{xy}}{}$
f_2	1.73	0.47
f_3	1.78	0.39

For a C-H stretching vibration (2 fold degenerate)

$$f_2 = 4.9048 \times 10^5 \text{ dynes cm}^{-1}$$

$$f_3 = 10.0964 \times 10^{13} \text{ dynes cm}^{-2}$$

$$D_e = 5.7876 \times 10^{-12} \text{ ergs molecule}^{-1} = 83.29 \text{ kcal mole}^{-1}$$

$$D_e^{-1} = 0.01200$$

For a C-F stretching vibration (4 fold degenerate)

$$f_2 = 6.4344 \times 10^5 \text{ dynes cm}^{-1}$$

$$f_3 = 12.6638 \times 10^{13} \text{ dynes cm}^{-2}$$

$$D_e = 8.3055 \times 10^{-12} \text{ ergs molecule}^{-1} = 119.52 \text{ kcal mole}^{-1}$$

$$D_e^{-1} = 0.00837$$


For a C-C stretching vibration

$$f_2 = 2.8253 \times 10^5 \text{ dynes cm}^{-1}$$

$$f_3 = 4.6967 \times 10^{13} \text{ dynes cm}^{-2}$$

$$D_e = 5.1118 \times 10^{-12} \text{ ergs molecule}^{-1} = 73.56 \text{ kcal mole}^{-1}$$


$$D_e^{-1} = 0.01360$$

For a  bending mode [108] (4 fold degenerate)

$$k = 0.76 \times 10^5 \text{ dynes cm}^{-1}$$

$$D_e = 54.68 \text{ kcal mole}^{-1}$$

$$D_e^{-1} = 0.01828$$

For a  bending mode [108] (7 fold degenerate)

$$k = 0.7 \times 10^5 \text{ dyne cm}^{-1}$$

$$D_e = 51.08 \text{ kcal mole}^{-1}$$

$$D_e^{-1} = 0.01957$$

$$\langle D_e^{-1} \rangle = \frac{1}{17} (2 \times 0.01200 + 3 \times 0.00837 + 0.01360 + 4 \times 0.01828 + 7 \times 0.01957)$$

$$= 0.0160$$

$$D = 62.31 \text{ kcal mole}^{-1}$$

B. The Complex

The C-H and C-F distances in the complex are identical with those in the molecule. As a result the average dissociation energies are also the same.

$$\langle D_e^{-1} \rangle = (1/12) (4 \times 0.00837 + 2 \times 0.012 + 2 \times 0.01828 + 4 \times 0.01957)$$

$$= 0.01436$$

$$D = 69.64 \text{ kcal mole}^{-1}$$

5.2.1.7 Evaluation of k_{uni}/k_{∞} A. Centrifugal Effects are NeglectedTABLE 5.36 - Parameters for k_{uni}/k_{∞} for $C_2H_2F_4$ (Model I)
Neglecting Centrifugal Effects

E_0	91.14 kcal mole ⁻¹
E_Z	9987 cm ⁻¹ = 28.55 kcal mole ⁻¹
E_Z^+	8007 cm ⁻¹ = 22.89 kcal mole ⁻¹
s	17
s^+	12
r	1
r^*	5
α	16.5
α^+	14.5
$\Gamma(\alpha+1)$	8.563×10^{13}
$\Gamma(\alpha^++1)$	3.348×10^{11}
$\Gamma(1+r^*/2)$	3.2333
$\prod_{i=1}^s \nu_i$	4.821×10^{50} cm ⁻¹⁷
$\prod_{i=1}^{s^+} \nu_i^+$	6.062×10^{36} cm ⁻¹²
$(E_Z^+)^{\alpha^+-\alpha}$	1.559×10^{-8} cm ²
$(E_Z^+)^{\alpha^++1}$	3.190×10^{60} cm ^{-15.5}
$(E_Z^+)^{s^+}$	6.944×10^{46} cm ⁻¹²
$(RT)^{1+r^*/2}$	2.531×10^{10} cm ^{-3.5}

./....

Table 5.36 continued...

$(RT)(r^*-r)/2$	$8.804 \times 10^5 \text{ cm}^{-2}$
$\langle v^2 \rangle$	$1974208.1 \text{ cm}^{-2}$
$\langle v \rangle$	1174.94 cm^{-1}
$\langle v \rangle^2$	1380484 cm^{-2}
β	1.3855
$\langle v^{+2} \rangle$	$2397447.9 \text{ cm}^{-2}$
$\langle v^+ \rangle$	1334.5 cm^{-1}
$\langle v^+ \rangle^2$	$1780890.3 \text{ cm}^{-2}$
β^+	1.4911
Z	$3.2104 \times 10^6 \text{ Torr}^{-1} \text{ sec}^{-1} *$
C_0	8.533
C_1	0.580
θ	0.0810
$G_1(x)$	$18.80x^{2.5}$
$G_2(x)$	$[x+1-1.4911/(5.00x+2.73x^{0.5}+3.51)]^{14.5}$
$G_3(x)$	$[x+1-1.4911 \exp(-2.419x^{0.25})]^{14.5}$
$H(x)$	$(x + 5.229)^{16.5}$
C_2/P	$7.68 \times 10^{11}/P$

* The collision diameter σ_c , to calculate Z , is not found in the literature. It has been calculated using the 28:7 potential [112]. The Mie m, n potential being a composite function obtained by adding an attraction term to a repulsion term can be written as [113]

$$\phi_{i,j}^M = K \epsilon [(\sigma/r)^n - (\sigma/r)^m]$$

where

$$K = (n/(n-m)(n/m)^{m/(n-m)})$$

$$\sigma = r_0(4)^{-1/21}$$

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B. Centrifugal Effects are Included

I. *The Direct Method*

In this method all the parameters in Table 5.36, except $H(x)$, are the same as those used in the determination of the fall-off region without centrifugal effects.

$$\begin{aligned}\langle \Delta E_j \rangle &= -(1.987 \times 10^{-3})(1350)(6.629) \\ &= -17.78 \text{ kcal mole}^{-1}\end{aligned}$$

$$\begin{aligned}H(x) &= \left(x + \frac{91.14 - 17.78 + 28.55}{22.89}\right)^{16.5} \\ &= (x + 4.452)^{16.5}\end{aligned}$$

II. *The Waage-Rabinovitch Approximation*

$$\begin{aligned}a &= 1 - 1.3855 \exp\left[\frac{-2.419(91.14 - 17.78 + 25.29)}{28.55}\right]^{0.25} \\ &= 0.9488\end{aligned}$$

$$\begin{aligned}F^{-1} &= 1 + \frac{(17 + 0.5 - 1)(7.629 - 1)(1.987 \times 10^{-3} \times 1350)}{91.14 + 0.9488 \times 28.55} \\ &= 3.482\end{aligned}$$

$$F = 0.287$$

The $k_{\text{uni}}/k_{\infty}$ ratio equals 0.5 at $P = 2125$ Torr.

./...

In this case

$$\sigma = r_o (m/n)^{1/(n-m)}$$

From the average distance $\langle R \rangle_{\text{av}}$ calculated at 400°K , $\sigma_{\text{C}_2\text{H}_2\text{F}_4}$ is found to be equal to 5.09 Å. Since the thermal decomposition of $\text{C}_2\text{H}_2\text{F}_4$ mixture of 1,1,2,2 tetrafluoroethane and argon has been studied, the mean of the collision diameters, $\sigma = 4.37$ Å, should be considered.

$$(\sigma = (\sigma_{\text{Ar}} + \sigma_{\text{C}_2\text{H}_2\text{F}_4})/2, \text{ where } \sigma_{\text{Ar}} = 3.64 \text{ Å} [104]).$$

TABLE 5.37 - Contribution of Centrifugal Effects to k_{uni}/k_{∞}
for $C_2H_2F_4$ at $1350^{\circ}K$ (Model I)

P (Torr)	$(k_{uni}/k_{\infty})^a$	$(k_{uni}/k_{\infty})^b$
10^{-1}	0.0043	0.0006
1	0.0222	0.0042
10^1	0.0897	0.0226
10^2	0.2685	0.0945
10^3	0.5704	0.2888
10^4	0.8567	0.6106
10^5	0.9910	0.8903
10^6	1.0212	1.0020
10^7	1.0250	1.0228
10^8	1.0255	1.0251
10^9	1.0255	1.0255

^a Neglecting centrifugal effects ($k_{uni}/k_{\infty} = 0.5$ at $P = 610$ Torr)

^b Including centrifugal effects ($k_{uni}/k_{\infty} = 0.5$ at $P = 4800$ Torr).

5.2.1.8 Calculation of $k_a(E^*)$

The input data to calculate $k_a(E^*)$ is given in Table 5.38.

TABLE 5.38 - Properties of the Active Molecule and Activated Complex
 ($C_2H_2F_4$, Model I)

	Molecule	Complex
Frequencies (cm^{-1})	3015	3000 (2)
	1440	
	1360	11655(2)
	901	
	622	700 (2)
	361	
	1440	650 (2)
	1080	
	478	1317 (2)
	1322	
	1125	1175 (2)
	271	
	3000	
	1336	
	1134	
	539	
	549	
E_0 (cal mole $^{-1}$)		91.14
s	17	12
r	1	5
Moments of Inertia (amu \AA^2)		
I_{xx}	164.228	719.22
I_{yy}	220.656	782.50
I_{zz}	123.152	133.90
I_{ir}	31.80	33.53
Symmetry number for internal rotation		
σ	1	2 (4) and 1 (1)
Average bond energy (kcal mole $^{-1}$)		
D	62.31	69.64
Increment for the summation (kcal mole $^{-1}$)		
ΔE^\ddagger		0.05
Number of rate constants to be calculated		
NEN		1200
L^\ddagger		1
Temperature ($^\circ K$)		
T		1350
Pressure (Torr)		
P		3500
Collision number (Torr $^{-1}$ sec $^{-1}$)		
Z		3.2104×10^6

The results at $E^\ddagger = 25.29 \text{ kcal mole}^{-1}$ are shown below.

$$k_a(E^\ddagger + E_0) = 0.3277 \times 10^{10} \text{ sec}^{-1}$$

$$k_a(E^\ddagger + E_0 + \langle \Delta E_J \rangle) = 0.9550 \times 10^{10} \text{ sec}^{-1}$$

$$k_a(E^\ddagger + E_0)_{\text{anh}} = 0.1157 \times 10^{10} \text{ sec}^{-1}$$

$$k_a(E^\ddagger + E_0 + \langle \Delta E_J \rangle)_{\text{anh}} = 0.3708 \times 10^{10} \text{ sec}^{-1}$$

5.2.1.9 Calculation of k_{uni}

The input data for the computer program which evaluates k_{uni} is given in Table 5.37.

A. Neglecting Centrifugal Effects

$$k_{\text{uni}} = \frac{2.9373 \times 10^6}{(9.537 \times 10^{-14})(6.9712 \times 10^5)(6472.55)(74.51)} e^{-(91.14/1.987 \times 10^3 \times 1350)} \cdot (0.05)(6.9830 \times 10^{10})$$

$$= 5.61 \times 10^2 \text{ sec}^{-1}$$

$$k_{\text{uni}}(\text{anh}) = (8.0379 \times 10^{-9})(8.1500 \times 10^{10})$$

$$= 6.55 \times 10^2 \text{ sec}^{-1}$$

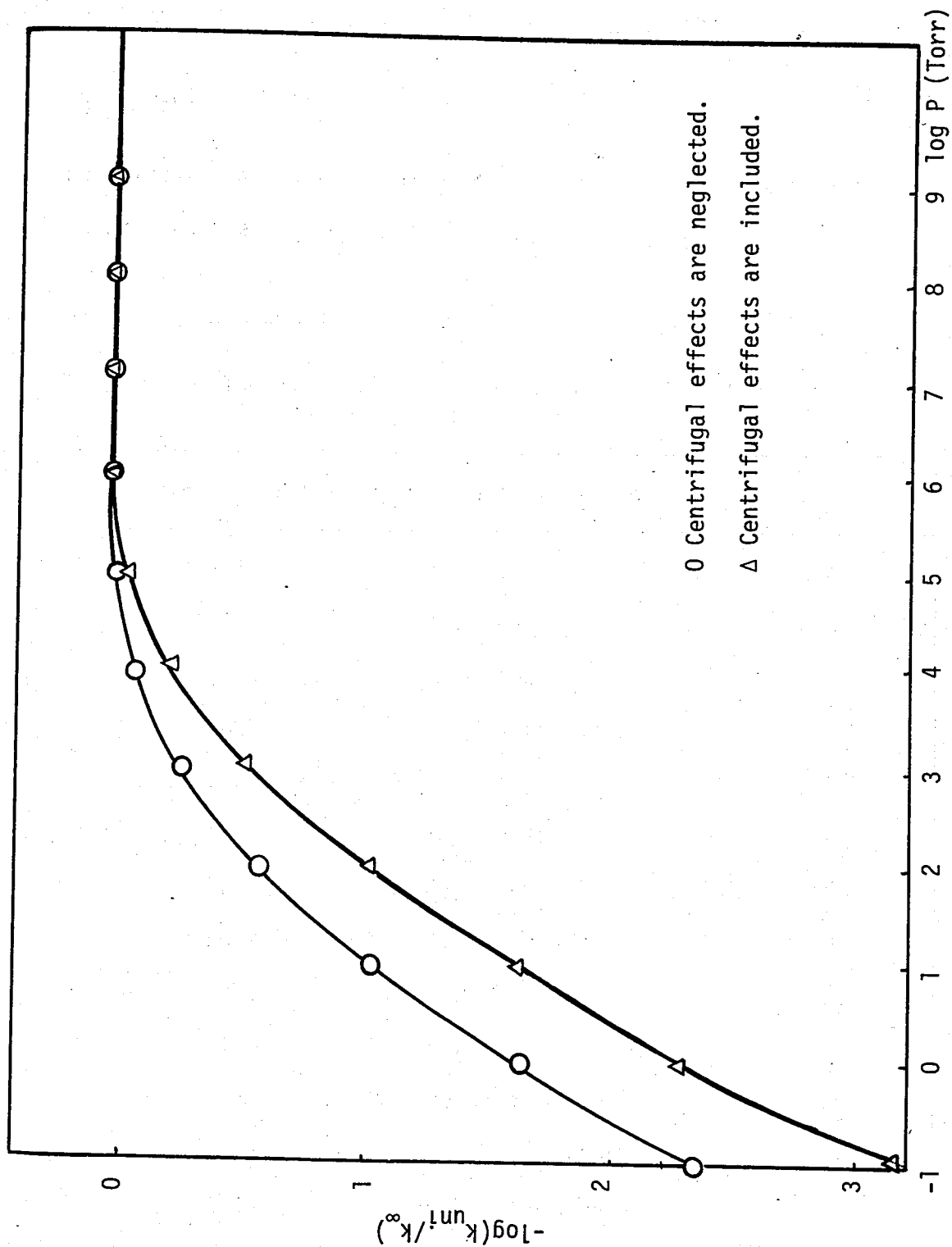
B. Including Centrifugal Effects

$$k_{\text{uni}} = (8.0379 \times 10^{-9})(5.3420 \times 10^{10})$$

$$= 4.29 \times 10^2 \text{ sec}^{-1}$$

$$k_{\text{uni}}(\text{anh}) = (8.0379 \times 10^{-9})(6.6420 \times 10^{10})$$

$$= 5.34 \times 10^2 \text{ sec}^{-1}$$



5.2.2 Model II

5.2.2.1 DataA. The Molecule

The molecule has the vibration frequencies given in Table 5.30 and the molecular parameters given in Table 5.31.

B. The Activated ComplexTABLE 5.39 - The Vibrational Frequencies of $C_2H_2F_4^+$ (Model II)

	Wave number (cm^{-1})	Type of vibration	Species
ν_1	3015	C-H stretching	A_g
ν_2	1440	C-H bending	A_g
ν_3	1360	C-F stretching	A_g
ν_4	622	CHF_2 deformation	A_g
ν_5	$361\exp[-\alpha(r^+-1.518)]$	rocking	A_g
ν_6	1440	C-H bending	B_g
ν_7	1080	C-F stretching	B_g
ν_8	$478\exp[-\alpha(r^+-1.518)]$	rocking	B_g
ν_9	1322	C-H bending	A_u
ν_{10}	1125	C-F bending	A_u
ν_{11}	$271\exp[-\alpha(r^+-1.518)]$	rocking	A_u
ν_{12}	3000	C-H stretching	A_u
ν_{13}	1336	C-F stretching	B_u
ν_{14}	1134	C-H bending	B_u
ν_{15}	539	CHF_2 deformation	B_u
ν_{16}	$549\exp[-\alpha(r^+-1.518)]$	rocking	B_u

According to (5.16)

$$V(r^+) = D[1 - e^{-\beta(r^+ - 1.518)}]^2 + E_Z^+ - E_Z^m$$

$$\Delta H^0(\text{CHF}_2 - \text{CHF}_2) = 91.4 \text{ kcal mole}^{-1} \quad [90]$$

$$\Delta H_0^0 = 89 \text{ kcal mole}^{-1} \quad (\Delta H_0^0 = \Delta H^0 - 2.4)^* \quad [114]$$

$$E_Z^m = 28.73 \text{ kcal mole}^{-1}$$

$$E_Z^p = 22.89 \text{ kcal mole}^{-1}$$

$$f = 5.35 \times 10^5 \text{ dynes cm}^{-1}$$

$$v_a = 361 \exp[-\alpha(r^+ - 1.518)]$$

$$v_b = 478 \exp[-\alpha(r^+ - 1.518)]$$

$$v_c = 271 \exp[-\alpha(r^+ - 1.518)]$$

$$v_d = 549 \exp[-\alpha(r^+ - 1.518)]$$

Thus $D = 94.84 \text{ kcal mole}^{-1}$

$$\beta = 2.01 \times 10^{-8} \text{ cm}^{-1}$$

$\alpha = 0.75$ (The adjustable parameter has been chosen such that the theoretically calculated Arrhenius parameters agree with the experimental ones).

$$E_Z^+ - E_Z^m = 2.372[\exp(-0.75(r^+ - 1.518))] - 3.846 \text{ kcal mole}^{-1}$$

$$V(r^+) = 94.84[1 - e^{-2.01(r^+ - 1.518)}]^2 + 2.372[\exp(-0.75(r^+ - 1.518))] - 3.846$$

* The value of the force constant for $C_2H_2F_4$ has been calculated by considering the force constants of C_2H_6 and C_2F_6 and supposing that this trend is in agreement with the increasing number of fluorines. "The increase in force constants parallels the increase in bond energies" [108].

TABLE 5.40 - Potential Energy and Vibration Frequencies as a Function of r^+ for $C_2H_2F_4^+$ (Model II)

r (Å)	$V(r^+)$ (kcal mole ⁻¹)	ν_a (cm ⁻¹)	ν_b (cm ⁻¹)	ν_c (cm ⁻¹)	ν_d (cm ⁻¹)
3.000	82.37	119	157	89	181
3.250	85.90	98	130	74	150
3.500	88.03	82	108	61	124
3.750	89.31	68	90	51	103
4.000	90.07	56	74	42	85
4.250	90.52	47	62	35	71
4.500	90.77	39	51	29	59
4.750	90.92	32	42	24	49
5.000	91.00	27	35	20	40

5.2.2.2 The Moments of Inertia

A. The Molecule

I. *External Rotation (same as Model I)*

$$I_{xx} = 164.228 \text{ amu } \text{Å}^2 = 272.62 \times 10^{-40} \text{ g.cm}^2$$

$$I_{yy} = 220.656 \text{ amu } \text{Å}^2 = 366.29 \times 10^{-40} \text{ g.cm}^2$$

$$I_{zz} = 123.152 \text{ amu } \text{Å}^2 = 204.43 \times 10^{-40} \text{ g.cm}^2$$

II. *Internal Rotation (same as Model I)*

$$I_{ir} = 31.80 \text{ amu } \text{Å}^2 = 52.80 \times 10^{-40} \text{ g.cm}^2$$

B. The Complex

I. *External Rotation*

The value of x^+ changes from $x^+ = 1.087 \text{ \AA}$ in the molecule to $x^+ = 1.139 \text{ \AA}$.

The value of y^+ changes from $y^+ = 1.030 \text{ \AA}$ (for the hydrogens) and $y^+ = 0.641 \text{ \AA}$ (for the fluorines) in the molecule to $y^+ = 1.071 \text{ \AA}$ (for the hydrogens) and $y^+ = 0.659$ for the fluorines in the complex.

The values of z^+ , the perpendicular distances from the hydrogens and the fluorines to the carbon, change from 0.381 \AA (for the hydrogens) in the molecule where $r_e = 1.518 \text{ \AA}$ to 0.241 \AA and from 0.468 \AA (for the fluorines) to 0.297 \AA where $r^+ = 4.72 \text{ \AA}$.

TABLE 5.41 - Parameters for Evaluation of Moment of Inertia Product as a Function of r^+ for $C_2H_2F_4$ (Model II)

r^+	Δr^+	$\Delta z^+(H)$	$z^+(H)$	$\Delta z^+(F)$	$z^+(F)$	$\Delta x^+(F)$	$x^+(F)$	$\Delta y^+(H)$	$y^+(H)$	$\Delta y^+(F)$	$y^+(F)$
3.000	1.482	0.065	0.316	0.079	0.389	0.024	1.111	0.019	1.049	0.008	0.644
3.250	1.732	0.075	0.306	0.092	0.376	0.028	1.115	0.022	1.052	0.010	0.655
3.500	1.982	0.087	0.294	0.105	0.363	0.032	1.119	0.025	1.055	0.011	0.655
3.750	2.232	0.098	0.283	0.119	0.349	0.036	1.123	0.029	1.059	0.013	0.655
4.000	2.482	0.109	0.272	0.133	0.335	0.040	1.127	0.032	1.062	0.014	0.655
4.250	2.732	0.119	0.262	0.146	0.322	0.044	1.131	0.035	1.065	0.015	0.655
4.500	2.982	0.130	0.251	0.159	0.309	0.048	1.135	0.038	1.068	0.017	0.655
4.750	3.232	0.141	0.241	0.173	0.297	0.052	1.139	0.041	1.071	0.018	0.655
5.000	3.232	0.141	0.241	0.173	0.297	0.052	1.139	0.041	1.071	0.018	0.655

$$\Delta r^+ = (r^+ - 1.518)$$

$$\Delta z_H^+ = \Delta r^+(0.14)/(4.72 - 1.518)$$

$$z_H^{+1} = 0.3181 - \Delta z^+ ; z_F^{+1} = 0.468 - \Delta z^+$$

$$\Delta z_F^+ = \Delta r^+(0.171)/(4.72 - 1.518)$$

$$\Delta x_F^+ = \Delta r^+(1.139 - 1.087)/(4.72 - 1.518)$$

$$x_F^+ = 1.087 + \Delta x$$

$$\Delta y_H^+ = \Delta r^+(0.041)/(4.72 - 1.518)$$

$$y_H^+ = 1.030 + \Delta y^+$$

$$\Delta y_F^+ = \Delta r^+(0.018)/(4.72 - 1.518)$$

$$y_F^+ = 1.030 + \Delta y^+$$

TABLE 5.42 - Change in x^+ as a Function of r^+ for $C_2H_2F_4^+$
(Model II)

r^+	3.000	3.250	3.500	3.750	4.000	4.250	4.500	4.750	5.000
	x^+	x^+	x^+	x^+	x^+	x^+	x^+	x^+	x^+
C_1	0	0	0	0	0	0	0	0	0
C_2	0	0	0	0	0	0	0	0	0
H_1	0	0	0	0	0	0	0	0	0
F_1	1.111	1.115	1.119	1.123	1.127	1.131	1.135	1.139	1.139
F_2	-1.111	-1.115	-1.119	-1.123	-1.127	-1.131	-1.135	-1.139	-1.139
H_2	0	0	0	0	0	0	0	0	0
F_3	-1.111	-1.115	-1.119	-1.123	-1.127	-1.131	-1.135	-1.139	-1.139
F_4	1.111	1.115	1.119	1.123	1.127	1.131	1.135	1.139	1.139
$\sum m_i x_i^{+2}$	93.799	94.475	95.154	95.836	96.520	97.206	97.895	98.588	98.588

TABLE 5.43 - Change in y^+ as a Function of r^+ for $C_2H_2F_4^+$
(Model II)

r^+	3.000	3.250	3.500	3.750	4.000	4.250	4.500	4.750	5.000
	y^+	y^+	y^+	y^+	y^+	y^+	y^+	y^+	y^+
C_1	0	0	0	0	0	0	0	0	0
C_2	0	0	0	0	0	0	0	0	0
H_1	1.049	1.052	1.055	1.059	1.062	1.065	1.068	1.071	1.071
F_1	-0.649	-0.651	-0.652	-0.654	-0.655	-0.656	-0.658	-0.659	-0.659
F_2	-0.649	-0.651	-0.652	-0.654	-0.655	-0.656	-0.658	-0.659	-0.659
H_2	-1.049	-1.052	-1.055	-1.059	-1.062	-1.065	-1.068	-1.071	-1.071
F_3	0.649	0.651	0.652	0.654	0.655	0.656	0.658	0.659	0.659
F_4	0.649	0.651	0.652	0.654	0.655	0.656	0.658	0.659	0.659
$\sum m_i y_i^{+2}$	34.226	34.437	34.548	34.764	34.876	34.989	35.201	35.314	35.314

TABLE 5.44 - Change in z^+ as a Function of r^+ for $C_2H_2F_4^+$ (Model II)

r^+	3.000	3.250	3.500	3.750	4.000	4.250	4.500	4.750	5.000
	z^+	z^+	z^+	z^+	z^+	z^+	z^+	z^+	z^+
C_1	1.500	1.625	1.750	1.875	2.000	2.125	2.250	2.375	2.500
C_2	-1.500	-1.625	-1.750	-1.875	-2.000	-2.125	-2.250	-2.375	-2.500
H_1	1.816	1.931	2.044	2.158	2.272	2.387	2.501	2.616	2.741
F_1	1.889	2.001	2.113	2.224	2.335	2.447	2.559	2.672	2.797
F_2	1.889	2.001	2.113	2.224	2.335	2.447	2.559	2.672	2.797
H_2	-1.816	-1.931	-2.044	-2.158	-2.272	-2.387	-2.501	-2.616	-2.741
F_3	-1.889	-2.001	-2.113	-2.224	-2.335	-2.447	-2.559	-2.672	-2.797
F_4	-1.889	-2.001	-2.113	-2.224	-2.335	-2.447	-2.559	-2.672	-2.797
$\sum m_i z_i^2$	331.862	375.224	421.278	469.708	520.818	574.984	631.854	691.848	759.784

TABLE 5.45 - Moments of Inertia as a Function of r^+ for $C_2H_2F_4^+$ (Model II)

$r^+(A)$	I_{xx}^+ (amu Å^2)	I_{yy}^+ (amu Å^2)	I_{zz}^+ (amu Å^2)
3.000	366.088	425.661	128.025
3.250	409.661	469.699	128.912
3.500	455.826	516.432	129.702
3.750	504.472	565.544	130.600
4.000	555.694	617.338	131.396
4.250	609.973	672.190	132.195
4.500	667.055	729.749	133.096
4.750	727.162	790.434	133.900
5.000	795.098	858.372	133.902

II. Internal Rotation

The moment of inertia for internal rotation is a function ℓ . The variation of ℓ is from 1.283 (for the fluorines) and 1.030 (for the hydrogens) to 1.317 (for the fluorines) and to 1.071 (for the hydrogens).

TABLE 5.46 - Parameters for Evaluation of the Moment of Inertia for Internal Rotation as Function of r^+ for $C_2H_2F_4$ (Model II)

r^+ (Å)	Δr^+ (Å)	$\Delta \ell_{(H)}^+$ (Å)	$\Delta \ell_{(F)}^+$ (Å)	$\ell_{(H)}^+$ (Å)	$\ell_{(F)}^+$ (Å)
3.000	1.482	0.019	0.016	1.049	1.299
3.250	1.732	0.022	0.018	1.052	1.301
3.500	1.982	0.025	0.021	1.055	1.304
3.750	2.232	0.029	0.024	1.059	1.307
4.000	2.482	0.032	0.026	1.062	1.309
4.250	2.732	0.035	0.029	1.065	1.312
4.500	2.982	0.038	0.032	1.068	1.315
4.750	3.232	0.041	0.034	1.071	1.317
5.000	3.232	0.041	0.034	1.071	1.317

$$\Delta \ell_{(H)}^+ = \frac{\Delta r^+ (1.071 - 1.030)}{4.72 - 1.518}$$

$$\Delta \ell_{(F)}^+ = \frac{\Delta r^+ (1.317 - 1.283)}{4.72 - 1.518}$$

$$\ell_{(H)}^+ = 1.030 + \Delta \ell^+$$

$$\ell_{(F)}^+ = 1.283 + \Delta \ell^+$$

TABLE 5.47 - Moments of Inertia for Internal Rotation as a Function of r^+ for $C_2H_2F_4^+$ (Model II)

r^+ (Å)	I_{ir}^+ (amu Å ²)
3.000	32.60
3.250	32.72
3.500	32.86
3.750	33.01
4.000	33.11
4.250	33.27
4.500	33.42
4.750	33.52
5.000	33.53

5.2.2.3 Calculation of the Partition Functions

Neglecting Centrifugal Effects

A. The Molecule

I. *Vibrational Partition Function*

The molecule has 18 vibrational degrees of freedom (Table 5.30)

$$Q_v = 5.0027 \times 10^4$$

II. *Rotational Partition Function*

$$Q_r = 6.9712 \times 10^5$$

B. The Activated Complex

The activated complex is located at $r^+ = 3.45 \text{ Å}$.

I. *Vibrational Partition Function*

$$v_a = 361 \exp[-0.75(3.45 - 1.518)] = 85 \text{ cm}^{-1}$$

$$v_b = 478 \exp[-0.75(3.45 - 1.518)] = 112 \text{ cm}^{-1}$$

$$v_c = 271 \exp[-0.75(3.45 - 1.518)] = 64 \text{ cm}^{-1}$$

$$v_d = 549 \exp[-0.75(3.45 - 1.518)] = 129 \text{ cm}^{-1}$$

$$Q_v^+ = 6.8604 \times 10^5$$

II. *Rotational Partition Function*

$r^+(A)$	$\Delta r^+(A)$	$\Delta x^+(F)$	$x^+(F)$	$\Delta y^+(H)$	$y^+(H)$	$\Delta y^+(F)$	$y^+(F)$
3.450	1.932	0.031	1.118	0.025	1.055	0.011	0.652
$\Delta z^+(H)$	$z^+(H)$	$\Delta z^+(F)$	$z^+(F)$				
0.084	0.297	0.103	0.365				

TABLE 5.48 - Parameters for Evaluation of Moment of Inertia Product of $C_2H_2F_4$ (Model II, neglecting Centrifugal Effects)

Atom	m_i	x_i^+	y_i^+	z_i^+	$y_i^+ z_i^+$
C ₁	12.011	0	0	1.725	0
C ₂	12.011	0	0	-1.725	0
H ₁	1.0079	0	1.055	2.022	2.133
F ₁	18.998	1.118	-0.652	2.090	-1.363
F ₂	18.998	-1.118	-0.652	2.090	-1.363
H ₂	1.0079	0	-1.055	-2.022	2.133
F ₃	18.998	1.118	0.652	-2.090	-1.363
F ₄	18.998	-1.118	0.652	-2.090	-1.363
	94.984	34.548	411.663	99.277	
	$(\sum m_i x_i^2)$	$(\sum m_i y_i^2)$	$(\sum m_i z_i^2)$	$(\sum m_i y_i^+ z_i^+)$	

$$I_{xx}^+ = 446.211 \text{ amu } \overset{0}{\text{A}}^2$$

$$I_{yy}^+ = 506.647 \text{ amu } \overset{0}{\text{A}}^2$$

$$I_{zz}^+ = 129.532 \text{ amu } \overset{0}{\text{A}}^2$$

$$I_{yz}^+ = 99.277 \text{ amu } \overset{0}{\text{A}}^2$$

$$\begin{aligned} ABC^+ &= I_{xx}^+ (I_{yy}^+ I_{zz}^+ - I_{yz}^{+2}) \\ &= 2.4886 \times 10^7 \text{ amu}^3 \overset{0}{\text{A}}^6 \\ &= 1.14 \times 10^{-112} \text{ g}^3 \text{cm}^6 \end{aligned}$$

$$\begin{aligned} Q_r^+ &= \frac{\sqrt{3.14} (8) (3.14)^2 (1.3805 \times 10^{-16}) (1350)}{2 (6.6262 \times 10^{-27})^2}^{3/2} (1.14 \times 10^{-112})^{1/2} \\ &= 1.833 \times 10^6 \end{aligned}$$

III. Partition Function for Internal Rotation

$r^+(\overset{0}{\text{A}})$	$\Delta r^+(\overset{0}{\text{A}})$	$\Delta \ell_{(\text{H})}^+(\overset{0}{\text{A}})$	$\Delta \ell_{(\text{F})}^+(\overset{0}{\text{A}})$	$\ell_{(\text{H})}^+(\overset{0}{\text{A}})$	$\ell_{(\text{F})}^+(\overset{0}{\text{A}})$
3.450	1.932	0.025	0.021	1.055	1.304

$$\begin{aligned} I_{ir}^+ &= \frac{1}{2} ((1.0079)(1.055)^2 + (2)(18.998)(1.304))^2 \\ &= 32.87 \text{ amu } \overset{0}{\text{A}}^2 \\ &= 54.56 \times 10^{-40} \text{ g.cm}^2 \end{aligned}$$

$$\begin{aligned} Q_{ir}^+ &= \frac{((8)(3.14)^3 (54.56 \times 10^{-40}) (1.3805 \times 10^{-16}) (1350))^{1/2}}{(6.6262 \times 10^{-27})(1)} \\ &= 75.79 \end{aligned}$$

Including Centrifugal EffectsA. The Molecule (See Section 5.2.2.3)I. *Vibrational Partition Function*

$$Q_V = 5.0027 \times 10^4$$

II. *Rotational Partition Function*

$$Q_r = 6.9712 \times 10^5$$

B. The Activated ComplexI. *Vibrational Partition Function*

The activated complex is located at $r^+ = 3.65 \text{ \AA}$.

$$\nu_a = 361 \exp[-0.75(3.65 - 1.518)] = 73 \text{ cm}^{-1}$$

$$\nu_b = 478 \exp[-0.75(3.65 - 1.518)] = 97 \text{ cm}^{-1}$$

$$\nu_c = 271 \exp[-0.75(3.65 - 1.518)] = 55 \text{ cm}^{-1}$$

$$\nu_d = 549 \exp[-0.75(3.65 - 1.518)] = 111 \text{ cm}^{-1}$$

Q_V^+ is evaluated by replacing the rocking frequencies in Table 5.30 by the ones calculated above.

$$Q_V^+ = 1.2126 \times 10^6$$

II. Rotational Partition Function

$r^+(\text{Å})$	$\Delta r^+(\text{Å})$	$\Delta x_{(\text{F})}^+(\text{Å})$	$x_{(\text{F})}^+(\text{Å})$	$\Delta y_{(\text{H})}^+(\text{Å})$	$y_{(\text{H})}^+(\text{Å})$	$\Delta y_{(\text{F})}^+(\text{Å})$	$y_{(\text{F})}^+(\text{Å})$
3.650	2.132	0.035	1.122	0.027	1.057	0.012	0.653
$\Delta z_{(\text{H})}^+(\text{Å})$	$z_{(\text{H})}^+(\text{Å})$	$\Delta z_{(\text{F})}^+(\text{Å})$	$z_{(\text{F})}^+(\text{Å})$				
0.093	0.288	0.114	0.354				

TABLE 5.49 - Parameters for Evaluation of Moment of Inertia Product of $\text{C}_2\text{H}_2\text{F}_4^+$ (Model II, including Centrifugal Effects)

Atom	m_i	x_i^+	y_i^+	z_i^+	$y_i^+ z_i^+$
C ₁	12.011	0	0	1.825	0
C ₂	12.011	0	0	-1.825	0
H ₁	1.0079	0	1.057	2.113	2.2513
F ₁	18.998	1.122	-0.653	2.179	-27.0320
F ₂	18.998	-1.122	-0.653	2.179	-27.0320
H ₂	1.0079	0	-1.057	-2.113	2.2513
F ₃	18.998	1.122	0.653	-2.179	-27.0320
F ₄	18.998	-1.122	0.653	-2.179	-27.0320
		$\sum m_i x_i^{*2} = 95.665$	$\sum m_i y_i^{*2} = 34.656$	$\sum m_i z_i^{*2} = 449.82$	$\sum m_i y_i^+ z_i^+ = 103.625$

$$I_{xx}^+ = 484.476 \text{ amu } \text{Å}^2$$

$$I_{yy}^+ = 545.485 \text{ amu } \text{Å}^2$$

$$I_{zz}^+ = 130.321 \text{ amu } \text{Å}^2$$

$$I_{yz}^+ = 103.625 \text{ amu } \text{Å}^2$$

$$ABC^+ = I_{xx}^+ (I_{yy}^+ I_{zz}^+ - I_{yz}^{+2})$$

$$= 2.924 \times 10^7 \text{ amu}^3 \text{Å}^6$$

$$= 1.34 \times 10^{-112} \text{ g}^3 \text{cm}^6$$

$$Q_r^+ = \frac{\sqrt{3.14} (8)(3.14)^2 (1.3805 \times 10^{-16})(1350)}{2 (6.6262 \times 10^{-27})^2}^{3/2} (1.34 \times 10^{-112})^{1/2}$$

$$= 2.0234 \times 10^6$$

III. Partition Function for Internal Rotation

$r^+(\text{A})$	$\Delta r^+(\text{A})$	$\Delta \ell_{(\text{H})}^+(\text{A})$	$\Delta \ell_{(\text{F})}^+(\text{A})$	$\ell_{(\text{H})}^+(\text{A})$	$\ell_{(\text{F})}^+(\text{A})$
3.650	2.132	0.027	0.023	1.057	1.306

$$I_{ir}^+ = \frac{1}{2} ((1.0079)(1.057)^2 + (2)(18.998)(1.306)^2)$$

$$= 32.97 \text{ amu } \text{\AA}^2$$

$$= 54.72 \times 10^{-40} \text{ g.cm}^2$$

$$Q_{ir}^+ = \frac{((8)(3.14)^3 (54.72 \times 10^{-40})(1.3805 \times 10^{-16})(1350))^{1/2}}{(6.6262 \times 10^{-27})(1)}$$

$$= 75.90$$

5.2.2.4 Calculation of $\langle E_V \rangle$, $\langle E_V^+ \rangle$ and E^+

A. Calculation of $\langle E_V \rangle$

$$T \partial \ln Q_V / \partial T = 9.765$$

$$\langle E_V \rangle = 26.20 \text{ kcal mole}^{-1}$$

B. Calculation of $\langle E_V^+ \rangle$

I. Neglecting Centrifugal Effects

$$T \partial \ln Q_V^+ / \partial T = 8.849$$

$$\langle E_V^+ \rangle = 23.74 \text{ kcal mole}^{-1}$$

II. Including Centrifugal Effects

$$T \partial \ln Q_V^+ / \partial T = 8.877$$

$$\langle E_V^+ \rangle = 23.81 \text{ kcal mole}^{-1}$$

C. Calculation of E^+

$$\begin{aligned} E^+ &= (1 + 0.5)(1.987 \times 10^{-3})(1350) + (2.859 \times 10^{-3})(8302.70) \\ &= 27.76 \text{ kcal mole}^{-1} \end{aligned}$$

5.2.2.5 Calculation of ΔS^\ddagger , k_∞ and A_∞

A. Neglecting Centrifugal Effects

The value of E_0 is 87.67. The value of E_∞ which corresponds to E_0 is

$$\begin{aligned} E_\infty &= 87.67 + \frac{1}{2}(1 - 0 + 2)(1.987 \times 10^{-3})(1350) - 26.20 + 23.74 \\ &= 89.23 \text{ kcal mole}^{-1} \end{aligned}$$

$$\begin{aligned} S_V &= 1.987(\ln 5.0027 \times 10^4 + 9.765) \\ &= 40.90 \text{ kcal mole}^{-1} \end{aligned}$$

$$S_r = 29.72 \text{ cal mole}^{-1} \text{ deg}^{-1}$$

$$S_{th} = 70.62 \text{ cal mole}^{-1} \text{ deg}^{-1}$$

$$\begin{aligned} S_V^+ &= 1.987(\ln 6.8604 \times 10^5 + 8.849) \\ &= 44.29 \text{ cal mole}^{-1} \text{ deg}^{-1} \end{aligned}$$

$$\begin{aligned} S_r^+ &= 1.987(\ln 1.8331 \times 10^6 + 1.5) \\ &= 31.64 \text{ cal mole}^{-1} \text{ deg}^{-1} \end{aligned}$$

$$S_{ir}^+ = 1.987(\ln 75.90 + 0.5)$$

$$= 9.60 \text{ cal mole}^{-1} \text{ deg}^{-1}$$

$$S_{th}^+ = 85.53 \text{ cal mole}^{-1} \text{ deg}^{-1}$$

$$\Delta S_{th}^\ddagger = 14.91 \text{ cal mole}^{-1} \text{ deg}^{-1}$$

$$k_{\infty,th} = \frac{(1.3805 \times 10^{-16})(1350)}{6.6262 \times 10^{-27}} \frac{(6.8604 \times 10^5)(1.8331 \times 10^6)(75.90)}{(5.0027 \times 10^4)(6.9712 \times 10^5)}$$

$$= 4.93 \times 10^2 \text{ sec}^{-1} \quad \times \exp\left(\frac{-87.67}{(1.987 \times 10^{-3})(1350)}\right)$$

$$A_{\infty,th} = \frac{(2.718)(1.3805 \times 10^{-16})(1350)}{(6.6262 \times 10^{-27})} e^{14.91/1.987} = 10^{17.14}$$

B. Including Centrifugal Effects

The value of E_0 is $88.86 \text{ kcal mole}^{-1}$. The value of E_∞ which corresponds to E_0 is

$$E_\infty = 90.49 \text{ kcal mole}^{-1}$$

$$S_{th} = 70.62 \text{ cal mole}^{-1} \text{ deg}^{-1}$$

$$S_V^+ = 1.987(\ln 1.2126 \times 10^6 + 8.877)$$

$$= 45.47 \text{ cal mole}^{-1} \text{ deg}^{-1}$$

$$S_r^+ = 1.987(\ln 2.0234 \times 10^6 + 1.5)$$

$$= 31.83 \text{ cal mole}^{-1} \text{ deg}^{-1}$$

$$S_{ir}^+ = 1.987(\ln 75.90 + 0.5)$$

$$= 9.60 \text{ cal mole}^{-1} \text{ deg}^{-1}$$

$$S_{th}^+ = 86.90 \text{ cal mole}^{-1} \text{ deg}^{-1}$$

$$\Delta S_{th}^\ddagger = 16.28 \text{ cal mole}^{-1} \text{ deg}^{-1}$$

$$k_{\infty,th} = 6.08 \times 10^2 \text{ sec}^{-1}$$

$$A_{\infty,th} = 10^{17.44}$$

5.2.2.6 Calculation of the Anharmonicity Corrections

A. The Molecule

In the molecule there are

- 2 C-H stretching frequencies ($D_e^{-1} = 0.01200$) (Model I)
- 3 C-F stretching frequencies ($D_e^{-1} = 0.00837$) (Model I)
- 1 C-C stretching frequency ($D_e^{-1} = 0.01360$) (Model I)
- 4 C-H bending frequencies ($D_e^{-1} = 0.01828$) (Model I)
- 7 C-F bending frequencies ($D_e^{-1} = 0.01957$) (Model I)
- 1 torsion frequency ($D_e^{-1} = 0.17570$) *

$$\begin{aligned} \langle D_e^{-1} \rangle &= \frac{1}{18} ((2)(0.01200) + (3)(0.00837) + 0.01360 + (4)(0.01828) \\ &\quad + (7)(0.01957) + 0.17570) \\ &= 0.02492 \end{aligned}$$

$$D = 40.13 \text{ kcal mole}^{-1}$$

B. The Activated Complex

In the activated complex there are

- 2 C-H stretching frequencies
- 3 C-F stretching frequencies
- 4 C-H bending frequencies
- 7 C-F bending frequencies

$$\begin{aligned} \langle D_e^{-1} \rangle &= \frac{1}{16} ((2)(0.01200) + (3)(0.00837) + (4)(0.01828) + (7)(0.01957)) \\ &= 0.01620 \end{aligned}$$

$$D = 61.72 \text{ kcal mole}^{-1}$$

* The dissociation energy corresponding to the torsion frequency of $C_2H_2F_4$ is estimated by comparing the potential barrier ($V = 3.5 \text{ kcal mole}^{-1}$) of this molecule to that of C_2H_6 ($V = 2.87 \text{ kcal mole}^{-1}$) and taking into consideration the known dissociation energy in C_2H_6 ($D_e^{-1} = 0.2387 \text{ kcal}^{-1} \text{ mole}$) of the same frequency [115].

5.2.2.7 Evaluation of k_{uni}/k_{∞} TABLE 5.50 - Parameters for k_{uni}/k_{∞} for $C_2H_2F_4$ (Model II)

	Centrifugal effects are neglected	Centrifugal effects are included
E_0	87.67 kcal mole ⁻¹	88.86 kcal mole ⁻¹
E_z^+	10051.5 cm ⁻¹ = 28.73 kcal mole ⁻¹	10051.5 cm ⁻¹ = 28.73 kcal mole ⁻¹
E_z	8901.5 cm ⁻¹ = 25.45 kcal mole ⁻¹	8874.5 cm ⁻¹ = 25.37 kcal mole ⁻¹
s	18	18
s^+	16	16
r	0	0
r^+	1	1
α	17	17
α^+	16.5	16.5
$\Gamma(\alpha+1)$	3.557×10^{14}	3.557×10^{14}
$\Gamma(\alpha^++1)$	8.563×10^{13}	8.563×10^{13}
$\Gamma(1+r^*/2)$	0.886	0.886
$\prod_{i=1}^s v_i$	6.258×10^{52} cm ⁻¹⁸	6.258×10^{52} cm ⁻¹⁸
$\prod_{i=1}^{s^+} v_i^+$	1.636×10^{45} cm ⁻¹⁶	8.996×10^{44} cm ⁻¹⁶
$(E_z^+)^{\alpha^+-\alpha}$	0.0106 cm ^{0.5}	0.0106 cm ^{0.5}
$(E_z^+)^{\alpha^++1}$	1.3050×10^{69} cm ^{-17.5}	1.2374×10^{69} cm ^{-17.5}
$(E_z^+)^{s^+}$	1.5539×10^{63} cm ⁻¹⁶	1.4801×10^{63} cm ⁻¹⁶
$(RT)^{1+r^*/2}$	28742.67 cm ^{-1.5}	28742.67 cm ^{-1.5}
$(RT)^{(r^*-r)/2}$	30.63 cm ^{-0.5}	30.63 cm ^{-0.5}
$\langle v^{+2} \rangle$	2003468.5 cm ⁻²	2002817.2 cm ⁻²
$\langle v^+ \rangle$	1112.6875 cm ⁻¹	1109.3125 cm ⁻¹
$\langle v^{+2} \rangle^2$	1238073.5 cm ⁻²	1230574.2 cm ⁻²
β^+	1.5645	1.5735
Z	3.2106×10^6 Torr ⁻¹ sec ⁻¹	3.2106×10^6 Torr ⁻¹ sec ⁻¹
		./...

Table 5.50 continued...

	Centrifugal effects are neglected	Centrifugal effects are included
C_0	9.487	9.458
C_1	0.4724	0.4609
θ	0.0072	0.0062
$G_1(x)$	$1.0175 \times 10^{-4} x^{0.5}$	$5.8742 \times 10^{-5} x^{0.5}$
$G_2(x)$	$[x+1-1.5645/(5.00x+2.73x^{0.5}+3.51)]^{16.5}$	$[x+1-1.5735/(5.00x+2.73x^{0.5}+3.51)]^{16.5}$
$G_3(x)$	$[x+1-1.5645 \exp(-2.419x^{0.25})]^{16.5}$	$[x+1-1.5735 \exp(-2.419x^{0.25})]^{16.5}$
$H(x)$	$(x + 4.574)^{17}$	$(x + 4.332)^{17*}$
C_2/P	$3.9128 \times 10^{10}/P$	$7.1251 \times 10^{10}/P$

$$\begin{aligned}
 * \quad \langle \Delta E_J \rangle &= (1.987 \times 10^{-3})(1350) \left(1 - \frac{(484.476)(545.485)(130.321)}{(155.812)(212.240)(123.152)} \right)^{1/2} (1.5) \\
 &= -7.68 \text{ kcal mole}^{-1}
 \end{aligned}$$

TABLE 5.51 - Contribution of Centrifugal Effects to $k_{\text{uni}}/k_{\infty}$ for $\text{C}_2\text{H}_2\text{F}_4 \rightarrow 2\text{CHF}_2$ at 1350°K (Model II)

P (Torr)	$(k_{\text{uni}}/k_{\infty})^a$	$(k_{\text{uni}}/k_{\infty})^b$
10^{-1}	0.0081	0.0028
1	0.0362	0.0142
10^1	0.1273	0.0599
10^2	0.3346	0.1924
10^3	0.6354	0.4513
10^4	0.8842	0.7560
10^5	0.9898	0.9473
10^6	1.0123	1.0061
10^7	1.0152	1.0156
10^8	1.0156	1.0167
10^9	1.0156	1.0167

^a Neglecting centrifugal effects ($k_{\text{uni}}/k_{\infty} = 0.5$ at $P = 370$ Torr)

^b Including centrifugal effects ($k_{\text{uni}}/k_{\infty} = 0.5$ at $P = 1514$ Torr)

5.2.2.8 Calculation of $k_a(E^*)$ TABLE 5.52 - Properties of the Active Molecule and Activated Complex
($C_2H_2F_4$, Model II)

	Molecule	Complex								
		Neglecting C.E.				Including C.E.				
Frequencies (cm^{-1})	3015	3015								
	1440	1440								
	1360	1360								
	901	622								
	622	1440								
	361	1080								
	1440	1322								
	1080	1125								
	478	3000								
	1322	1336								
	1125	1134								
	271	539								
	130	r^+	3.00	3.25	3.50	3.75	4.00	4.25	4.50	4.75
	3000		119	98	82	68	56	47	39	31
	1336		157	130	108	90	74	62	51	41
	1134		89	74	61	51	42	35	29	22
	539		181	150	124	103	85	71	59	49
	549									
E_0 (kcal mole $^{-1}$)			87.67				88.86			
s	18						16			
r	0						1			
Moments of Inertia (amu A 2)		r^+	I_{xx}^+	I_{yy}^+	I_{zz}^+					
I_{xx}	155.812	3.000	366.088	425.661	128.025					
I_{yy}	212.24	3.250	409.661	469.699	128.912					
I_{zz}	123.152	3.500	455.826	516.432	129.702					
		3.750	504.472	565.544	130.600					
		4.000	555.694	617.338	131.396					
		4.250	609.973	672.190	132.195					
		4.500	667.055	729.749	133.096					
		4.750	727.162	790.434	133.900					
		5.000	795.098	858.372	133.902					
Symmetry number for internal rotation						1				
Average bond energy (kcal mole $^{-1}$)										
D	40					61.7				

Table 5.52 continued...

Molecule	Complex									
	Neglecting C.E.					Including C.E.				
Increment for the summation (kcal mole ⁻¹) ΔE^+	0.1									
Number of rate constants to be calculated (for k_{uni})										
NEN	1000									
L [‡]	1									
Temperature (°K) T	1350									
Pressure (Torr) P	3500									
Collision number (Torr ⁻¹ sec ⁻¹) Z	3.2104x10 ⁶									
Internal energy of energized molecule (kcal mole ⁻¹) ECC	112.35					102.35				
Number of reaction coordinate intervals NN						8				
Potential energy of reaction coordinate (kcal mole ⁻¹) $V(r^+)$	r^+	3.00	3.25	3.50	3.75	4.00	4.25	4.50	4.75	5.00
		82.37	85.90	88.03	89.31	90.07	90.52	90.77	90.92	91.00
Reduced moment of inertia changing with r^+ I_{ir}^+ (amu A ²)	r^+	3.00	3.25	3.50	3.75	4.00	4.25	4.50	4.75	5.00
		32.60	32.72	32.86	33.01	33.11	33.27	33.42	33.52	33.52

The results at $E^+ = 27.76$ kcal mole⁻¹ are given below.

$$k_a(E^+ + E_0) = 0.1343 \times 10^{10} \text{ sec}^{-1}$$

$$k_a(E^+ + E_0)_{\text{anh}} = 0.2007 \times 10^9 \text{ sec}^{-1}$$

$$k_a(E^+ + E_0 + \langle \Delta E_J \rangle) = 0.5667 \times 10^{10} \text{ sec}^{-1}$$

$$k_a(E^+ + E_0 + \langle \Delta E_J \rangle)_{\text{anh}} = 0.9761 \times 10^9 \text{ sec}^{-1}$$

5.2.2.9 Calculation of k_{uni}

The input data for the computer program which evaluates k_{uni} is given in Table 5.52.

A. Neglecting Centrifugal Effects

$$\begin{aligned} k_{\text{uni}} &= \frac{1.8331 \times 10^6}{(9.537 \times 10^{-14})(6.9712 \times 10^5)(5.0027 \times 10^4)} \exp\left(\frac{-87.67}{1.987 \times 10^{-3} \times 1350}\right) (0.1) \\ &= (3.5261 \times 10^{-7})(0.1106 \times 10^{10}) \quad \times (0.1106 \times 10^{10}) \\ &= 3.90 \times 10^2 \end{aligned}$$

$$\begin{aligned} k_{\text{uni}}(\text{anh}) &= (3.5261 \times 10^{-7})(0.1333 \times 10^{10}) \\ &= 4.70 \times 10^2 \end{aligned}$$

B. Including Centrifugal Effects

$$\begin{aligned} k_{\text{uni}} &= \frac{2.0234 \times 10^6}{(9.537 \times 10^{-14})(6.9712 \times 10^5)(5.0027 \times 10^4)} \exp\left(\frac{-88.86}{1.987 \times 10^{-3} \times 1350}\right) (0.1) \\ &= (2.4976 \times 10^{-7})(0.1499 \times 10^{10}) \quad \times (0.1499 \times 10^{10}) \\ &= 3.67 \times 10^2 \end{aligned}$$

$$\begin{aligned} k_{\text{uni}}(\text{anh}) &= (2.4976 \times 10^{-7})(0.2049 \times 10^{10}) \\ &= 5.12 \times 10^2 \end{aligned}$$

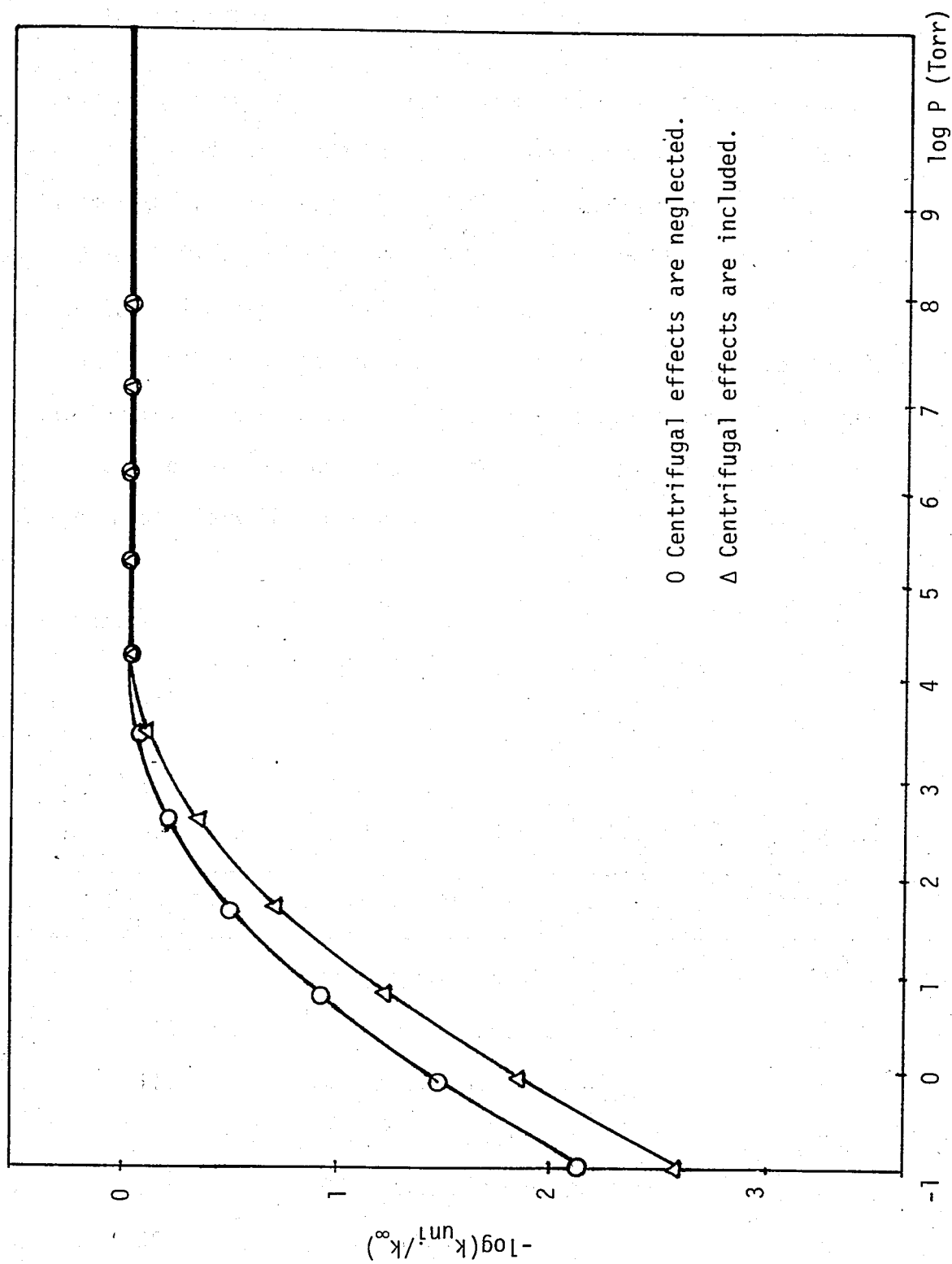


Figure 5.6 - Calculated fall-off curves for 1,1,2,2-tetrafluoroethane decomposition at 1350K (Model II)

5.3 PENTAFLUOROETHANE

The kinetics of the gas phase decomposition of a dilute mixture of pentafluoroethane in argon has been studied in a single pulse shock tube in the temperature range 1180-1370⁰K at total pressures of about 2900-4000 Torr [91]. At high temperatures ($T > 1350^0\text{K}$) there is a significant contribution from the C-C bond rupture.

In the following sections the fall-off region as well as the rate constant for this C-C bond fission reaction are evaluated. Good agreement is obtained between the experimental Arrhenius parameters and the results of Model II with centrifugal effects.

5.3.1 Model I

5.3.1.1 Data

A. The Molecule*

TABLE 5.53 - Vibrational Frequencies of C_2HF_5 [116] (C_s symmetry)

	Wave number (cm^{-1})	Type of vibration	Species
ν_1	1218	CF_3 asymmetric stretching	A'
ν_2	1198	CF_3 symmetric stretching	A'
ν_3	1111	CF_2 symmetric stretching	A'
ν_4	867	C-C stretching	A'
ν_5	725	CF_3 symmetric deformation	A'
ν_6	654	CF_2 deformation	A'
			./...

* The energized C_2HF_5 molecule has the same configuration as the energized C_2H_6 molecule.

Table 5.53 continued....

	Wave number (cm^{-1})	Type of vibration	Species
ν_7	523	CF_3 asymmetric deformation	A'
ν_8	361	CF_2 wagging	A'
ν_9	3008	C-H stretching	A'
ν_{10}	217	CF_3 rocking	A'
ν_{11}	1393	CCH deformation	A'
ν_{12}	1309	CF_3 asymmetric stretching	A''
ν_{13}	1145	CF_2 antisymmetric stretching	A''
ν_{14}	577	CF_3 asymmetric deformation	A''
ν_{15}	413	CF_2 twisting	A''
ν_{16}	1359	CCH bending	A''
ν_{17}	247	CF_3 rocking	A''
ν_{18}	74	torsion	A''

TABLE 5.54 - Molecular Parameters of C_2HF_5 [117] (C_s symmetry)

$R(\text{C}-\overset{\circ}{\text{C}})$ ($\overset{\circ}{\text{A}}$)	1.525 ($\overset{\circ}{\text{A}}$)
$R(\text{C}-\overset{\circ}{\text{H}})$ ($\overset{\circ}{\text{A}}$)	1.09 ($\overset{\circ}{\text{A}}$)
$R(\text{C}-\overset{\circ}{\text{F}})(\overset{\circ}{\text{CHF}}_2)$ ($\overset{\circ}{\text{A}}$)	1.347 ($\overset{\circ}{\text{A}}$)
$R(\text{C}-\overset{\circ}{\text{F}})(\overset{\circ}{\text{CF}}_3)$ ($\overset{\circ}{\text{A}}$)	1.327 ($\overset{\circ}{\text{A}}$)
ΔCCH	109°
ΔCCF	110°
ϕ	$118^\circ 48'$ (angle between the two CCF planes associated with the $-\text{CHF}_2$ group)
ΔFCH	$109^\circ 54'$
$\Delta \text{FCF}(-\overset{\circ}{\text{CHF}}_2)$	108°
$\Delta \text{FCF}(-\overset{\circ}{\text{CF}}_3)$	109°

B. The Activated Complex

The activated complex is supposed to have the vibrational frequencies and molecular parameters of CHF_2^\ddagger and CF_3^\ddagger (Tables 5.32, 5.33, 5.75 and 5.76).

5.3.1.2. The Moments of Inertia

A. The Molecule (Table 5.54)

I. *External Rotation*

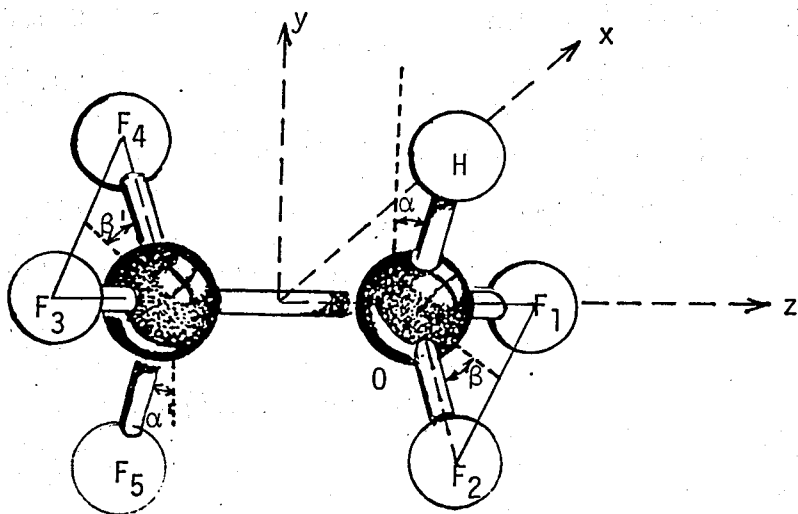


Figure 5.7 - Geometrical representation of C_2HF_5 .

Calculation of the coordinates

$$\alpha = 109^{\circ} - 90^{\circ} = 19^{\circ}$$

$$\alpha' = 110^{\circ} - 90^{\circ} = 20^{\circ}$$

$$\beta = 108^{\circ}/2 = 54^{\circ}$$

$$\beta' = 109^{\circ}/2 = 54^{\circ}30' = 54.5^{\circ}$$

The -CHF₂ Group

$$x_{C_1} = 0$$

$$y_{C_1} = 0$$

$$x_H = 0$$

$$y_H = \cos 19^{\circ}(1.09)$$

$$x_{F_1} = \sin 54^{\circ}(1.347)$$

$$= 1.031$$

$$= 1.090$$

$$y_{F_1, F_2} = -(\sin(90^{\circ} - \frac{118.8^{\circ}}{2}))(1.266)$$

$$x_{F_2} = -1.090$$

$$= -0.644$$

$$\text{where } C_0 = \cos 20^{\circ}(1.347)$$

$$z_{C_1} = 0.763$$

$$= 1.266$$

$$z_{H_1} = (\sin 19^{\circ}(1.09)) + 0.763$$

$$= 1.118$$

$$z_{F_1, F_2} = (\sin 20^{\circ}(1.347)) + 0.763$$

$$= 1.224$$

The -CF₃ Group

$$x_{C_2} = 0$$

$$y_{C_2} = 0$$

$$x_{F_5} = 0$$

$$y_{F_5} = -(\cos 20^{\circ}(1.327))$$

$$x_{F_4} = \sin 54.5^{\circ}(1.327)$$

$$= -1.247$$

$$= 1.080$$

$$y_{F_3, F_4} = \sin 30^{\circ}(1.247)$$

$$x_{F_3} = -1.080$$

$$= 0.624$$

$$z_{C_2} = -0.763$$

$$z_{F_3, F_4, F_5} = -(\sin 20^{\circ}(1.327)) + 0.763$$

$$= -1.217$$

TABLE 5.55 - Parameters for Evaluation of Moment of Inertia Product of C₂H₅F

Atom	m _i	X _i	Y _i	Z _i	m _i X _i	m _i Y _i	m _i Z _i	m _i X _i ²	m _i Y _i ²	m _i Z _i ²	m _i X _i Y _i	m _i X _i Z _i	m _i Y _i Z _i
C ₁	12.011	0	0	0.763	0	0	9.164	0	0	6.992	0	0	0
C ₂	12.011	0	0	-0.763	0	0	-9.164	0	0	6.992	0	0	0
H ₁	1.008	0	1.031	1.118	0	1.039	1.127	0	1.071	1.260	0	0	1.162
F ₁	18.998	1.090	-0.644	1.224	20.708	-12.235	23.254	22.572	7.879	28.462	-13.336	25.346	-14.975
F ₂	18.998	-1.090	-0.644	1.224	-20.708	-12.235	23.254	22.572	7.879	28.462	13.336	-25.346	-14.975
F ₃	18.998	-1.080	0.624	-1.224	-20.708	11.855	-23.254	22.572	7.879	28.462	-12.803	25.113	-14.510
F ₄	18.998	1.080	0.624	-1.224	20.708	11.855	-23.254	22.572	7.879	28.462	12.803	-25.113	-14.510
F ₅	18.998	0	-1.247	-1.224	0	-23.691	-23.254	0	29.542	28.462	0	0	28.997
					0	-23.412	-22.127	90.288	62.129	157.554	0	0	-28.811

$$\Sigma m_i X_i^2 = \Sigma m_i X_i^2 - (\Sigma m_i X_i)^2 / M \quad (5.23)$$

$$= 90.288$$

$$\Sigma m_i Z_i^2 = \Sigma m_i Z_i^2 - (\Sigma m_i Z_i)^2 / M \quad (5.25)$$

$$= 157.554 - (-22.127)^2 / 120$$

$$\Sigma m_i Y_i^2 = \Sigma m_i Y_i^2 - (\Sigma m_i Y_i)^2 / M \quad (5.24)$$

$$= 153.474$$

$$= 62.129 - (-23.412)^2 / 120$$

$$= 57.561$$

$$\Sigma m_i Y_i Z_i = \Sigma m_i Y_i Z_i - (\Sigma m_i Y_i)(\Sigma m_i Z_i) / M \quad (5.26)$$

$$= -28.811 - (-23.412)(-22.127) / 120$$

$$= -33.128$$

$$I_{xx} = 57.561 + 153.474 = 211.035 \text{ amu } \overset{0}{\text{A}}^2$$

$$I_{yy} = 90.288 + 153.474 = 243.762 \text{ amu } \overset{0}{\text{A}}^2$$

$$I_{zz} = 90.288 + 57.561 = 147.849 \text{ amu } \overset{0}{\text{A}}^2$$

$$ABC = 7.374 \times 10^6 \text{ amu}^3 \overset{0}{\text{A}}^6$$

$$= 33.70 \times 10^{-114} \text{ g}^3 \text{cm}^{-6}$$

II. Internal Rotation

The moment of inertia for internal rotation can be calculated in the following way.

$$I_{ir} = \frac{I_1 I_2}{I_1 + I_2}$$

$$= 37.05 \text{ amu } \overset{0}{\text{A}}^2$$

$$= 61.51 \times 10^{-40} \text{ g.cm}^2$$

$$I_1 = 63.60 \text{ amu } \overset{0}{\text{A}}^2 \text{ from } I_{ir} \text{ of } \text{C}_2\text{H}_2\text{F}_4 \text{ (Section 5.2.1.2)}$$

$$I_2 = 88.76 \text{ amu } \overset{0}{\text{A}}^2 \text{ from } I_{ir} \text{ of } \text{C}_2\text{F}_6 \text{ (Section 5.4.1.2)}$$

B. The Complex

I. External Rotation

Calculation of $\langle R_c \rangle_{av}$ at $T = 1400^\circ \text{K}$

$$a_{es} = \frac{2(1.77 \times 10^{-18})^2 (1.5 \times 10^{-18})^2}{3(1.3805 \times 10^{-16})(1400)}$$

$$= 0.24 \times 10^{-58} \text{ ergs cm}^6$$

$$a_{ind} = (2.008 \times 10^{-24})(1.5 \times 10^{-18})^2 + (2.650 \times 10^{-24})(1.77 \times 10^{-18})^2$$

$$= 0.13 \times 10^{-58} \text{ ergs cm}^6$$

$$a_{\text{dis}} = (3/2) \left(\frac{(4.8033 \times 10^{-10})(6.6262 \times 10^{-27})}{2(3.14)(9.1096 \times 10^{-28})^{1/2}} \right) (2.008 \times 2.650 \times 10^{-48}) / \left[\left(\frac{2.008 \times 10^{-24}}{19} \right)^2 + \left(\frac{2.650 \times 10^{-24}}{25} \right)^2 \right]$$

$$= 2.06 \times 10^{-58} \text{ ergs cm}^6$$

$$a = 2.43 \times 10^{-58} \text{ ergs cm}^6$$

$$\langle R_c \rangle_{\text{av}} = 4.83 \times 10^{-8} \text{ cm.}$$

Calculation of the coordinates

-CHF₂ (See Section 5.2.1.2)

$$\begin{array}{lll} x_{C_1} = 0 & y_{C_1} = 0 & z_{C_1} = 2.415 \\ x_H = 0 & y_H = 1.071 & z_H = 2.415 + 0.241 = 2.656 \\ x_{F_1} = 1.139 & y_{F_1, F_2} = -0.659 & z_{F_1, F_2} = 2.415 + 0.297 = 2.712 \\ x_{F_2} = -1.139 & & \end{array}$$

-CF₃ (from C₂F₆⁺)

$$\begin{array}{lll} x_{C_2} = 0 & y_{C_1} = 0 & z_C = -2.415 \\ x_{F_5} = 0 & y_{F_3} = -1.286 & z_{F_3, F_4, F_5} = -2.712 \\ x_{F_4} = 1.114 & y_{F_4, F_5} = 0.643 & \\ x_{F_3} = -1.114 & & \end{array}$$

TABLE 5.56 - Parameters for Evaluation of Moment of Inertia Product of C₂HF₅⁺

Atom	m _i	X _i ⁺	Y _i ⁺	Z _i ⁺	m _i X _i ⁺	m _i Y _i ⁺	m _i Z _i ⁺	m _i X _i ²	m _i Y _i ²	m _i Z _i ²	m _i X _i Y _i ⁺	m _i X _i Z _i ⁺	m _i Y _i Z _i ⁺	m _i X _i ² Z _i ⁺	m _i Y _i ² Z _i ⁺
C ₁	12.011	0	0	2.415	0	0	29.007	0	0	70.051	0	0	0	0	0
C ₂	12.011	0	0	-2.415	0	0	-29.007	0	0	70.051	0	0	0	0	0
H ₁	1.0079	0	1.071	2.656	0	1.080	2.677	0	1.156	7.111	0	0	0	0	2.867
F ₁	18.998	1.139	-0.659	2.712	21.639	-12.520	51.523	24.647	8.251	139.729	-14.260	58.684	-33.953	-14.260	58.684
F ₂	18.998	-1.139	-0.659	2.712	-21.639	-12.520	51.523	24.647	8.251	139.729	14.260	-58.684	-33.953	14.260	-58.684
F ₃	18.998	-1.114	0.643	-2.712	-21.639	12.216	-51.523	23.576	7.857	139.729	-13.608	57.396	-33.129	-13.608	57.396
F ₄	18.998	1.114	0.643	-2.712	21.639	12.216	-51.523	23.576	7.857	139.729	13.608	-57.396	-33.129	13.608	-57.396
F ₅	18.998	0	-1.286	-2.712	0	-24.431	-51.523	0	31.429	139.729	0	0	0	0	66.258
					0	-23.960	-48.846	96.446	64.801	845.858	0	0	0	0	-65.039

$$\begin{aligned} \Sigma m_i X_i^2 &= \Sigma m_i X_i^2 - (\Sigma m_i X_i^+)^2 / M & \Sigma m_i Z_i^2 &= \Sigma m_i Z_i^2 - (\Sigma m_i Z_i^+)^2 / M & I_{xx}^+ &= 885.992 \text{ amu } \text{Å}^2 \\ &= 96.446 & &= 845.858 - (-48.846)^2 / 120 & I_{yy}^+ &= 922.421 \text{ amu } \text{Å}^2 \\ \Sigma m_i Y_i^2 &= \Sigma m_i Y_i^2 - (m_i Y_i^+)^2 / M & &= 825.975 & I_{zz}^+ &= 156.463 \text{ amu } \text{Å}^2 \\ &= 64.801 - (23.960)^2 / 120 & \Sigma m_i Y_i^+ Z_i^+ &= \Sigma m_i Y_i^+ Z_i^+ - (\Sigma m_i Y_i^+)(\Sigma m_i Z_i^+) / M & ABC &= I_{xx}^+ I_{yy}^+ I_{zz}^+ - I_{yz}^{+2} \\ &= 60.017 & &= -65.039 - (-23.960)(-48.846) / 120 & &= 1.229 \times 10^8 \text{ amu}^3 \text{Å}^6 \\ & & &= -74.792 & &= 5.62 \times 10^{-112} \text{ g}^3 \text{cm}^{-6} \end{aligned}$$

II. *Internal Rotation*

$$I_{ir}^+ = \frac{I_1^+ I_2^+}{I_1^+ + I_2^+} \quad \begin{array}{l} I_1^+ = 67.06 \text{ amu } \text{\AA}^2 \text{ from } I_{ir}^+ \text{ of } C_2H_2F_4^+ \text{ (Model I)} \\ I_2^+ = 94.26 \text{ amu } \text{\AA}^2 \text{ from } I_{ir}^+ \text{ of } C_2F_6^+ \text{ (Model I)} \end{array}$$

$$= 39.18 \text{ amu } \text{\AA}^2$$

$$= 65.04 \times 10^{-40} \text{ g.cm}^2$$

5.3.1.3 Calculation of the Partition Functions

A. The Molecule

I. *Vibrational Partition Function*

$$Q_v = 76610.56$$

II. *Rotational Partition Function*

$$Q_r = \frac{\sqrt{3.14} (8) (3.14)^2 (1.3805 \times 10^{-16}) (1400)}{1 (6.6262 \times 10^{-27})^2} \text{ }^{3/2} (33.70 \times 10^{-114}) \text{ }^{1/2}$$

$$= 2.1083 \times 10^6$$

III. *Partition Function for Internal Rotation*

$$Q_{ir} = \frac{((8)(30.96)(61.51 \times 10^{-40})(1.3805 \times 10^{-16})(1400)) \text{ }^{1/2}}{(6.6262 \times 10^{-27})(3)}$$

$$= 27.30$$

B. The Activated Complex

I. *Vibrational Partition Function*

$$Q_v^+ = 380.152$$

II. *Rotational Partition Function*

$$Q_r^+ = \frac{\sqrt{3.14} \cdot (8)(3.14)^2(1.3805 \times 10^{-16})(1400)}{1 \cdot (6.6262 \times 10^{-27})^2}^{3/2} (5.62 \times 10^{-112})^{1/2}$$

$$= 8.6074 \times 10^6$$

III. *Partition Function for Internal Rotations*

$$Q_{ir}^+ = [((8)(3.14)^3(65.04 \times 10^{-40})(1.3805 \times 10^{-16})(1400))^{1/2} / 6.6262 \times 10^{-27} \times 1]$$

$$\times [((8)(3.14)^2(65.04 \times 10^{-40})(1.3805 \times 10^{-16})(1400))^{1/2} / 6.6262 \times 10^{-27} \times 2]^4$$

$$= 26.9134 \times 10^6$$

5.3.1.4 Calculation of $\langle E_V \rangle$, $\langle E_V^+ \rangle$, E_0 and E^+

A. Calculation of $\langle E_V \rangle$

$$T \partial \ln Q_V / \partial T = 10.48$$

$$\langle E_V \rangle = 29.15 \text{ kcal mole}^{-1}$$

B. Calculation of $\langle E_V^+ \rangle$

$$T \partial \ln Q_V^+ / \partial T = 6.765$$

$$\langle E_V^+ \rangle = 18.82 \text{ kcal mole}^{-1}$$

C. Calculation of E_0

$$E_0 = 93.50 - (1/2)(5 - 1 + 2)(1.987 \times 10^{-3})(1400) + 29.15 - 18.82$$

$$= 95.48 \text{ kcal mole}^{-1}$$

D. Calculation of E^+

$$E^+ = (1 + 2.5)(1.987 \times 10^{-3})(1400) + (2.859 \times 10^{-3})(6580.53)$$

$$= 28.55 \text{ kcal mole}^{-1}$$

5.3.1.5 Calculation of ΔS^\ddagger , k_∞ and A_∞

The experimental [91] Arrhenius parameters are

$$A_\infty = 10^{16.6} \text{ sec}^{-1}$$

$$E_\infty = 93.5 \text{ kcal mole}^{-1}$$

$$\Delta S^\ddagger = 12.35 \text{ cal mole}^{-1} \text{ deg}^{-1}$$

$$k_\infty = 4.01 \times 10^2 \text{ sec}^{-1}$$

The corresponding theoretical values are

$$S_v = 1.987(\ln 76610.560 + 10.480)$$

$$= 43.17 \text{ cal mole}^{-1} \text{ deg}^{-1}$$

$$S_r = 1.987(\ln 2.1083 \times 10^6 + 1.5)$$

$$= 31.91 \text{ cal mole}^{-1} \text{ deg}^{-1}$$

$$S_{ir} = 1.987(\ln 27.30 + 0.5)$$

$$= 7.56 \text{ cal mole}^{-1} \text{ deg}^{-1}$$

$$S_{th} = 82.64 \text{ cal mole}^{-1} \text{ deg}^{-1}$$

$$S_v^+ = 1.987(\ln 380.152 + 6.765)$$

$$= 25.25 \text{ cal mole}^{-1} \text{ deg}^{-1}$$

$$S_r^+ = 1.987(\ln 8.6074 \times 10^6 + 1.5)$$

$$= 34.71 \text{ cal mole}^{-1} \text{ deg}^{-1}$$

$$S_{ir}^+ = 1.987(\ln 26.9134 \times 10^6 + 2.5)$$

$$= 38.96 \text{ cal mole}^{-1} \text{ deg}^{-1}$$

$$S_{th}^+ = 98.92 \text{ cal mole}^{-1} \text{ deg}^{-1}$$

$$\Delta S_{th}^\ddagger = 16.28 \text{ cal mole}^{-1} \text{ deg}^{-1}$$

$$k_{\infty, th} = \frac{(1)(1.3805 \times 10^{-16})(1400)}{6.6262 \times 10^{-27}} \frac{380.152 \times 8.6074 \times 10^6 \times 26.9134 \times 10^6}{76610.560 \times 2.1083 \times 10^6 \times 27.30}$$

$$\times \exp\left(\frac{-95.49}{1.987 \times 10^{-3} \times 1400}\right)$$

$$= 7.20 \times 10^2$$

$$A_{\infty, th} = \frac{(2.718)(1.3805 \times 10^{-16})(1400)}{6.6262 \times 10^{-27}} e^{16.28/1.987}$$

$$= 10^{17.46}$$

5.3.1.6 Calculation of the Anharmonicity Corrections

As previously mentioned, the values of a_{xy} and b_{xy} to calculate f_2 and f_3 are taken from the tables [85].

A. The Molecule

For C-H stretching

$$f_2 = 5.0480 \times 10^5 \text{ dynes cm}^{-1}$$

$$f_3 = 10.4914 \times 10^{13} \text{ dynes cm}^{-2}$$

$$D_e = 5.8433 \times 10^{-12} \text{ ergs molecule}^{-1} = 84.09 \text{ kcal mole}^{-1}$$

$$D^{-1} = 0.01189$$

For C-F stretching (in $-\text{CHF}_2$) (2 fold degenerate)

$$f_2 = 6.5297 \text{ dynes cm}^{-1}$$

$$f_3 = 12.8901 \text{ dynes cm}^{-1}$$

$$D_e = 8.3780 \times 10^{-12} \text{ ergs molecule}^{-1} = 120.56 \text{ kcal mole}^{-1}$$

$$D^{-1} = 0.00829$$

For C-F stretching (in $-\text{CF}_3$) (3 fold degenerate)

$$f_2 = 7.2019 \times 10^5 \text{ dynes cm}^{-1}$$

$$f_3 = 14.5057 \times 10^{13} \text{ dynes cm}^{-1}$$

$$D_e = 8.8763 \times 10^{-12} \text{ ergs molecule}^{-1} = 127.73 \text{ kcal mole}^{-1}$$

$$D_e^{-1} = 0.00783$$

For C-C stretching

$$f_2 = 2.7300 \text{ dynes cm}^{-1}$$

$$f_3 = 4.5066 \text{ dynes cm}^{-1}$$

$$D_e = 5.0091 \times 10^{-12} \text{ ergs molecule}^{-1} = 72.08 \text{ kcal mole}^{-1}$$

$$D_e^{-1} = 0.01387$$

For bending nodes

C-H bending (2 fold degenerate) (from previous calculations)

$$D_e^{-1} = 0.01828$$

C-F bending (8 fold degenerate) (from previous calculations)

$$D_e^{-1} = 0.01957$$

$$\langle D_e^{-1} \rangle = \frac{1}{17} (0.01189 + (2)(0.00829) + (3)(0.00783) + 0.01387 \\ + (2)(0.01828) + (8)(0.01957))$$

$$\langle D_e^{-1} \rangle = 0.01520$$

$$D = 65.65 \text{ kcal mole}^{-1}$$

B. The Complex

$$\langle D_e^{-1} \rangle = \frac{1}{12} ((3)(0.00767) + (3)(0.01957) + (2)(0.0837) + 0.012 \\ + 0.01828 + (2)(0.0195))$$

$$= 0.01398 \text{ (from the data of } \text{C}_2\text{F}_6 \text{ and } \text{C}_2\text{H}_2\text{F}_4)$$

$$D = 71.54 \text{ kcal mole}^{-1}$$

5.3.1.7 Evaluation of $k_{\text{uni}}/k_{\infty}$ A. Centrifugal Effects are NeglectedTABLE 5.57 - Parameters for $k_{\text{uni}}/k_{\infty}$ for C_2HF_5 (Model I)
Neglecting Centrifugal Effects

E_0	95.49 kcal mole ⁻¹
E_Z	8162.5 cm ⁻¹ = 23.33 kcal mole ⁻¹
E_Z^+	6661.5 cm ⁻¹ = 19.04 kcal mole ⁻¹
s	17
s^+	12
r	1
r^*	5
α	16.5
α^+	14.5
$\Gamma(\alpha+1)$	8.563×10^{13}
$\Gamma(\alpha^++1)$	3.348×10^{11}
$\Gamma(1+r^*/2)$	3.2333
$\prod_{i=1}^s \nu_i$	$1.372 \times 10^{49} \text{ cm}^{-17}$
$\prod_{i=1}^{s^+} \nu_i^+$	$7.718 \times 10^{35} \text{ cm}^{-12}$
$(E_Z^+)^{\alpha^+-\alpha}$	$2.253 \times 10^{-8} \text{ cm}^2$
$(E_Z^+)^{\alpha^++1}$	$1.842 \times 10^{59} \text{ cm}^{-15.5}$
$(E_Z^+)^{s^+}$	$7.640 \times 10^{45} \text{ cm}^{-12}$
$(RT)^{1+r^*/2}$	$2.874 \times 10^{10} \text{ cm}^{-3.5}$
$(RT)^{(r^*-r)/2}$	$9.469 \times 10^5 \text{ cm}^{-2}$

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Table 5.57 continued...

$\langle v^2 \rangle$	1337260.3 cm ⁻²
$\langle v \rangle$	960.294 cm ⁻¹
$\langle v \rangle^2$	922164.57 cm ⁻²
β	1.4050
$\langle v^{+2} \rangle$	1642896.3 cm ⁻²
$\langle v^+ \rangle$	1110.250 cm ⁻¹
$\langle v^+ \rangle^2$	1232655.10 cm ⁻²
β^+	1.4763
Z	$2.9358 \times 10^6 \text{ Torr}^{-1} \text{ sec}^{-1} *$
C_0	6.846
C_1	0.0652
θ	0.0976
$G_1(x)$	$10.47x^{2.5}$
$G_2(x)$	$[x+1-1.4763/(5.00x+2.73x^{0.5}+3.51)]^{14.5}$
$G_3(x)$	$[x+1-1.4763\exp(-2.419x^{0.25})]^{14.5}$
H(x)	$(x + 6.239)^{16.5}$
C_2/P	$11.13 \times 10^{11}/P$

* The collision diameter used in the evaluation of Z is not given in the literature. It is calculated using the 28:7 potential (as done for $C_2H_2F_4$). $\sigma_{C_2HF_5}$ is found to be equal to 5.14 Å. The mean of the collision diameters (C_2HF_5 and argon) is 4.39 Å

B. Centrifugal Effects are Included

I. *The Direct Method*

The value of $H(x)$, calculated below, is used with the parameters of Table 5.57 to determine the fall off region.

$$\begin{aligned}\langle \Delta E_J \rangle &= (-1.987 \times 10^{-3})(1400)(6.92) \\ &= -19.25 \text{ kcal mole}^{-1}\end{aligned}$$

$$\begin{aligned}H(x) &= \left(x + \frac{95.48 - 19.25 + 23.33}{19.04} \right)^{16.5} \\ &= (x + 5.229)^{16.5}\end{aligned}$$

II. *The Waage-Rabinovitch Approximation*

$$\begin{aligned}a &= 1 - 1.4050 \exp[-2.419 \left(\frac{95.48 - 19.25 + 28.55}{23.33} \right)^{0.25}] \\ &= 0.9585\end{aligned}$$

$$\begin{aligned}F^{-1} &= 1 + \frac{(17 + 0.5 - 1)(7.92 - 1)(1.987 \times 10^{-3} \times 1400)}{(95.48 + (0.9585 \times 23.33))} \\ &= 3.695\end{aligned}$$

$$F = 0.270$$

The $k_{\text{uni}}/k_{\infty}$ ratio equals 0.5 at $P = 2074$ Torr.

TABLE 5.58 - Contribution of Centrifugal Effects to $k_{\text{uni}}/k_{\infty}$
for $\text{C}_2\text{HF}_5 \rightarrow \text{CF}_3\cdot + \text{CHF}_2\cdot$ at 1400°K (Model I)

P (Torr)	$(k_{\text{uni}}/k_{\infty})^{\text{a}}$	$(k_{\text{uni}}/k_{\infty})^{\text{b}}$
10^{-1}	0.0053	0.0006
1	0.0258	0.0041
10^1	0.0988	0.0213
10^2	0.2833	0.0756
10^3	0.5831	0.2720
10^4	0.8578	0.5850
10^5	0.9831	0.8692
10^6	1.0106	0.9884
10^7	1.0141	1.0114
10^8	1.0144	1.0142
10^9	1.0145	1.0144

^aCentrifugal effects are neglected ($k_{\text{uni}}/k_{\infty} = 0.5$ at $P = 560$ Torr).

^bCentrifugal effects are included ($k_{\text{uni}}/k_{\infty} = 0.5$ at $P = 6000$ Torr).

5.3.1.8 Calculation of $k_a(E^*)$

The input data for the computer program to calculate $k_a(E^*)$ is given in Table 5.59.

TABLE 5.59 - Properties of the Active Molecule and the Activated
 Complex
 (C_2HF_5 , Model I)

	Molecule	Complex
Frequencies (cm^{-1})	1218	3000
	1198	1166
	1111	700
	867	650
	725	1317
	654	1175
	523	1087
	361	703
	3008	1251 (2)
	217	512 (2)
	1393	
	1309	
	1145	
	577	
	413	
	1359	
	247	
E_0 (kcal mole $^{-1}$)		95.49
s	17	12
r	1	5
Moments of inertia (amu \AA^2)		
I_{xx}	211.035	885.992
I_{yy}	243.762	922.421
I_{zz}	147.849	156.463
I_{ir}	37.05	39.18
Symmetry number for internal rotation		
σ	3	2 (4) and 1 (1)
Average bond energy (kcal mole $^{-1}$)		
D	65.65	71.54
Increment for the summation (kcal mole $^{-1}$) ΔE^{\ddagger}		0.05
Number of rate constants to be calculated NEN	1200	

./...

Table 5.59 continued....

	Molecule	Complex
L^\ddagger		1
Temperature ($^{\circ}\text{K}$) T		1400
Pressure (Torr) P		3500
Collision number ($\text{Torr}^{-1}\text{sec}^{-1}$) Z		2.936×10^6

The results at $E^\ddagger = 28.55 \text{ kcal mole}^{-1}$ are shown below.

$$k_a(E^\ddagger + E_0) = 0.2469 \times 10^{10} \text{ sec}^{-1}$$

$$k_a(E^\ddagger + E_0 + \langle \Delta E_J \rangle) = 0.2562 \times 10^{11} \text{ sec}^{-1}$$

$$k_a(E^\ddagger + E_0)_{\text{anh}} = 0.9118 \times 10^9 \text{ sec}^{-1}$$

$$k_a(E^\ddagger + E_0 + \langle \Delta E_J \rangle)_{\text{anh}} = 0.1143 \times 10^{11} \text{ sec}^{-1}$$

5.3.1.9 Calculation of k_{uni}

The input data for this calculation is given in Table 5.59.

A. Neglecting Centrifugal Effects

$$k_{\text{uni}} = \frac{8.6074 \times 10^6}{(9.537 \times 10^{-14})(2.1083 \times 10^6)(76610.56)(27.30)} e^{-95.49 / 1.987 \times 10^{-3} \times 1400} \\ = 5.47 \times 10^2 \text{ sec}^{-1} \cdot (0.05)(4.3239 \times 10^{11})$$

$$k_{\text{uni}}(\text{anh}) = (1.2652 \times 10^{-9})(4.9705 \times 10^{11}) \\ = 6.29 \times 10^2 \text{ sec}^{-1}$$

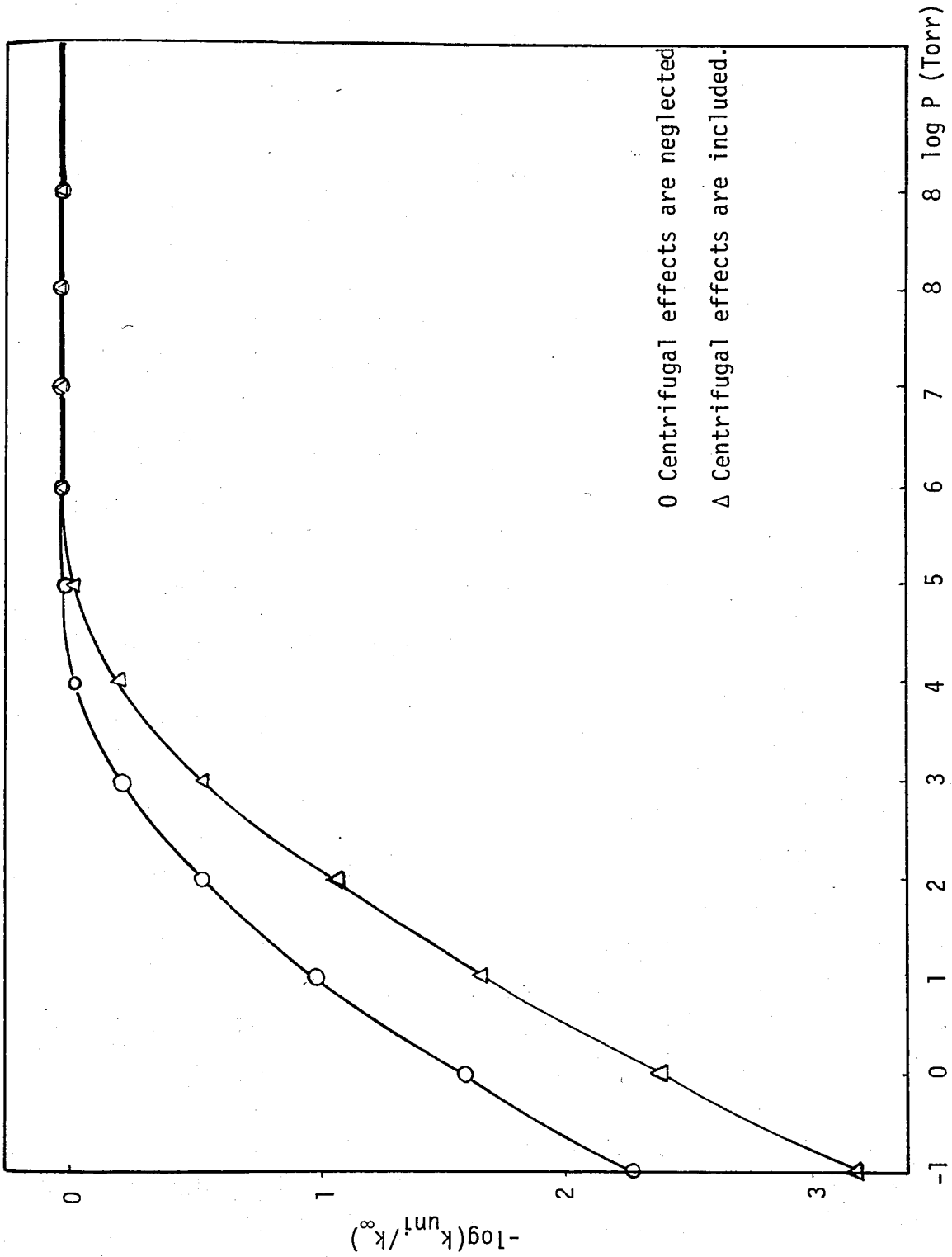


Figure 5.8 - Calculated fall-off curves for pentafluoroethane decomposition at 1400^oK (Model I)

B. Including Centrifugal Effects

$$k_{\text{uni}} = (1.2652 \times 10^{-9})(2.4353 \times 10^{11})$$

$$= 3.08 \times 10^2 \text{ sec}^{-1}$$

$$k_{\text{uni(anh)}} = (1.2652 \times 10^{-9})(3.1202 \times 10^{11})$$

$$= 3.95 \times 10^2 \text{ sec}^{-1}$$

5.3.2 Model I I

5.3.2.1 Data

A. The Molecule

The molecule has the vibrational frequencies given in Table 5.53 and the molecular parameters given in Table 5.54.

B. The Activated Complex

TABLE 5.60 - The Vibrational Frequencies of C_2HF_5 (Model II).

	Wave number (cm^{-1})	Type of Vibration	Species
ν_1	1218	CF_3 asymmetric stretching	A'
ν_2	1198	CF_3 symmetric stretching	A'
ν_3	1111	CF_2 symmetric stretching	A'
ν_4	725	CF_3 symmetric deformation	A'
ν_5	654	CF_2 deformation	A'
ν_6	523	CF_3 asymmetric deformation	A'
ν_7	$361 \exp[-\alpha(r^+ - 1.525)]$	CF_2 wagging	A'
ν_8	3008	C-H stretching	A'
			./...

Table 5.60 continued...

	Wave number (cm ⁻¹)	Type of vibration	Species
ν_9	217exp[- $\alpha(r^+ - 1.525)$]	CF ₃ rocking	A'
ν_{10}	1393	CCH deformation	A'
ν_{11}	1309	CF ₃ asymmetric stretching	A''
ν_{12}	1145	CF ₂ asymmetric stretching	A''
ν_{13}	577	CF ₃ asymmetric deformation	A''
ν_{14}	413exp[- $\alpha(r^+ - 1.525)$]	CF ₂ twisting	A''
ν_{15}	1359	CCH bending	A''
ν_{16}	247exp[- $\alpha(r^+ - 1.525)$]	CF ₃ rocking	A''

The potential energy is

$$V(r^+) = D[1 - e^{-\beta(r^+ - 1.525)}]^2 + E_Z^+ - E_Z^m$$

$$\Delta H^0(\text{CF}_3 - \text{CHF}_2) = 93.5 \text{ kcal mole}^{-1}$$

$$\Delta H_0^0 = 91.1 \text{ kcal mole}^{-1} \text{ [114]}$$

$$E_Z^m = 23.44 \text{ kcal mole}^{-1}$$

$$E_Z^p = 19.04 \text{ kcal mole}^{-1}$$

$$f = 5.40 \times 10^5 \text{ dynes cm}^{-1} *$$

$$\nu_a = 361 \exp[-\alpha(r^+ - 1.525)]$$

$$\nu_b = 217 \exp[-\alpha(r^+ - 1.525)]$$

$$\nu_c = 413 \exp[-\alpha(r^+ - 1.525)]$$

$$\nu_d = 247 \exp[-\alpha(r^+ - 1.525)]$$

$$D = 95.51 \text{ kcal mole}^{-1}$$

$$\beta = 2.02 \times 10^{-8} \text{ cm}^{-1}$$

$$\alpha = 0.80 \text{ (The adjustable parameter has been chosen as done previously)}$$

$$E_Z^+ - E_Z^m = 1.77[\exp(-0.80(r^+ - 1.525))] - 3.115 \text{ kcal mole}^{-1}$$

*

It has been calculated in the same way as in C₂H₂F₄.

$$V(r^+) = 95.50[1 - e^{-2.02(r^+ - 1.525)}]^2 + 1.77[\exp(-0.80(r^+ - 1.525))] - 3.115 \text{ kcal mole}^{-1}$$

TABLE 5.61 - Potential Energy and Vibrational Frequencies as a Function of r^+ for $C_2HF_5^+$ (Model II)

r^+ (Å)	$V(r^+)$ (kcal mole ⁻¹)	ν_a (cm ⁻¹)	ν_b (cm ⁻¹)	ν_c (cm ⁻¹)	ν_d (cm ⁻¹)
3.000	83.55	111	67	127	76
3.250	87.07	91	55	104	62
3.500	89.24	74	45	85	51
3.750	90.56	61	37	70	42
4.000	91.34	50	30	57	34
4.250	91.80	41	25	47	28
4.500	92.08	33	20	38	23
4.750	92.24	27	16	31	19
5.000	92.32	22	13	26	15

5.3.2.2 The Moments of Inertia

A. The Molecule (Same as Model I)

$$I_{xx} = 211.035 \text{ amu } \text{Å}^2 = 350.32 \times 10^{-40} \text{ g.cm}^2$$

$$I_{yy} = 243.762 \text{ amu } \text{Å}^2 = 404.65 \times 10^{-40} \text{ g.cm}^2$$

$$I_{zz} = 147.849 \text{ amu } \text{Å}^2 = 245.43 \times 10^{-40} \text{ g.cm}^2$$

B. The Complex

I. *External Rotation*

The value of x^+ for the fluorines changes from $x^+ = 1.090$ to 1.139 (for the $-\text{CHF}_2$ group) and from 1.080 to 1.114 (for the $-\text{CF}_3$ group). The value of y^+ changes from $y^+ = 1.031$ to 1.071 (for the hydrogen) from 0.644 to 0.659 (for the fluorines of the $-\text{CHF}_2$ group), from 1.247 to 1.286 and from 0.624 to 0.643 (for the fluorines of the $-\text{CF}_3$ group). The values of z^+ , the perpendicular distances from the hydrogens and the fluorines to the carbon, change from 0.355 (for the hydrogen) in the molecule where $r_e = 1.525$ to 0.241 and from 0.461 to 0.297 (for the fluorines of the $-\text{CHF}_2$ group) from 0.454 to 0.297 (for the fluorines of the CF_3 group) in the complex where $r^+ = 4.83 \overset{0}{\text{A}}$.

TABLE 5.62 - Parameters for Evaluation of Moment of Inertia Product as a Function of r^+ for $C_2HF_5^+$ (Model II)

r^+	Δr^+	$\Delta x^+(-CHF_2)$	$x^+(-CF_3)$	$\Delta x^+(-CF_3)$	$\Delta y^+(H)$	$y^+(H)$	$\Delta y^+(-CHF_2)$	$y^+(-CHF_2)$	$\Delta y^+(-CF_3)$	$y^+(-CF_3)$	$\Delta z^+(H)$	$z^+(H)$	$\Delta z^+(-CHF_2)$	$z^+(-CHF_2)$
3.000	1.475	0.022	1.112	0.015	1.095	0.018	1.049	0.007	0.651	1.264	0.051	0.304	0.073	0.388
3.250	1.725	0.026	1.116	0.018	1.098	0.021	1.052	0.008	0.652	1.267	0.059	0.296	0.085	0.376
3.500	1.975	0.029	1.119	0.020	1.100	0.024	1.055	0.009	0.653	1.270	0.068	0.287	0.098	0.363
3.750	2.225	0.033	1.123	0.023	1.103	0.027	1.058	0.010	0.654	1.273	0.077	0.278	0.110	0.351
4.000	2.475	0.037	1.127	0.025	1.105	0.030	1.061	0.011	0.655	1.276	0.085	0.270	0.123	0.338
4.250	2.725	0.040	1.130	0.028	1.108	0.033	1.064	0.012	0.656	1.279	0.094	0.261	0.135	0.326
4.500	2.975	0.044	1.134	0.031	1.111	0.036	1.067	0.014	0.658	1.282	0.103	0.252	0.147	0.314
4.750	3.225	0.048	1.138	0.033	1.113	0.039	1.070	0.015	0.659	1.285	0.111	0.244	0.160	0.301
5.000	3.475	0.049	1.139	0.034	1.114	0.040	1.071	0.015	0.659	1.286	0.111	0.241	0.164	0.297

$\Delta z^+(-CF_3)$	$z^+(-CF_3)$
0.070	0.384
0.082	0.372
0.094	0.360
0.106	0.348
0.118	0.336
0.129	0.325
0.141	0.313
0.153	0.301
0.153	0.297

$$\Delta r^+ = (r^+ - 1.525)$$

$$\Delta x^+(-CHF_2) = \frac{\Delta r^+(1.139 - 1.090)}{4.830 - 1.525}$$

$$x^+(-CHF_2) = 1.090 + \Delta x^+$$

$$\Delta x^+(-CF_3) = \frac{\Delta r^+(1.114 - 1.080)}{4.830 - 1.525}$$

$$x^+(-CF_3) = 1.080 + \Delta x^+$$

$$\Delta y^+(H) = \frac{\Delta r^+(1.071 - 1.031)}{4.830 - 1.525}$$

$$y^+(H) = 1.031 + \Delta y^+$$

$$\Delta y^+(-CHF_2) = \frac{\Delta r^+(0.659 - 0.644)}{4.830 - 1.525}$$

$$y^+(-CHF_2) = \Delta y^+ + 0.644$$

$$\Delta y^+(-CF_3) = \frac{\Delta r^+(1.286 - 1.247)}{4.830 - 1.525}$$

$$y^+(-CF_3) = \Delta y^+ + 1.247$$

$$\Delta z^+(H) = \frac{\Delta r^+(0.241 - 0.355)}{4.830 - 1.525}$$

$$z^+(H) = 0.355 - \Delta z^+$$

$$\Delta z^+(-CHF_2) = \frac{\Delta r^+(0.461 - 0.297)}{4.830 - 1.525}$$

$$z^+(-CHF_2) = 0.461 - \Delta z^+$$

$$\Delta z^+(-CF_3) = \frac{\Delta r^+(0.454 - 0.297)}{4.830 - 1.525}$$

$$z^+(-CF_3) = 0.454 - \Delta z^+$$

TABLE 5.63 - Change in X^+ as a Function of r^+ for $C_2HF_5^+$ (Model II)

r^+	3.000	3.250	3.500	3.750	4.000	4.250	4.500	4.750	5.000
C_1	0	0	0	0	0	0	0	0	0
C_2	0	0	0	0	0	0	0	0	0
H	0	0	0	0	0	0	0	0	0
F_1	1.112	1.116	1.119	1.123	1.127	1.130	1.134	1.138	1.142
F_2	-1.112	-1.116	-1.119	-1.123	-1.127	-1.130	-1.134	-1.138	-1.142
F_3	-1.095	-1.098	-1.100	-1.103	-1.105	-1.108	-1.111	-1.113	-1.114
F_4	1.095	1.098	1.100	1.103	1.105	1.108	1.111	1.113	1.114
F_5	0	0	0	0	0	0	0	0	0
$\sum m_1 X_1^{+2}$	92.542	93.130	93.552	94.144	94.654	95.163	95.760	96.275	96.706

TABLE 5.64 - Change in Y^+ as a Function of r^+ for $C_2HF_5^+$ (Model II)

r^+	3.000	3.250	3.500	3.750	4.000	4.250	4.500	4.750	5.000
C_1	0	0	0	0	0	0	0	0	0
C_2	0	0	0	0	0	0	0	0	0
H	1.049	1.052	1.055	1.058	1.061	1.064	1.067	1.070	1.071
F_1	-0.651	-0.652	-0.653	-0.654	-0.655	-0.656	-0.658	-0.659	-0.659
F_2	-0.651	-0.652	-0.653	-0.654	-0.655	-0.656	-0.658	-0.659	-0.659
F_3	-1.264	-1.267	-1.270	-1.273	-1.276	-1.279	-1.282	-1.285	-1.286
F_4	0.632	0.634	0.635	0.637	0.638	0.640	0.641	0.643	0.643
F_5	0.632	0.634	0.635	0.637	0.638	0.640	0.641	0.643	0.643
$\sum m_1 Y_1^{+2}$	62.742	63.038	63.287	63.584	63.834	64.133	64.434	64.734	64.785

TABLE 5.65 - Change in Z^+ as a Function of r^+ for CHF_5^+ (Model II)

r^+	3.000	3.250	3.500	3.750	4.000	4.250	4.500	4.750	5.000
C_1	1.500	1.625	1.750	1.875	2.000	2.125	2.250	2.375	2.500
C_2	-1.500	-1.625	-1.750	-1.875	-2.000	-2.125	-2.250	-2.375	-2.500
H	1.804	1.921	2.037	2.153	2.270	2.386	2.502	2.620	2.741
F_1	1.888	2.001	2.113	2.226	2.338	2.451	2.563	2.676	2.797
F_2	1.888	2.001	2.113	2.226	2.338	2.451	2.563	2.676	2.797
F_3	-1.884	-1.997	-2.110	-2.223	-2.336	-2.450	-2.563	-2.676	-2.797
F_4	-1.884	-1.997	-2.110	-2.223	-2.336	-2.450	-2.563	-2.676	-2.797
F_5	-1.884	-1.997	-2.110	-2.223	-2.336	-2.450	-2.563	-2.676	-2.797
$\sum m_i Z_i^{+2}$	395.066	445.218	501.136	559.047	619.988	684.577	748.120	818.361	893.812

TABLE 5.66 - Moments of Inertia as a Function of r^+ ($\text{amu } \text{Å}^2$) for C_2HF_5^+ (Model II)

$r^+ (\text{Å})$	I_{xx}^+ ($\text{amu } \text{Å}^2$)	I_{yy}^+ ($\text{amu } \text{Å}^2$)	I_{zz}^+ ($\text{amu } \text{Å}^2$)
3.000	457.807	487.608	155.284
3.250	509.595	538.348	156.168
3.500	564.424	594.688	156.839
3.750	622.606	653.191	157.728
4.000	683.823	714.642	158.488
4.250	748.688	779.740	159.296
4.500	812.554	843.880	160.194
4.750	883.095	914.636	161.009
5.000	958.597	990.518	161.491

II. *Internal Rotation*

TABLE 5.67 - Moment of Inertia for Internal Rotation as a Function of r^+ for $C_2HF_5^+$ (Model II)

$r^+(A)$	I_1^+ (from $C_2H_2F_4$) (amu A^2)	I_2^+ (from C_2F_6) (amu A^2)	$I_{irO_2}^+$ (amu A^2)
3.000	65.20	91.06	38.00
3.250	65.44	91.48	38.15
3.500	65.72	91.88	38.31
3.750	66.02	92.28	38.49
4.000	66.22	92.68	38.62
4.250	66.54	93.08	38.80
4.500	66.84	93.48	38.97
4.750	67.04	93.90	39.11
5.000	67.06	94.26	39.18

5.3.2.3 Calculation of the Partition Functions

Neglecting Centrifugal Effects

A. The Molecule

I. *Vibrational Partition Function*

The molecule has 18 vibrational degrees of freedom (Table 5.53)

$$Q_V = 1.0459 \times 10^6$$

II. Rotational Partition Function

$$Q_r = 2.1083 \times 10^6$$

B. The Activated Complex

I. Vibrational Partition Function

The activated complex is located $r^+ = 3.350 \text{ \AA}$

$$\nu_a = 361 \exp[-0.80(3.35 - 1.525)] = 84 \text{ cm}^{-1}$$

$$\nu_b = 217 \exp[-0.80(3.35 - 1.525)] = 50 \text{ cm}^{-1}$$

$$\nu_c = 413 \exp[-0.80(3.35 - 1.525)] = 96 \text{ cm}^{-1}$$

$$\nu_d = 247 \exp[-0.80(3.35 - 1.525)] = 57 \text{ cm}^{-1}$$

$$Q_v^+ = 9.797 \times 10^6$$

II. Rotational Partition Function

$r^+(\text{A})$	$\Delta r^+(\text{A})$	$\Delta x^+(-\text{CHF}_2)$	$x^+(-\text{CHF}_2)$	$\Delta x^+(-\text{CF}_3)$	$x^+(-\text{CF}_3)$	$\Delta y^+(\text{H})$	$y^+(\text{H})$
3.35	1.825	0.027	1.117	0.019	1.099	0.022	1.053

$\Delta y^+(-\text{CHF}_2)$	$y^+(-\text{CHF}_2)$	$\Delta y^+(-\text{CF}_3)$	$y^+(-\text{CF}_3)$	$\Delta z^+(\text{H})$	$z^+(\text{H})$
0.008	0.652	0.022	1.269	0.063	0.292

$\Delta z^+(-\text{CHF}_2)$	$z^+(-\text{CHF}_2)$	$\Delta z^+(-\text{CF}_3)$	$z^+(-\text{CF}_3)$
0.090	0.370	0.087	0.367

III. Internal Rotation

The moment of inertia at $r^+ = 3.35 \text{ \AA}$ is evaluated by interpolation in Table 5.67. The corresponding value for I_{ir}^+ is 38.21 amu \AA^2 .

$$Q_{ir}^+ = \frac{((8)(3.14)^3(63.44 \times 10^{-40})(1.3805 \times 10^{-16})(1400))^{1/2}}{(6.6262 \times 10^{-27}) (3)}$$

$$= 27.74$$

Including Centrifugal Effects

A. The Molecule

I. Vibrational Partition Function

$$Q_v = 1.0459 \times 10^6$$

II. Rotational Partition Function

$$Q_r = 2.1083 \times 10^6$$

B. The Activated Complex

I. Vibrational Partition Function

The activated complex is located $r^+ = 3.550 \text{ \AA}$

$$\nu_a = 361 \exp[-0.80(3.550 - 1.525)] = 71 \text{ cm}^{-1}$$

$$\nu_b = 217 \exp[-0.80(3.550 - 1.525)] = 43 \text{ cm}^{-1}$$

$$\nu_c = 413 \exp[-0.80(3.550 - 1.525)] = 82 \text{ cm}^{-1}$$

$$\nu_d = 247 \exp[-0.80(3.550 - 1.525)] = 49 \text{ cm}^{-1}$$

$$Q_v^+ = 1.7968 \times 10^7$$

TABLE 5.69 - Parameters for Evaluation of Moment of Inertia Product of C_2HF_5
(Model II, including Centrifugal Effects)

Atom	m_i	X_i^+	Y_i^+	Z_i^+	$m_i Y_i^+$	$m_i Z_i^+$	$m_i X_i^{+2}$	$m_i Y_i^{+2}$	$m_i Z_i^{+2}$	$m_i Y_i^+ Z_i^+$	$m_i Y_i^+ Z_i^{+2}$
C ₁	12.011	0	0	1.775	0	21.320	0	0	37.842	0	0
C ₂	12.011	0	0	-1.775	0	-21.320	0	0	37.842	0	0
H	1.008	0	1.056	2.060	1.064	2.076	0	1.124	4.278	2.193	2.193
F ₁	18.998	1.120	-0.653	2.136	-12.406	40.580	23.831	8.101	86.678	-26.499	-26.499
F ₂	18.998	-1.120	-0.653	2.136	-12.406	40.580	23.831	8.101	86.678	-26.499	-26.499
F ₃	18.998	-1.101	0.636	-2.133	12.073	-40.523	23.029	7.673	86.435	-25.752	-25.752
F ₄	18.998	1.101	0.636	-2.133	12.073	-40.523	23.029	7.673	86.435	-25.752	-25.752
F ₅	18.998	0	-1.271	-2.133	-24.146	-40.523	0	30.690	86.435	51.503	51.503
					-23.748	-38.333	93.720	63.362	512.623	-50.806	-50.806

$$\begin{aligned} \Sigma m_i X_i^{+2} &= 93.720 & I_{xx}^+ &= 559.040 & ABC &= 4.904 \times 10^7 \text{ amu}^3 \text{ \AA}^6 \\ \Sigma m_i Y_i^{+2} &= 58.660 & I_{yy}^+ &= 594.100 & &= 2.24 \times 10^{-112} \text{ g}^3 \text{ cm}^6 \\ \Sigma m_i Z_i^{+2} &= 500.380 & I_{zz}^+ &= 152.380 \\ \Sigma m_i Y_i^+ Z_i^+ &= -58.392 & I_{yz}^+ &= 58.392 \end{aligned}$$

$$Q_r^+ = \frac{\sqrt{3.14} (8) (3.14)^2 (1.3805 \times 10^{-16}) (1400)^3 / 2 (2.24 \times 10^{-112})^{1/2}}{1 (6.6262 \times 10^{-27})^2} = 5.4355 \times 10^6$$

TABLE 5.69 - Parameters for Evaluation of Moment of Inertia Product of C_2HF_5
(Model II, including Centrifugal Effects)

Atom	m_i	X_i^+	Y_i^+	Z_i^+	$m_i Y_i^{+2}$	$m_i X_i^{+2}$	$m_i Y_i^{+2}$	$m_i Z_i^{+2}$	$m_i Y_i^+ Z_i^+$
C ₁	12.011	0	0	1.775	0	0	0	37.842	0
C ₂	12.011	0	0	-1.775	0	0	0	37.842	0
H	1.008	0	1.056	2.060	1.064	0	1.124	4.278	2.193
F ₁	18.998	1.120	-0.653	2.136	-12.406	23.831	8.101	86.678	-26.499
F ₂	18.998	-1.120	-0.653	2.136	-12.406	23.831	8.101	86.678	-26.499
F ₃	18.998	-1.101	0.636	-2.133	12.073	23.029	7.673	86.435	-25.752
F ₄	18.998	1.101	0.636	-2.133	12.073	23.029	7.673	86.435	-25.752
F ₅	18.998	0	-1.271	-2.133	<u>-24.146</u>	<u>0</u>	<u>30.690</u>	<u>86.435</u>	<u>51.503</u>
					-23.748	93.720	63.362	512.623	-50.806

$$\Sigma m_i X_i^{+2} = 93.720$$

$$I_{xx}^+ = 559.040$$

$$ABC = 4.904 \times 10^7 \text{ amu}^3 \text{ \AA}^6$$

$$\Sigma m_i Y_i^{+2} = 58.660$$

$$I_{yy}^+ = 594.100$$

$$= 2.24 \times 10^{-112} \text{ g}^3 \text{ cm}^6$$

$$\Sigma m_i Z_i^{+2} = 500.380$$

$$I_{zz}^+ = 152.380$$

$$\Sigma m_i Y_i^+ Z_i^+ = -58.392$$

$$I_{yz}^+ = 58.392$$

$$Q_r^+ = \frac{\sqrt{3.14} (8) (3.14)^2 (1.3805 \times 10^{-16}) (1400)^{3/2} (2.24 \times 10^{-112})^{1/2}}{1 (6.6262 \times 10^{-27})^2}$$

$$= 5.4355 \times 10^6$$

II. Rotational Partition Function

$r^+(\text{\AA})$	$\Delta r^+(\text{\AA})$	$\Delta x^+(-\text{CHF}_2)$	$x^+(-\text{CHF}_2)$	$\Delta x^+(-\text{CF}_3)$	$x^+(-\text{CF}_3)$	$\Delta y^+(\text{H})$	$y^+(\text{H})$
3.550	2.025	0.030	1.120	0.021	1.101	0.025	1.056
	$\Delta y^+(-\text{CHF}_2)$	$y^+(-\text{CHF}_2)$	$\Delta y^+(-\text{CF}_3)$	$y^+(-\text{CF}_3)$	$\Delta z^+(\text{H})$	$z^+(\text{H})$	
	0.009	0.653	0.024	1.271	0.070	0.285	
	$\Delta z^+(-\text{CHF}_2)$	$z^+(-\text{CHF}_2)$	$\Delta z^+(-\text{CF}_3)$	$z^+(-\text{CF}_3)$			
	0.100	0.361	0.096	0.358			

III. Internal Rotation

The moment of inertia at $r^+ = 3.550 \text{\AA}$ is evaluated by interpolation in Table 5.67. The corresponding value for I_{ir}^+ is 38.35 amu \AA^2 .

$$Q_{ir}^+ = \frac{((8)(3.14)^3(63.65 \times 10^{-40})(1.3805 \times 10^{-16})(1400))^{1/2}}{(6.6262 \times 10^{-27})(3)}$$

$$= 27.79$$

5.3.2.4 Calculation of $\langle E_V \rangle$, $\langle E_V^+ \rangle$ and E^+

A. Calculation of $\langle E_V \rangle$

$$T \ln Q_V / \partial T = 11.442$$

$$\langle E_V \rangle = 31.83 \text{ kcal mole}^{-1}$$

B. Calculation of $\langle E_V^+ \rangle$

I. Centrifugal effects are neglected

$$T \ln Q_V^+ / \partial T = 10.31 \quad ; \quad \langle E_V^+ \rangle = 28.69 \text{ kcal mole}^{-1}$$

II. *Centrifugal Effects are Included*

$$T \partial \ln Q_V^+ / \partial T = 10.34$$

$$E_V^+ = 28.75 \text{ kcal mole}^{-1}$$

C. Calculation of E^+

$$\begin{aligned} E^+ &= (1 + 0.5)(1.987)(1400) + (2.859 \times 10^{-3})(1.0032 \times 10^4) \\ &= 32.85 \text{ kcal mole}^{-1} \end{aligned}$$

5.3.2.5 Calculation of ΔS^\ddagger , k_∞ and A_∞

A. Neglecting Centrifugal Effects

The value of E_0 is $88.10 \text{ kcal mole}^{-1}$. The value of E_∞ which corresponds to E_0 is

$$E_\infty = 89.13 \text{ kcal mole}^{-1}$$

$$\begin{aligned} S_V &= 1.987(\ln 1.0459 \times 10^6 + 11.442) \\ &= 50.28 \text{ cal mole}^{-1} \text{ deg}^{-1} \end{aligned}$$

$$\begin{aligned} S_r &= 1.987(\ln 2.1083 \times 10^6 + 1.5) \\ &= 31.91 \text{ cal mole}^{-1} \text{ deg}^{-1} \end{aligned}$$

$$S_{th} = 82.19 \text{ cal mole}^{-1} \text{ deg}^{-1}$$

$$\begin{aligned} S_V^+ &= 1.987(\ln 9.7970 \times 10^6 + 10.314) \\ &= 52.48 \text{ cal mole}^{-1} \text{ deg}^{-1} \end{aligned}$$

$$\begin{aligned} S_r^+ &= 1.987(\ln 4.9928 \times 10^6 + 1.5) \\ &= 33.63 \text{ cal mole}^{-1} \text{ deg}^{-1} \end{aligned}$$

$$S_{ir}^+ = 1.987(\ln 27.74 + 0.5)$$

$$= 7.60 \text{ cal mole}^{-1} \text{ deg}^{-1}$$

$$S_{th}^+ = 93.71 \text{ cal mole}^{-1} \text{ deg}^{-1}$$

$$\Delta S_{th}^\ddagger = 11.52 \text{ cal mole}^{-1} \text{ deg}^{-1}$$

$$k_{\infty, th} = \frac{(1.3805 \times 10^{-16})(1400)}{6.6262 \times 10^{-27}} \frac{(9.797 \times 10^6)(4.9928 \times 10^6)(27.74)}{(1.0459 \times 10^6)(2.1083 \times 10^6)}$$

$$\times \exp\left(-\frac{88.10}{(1.987 \times 10^{-3})(1400)}\right)$$

$$= 3.16 \times 10^2 \text{ sec}^{-1}$$

$$A_{\infty, th} = \frac{(2.718)(1.3805 \times 10^{-16})(1400)}{6.6262 \times 10^{-27}} e^{11.52/1.987}$$

$$= 10^{16.42}$$

B. Including Centrifugal Effects

The value of E_0 is $89.57 \text{ kcal mole}^{-1}$. The value of E_∞ which corresponds to E_0 is

$$E_\infty = 90.66 \text{ kcal mole}^{-1}$$

$$S_{th} = 82.19 \text{ cal mole}^{-1} \text{ deg}^{-1}$$

$$S_v^+ = 1.987(\ln 1.7968 \times 10^7 + 10.34)$$

$$= 53.74 \text{ cal mole}^{-1} \text{ deg}^{-1}$$

$$S_r^+ = 1.987(\ln 5.4355 \times 10^6 + 1.5)$$

$$= 33.80 \text{ cal mole}^{-1} \text{ deg}^{-1}$$

$$S_{ir}^+ = 1.987(\ln 27.79 + 0.5)$$

$$= 7.60 \text{ cal mole}^{-1} \text{ deg}^{-1}$$

$$S_{th}^+ = 95.14 \text{ cal mole}^{-1} \text{ deg}^{-1}$$

$$\Delta S_{th}^{\ddagger} = 12.95 \text{ cal mole}^{-1} \text{ deg}^{-1}$$

$$k_{\infty,th} = 3.73 \times 10^2 \text{ sec}^{-1}$$

$$A_{\infty,th} = 10^{16.13}$$

5.3.2.6 Calculation of the Anharmonicity Corrections

A. The Molecule

In the molecule there are

1 C-H stretching frequency	$(D_e^{-1} = 0.01189)$ (Model I)
2 C-F stretching frequencies (in $-\text{CHF}_2$)	$(D_e^{-1} = 0.00829)$ (Model I)
3 C-F stretching frequencies (in $-\text{CF}_3$)	$(D_e^{-1} = 0.00783)$ (Model I)
1 C-C stretching frequency	$(D_e^{-1} = 0.01387)$ (Model I)
2 C-H bending frequencies	$(D_e^{-1} = 0.01828)$ (Model I)
8 C-F bending frequencies	$(D_e^{-1} = 0.01957)$ (Model I)
1 torsion frequency	$(D_e^{-1} = 0.17490)^*$

$$\langle D_e^{-1} \rangle = \frac{1}{18} (0.01189 + (2)(0.00829) + (3)(0.00783) + 0.01387$$

$$+ (2)(0.01828) + (8)(0.01957) + 0.17490)$$

$$= 0.02410$$

$$D = 41.49 \text{ kcal mole}^{-1}$$

* The dissociation energy corresponding to the torsion frequency of C_2HF_5 ($V = 3.51 \text{ kcal mole}^{-1}$) is calculated as done before for $\text{C}_2\text{H}_2\text{F}_4$. [115]

B. The Complex

In the activated complex there are

- 1 C-H stretching frequency
- 2 C-F stretching frequencies
- 3 C-F stretching frequencies
- 2 C-H bending frequencies
- 8 C-F bending frequencies

$$\langle D_e^{-1} \rangle = \frac{1}{16} (0.01189 + (2)(0.00829) + (3)(0.00783) + (2)(0.01828) + (8)(0.01957))$$

$$= 0.0153$$

$$D = 65.28 \text{ kcal mole}^{-1}$$

5.3.2.7 Evaluation of $k_{\text{uni}}/k_{\infty}$

TABLE 5.70 - Parameters for $k_{\text{uni}}/k_{\infty}$ for C_2HF_5 (Model II)

	Centrifugal effects are neglected	Centrifugal effects are included
E_0	88.10 kcal mole ⁻¹	89.57 kcal mole ⁻¹
E_z	8199.5 cm ⁻¹ = 23.44 kcal mole ⁻¹	8199.5 cm ⁻¹ = 23.44 kcal mole ⁻¹
E_z^+	7253.5 cm ⁻¹ = 20.74 kcal mole ⁻¹	7232.5 cm ⁻¹ = 20.68 kcal mole ⁻¹
s	18	18
s^+	16	16
r	0	0
r^*	1	1
		./...

Table 5.70 continued...

	Centrifugal effects are neglected	Centrifugal effects are included
α	17	17
α^+	16.5	16.5
$\Gamma(\alpha+1)$	3.557×10^{14}	3.557×10^{14}
$\Gamma(\alpha^++1)$	8.563×10^{13}	8.563×10^{13}
$\Gamma(1+r^*/2)$	0.886	0.886
$\prod_{i=1}^S v_i$	$1.015 \times 10^{51} \text{ cm}^{-18}$	$1.015 \times 10^{51} \text{ cm}^{-18}$
$\prod_{i=1}^{S^+} v_i^+$	$4.550 \times 10^{43} \text{ cm}^{-16}$	$2.429 \times 10^{43} \text{ cm}^{-16}$
$(E_Z^+)^{\alpha^+-\alpha}$	$0.0117 \text{ cm}^{0.5}$	$0.0118 \text{ cm}^{0.5}$
$(E_Z^+)^{\alpha^++1}$	$3.627 \times 10^{67} \text{ cm}^{-17.5}$	$3.448 \times 10^{67} \text{ cm}^{-17.5}$
$(E_Z^+)^{S^+}$	$5.872 \times 10^{61} \text{ cm}^{-16}$	$5.606 \times 10^{61} \text{ cm}^{-16}$
$(RT)^{1+r^*/2}$	$30354.184 \text{ cm}^{-1.5}$	$30354.184 \text{ cm}^{-1.5}$
$(RT)^{(r^*-r)/2}$	$31.19 \text{ cm}^{-0.5}$	$31.19 \text{ cm}^{-0.5}$
$\langle v^{+2} \rangle$	$1349673.1 \text{ cm}^{-2}$	$1349297.7 \text{ cm}^{-2}$
$\langle v^+ \rangle$	906.688 cm^{-1}	904.063 cm^{-1}
$\langle v^+ \rangle^2$	$822083.13 \text{ cm}^{-2}$	$817329.91 \text{ cm}^{-2}$
β^+	1.5873	1.5960
Z	$2.9358 \times 10^6 \text{ Torr}^{-1} \text{ sec}^{-1}$	$2.9358 \times 10^6 \text{ Torr}^{-1} \text{ sec}^{-1}$
C_0	7.454	7.433
C_1	3.1307×10^{-2}	3.0399×10^{-2}
θ	0.0069	0.0059
$G_1(x)$	$7.4891 \times 10^{-5} x^{0.5}$	$4.1871 \times 10^{-5} x^{0.5}$
$G_2(x)$	$[x+1-1.5873/(5.00x+2.73x^{0.5}+3.51)]^{16.5}$	$[x+1-1.5960/(5.00x+2.73x^{0.5}+3.51)]^{16.5}$
$G_3(x)$	$[x+1-1.5873 \exp(-2.419 x^{0.25})]^{16.5}$	$[x+1-1.5960 \exp(-2.419 x^{0.25})]^{16.5}$

./...

Table 5.70 continued...

	Centrifugal effects are neglected	Centrifugal effects are included
H(x)	$(x + 5.379)^{17}$	$(x + 5.128)^{17}$ *
C ₂ /P	9.9024x10 ⁹	1.8745x10 ¹⁰

$$* \langle \Delta E_J \rangle = 1.5 \left(1 - \frac{(559.040)(594.100)(152.380)}{(211.035)(243.762)(147.849)} \right)^{1/2} (1.987 \times 10^{-3})(1400)$$

$$= -6.59 \text{ kcal mole}^{-1}$$

TABLE 5.71 - Contribution of Centrifugal Effects to $k_{\text{uni}}/k_{\infty}$
for $\text{C}_2\text{HF}_5 \rightarrow \text{CF}_3 \cdot + \text{CHF}_2 \cdot$ at 1400^oK (Model II)

P (Torr)	$(k_{\text{uni}}/k_{\infty})^a$	$(k_{\text{uni}}/k_{\infty})^b$
10 ⁻¹	0.0192	0.0076
1	0.0742	0.0341
10 ¹	0.2217	0.1212
10 ²	0.4884	0.3237
10 ³	0.7800	0.6247
10 ⁴	0.9509	0.8771
10 ⁵	1.0009	0.9837
10 ⁶	1.0087	1.0060
10 ⁷	1.0096	1.0088
10 ⁸	1.0097	1.0091
10 ⁹	1.0097	1.0091

neglecting centrifugal effects ($k_{\text{uni}}/k_{\infty} = 0.5$ at $P = 112$ Torr)

including centrifugal effects ($k_{\text{uni}}/k_{\infty} = 0.5$ at $P = 400$ Torr).

5.3.2.8 Calculation of $k_a(E^*)$ TABLE 5.72 - Properties of the Active Molecule and Activated Complex (C_2HF_5 , Model II)

Molecule		Complex								
		Neglecting C.E.				Including C.E.				
Frequencies (cm^{-1})	1218					1218				
	1198					1198				
	1111					1111				
	867					725				
	725					654				
	654					523				
	523					3008				
	361					1393				
	3008					1309				
	217					1145				
	1393					577				
	1309					1359				
	1145									
	577	r^+	3.000	3.250	3.500	3.750	4.000	4.250	4.500	4.750
413										
1359		111	91	74	61	50	41	33	27	22
247		67	55	45	37	30	25	20	16	13
74		127	104	85	70	57	47	38	31	26
		76	62	51	42	34	28	23	19	15
E_0 (kcal mole $^{-1}$)				88.10				89.57		
s		18				16				
r		0				1				
Moments of inertia (amu Å^2)										
I_{xx}	I_{yy}	I_{zz}	r^+	I_{xx}^+	I_{yy}^+	I_{zz}^+				
211.035	243.762	147.849	3.000	457.807	487.608	155.284				
			3.250	509.595	538.348	156.168				
			3.500	564.424	594.688	156.839				
			3.750	622.606	653.191	157.728				
			4.000	683.823	714.642	158.488				
			4.250	748.688	779.740	159.296				
			4.500	812.554	843.880	160.194				
			4.750	883.095	914.636	161.009				
			5.000	958.597	990.518	161.491				

Symmetry number for internal rotation

 σ

3

Table 5.72 continued...

Molecule	Complex																					
	<u>Neglecting C.E.</u>	<u>Including C.E.</u>																				
Average bond energy (kcal mole ⁻¹) D	41.49	65.28																				
Increment for the summation (kcal mole ⁻¹) ΔE^\ddagger	0.1																					
Number of rate constants to be calculated NEN	1000																					
L^\ddagger	1																					
Temperature (°K) T	1400																					
Pressure (Torr) P	3500																					
Collision number (Torr ⁻¹ sec ⁻¹) Z	2.9358x10 ⁶																					
Internal energy of activated molecule (kcal mole ⁻¹) ECC		119.35 kcal mole ⁻¹ 109.35 kcal mole ⁻¹																				
Number of reaction coordinate intervals NN		8																				
Potential energy of reaction coordinate (kcal mole ⁻¹) V(r ⁺)	<table border="1"> <thead> <tr> <th>r⁺</th> <th>3.000</th> <th>3.250</th> <th>3.500</th> <th>3.750</th> <th>4.000</th> <th>4.250</th> <th>4.500</th> <th>4.750</th> <th>5.000</th> </tr> </thead> <tbody> <tr> <td></td> <td>83.55</td> <td>87.07</td> <td>89.24</td> <td>90.56</td> <td>91.34</td> <td>91.80</td> <td>92.08</td> <td>92.24</td> <td>92.32</td> </tr> </tbody> </table>		r ⁺	3.000	3.250	3.500	3.750	4.000	4.250	4.500	4.750	5.000		83.55	87.07	89.24	90.56	91.34	91.80	92.08	92.24	92.32
r ⁺	3.000	3.250	3.500	3.750	4.000	4.250	4.500	4.750	5.000													
	83.55	87.07	89.24	90.56	91.34	91.80	92.08	92.24	92.32													
Reduced moment of inertia changing with r ⁺ (amu Å ²) I _{ir} ⁺	<table border="1"> <thead> <tr> <th>r⁺</th> <th>I_{ir}⁺</th> </tr> </thead> <tbody> <tr><td>3.000</td><td>38.00</td></tr> <tr><td>3.250</td><td>38.15</td></tr> <tr><td>3.500</td><td>38.31</td></tr> <tr><td>3.750</td><td>38.49</td></tr> <tr><td>4.000</td><td>38.62</td></tr> <tr><td>4.250</td><td>38.80</td></tr> <tr><td>4.500</td><td>38.97</td></tr> <tr><td>4.750</td><td>39.11</td></tr> <tr><td>5.000</td><td>39.18</td></tr> </tbody> </table>		r ⁺	I _{ir} ⁺	3.000	38.00	3.250	38.15	3.500	38.31	3.750	38.49	4.000	38.62	4.250	38.80	4.500	38.97	4.750	39.11	5.000	39.18
r ⁺	I _{ir} ⁺																					
3.000	38.00																					
3.250	38.15																					
3.500	38.31																					
3.750	38.49																					
4.000	38.62																					
4.250	38.80																					
4.500	38.97																					
4.750	39.11																					
5.000	39.18																					

The results at $E^+ = 32.85 \text{ kcal mole}^{-1}$ are given below.

$$k_a(E^+ + E_0) = 0.4688 \times 10^9 \text{ sec}^{-1}$$

$$k_a(E^+ + E_0)_{\text{anh}} = 0.7820 \times 10^9 \text{ sec}^{-1}$$

$$k_a(E^+ + E_0 + \langle \Delta E_J \rangle) = 0.1741 \times 10^{10} \text{ sec}^{-1}$$

$$k_a(E^+ + E_0 + \langle \Delta E_J \rangle)_{\text{anh}} = 0.3230 \times 10^9 \text{ sec}^{-1}$$

5.3.2.9 Calculation of k_{uni}

The input data for the computer program which evaluate k_{uni} is given in Table 5.72.

A. Neglecting Centrifugal Effects

$$k_{\text{uni}} = \frac{4.9928 \times 10^6 \exp(-88.10/1.987 \times 10^{-3}(1400))}{(9.537 \times 10^{-14})(2.1083 \times 10^6)(1.0459 \times 10^6)} (0.1)(0.6605 \times 10^{10})$$

$$= 2.76 \times 10^2 \text{ sec}^{-1}$$

$$k_{\text{uni}}(\text{anh}) = (4.1816 \times 10^{-8})(0.7289 \times 10^{10})$$

$$= 3.05 \times 10^2 \text{ sec}^{-1}$$

B. Including Centrifugal Effects

$$k_{\text{uni}} = \frac{5.4355 \times 10^6 \exp(-89.57/1.987 \times 10^{-3}(1400))}{(9.537 \times 10^{-14})(2.1083 \times 10^6)(1.0459 \times 10^6)} (0.1)(0.1063 \times 10^{11})$$

$$= 2.85 \times 10^2 \text{ sec}^{-1}$$

$$k_{\text{uni}}(\text{anh}) = (2.6837 \times 10^{-8})(0.1279 \times 10^{11})$$

$$= 3.43 \times 10^2 \text{ sec}^{-1}$$

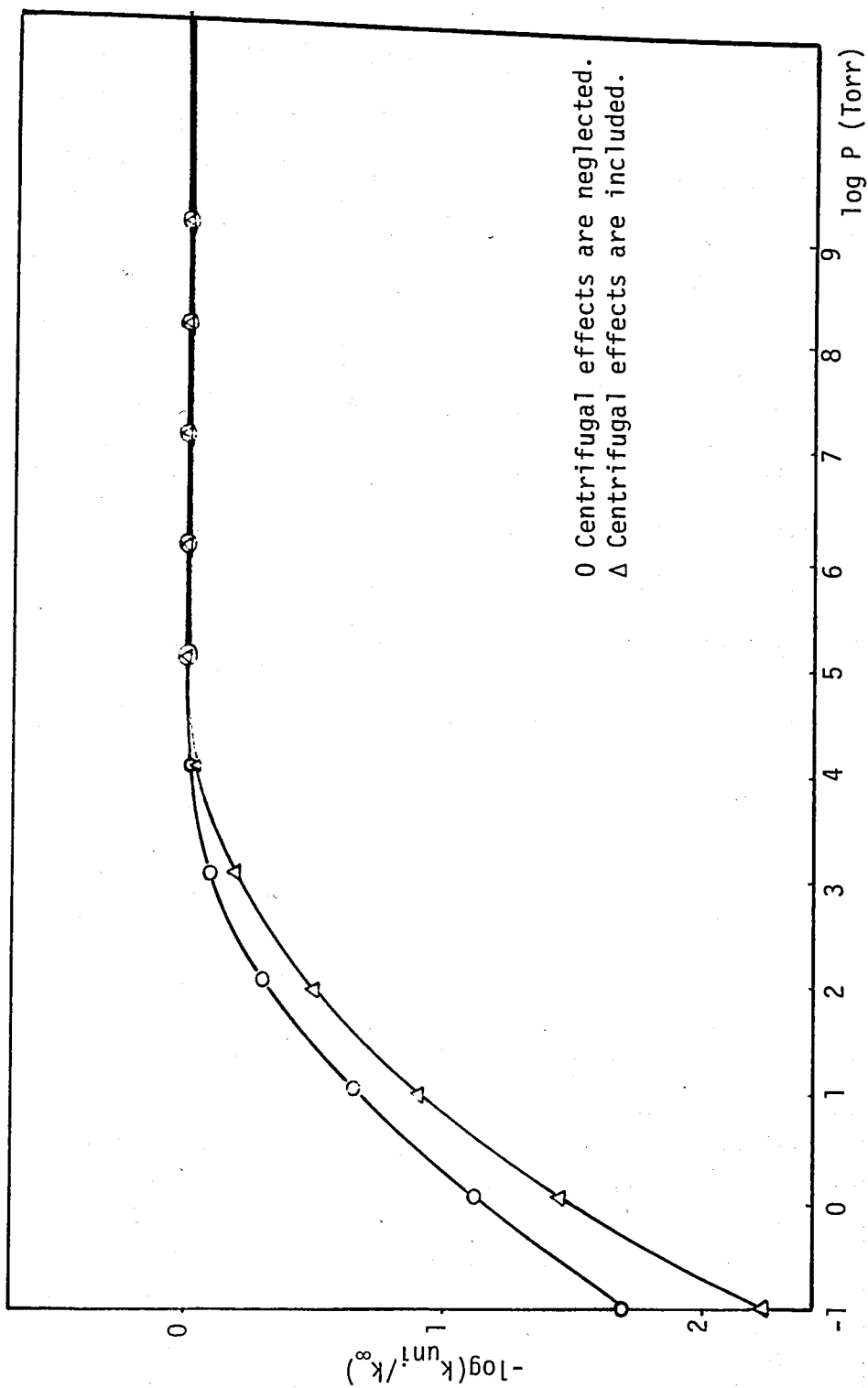


Figure 5.9 - Calculated fall-off curves for pentafluoroethane decomposition at 1400°K (Model II)

5.4 HEXAFLUOROETHANE

E. Tschuikow-Roux [103] performed the thermal decomposition of hexafluoroethane in a shock-tube over the temperature range 1300-1600^oK and total pressures in the neighbourhood of 4 atm. The author discussed this reaction in terms of the RRKM theory [104]. The results are misleading due to the lack of the negative sign in front of the quantity $\langle \Delta E_j \rangle$.

Calculations are carried out in the following sections to find out the fall-off region and the rate constant for this reaction.

In this case Model I agrees better with the experimental results. However, the adjustable parameter α has the value of 1 in the calculations for Model II. Any change in α would improve the agreement of the results for Model II.

5.4.1 Model I

5.4.1.1 Data

A. The Molecule*TABLE 5.73 - Vibrational Frequencies of C_2F_6 [118] (D_{3d} symmetry)

	Wave number (cm^{-1})	Type of vibration	Species
ν_1	1420	C-F stretching	A_{1g}
ν_2	807	CF_3 deformation	A_{1g}
ν_3	349	C-C stretching	A_{1g}
ν_4	68	twisting	A_{1u}
ν_5	1116	C-F stretching	A_{2u}
ν_6	714	CF_3 deformation	A_{2u}

* The energized C_2F_6 molecule has the same configuration as the energized C_2H_6 molecule.

Table 5.73 continued...

	Wave number (cm^{-1})	Type of vibration	Species
ν_7	1250	C-F stretching	E_u
ν_8	522	CF_3 deformation	E_u
ν_9	219	CF_3 -C rocking	E_u
ν_{10}	1237	C-F stretching	E_g
ν_{11}	620	CF_3 deformation	E_g
ν_{12}	380	CF_3 -C rocking	E_g

TABLE 5.74 - Molecular parameters of C_2F_6 (D_{3d} symmetry)

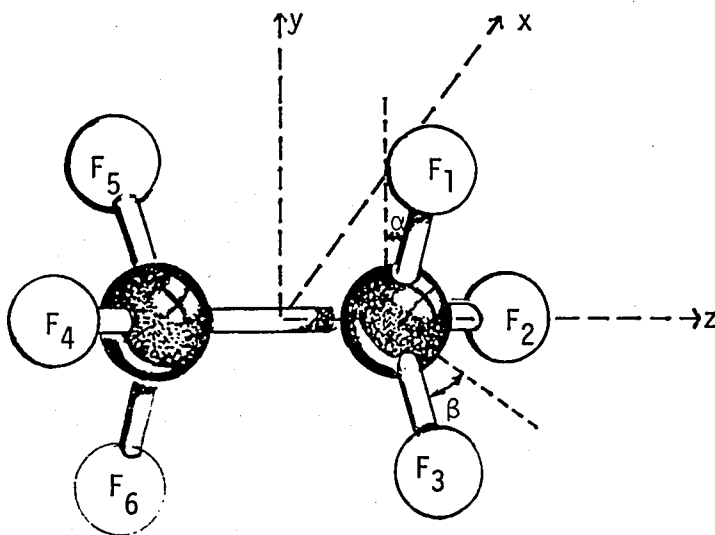
$R(\text{C}-\overset{\text{O}}{\underset{\text{O}}{\text{C}}})(\text{A})[119]$	1.545
$R(\text{C}-\text{F})(\text{A})[119]$	1.326
$\angle \text{CCF}[119]$	$109^{\circ}42'$
$\angle \text{FCF}[120]$	$109^{\circ}28'$

B. The Activated ComplexTable 5.75 - Vibrational Frequencies of CF_3 (C_{3v}) [121]

	Wave number (cm^{-1})	Type of vibration	Species
ν_1	1087	C-F stretching	A_1
ν_2	703	out of plane bending	A_1
ν_3	1251	asymmetric stretching	E
ν_4	512	bending	E

Table 5.76 - Molecular Parameters of CF_3 (C_{3v})

$R(\text{C-F})(\text{\AA})[121]$	1.32
$\Delta\text{FCF}[122]$	$109^{\circ}28'$
Deviation from planarity	13°

5.4.1.2 The Moments of InertiaA. The Molecule* (Table 5.74)I. *External Rotation*Figure 5.10 - Geometric representation of C_2F_6 .

Calculation of the coordinates

$$\alpha = 109^{\circ}42' - 90^{\circ} = 19^{\circ}42' = 19.7^{\circ}$$

$$\beta = 109^{\circ}28' / 2 = 54^{\circ}44' = 54.73^{\circ}$$

$$x_{C_1, C_2} = 0$$

$$y_{C_1, C_2} = 0$$

$$x_{F_1, F_6} = 0$$

$$y_{F_1} = \cos 19.7^\circ \times 1.326$$

$$x_{F_2, F_5} = \sin(54.73^\circ \times 1.326)$$

$$= 1.248$$

$$= 1.083$$

$$y_{F_6} = -1.248$$

$$x_{F_3, F_4} = -1.083$$

$$y_{F_2, F_3} = -(\sin 30^\circ \times 1.248)$$

$$= -0.624$$

$$y_{F_4, F_5} = 0.624$$

$$z_{C_1} = 0.773$$

$$z_{C_2} = -0.773$$

$$z_{F_1, F_2, F_3} = (\sin 19.7^\circ \times 1.326) + 0.772$$

$$= 1.219$$

$$z_{F_4, F_5, F_6} = -1.219$$

Table 5.77 - Parameters for Evaluation of Moment of Inertia Product of C_2F_6

Atom	m_i	x_i	y_i	z_i	$m_i x_i^2$	$m_i y_i^2$	$m_i z_i^2$
C_1	12.011	0	0	0.773	0	0	7.177
C_2	12.011	0	0	-0.773	0	0	7.177
F_1	18.998	0	1.248	1.219	0	29.589	28.230
F_2	18.998	-1.083	-0.624	1.219	22.277	7.397	28.230
F_3	18.998	-1.083	-0.624	1.219	22.277	7.397	28.230
F_4	18.998	-1.083	0.624	-1.219	22.277	7.397	28.230
F_5	18.998	1.083	0.624	-1.219	22.277	7.397	28.230
F_6	18.998	0	-1.248	-1.219	0	29.589	28.230
					89.108	88.768	183.735

$$I_{xx} = I_{yy} = 272.673 \text{ amu } \text{Å}^2 = 452.64 \times 10^{-40} \text{ g.cm}^2$$

$$I_{zz} = 177.876 \text{ amu } \text{Å}^2 = 295.27 \times 10^{-40} \text{ g.cm}^2$$

II. Internal Rotation

$$\begin{aligned}
 I_{i,r} &= \frac{3}{2} \times 18.998 \times 1.248^2 & \ell &= 1.326 \times \sin(180^\circ - 109.7^\circ) \\
 &= 44.384 \text{ amu } \text{Å}^2 & &= 1.248 \\
 &= 73.68 \times 10^{-40} \text{ g.cm}^2
 \end{aligned}$$

B. The Complex

I. External Rotation

Calculation of $\langle R_C \rangle_{av}$ at $T = 1450^\circ \text{K}$

$$a_{es} = 2(1.5 \times 10^{-18})^4 / (3 \times 1.3805 \times 10^{-16} \times 1450)$$

$$= 0.17 \times 10^{-58} \text{ erg} \cdot \text{cm}^6$$

$$a_{\text{ind}} = 2 \times 2.65 \times 10^{-24} \times (1.5 \times 10^{-18})^2$$

$$= 0.12 \times 10^{-58} \text{ ergs cm}^6$$

$$a_{\text{dis}} = 1.5 \times \left(\frac{4.802 \times 10^{-10} \times 6.6262 \times 10^{-27}}{2 \times 3.14 \times (9.105 \times 10^{-28})^{1/2}} \right) \times \left[\frac{(2.65 \times 10^{-24})^2}{2 \times (2.65 \times 10^{-24} / 25)^{1/2}} \right]$$

$$= 2.72 \times 10^{-58} \text{ ergs cm}^6$$

$$a = 3.01 \times 10^{-58} \text{ ergs cm}^6$$

$$\langle R_c \rangle_{\text{av}} = 4.97 \times 10^{-8} \text{ cm}$$

Calculation of the coordinates

$$x_{C_1, C_2} = 0$$

$$y_{C_1, C_2} = 0$$

$$x_{F_1, F_6} = 0$$

$$y_{F_1} = \cos 13^\circ \times 1.32$$

$$x_{F_2, F_5} = \cos 30^\circ \times 1.286$$

$$= 1.286$$

$$= 1.114$$

$$y_{F_6} = -1.286$$

$$y_{F_2, F_3} = -(\sin 30^\circ \times 1.286)$$

$$x_{F_3, F_4} = -1.114$$

$$=-0.643$$

$$y_{F_4, F_5} = 0.643$$

$$z_{C_1} = 2.485$$

$$z_{C_2} = -2.485$$

$$z_{F_1, F_2, F_3} = (\sin 13^\circ \times 1.32) + 2.485$$

$$= 2.782$$

$$z_{F_4, F_5, F_6} = -2.782$$

Table 5.78 - Parameters for Evaluation of Moment of Inertia Product of $C_2F_6^+$ (Model I)

Atom	m_i	x_i^+	y_i^+	z_i^+	$m_i x_i^{+2}$	$m_i y_i^{+2}$	$m_i z_i^{+2}$
C ₁	12.011	0	0	2.485	0	0	74.171
C ₂	12.011	0	0	-2.485	0	0	74.171
F ₁	18.998	0	1.286	2.782	0	31.429	147.025
F ₂	18.998	1.114	-0.643	2.782	23.576	7.857	147.025
F ₃	18.998	-1.114	-0.643	2.782	23.576	7.857	147.025
F ₄	18.998	-1.114	0.643	-2.782	23.576	7.857	147.025
F ₅	18.998	1.114	0.643	-2.782	23.576	7.857	147.025
F ₆	18.998	0	-1.286	-2.782	0	31.429	147.025
					94.304	94.286	1030.492

$$I_{xx}^+ = I_{yy}^+ = 1124.787 \text{ amu } \overset{0}{\text{A}}^2 = 1867.15 \times 10^{-40} \text{ g.cm}^2$$

$$I_{zz}^+ = 188.608 \text{ amu } \overset{0}{\text{A}}^2 = 313.06 \times 10^{-40} \text{ g.cm}^2$$

II. Internal Rotation

$$\begin{aligned}
 I_{ir}^+ &= \frac{3}{2} \times 18.998 \times 1.286^2 & \ell &= 1.32 \times \sin(180^\circ - 77^\circ) \\
 &= 47.13 \text{ amu } \overset{0}{\text{A}}^2 & &= 1.286 \\
 &= 78.23 \times 10^{-40} \text{ g.cm}^2
 \end{aligned}$$

5.4.1.3 Calculation of the Partition Functions

A. The Molecule

I. *Vibrational Partition Function*

$$Q_v = 7.3599 \times 10^5$$

II. Rotational Partition Function

$$Q_r = \frac{\sqrt{3.14}}{6} \times \left(\frac{8 \times 3.14^2 \times 1.3805 \times 10^{-16} \times 1450}{(6.6262 \times 10^{-27})^2} \right)^{3/2} (452.64^2 \times 295.27 \times 10^{-120})^{1/2}$$

$$= 4.9623 \times 10^5$$

Where

$$I_{xx} = I_{yy} = 452.64 \times 10^{-40} \text{ g.cm}^2$$

$$I_{zz} = 295.27 \times 10^{-40} \text{ g.cm}^2$$

$$T = 1450^{\circ}\text{K}$$

$$\sigma = 6$$

III. Partition Function for Internal Rotation

$$Q_{ir} = (8 \times 30.96 \times 73.68 \times 10^{-40} \times 1.3805 \times 10^{-16} \times 1450)^{1/2} / 6.6262 \times 10^{-27} \times 3$$

$$= 30.40$$

B. The Activated Complex

I. Vibrational Partition Function

$$Q_v^+ = 1439.88$$

II. Rotational Partition Function

$$Q_r^+ = \frac{\sqrt{3.14}}{2} \times \left(\frac{8 \times 3.14^2 \times 1.3805 \times 10^{-16} \times 1450}{(6.6262 \times 10^{-27})^2} \right)^{3/2} \times (1867.15^2 \times 313.06 \times 10^{-120})^{1/2}$$

$$= 6.3216 \times 10^6$$

III. Partition Function for Internal Rotations

$$Q_{ir}^+ = \left[\frac{(8 \times 3.14^3 \times 78.23 \times 10^{-40} \times 1.3805 \times 10^{-16} \times 1450)^{1/2}}{6.6262 \times 10^{-27} \times 1} \right] \left[\frac{(8 \times 3.14^2 \times 78.23 \times 10^{-40} \times 1.3805 \times 10^{-16} \times 1450)^{1/2}}{6.6262 \times 10^{-27} \times 2} \right]^4$$

$$= 4.6619 \times 10^7$$

5.4.1.4 Calculation of $\langle E_V \rangle$, $\langle E_V^+ \rangle$, E_0 and E^+

A. Calculation of $\langle E_V \rangle$

$$\frac{T \partial \ln Q_V}{\partial T} = 11.62$$

$$\langle E_V \rangle = 33.48 \text{ kcal mole}^{-1}$$

B. Calculation of $\langle E_V^+ \rangle$

$$\frac{T \partial \ln Q_V^+}{\partial T} = 7.58$$

$$\langle E_V^+ \rangle = 21.84 \text{ kcal mole}^{-1}$$

C. Calculation of E_0

$$E_0 = 94.40 - \frac{1}{2}(5-1+2) \times 1.987 \times 10^{-3} \times 1450 - 33.48 - 21.84$$

$$= 97.40 \text{ kcal mole}^{-1}$$

D. Calculation of E^+

$$E^+ = (1+2.5) \times 1.987 \times 10^{-3} \times 1450 + 2.859 \times 10^{-3} \times 7641.08$$

$$= 31.93 \text{ kcal mole}^{-1}$$

5.4.1.5 Calculation of ΔS^\ddagger , k_∞ and A_∞

$$A_\infty = 10^{17.63} \text{ sec}^{-1}$$

$$E_\infty = 94.40 \text{ kcal mole}^{-1}$$

$$\Delta S^\ddagger = 17.01 \text{ cal mole}^{-1} \text{ deg}^{-1}$$

$$k_\infty = 2.54 \times 10^3 \text{ sec}^{-1}$$

$$\begin{aligned} S_v &= 1.987 (\ln 7.3599 \times 10^5 + 11.62) \\ &= 49.91 \text{ cal mole}^{-1} \text{ .deg}^{-1} \end{aligned}$$

$$\begin{aligned} S_r &= 1.987 (\ln 4.9623 \times 10^5 + 1.5) \\ &= 29.04 \text{ cal mole}^{-1} \text{ .deg}^{-1} \end{aligned}$$

$$\begin{aligned} S_{ir} &= 1.987 (\ln 30.40 + 0.5) \\ &= 7.78 \text{ cal mol}^{-1} \text{ .deg}^{-1} \end{aligned}$$

$$S_{th} = 86.73 \text{ cal mole}^{-1} \text{ .deg}^{-1}$$

$$\begin{aligned} S_v^+ &= 1.987 (\ln 1439.88 + 7.58) \\ &= 29.51 \text{ cal mole}^{-1} \text{ .deg}^{-1} \end{aligned}$$

$$\begin{aligned} S_r^+ &= 1.987 (\ln 6.3216 \times 10^6 + 1.5) \\ &= 34.10 \text{ cal mole}^{-1} \text{ .deg}^{-1} \end{aligned}$$

$$\begin{aligned} S_{ir}^+ &= 1.987 (\ln 4.6618 \times 10^7 + 2.5) \\ &= 40.05 \text{ cal mole}^{-1} \text{ .deg}^{-1} \end{aligned}$$

$$S_{th}^+ = 103.66 \text{ cal mole}^{-1} \text{ .deg}^{-1}$$

$$\Delta S_{th}^\ddagger = 16.93 \text{ cal mole}^{-1} \text{ .deg}^{-1}$$

$$k_{\infty, th} = 3 \times \frac{1.3805 \times 10^{-16} \times 1450}{6.6262 \times 10^{-27}} \times \frac{1439.88 \times 2 \times 6.3216 \times 10^6 \times 4.6618 \times 10^7}{7.3599 \times 10^5 \times 6 \times 4.9623 \times 10^5 \times 30.40} \times \exp\left(-\frac{97.400}{1.987 \times 1.450}\right) \times 10^{-3}$$

$$= 2.40 \times 10^3 \text{ sec}^{-1}$$

$$A_{\infty, th} = \frac{2.718 \times 1.3805 \times 10^{-16} \times 1450}{6.6262 \times 10^{-27}} \times e^{16.93/1.987}$$

$$= 10^{17.61} \text{ sec}^{-1}$$

5.4.1.6 Calculation of the Anharmonicity Corrections

As previously mentioned, the values of a_{xy} and b_{xy} are taken from the tables [85].

A. The Molecule

For C-F stretching (6 fold degenerate)

$$f_2 = 7.2373 \times 10^5 \text{ dynes cm}^{-1}$$

$$f_3 = 14.5916 \times 10^{13} \text{ dynes cm}^{-2}$$

$$D_e = 8.9021 \times 10^{-12} \text{ ergs molecule}^{-1} = 128.10 \text{ kcal mole}^{-1}$$

$$D_e^{-1} = .00780$$

For C-C stretching

$$f_2 = 2.4752 \times 10^5 \text{ dynes cm}^{-1}$$

$$f_3 = 4.0046 \times 10^{13} \text{ dynes cm}^{-2}$$

$$D_e = 4.7280 \times 10^{-12} \text{ ergs molecule}^{-1} = 68.04 \text{ kcal mole}^{-1}$$

$$D_e^{-1} = .01470$$

For bending modes (10 fold degenerate)

$$D_e^{-1} = 0.01957$$

$$\langle D_e^{-1} \rangle = \frac{1}{17} (10 \times 0.01957 + 6 \times 0.00780 \times 0.01470)$$

$$= 0.01513$$

$$D = 66.09 \text{ kcal mole}^{-1}$$

B. The Complex

For C-F stretching (6 fold degenerate)

$$f_2 = 7.4532 \times 10^5 \text{ dynes cm}^{-1}$$

$$f_3 = 15.1178 \times 10^{13} \text{ dynes cm}^{-2}$$

$$D_e = 9.0578 \times 10^{-12} \text{ ergs molecule}^{-1} = 130.34 \text{ kcal mole}^{-1}$$

$$D_e^{-1} = 0.00767$$

For C-F bending (6 fold degenerate)

$$D_e^{-1} = 0.01957$$

$$\langle D_e^{-1} \rangle = \frac{1}{12} (6 \times 0.00767 + 6 \times 0.01957)$$

$$= 0.01362$$

$$D = 73.42 \text{ kcal mole}^{-1}$$

5.4.1.7 Evaluation of $k_{\text{uni}}/k_{\infty}$

A. Centrifugal Effects are Neglected

TABLE 5.79 - Parameters for $k_{\text{uni}}/k_{\infty}$ for C_2F_6 (Model I), Neglecting Centrifugal Effects

E_0	97.40 kcal mole ⁻¹
E_Z	6431 cm ⁻¹ = 18.38 kcal/mole
E_Z^+	5316 cm ⁻¹ = 15.20 kcal/mole
s	17
s ⁺	12
	./...

Table 5.79 - Continued

r	1
r^*	5
α	16.5
α^+	14.5
$\Gamma(\alpha+1)$	8.563×10^{13}
$\Gamma(\alpha^++1)$	3.348×10^{11}
$\Gamma(1 + \frac{r^*}{2})$	3.2333
$\prod^s v_i$	$5.53 \times 10^{47} \text{ cm}^{-17}$
$\prod^{s+} v_i^+$	$9.828 \times 10^{34} \text{ cm}^{-12}$
$(E_z^+)^{\alpha+-\alpha}$	$3.540 \times 10^{-8} \text{ cm}^2$
$(E_z^+)^{\alpha^++1}$	$5.579 \times 10^{57} \text{ cm}^{-15.5}$
$(E_z^+)^{s+}$	$5.094 \times 10^{44} \text{ cm}^{-12}$
$(RT)^{1+r^*/2}$	$3.249 \times 10^{10} \text{ cm}^{-3.5}$
$(RT)^{(r^*-r)/2}$	$1.016 \times 10^6 \text{ cm}^{-2}$
$\langle v^2 \rangle$	$4092174.2 \text{ cm}^{-2}$
$\langle v \rangle$	1839.59 cm^{-1}
$\langle v \rangle^2$	$3384084.9 \text{ cm}^{-2}$
β	1.1716
$\langle v^{+2} \rangle$	$888344.67 \text{ cm}^{-2}$
$\langle v^+ \rangle$	886.00 cm^{-1}
$\langle v^+ \rangle^2$	784996 cm^{-2}
β^+	1.2535
Z	$2.8257 \times 10^6 \text{ Torr}^{-1} \text{ sec}^{-1}$ where $\sigma_d = 4.5 \times 10^{-8} \text{ cm}$

Table 5.79 - Continued

C_0	5.275
C_1	3.624×10^{-3}
θ	0.0960
$G_1(x)$	$19.44x^{2.5}$
$G_2(x)$	$[x+1-1.2535/(5.00 \times 2.73x^{0.5}+3.51)]^{14.5}$
$G_3(x)$	$[x+1-1.2535 \exp(-2.419x^{0.25})]^{14.5}$
$H(x)$	$(x+7.620)^{16.5}$
$C_{2/P}$	$25.049 \times 10^{11}/P$

B. Centrifugal Effects are Included

I. Direct Method

The value of $H(x)$, calculated below, is used with the parameters of Table 5.79, to determine the fall-off region.

$$\begin{aligned} \langle \Delta E_j \rangle &= -1.987 \times 10^{-3} \times 1450 \times 7.186 \\ &= -20.70 \text{ kcal mole}^{-1} \end{aligned}$$

$$\begin{aligned} H(x) &= \left(x + \frac{97.40 - 20.70 + 18.38}{15.20} \right)^{16.5} \\ &= (x + 6.255)^{16.5} \end{aligned}$$

II. The Waage-Rabinovitch Approximation

$$\begin{aligned} a &= 1 - 1.2311 \exp \left[-2.419 \left(\frac{97.40 - 20.70 + 31.93}{18.38} \right)^{0.25} \right] \\ &= 0.9717 \end{aligned}$$

$$F^{-1} = 1 + \frac{(17+0.5-1)(8.186-1)(1.987 \times 10^{-3} \times 1450)}{(97.40 + (0.9717 \times 18.38))}$$

$$F^{-1} = 3.964$$

$$F = 0.252$$

The $k_{\text{uni}}/k_{\infty}$ ratio equals 0.5 at $P = 15873$ Torr.

TABLE 5.80 - Contribution of Centrifugal Effects to $k_{\text{uni}}/k_{\infty}$ for $\text{C}_2\text{F}_6 \rightarrow 2\text{CF}_3$ at 1450°K (Model I)

P (Torr)	$(k_{\text{uni}}/k_{\infty})^{\text{a}}$	$(k_{\text{uni}}/k_{\infty})^{\text{b}}$
10^{-1}	0.0010	0.0004
1	0.0058	0.0025
10^1	0.0286	0.0137
10^2	0.1111	0.0601
10^3	0.3189	0.2011
10^4	0.6369	0.4801
10^5	0.8878	0.7885
10^6	0.9772	0.9505
10^7	0.9923	0.9886
10^8	0.9940	0.9936
10^9	0.9941	0.9941

neglecting centrifugal effects ($(k_{\text{uni}}/k_{\infty})=0.5$ at $P=4000$ mmHg)

including centrifugal effects ($(k_{\text{uni}}/k_{\infty})=0.5$ at $P=16000$ mmHg)

5.4.1.8 Calculation of $k_a(E^*)$

The input data for the computer program to calculate $k_a(E^*)$ is given in Table. 5.81.

TABLE 5.81 - Properties of the Active Molecule and the Activated Complex
(C₂F₆, Model I)

	Molecule	Complex
Frequencies (cm ⁻¹)	1420	1087
	807	703
	349	1251 (2)
	1116	512 (2)
	714	
	1250 (2)	
	522 (2)	
	219 (2)	
	1237 (2)	
	620 (2)	
	380 (2)	
E ₀ (kcal mole ⁻¹)		97.40
s	17	12
r	1	5
Moments of Inertia (amu Å ²)		
I _{xx}	272.673	1124.787
I _{zz}	177.876	188.608
I _{ir}	44.38	47.13
Symmetry number for internal rotation		
σ	3	2 (4) and 1 (1)
Average bond energy (kcal mole ⁻¹)		
D	66.09	73.42
Increment for the summation ΔE ⁺ (kcal mole ⁻¹)		0.05
Number of rate constants to be calculated		
NEN		1200
L [‡]		3
Temperature		
T		1450
Pressure (Torr)		
P		3040
Collision number (Torr ⁻¹ Sec ⁻¹)		
Z		2.8257x10 ⁶

The results at $E^+ = 31.93 \text{ kcal mole}^{-1}$ are shown below

$$k_a(E^+ + E_0) = 0.3637 \times 10^{10} \text{ sec}^{-1}$$

$$k_a(E^+ + E_0 + \langle \Delta E_j \rangle) = 0.4506 \times 10^{11} \text{ sec}^{-1}$$

$$k_a(E^+ + E_0)_{\text{(anh)}} = 0.1346 \times 10^{10} \text{ sec}^{-1}$$

$$k_a(E^+ + E_0 + \langle \Delta E_j \rangle)_{\text{(anh)}} = 0.2037 \times 10^{11} \text{ sec}^{-1}$$

5.4.1.9 Calculation of k_{uni}

The input data for the computer program which evaluates k_{uni} is given in Table 5.81.

A. Neglecting the Centrifugal Effects

$$k_{\text{uni}} = \frac{6.3216 \times 10^6}{9.537 \times 10^{-14} \times 4.9623 \times 10^5 \times 735988.4 \times 30.40} \exp\left(-\frac{97.40}{1.987 \times 10^3 \times 1450}\right) \cdot (0.05)(2.5893 \times 10^{12})$$

$$= 1608.42 \text{ sec}^{-1}$$

$$k_{\text{uni}}(\text{anh}) = 6.2118 \times 10^{-10} \times 3.0715 \times 10^{12}$$

$$= 1907.95 \text{ sec}^{-1}$$

B. Including the Centrifugal Effects

$$k_{\text{uni}} = 6.2118 \times 10^{-10} \times 1.2405 \times 10^{12}$$

$$= 770.57 \text{ sec}^{-1}$$

$$k_{\text{uni}}(\text{anh}) = 6.2118 \times 10^{-10} \times 1.6468 \times 10^{12}$$

$$= 1022.96 \text{ sec}^{-1}$$

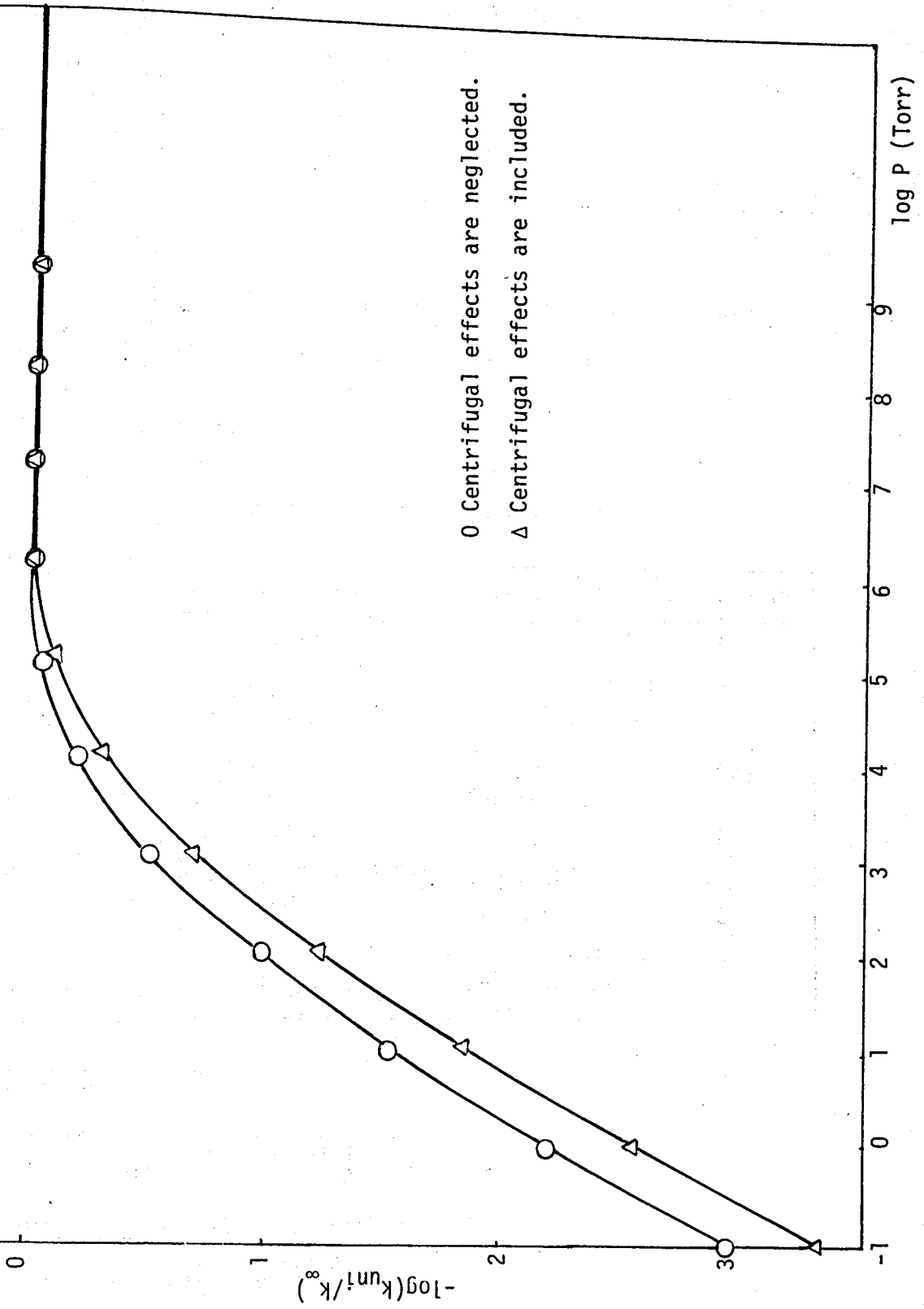


Figure 5.11 - Calculated fall-off curves for hexafluoroethane decomposition at 1450°K (Model I)

5.4.2 Model II

5.4.2.1 Data

A. The Molecule

The molecule has the vibrational frequencies given in Table 5.73 and the molecular parameters given in Table 5.74.

B. The Activated ComplexTABLE 5.82 - The Frequencies of $C_2F_6^+$ (Model II)

	Wave number (cm^{-1})	Type of Vibration	Species
ν_1	1420	C-F stretching	A_{1g}
ν_2	807	CF_3 deformation	A_{1g}
ν_3	1116	C-F stretching	A_{2u}
ν_4	714	CF_3 deformation	A_{2u}
ν_5	1250	C-F stretching	E_u
ν_6	522	CF_3 deformation	E_u
ν_7	$219\exp[-\alpha(r^+-1.545)]$	CF_3 Crocking	E_u
ν_8	1237	C-F stretching	E_g
ν_9	620	CF_3 deformation	E_g
ν_{10}	$380\exp[-\alpha(r^+-1.545)]$	CF_3 Crocking	E_g

The potential energy is

$$V(r^+) = D \left[1 - e^{-\beta(r^+ - 1.545)} \right]^2 + E_Z^+ - E_Z^m$$

$$\Delta H_0^0(CF_3-CF_3) = 96.9 \pm 2 \text{ kcal mole}^{-1} [123]$$

$$\Delta H_0^0 = 94.5 \text{ kcal mole}^{-1} [114]$$

$$E_Z^m = 18.48 \text{ kcal mole}^{-1}$$

$$E_Z^p = 15.20 \text{ kcal mole}^{-1}$$

$$f = 5.45 \times 10^5 \text{ dynes cm}^{-1} [124]$$

$$v_a = 219 \exp[-\alpha(r^+ - 1.545)] \quad (2)$$

$$v_b = 380 \exp[-\alpha(r^+ - 1.545)] \quad (2)$$

$$D = 97.79 \text{ kcal mole}^{-1}$$

$$\beta = 2.00 \times 10^{-8} \text{ cm}^{-1}$$

$$\alpha = 1.00$$

$$E_z^+ - E_z^m = 1.713 \left[\exp(-(r^+ - 1.545)) \right] - 2.309 \text{ kcal mole}^{-1}$$

$$V(r^+) = 97.79 \left[1 - e^{-2.00(r^+ - 1.545)} \right]^2 + 1.713 \left[\exp(-(r^+ - 1.545)) \right] - 2.309 \text{ kcal mole}^{-1}$$

The data concerning the potential energy and the rocking frequencies is given in Table 5.83.

TABLE 5.83 - Potential Energy and Vibrational Frequencies as a Function of r^+ for $C_2F_6^+$ (Model II)

$r^+(\text{\AA})$	$V(r^+) \text{ kcal mole}^{-1}$	$v_a (\text{cm}^{-1})$	$v_b (\text{cm}^{-1})$
3.000	85.51	51	89
3.250	89.43	40	69
3.500	91.84	31	54
3.750	93.30	24	42
4.000	94.19	19	33
4.250	94.72	15	25
4.500	95.04	11	20
4.750	95.22	9	15
5.000	95.34	7	12

5.4.2.2 The Moments of Inertia

A. The Molecule (same as Model I)

$$I_{xx} = I_{yy} = 272.615 \text{ amu } \overset{\circ}{\text{A}}^2 = 452.54 \times 10^{-40} \text{ g.cm}^2$$

$$I_{zz} = 177.876 \text{ amu } \overset{\circ}{\text{A}}^2 = 295.08 \times 10^{-40} \text{ g.cm}^2$$

B. The Complex

I. *External Rotation*

The value of x^+ changes from $x^+ = 1.081$ in the molecule to $x^+ = 1.114$ in the complex.

The value of z^+ , the perpendicular distance from the fluorines to the carbon, changes from 0.447 in the molecule where $r_e = 1.545$ to 0.297 in the Gorin model where $r_e = 4.97 \overset{\circ}{\text{A}}$.

Table 5.84 - Parameters for Evaluation of Moment of Inertia Product as a Function of r^+ for C_2F_6 (Model II)

r^+	Δr^+	Δx^+	x^+	Δz^+	z^+
	$(\Delta r^+ = r^+ - 1.545)$	$(\Delta x^+ = \frac{\Delta r^+(1.114 - 1.081)}{4.97 - 1.545})$	$(x^+ = 1.081 + \Delta x^+)$	$(\Delta z^+ = \frac{\Delta r^+ \times 0.1501}{4.97 - 1.545})$	$(z^+ = 0.447 - \Delta z^+)$
3.000	1.455	0.014	1.095	0.064	0.383
3.250	1.705	0.016	1.097	0.075	0.372
3.500	1.955	0.019	1.100	0.086	0.361
3.750	2.205	0.021	1.102	0.097	0.350
4.000	2.455	0.024	1.105	0.108	0.339
4.250	2.705	0.026	1.107	0.119	0.328
4.500	2.955	0.028	1.109	0.130	0.317
4.750	3.205	0.031	1.112	0.140	0.307
5.000	-	-	1.114	-	0.297

TABLE 5.85 - Change in x^+ as a Function of r^+ for $C_2F_6^+$ (Model II)

r^+	3.000	3.250	3.500	3.750	4.000	4.250	4.500	4.750	5.000
	x^+	x^+	x^+	x^+	x^+	x^+	x^+	x^+	x^+
C_1	0	0	0	0	0	0	0	0	0
C_2	0	0	0	0	0	0	0	0	0
F_1	0	0	0	0	0	0	0	0	0
F_2	1.095	1.097	1.100	1.102	1.105	1.107	1.109	1.112	1.114
F_3	-1.095	-1.097	-1.100	-1.102	-1.105	-1.107	-1.109	-1.112	-1.114
F_4	-1.095	-1.097	-1.100	-1.102	-1.105	-1.107	-1.109	-1.112	-1.114
F_5	1.095	1.097	1.100	1.102	1.105	1.107	1.109	1.112	-1.114
F_6	0	0	0	0	0	0	0	0	0
$\Sigma m_1 x_1^{+2}$	91.116	91.449	91.950	92.285	92.788	93.124	93.461	93.967	94.304

TABLE 5.86 - Change in z^+ as a Function of r^+ for $C_2F_6^+$ (Model II)

r^+	3.000	3.250	3.500	3.750	4.000	4.250	4.500	4.750	5.000
	z^+	z^+	z^+	z^+	z^+	z^+	z^+	z^+	z^+
C_1	1.500	1.625	1.750	1.875	2.000	2.125	2.250	2.375	2.500
C_2	-1.500	-1.625	-1.750	-1.875	-2.000	-2.125	-2.250	-2.375	-2.500
F_1	1.883	1.997	2.111	2.225	2.339	2.453	2.567	2.682	2.797
F_2	1.883	1.997	2.111	2.225	2.339	2.453	2.567	2.682	2.797
F_3	1.883	1.997	2.111	2.225	2.339	2.453	2.567	2.682	2.797
F_4	-1.883	-1.997	-2.111	-2.225	-2.339	-2.453	-2.567	-2.682	-2.797
F_5	-1.883	-1.997	-2.111	-2.225	-2.339	-2.453	-2.567	-2.682	-2.797
F_6	-1.883	-1.997	-2.111	-2.225	-2.339	-2.453	-2.567	-2.682	-2.797
$\Sigma m_1 z_1^{+2}$	458.216	518.018	581.535	648.764	719.707	794.805	872.734	955.429	1041.830

TABLE 5.87 - Moments of Inertia as a Function of r^+ ($\text{amu } \text{Å}^2$) for C_2F_6^+ (Model II)

r^+ (Å)	$I_{xx}^+ = I_{yy}^+$ ($\text{amu } \text{Å}^2$)	I_{zz}^+ ($\text{amu } \text{Å}^2$)
3.000	549.332	182.232
3.250	609.458	182.898
3.500	673.485	183.900
3.750	741.049	184.570
4.000	812.495	185.576
4.250	887.929	186.248
4.500	966.195	186.922
4.750	1049.770	187.934
5.000	1136.134	188.608

II. Internal Rotation

The internal moment of inertia changing with r^+ is a function of ℓ which changes from 1.248 Å in the molecule to 1.286 Å in the complex of the Gorin model.

TABLE 5.88 - Parameters for Evaluation of the Moment of Internal Rotation as a Function of r^+ for C_2F_6^+ (Model II)

r^+ (Å)	Δr^+ (Å)	$\Delta \ell^+$ (Å)	ℓ^+ (Å)
		$(\Delta \ell^+ = \frac{\Delta r^+ \times (1.286 - 1.248)}{4.970 - 1.545})$	$(\ell^+ = 1.248 + \Delta \ell^+)$
3.000	1.455	0.016	1.264
3.250	1.705	0.019	1.267
3.500	1.955	0.022	1.270
3.750	2.205	0.024	1.272
4.000	2.455	0.027	1.275
4.250	2.705	0.030	1.278
4.500	2.955	0.033	1.281
4.750	3.205	0.036	1.284
5.000	3.455	0.038	1.286

TABLE 5.89 - Moment of Inertia for Internal Rotation as a Function of r^+ for $C_2F_6^+$ (Model II)

r^+ (Å)	I_{ir}^+ (amu Å ²)
3.000	45.53
3.250	45.74
3.500	45.94
3.750	46.14
4.000	46.34
4.250	46.54
4.500	46.74
4.750	46.95
5.000	47.13

5.4.2.3 Calculation of the Partition Functions

Neglecting Centrifugal Effects

A. The Molecule

I. Vibrational Partition Function

The molecule has 18 vibrational degrees of freedom (Table 5.73).

$$Q_v = 1.1280 \times 10^7$$

II. Rotational Partition Function

$$Q_v = 4.9623 \times 10^5$$

B. The Activated Complex

The minimization procedure carried out by the computer located the activated complex at $r^+ = 3.250$ Å.

I. Vibrational Partition Function

$$v_a = 219 \exp(-1(3.250-1.545)) = 40 \text{ cm}^{-1} \quad (2)$$

$$v_b = 380 \exp(-1(3.250-1.545)) = 69 \text{ cm}^{-1} \quad (2)$$

$$Q_v^+ = 1.2230 \times 10^8$$

II. Rotational Partition Function

$r^+(A)$	$\Delta r^+(A)$	$\Delta x^+(A)$	$x^+(A)$	$\Delta z^+(A)$	$z^+(A)$
3.250	1.705	0.016	1.097	0.075	0.372

TABLE 5.90 - Parameters for Evaluation of Moment of Inertia Product of $C_2F_6^+$ (Model II, Neglecting Centrifugal Effects)

Atom	m_i	x_i^+	z_i^+
C ₁	12.011	0	1.625
C ₂	12.011	0	-1.625
F ₁	18.998	0	1.997
F ₂	18.998	1.097	1.997
F ₃	18.998	-1.097	1.997
F ₄	18.998	-1.097	-1.997
F ₅	18.998	1.097	-1.997
F ₆	18.998	0	-1.997
		$\sum m_i x_i^2 = 91.449$	$\sum m_i z_i^2 = 518.018$

$$I_{xx}^+ = I_{yy}^+ = 609.458 \text{ amu } A^2 = 1011.70 \times 10^{-40} \text{ g.cm}^2$$

$$I_{zz}^+ = 182.898 \text{ amu } A^2 = 303.61 \times 10^{-40} \text{ g.cm}^2$$

$$Q_r^+ = \frac{\sqrt{3.14}}{6} \left(\frac{8 \times 3.14^2 \times 1.3805 \times 10^{-16} \times 1450}{(6.6262 \times 10^{-27})^2} \right)^{3/2} (1011.70^2 \times 303.61 \times 10^{-120})^{1/2}$$

$$= 1.1247 \times 10^6$$

III. Partition Function for Internal Rotation

$r^+(A)$	$\Delta r^+(A)$	$\Delta \ell^+(A)$	$\ell^+(A)$	$I_{ir}^+(\text{amu}, A^2)$
3.250	1.705	0.019	1.267	45.74

$$Q_{ir}^+ = \frac{(8 \times 3.14^3 \times 75.93 \times 10^{-40} \times 1.3805 \times 10^{-16} \times 1450)^{1/2}}{6.6262 \times 10^{-27} \times 3}$$

$$= 30.89$$

Including Centrifugal Effects

A. The Molecule

I. Vibrational Partition Function

$$Q_v = 1.1280 \times 10^7$$

II. Rotational Partition Function

$$Q_r = 4.9623 \times 10^5$$

B. The Activated Complex

I. Vibrational Partition Function

The activated complex is located at $r^+ = 3.375 \text{ \AA}$

$$\nu_a = 219 \exp(-(3.375-1.545)) = 35 \text{ cm}^{-1} \quad (2)$$

$$\nu_b = 380 \exp(-(3.375-1.545)) = 61 \text{ cm}^{-1} \quad (2)$$

$$Q_v^+ = 2.0180 \times 10^8$$

II. Rotational Partition Function

$r^+(A)$	$\Delta r^+(A)$	$\Delta x^+(A)$	$x^+(A)$	$\Delta z^+(A)$	$z^+(A)$
3.375	1.83	0.018	1.099	0.080	0.353

TABLE 5.91 - Parameters for Evaluation of Moment of Inertia Product of $C_2F_6^+$ (Model II, Including Centrifugal Effects)

Atom	m_i	x_i^+	z_i^+
C_1	12.011	0	1.6875
C_2	12.011	0	-1.6875
F_1	18.998	0	2.0405
F_2	18.998	1.099	2.0405
F_3	18.998	-1.099	2.0405
F_4	18.998	-1.099	-2.0405
F_5	18.998	1.099	-2.0405
F_6	18.998	0	-2.0405
		$\sum m_i x_i^{+2} = 91.783$	$\sum m_i z_i^{+2} = 543.01$

$$I_{xx}^+ = I_{yy}^+ = 634.793 \text{ amu } \text{Å}^2 \quad 1053.76 \times 10^{-40} \text{ g.cm}^2$$

$$I_{zz}^+ = 183.566 \text{ amu } \text{Å}^2 \quad 304.72 \times 10^{-40} \text{ g.cm}^2$$

$$Q_r^+ = \frac{\sqrt{3.14} (8 \times 3.14^2 \times 1.3805 \times 10^{-16} \times 1450)^{3/2} (1053.76^2 \times 304.72 \times 10^{-120})^{1/2}}{6 (6.6262 \times 10^{-27})^2}$$

$$Q_r^+ = 1.1736 \times 10^6$$

III. Partition Function for Internal Rotation

$r^+(A)$	$\Delta r^+(A)$	$\Delta \ell^+(A)$	$\ell^+(A)$	$I_{j_r}^+(\text{amu } \text{Å}^2)$
3.375	1.83	0.020	1.268	45.84

$$Q_{ir}^+ = (8 \times 3.14^3 \times 76.09 \times 10^{-40} \times 1.3805 \times 10^{-16} \times 1450)^{1/2} / (6.6262 \times 10^{-27}) \times 3$$

$$= 30.92$$

5.4.2.4 Calculation of $\langle E_V \rangle$, $\langle E_V^+ \rangle$ and E^+

A. Calculation of $\langle E_V \rangle$

$$\frac{T \partial \ln Q_V}{\partial T} = 12.58$$

$$\langle E_V \rangle = 36.26 \text{ kcal mole}^{-1}$$

B. Calculation of $\langle E_V^+ \rangle$

I. *Neglecting Centrifugal Effects*

$$\frac{T \partial \ln Q_V^+}{\partial T} = 11.24$$

$$\langle E_V^+ \rangle = 32.37 \text{ kcal mole}^{-1}$$

II. *Including Centrifugal Effects*

$$\frac{T \partial \ln Q_V^+}{\partial T} = 11.25$$

$$\langle E_V^+ \rangle = 32.41 \text{ kcal mole}^{-1}$$

C. Calculation of E^+

$$E^+ = (1 + 0.5)(1.987 \times 10^{-3})(1450) + (2.859 \times 10^{-3})(1.132 \times 10^4)$$

$$= 36.71 \text{ kcal mole}^{-1}$$

5.4.2.5 Calculation of ΔS^\ddagger , k_∞ and A_∞

A. Neglecting Centrifugal Effects

The value of E_0 is 89.43 kcal mole⁻¹

The value of E_∞ which corresponds to E_0 is

$$E_\infty = 89.86 \text{ kcal mole}^{-1}$$

$$S_v = 1.987 (\ln 1.1280 \times 10^7 + 12.58) \\ = 57.26 \text{ cal mole}^{-1} \text{ deg}^{-1}$$

$$S_r = 29.04 \text{ cal mole}^{-1} \text{ deg}^{-1}$$

$$S_{th} = 86.30 \text{ cal deg}^{-1} \text{ mole}^{-1}$$

$$S_v^+ = 1.987 (\ln 1.2230 \times 10^8 + 11.24) \\ = 59.34 \text{ cal mole}^{-1} \text{ deg}^{-1}$$

$$S_r^+ = 1.987 (\ln 1.1247 \times 10^6 + 1.5) \\ = 30.67 \text{ cal mole}^{-1} \text{ deg}^{-1}$$

$$S_{ir}^+ = 1.987 (\ln 30.89 + 0.5) \\ = 7.81 \text{ cal mole}^{-1} \text{ deg}^{-1}$$

$$S_{th}^+ = 97.82 \text{ cal mole}^{-1} \text{ deg}^{-1}$$

$$\Delta S_{th}^\ddagger = 11.52 \text{ cal mole}^{-1} \text{ deg}^{-1}$$

$$k_{\infty th} = \frac{1.3805 \times 10^{-16} \times 1450}{6.6262 \times 10^{-27}} \times \frac{1.2230 \times 10^8 \times 1.1247 \times 10^6 \times 30.89}{1.1280 \times 10^7 \times 4.9623 \times 10^5} \times \\ = 7.59 \times 10^2 \text{ sec}^{-1}$$

$$\times \exp\left(-\frac{89.43}{1.987 \times 1450 \times 10^{-3}}\right)$$

$$A_{\infty th} = 10^{16.43}$$

B. Including Centrifugal Effects

The value of E_0 is 90.75 kcal mole⁻¹

The value of E_∞ corresponding to E_0 is

$$E_\infty = 91.23 \text{ kcal mole}^{-1}$$

$$S_{th} = 86.30 \text{ cal deg}^{-1} \text{ mole}^{-1}$$

$$S_v^+ = 1.987 (\ln 2.0180 \times 10^8 + 11.25) \\ = 60.35 \text{ cal mole}^{-1} \text{ deg}^{-1}$$

$$S_r^+ = 1.987 (\ln 1.1736 \times 10^6 + 1.5) \\ = 30.75 \text{ cal mole}^{-1} \text{ deg}^{-1}$$

$$s_{ir}^+ = 1.987 (\ln 30.92 + 0.5) \\ = 7.81 \text{ cal mole}^{-1} \text{ deg}^{-1}$$

$$S_{th}^+ = 98.91 \text{ cal mole}^{-1} \text{ deg}^{-1}$$

$$\Delta S_{th}^\ddagger = 12.61 \text{ cal mole}^{-1} \text{ deg}^{-1}$$

$$k_{\infty th} = 8.29 \times 10^2 \text{ sec}^{-1}$$

$$A_{\infty th} = 10^{16.67}$$

5.4.2.6 Calculation of the Anharmonicity Corrections

A. The Molecule

In the molecule there are

6 C-F stretching frequencies (Model I)

10 C-F bending frequencies (Model I)

1 C-C stretching frequency (Model I)

1 torsion frequency*

$$\langle D_e^{-1} \rangle = \frac{1}{18} (10 \times 0.01957 + 6 \times 0.00783 + 0.01470 + 0.11990)$$

$$= 0.02095$$

$$D = 47.73 \text{ kcal mole}^{-1}$$

* The dissociation energy corresponding to the torsion frequency of C_2F_6 is calculated by comparing the potential barrier ($V=4.35 \text{ kcal mole}^{-1}$) of this molecule to the one of C_2H_6 ($V=2.87 \text{ kcal mole}^{-1}$) considering also the known dissociation energy of the same frequency in C_2H_6 ($D^{-1}=0.2387 \text{ kcal mole}^{-1}$).

B. The Activated Complex

In the activated complex there are

6 C-F stretching frequencies

10 C-F bending frequencies

Thus

$$\langle D_e^{-1} \rangle = \frac{1}{16} (10 \times 0.01957 + 6 \times 0.00783)$$

$$= 0.01517$$

$$D = 65.92 \text{ kcal mole}^{-1}$$

5.4.2.7 Evaluation of $k_{\text{uni}}/k_{\infty}$

TABLE 5.92 - Parameters for $k_{\text{uni}}/k_{\infty}$ for C_2F_6 (Model II)

	Centrifugal effects are neglected	Centrifugal effects are included
E_0	89.43 kcal/mole	90.75 kcal/mole
E_Z^{\ddagger}	$6465 \text{ cm}^{-1} = 18.48 \text{ kcal mole}^{-1}$	$6465 \text{ cm}^{-1} = 18.48 \text{ kcal mole}^{-1}$
E_Z	$5766.5 \text{ cm}^{-1} = 16.49 \text{ kcal mole}^{-1}$	$5753.5 \text{ cm}^{-1} = 16.45 \text{ kcal mole}^{-1}$
s	18	18
s^+	16	16
r	0	0
r^*	1	1
α	17	17
α^+	16.5	16.5
$\Gamma(\alpha+1)$	3.557×10^{14}	3.557×10^{14}
$\Gamma(\alpha^++1)$	8.563×10^{13}	8.563×10^{13}
$\Gamma(1+r^*/2)$	0.886	0.886
$\prod_{i=1}^s \nu_i$	$3.758 \times 10^{49} \text{ cm}^{-18}$	$3.758 \times 10^{49} \text{ cm}^{-18}$
$\prod_{i=1}^{s^+} \nu_i^+$	$1.742 \times 10^{42} \text{ cm}^{-16}$	$1.042 \times 10^{42} \text{ cm}^{-16}$
		./...

Table 5.92 - Continued...

	Centrifugal effects are neglected	Centrifugal effects are included
$(E_Z^+)^{\alpha^+-\alpha}$	0.0132 cm ^{0.5}	0.0132 cm ^{0.5}
$(E_Z^+)^{\alpha^++1}$	6.546x10 ⁶⁵ cm ^{-17.5}	6.292x10 ⁶⁵ cm ^{-17.5}
$(E_Z^+)^{S+}$	1.495x10 ⁶⁰ cm ⁻¹⁶	1.442x10 ⁶⁰ cm ⁻¹⁶
$(RT)^{\frac{1+r^*}{2}}$	31994.735 cm ^{-1.5}	31994.735 cm ^{-1.5}
$(RT)^{r^*r/2}$	31.75 cm ^{-0.5}	31.75 cm ^{-0.5}
$\langle v^{+2} \rangle$	745920.56 cm ⁻²	745743.69 cm ⁻²
$\langle v^+ \rangle$	720.8125 cm ⁻¹	719.1875 cm ⁻¹
$\langle v^+ \rangle^2$	519570.66 cm ⁻²	517230.66 cm ⁻²
β^+	1.3880	1.3939
Z	2.8257x10 ⁶ Torr ⁻¹ sec ⁻¹	2.8257x10 ⁶ Torr ⁻¹ Sec ⁻¹
C_0	5.72	5.71
C_1	1.1215x10 ⁻³	1.0919x10 ⁻³
θ	0.0069	0.0061
$G_1(x)$	1.1260x10 ⁻⁴ x ^{0.5}	6.9868x10 ⁻⁵ x ^{0.5}
$G_2(x)$	$[x+1-1.3880/(5.00x+2.73x^{0.5}+3.51)]^{16.5}$	$[x+1-1.3939/(5.00x+2.73x^{0.5}+3.51)]^{16.5}$
$G_3(x)$	$[x+1-1.3880 \exp(-2.419x^{0.25})]^{16.5}$	$[x+1-1.3939 \exp(-2.419x^{0.25})]^{16.5}$
H(x)	(x+6.546) ¹⁷	(x+6.283) ^{17*}
C_2/P	1.2277x10 ¹⁰ /P	2.0538x10 ¹⁰ /P

$$* \langle \Delta E_j \rangle = 1.5 \times \left(1 - \frac{(634.793)^2 \times 183.566}{(272.615)^2 \times 177.76} \right)^{1/2} \times 1.987 \times 10^{-3} \times 1450$$

$$= -5.90$$

TABLE 5.93 - Contribution of Centrifugal Effects to $k_{\text{uni}}/k_{\infty}$ for $\text{C}_2\text{F}_6 \rightarrow 2\text{CF}_3$ at 1450 K (Model II)

P (Torr)	$(k_{\text{uni}}/k_{\infty})^a$	$(k_{\text{uni}}/k_{\infty})^b$
10^{-1}	0.0167	0.0078
1	0.0653	0.0344
10^1	0.1995	0.1208
10^2	0.4540	0.3245
10^3	0.7514	0.6181
10^4	0.9412	0.8712
10^5	1.0018	0.9802
10^6	1.0120	1.0034
10^7	1.0131	1.0064
10^8	1.0132	1.0067
10^9	1.0132	1.0068

Neglecting centrifugal effects ($k_{\text{uni}}/k_{\infty} = 0.5$ at $P=150$ Torr).

Including centrifugal effects ($k_{\text{uni}}/k_{\infty} = 0.5$ at $P=417$ Torr).

5.4.2.8 Calculation of $k_a(E^*)$

TABLE 5.94 - Properties of the Active Molecule and Activated Complex (C_2F_6 , Model II)

Frequencies (cm^{-1})	Molecule		Complex								
			Neglecting C.E.			Including C.E.					
	1420					1420					
	807					807					
	349					349					
	68					68					
	1116					1116					
	714					714					
	1250(2)					1250(2)					
	522(2)					522(2)					
	219(2)					1237(2)					
	1237(2)					620(2)					
	620(2) ^r		3.00	3.25	3.50	3.75	4.00	4.25	4.50	4.75	5.00
	380(2)		51	40	31	24	19	15	11	9	7
			89	69	54	42	33	25	20	15	12

./...

Table 5.94 - Continued...

Molecule		Complex		
E_0 (kcal mole ⁻¹)		89.43		90.75
s	18			16
r	0			1
Moments of inertia (amu Å ²)		r^+	$I_{xx}^+ = I_{yy}^+$	I_{zz}^+
$I_{xx} = I_{yy}$	272.62	3.000	549.332	182.232
I_{zz}	177.76	3.250	609.466	182.90
		3.500	673.498	183.900
		3.750	741.05	184.57
		4.000	812.50	185.58
		4.250	887.929	186.25
		4.500	966.20	186.92
		4.750	1049.77	187.93
		5.000	1136.13	188.61
Symmetry number for internal rotation σ	-			3
Average bond energy (kcal mole ⁻¹) D	47.73			65.98
Increment for the summation (kcal mole ⁻¹) ΔE^+		0.1		
Number of rate constants to be calculated (for k_{uni}) NEN		1200		
Reaction path degeneracy L^\ddagger		1		
Temperature (°K) T		1450		
Pressure (Torr) P		3040		
Collision Number (Torr ⁻¹ sec ⁻¹) Z		2.8257x10 ⁶		
Internal Energy of activated molecule (kcal mole ⁻¹) ECC		127.50		117.50
Number of reaction coordinate intervals NN		8		

./...

Table 5.94 - Continued...

Molecule	Complex
Potential Energy of reaction coordinate (kcal mole ⁻¹) V(r ⁺)	
	85.51 (r ⁺ =3.000 Å) ⁰
	89.43 (r ⁺ =3.250 Å) ⁰
	91.84 (r ⁺ =3.500 Å) ⁰
	93.30 (r ⁺ =3.750 Å) ⁰
	94.19 (r ⁺ =4.000 Å) ⁰
	94.72 (r ⁺ =4.250 Å) ⁰
	95.04 (r ⁺ =4.500 Å) ⁰
	95.22 (r ⁺ =4.750 Å) ⁰
	95.34 (r ⁺ =5.000 Å) ⁰
Reduced moment of inertia changing with r ⁺ I _{ir} ⁺ (amu Å ²)	
	45.53 (r ⁺ =3.000 Å) ⁰
	45.74 (r ⁺ =3.250 Å) ⁰
	45.94 (r ⁺ =3.500 Å) ⁰
	46.14 (r ⁺ =3.750 Å) ⁰
	46.34 (r ⁺ =4.000 Å) ⁰
	46.54 (r ⁺ =4.250 Å) ⁰
	46.74 (r ⁺ =4.500 Å) ⁰
	46.95 (r ⁺ =4.750 Å) ⁰
	47.13 (r ⁺ =5.000 Å) ⁰
The results at E ⁺ = 36.7] kcal mole ⁻¹ are	
k _a (E ⁺ +E ₀) = 0.5740 x 10 ⁹ sec ⁻¹	
k _a (E ⁺ +E ₀ +<ΔE _j >) = 0.1610x10 ¹⁰ sec ⁻¹	
k _a (E ⁺ +E ₀)(anh) = 0.1354x10 ⁹ sec ⁻¹	
k _a (E+E ₀ +<ΔE _j >)(anh) = 0.4073x10 ⁹ sec ⁻¹	

5.4.2.9 Calculation of k_{uni}

The input data for the computer program which evaluates k_{uni} is given in Table 5.94.

A. Neglecting Centrifugal Effects

$$\begin{aligned}
 k_{uni} &= \frac{1.1247 \times 10^6}{9.537 \times 10^{-14} \times 4.9623 \times 10^5 \times 1.1280 \times 10^7} \exp\left(\frac{-89.43}{1.987 \times 10^{-3} \times 1450}\right) \times 0.1 \times \\
 & \qquad \qquad \qquad \times 0.9339 \times 10^{11} \\
 &= 6.9706 \times 10^{-9} \times 0.9339 \times 10^{11} \\
 &= 6.51 \times 10^2
 \end{aligned}$$

$$\begin{aligned}
 k_{uni(anh)} &= 6.9706 \times 10^{-9} \times 0.1038 \times 10^{12} \\
 &= 7.23 \times 10^2
 \end{aligned}$$

B. Including Centrifugal Effects

$$\begin{aligned}
 k_{uni} &= \frac{1.1736 \times 10^6}{9.537 \times 10^{-14} \times 4.9623 \times 10^5 \times 1.1280 \times 10^7} \exp\left(\frac{-90.75}{1.987 \times 10^{-3} \times 1450}\right) \times 0.1 \times 0.1337 \times 10^{12} \\
 &= 6.15 \times 10^2
 \end{aligned}$$

$$\begin{aligned}
 k_{uni(anh)} &= 4.600210^{-9} \times 0.1578 \times 10^{12} \\
 &= 7.26 \times 10^2
 \end{aligned}$$

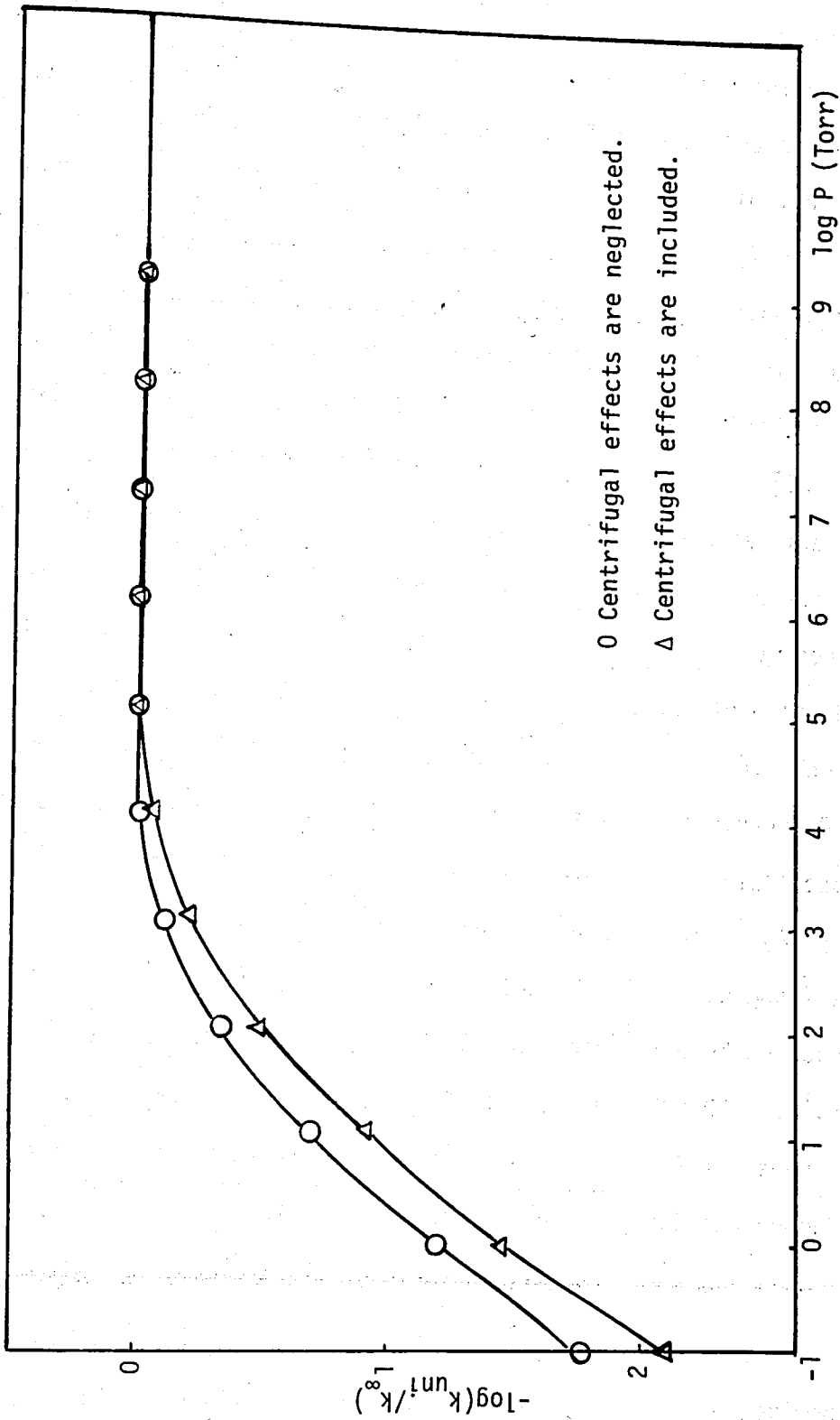


Figure 5.12 - Calculated fall-off curve for hexafluoroethane decomposition at 1450°K (Model II)

It has only been possible to compare some of the results obtained in this work with already published experimental studies and theoretical calculations. Since the ethane molecule has been widely studied, a comparison with previous investigations is made in what follows.

For Model I, good agreement is obtained with the Arrhenius parameters calculated by Waage and Rabinovitch [93], as well as with the experimental results of Quinn [97]. The fall-off curves obtained with this Model are less steep than those of Waage and Rabinovitch [93] obtained at the same temperature. On the other hand, the Arrhenius parameters calculated with Model II agree with the results of the experimental work of Trenwith [96]. The result for $P_{1/2}$ obtained by considering the centrifugal effect of adiabatic rotations is close to the one of this worker and to the value calculated by Hase [42a]. The measured rate constant, $k_a(E^*)$, for the decomposition of ethane [99] for $E_a = 85.8 \text{ kcal mole}^{-1}$ at $E^* = 114.9 \text{ kcal mole}^{-1}$ is $4.6 \times 10^{-9} \text{ sec}^{-1}$. The results of Hase at the same conditions are $5.8 \times 10^9 \text{ sec}^{-1}$ [42a] and $4.9 \times 10^9 \text{ sec}^{-1}$ [42b]. In this work, the value of $k_a(E^*)$ for Model II, at $E^* = 114.9 \text{ kcal mole}^{-1}$ and $E_0 = 85.97 \text{ kcal mole}^{-1}$ including corrections for anharmonicity and centrifugal effects is $3.39 \times 10^9 \text{ sec}^{-1}$. Furthermore, the magnitude of k_{uni} calculated with Model II is in satisfactory agreement with the one computed by Growcock and coworkers [99].

$$k_{\text{uni}} \approx 3.3 \times 10^{-6} \text{ sec}^{-1} \text{ (Present work)}$$

$$k_{\text{uni}} \approx 1.6 \times 10^{-6} \text{ sec}^{-1} \text{ (Growcock)}$$

The margin of numerical correspondance between theory and experiment for the majority of examples should be reasonable in view of the fact

that equation (3.20), upon which the calculations are based, does not contain arbitrary parameters for fitting the experimental values.

The following trends may be noted:

- a. The pressure at which the rate constant reaches one-half its limiting high pressure value increases with the number of fluorine atoms. This behaviour, which is observed in the calculations with Model I, is in harmony with the activation energies for the carbon-carbon bond scission, increasing with the number of fluorine atoms in the hydrocarbon. Since in Model II, a similar agreement between the theoretical and experimental entropies of activation is not observed, it is not possible to observe a trend in the $P^{1/2}$ values.
- b. At any constant value of $\log P$, where the pressure is very small, it is seen that the values of $\log k_{\text{uni}}/k_{\infty}$ become larger as the number of fluorine atoms decreases.

Factors influencing the unimolecular rate constant

1. *The de-energization Variable λZ*

The significant variable is the de-energization rate constant λZ which appears in the expression for k_{uni} as $\lambda Z P$. A change in λZ causes an inversely proportional change in the pressure required to produce a given value of k_{uni} or $k_{\text{uni}}/k_{\infty}$. The plot of $\log k_{\text{uni}}/k_{\infty}$ v.s. $\log P$ is shifted horizontally by a distance equal to the change in

$\log \lambda Z$ without any change in the shape. Uncertainties in λZ arise from the values of λ and the collision cross section σ_d . It has been demonstrated that the collision efficiency for deactivation varies for different gases [125]. Even if the collision efficiency is taken as unity for the parent gas, it is less than unity for an inert gas. Kohlmaier and Rabinovitch [126] have shown that in the case of sec-butyl radicals, the average energy removed per collision by argon is about 3 kcal mole^{-1} . In the case of C_2H_6^* at 873°K , the calculated average energy in excess of the critical energy in Model II is $11.29 \text{ kcal mole}^{-1}$. Based on a step-ladder model this indicates that an average of 4 collisions may be required to deactivate the C_2H_6^* molecule. The collision efficiency would be $\lambda \approx 0.25$. This factor would have the effect of shifting the fall-off curve to higher pressures by 0.60 log units. The value obtained in this way for $P^{1/2}$ including centrifugal effects would match exactly the experimental result of Trenwith [96]. The same assumption could be made for the other molecules to obtain the following collision efficiency parameters: 1,1,2,2-tetrafluoro ethane ≈ 0.11 , pentafluoroethane ≈ 0.09 , hexafluoroethane ≈ 0.08 .

On the other hand, the values used here for the hard-sphere collision diameters may not be exact. In the case of ethane different values of σ_d have been used in the theoretical calculations [93,95,98,102]. Any change in σ_d would have the effect of shifting the fall-off curve by about 0.3 log units to higher or lower pressures.

2. The Integration Procedure

In the integration procedure the variable parameters are the step length ΔE^+ and the maximum energy E^+ to which the integration is taken. The results of a series of calculations to illustrate these points are summarized in Table 5.95 for C_2F_6 .

TABLE 5.95 - Effect of ΔE^+ and E^+ on k_{uni} for C_2F_6 (Model I)

ΔE^{+*} (kcal mole ⁻¹)	0.05	0.1	E^{+*} (kcal mole ⁻¹)	50	59.97
$k_{uni}(+C.E.)$ (sec ⁻¹)	766.11	766.11	$k_{uni}(+C.E.)$ (sec ⁻¹)	764.88	766.11
$k_{uni}(+C.E.)$ (anh) (sec ⁻¹)	1017.04	1016.89	$k_{uni}(+C.E.)$ (anh)(sec ⁻¹)	1014.58	1017.04

* The remaining parameters for the integration are those of Table 5.81.

As seen in Table 5.94 none of variations tested introduces a considerable change in k_{uni} . In conclusion, the integration is insensitive to variations in the computational details.

3. The Whitten-Rabinovitch Approximation

An artifact of the approximation may be noted in that for certain molecules as the pressure becomes very large, the value of k_{uni}/k_{∞} converges toward slightly higher or slightly lower values than unity. The departure from unity for the molecules studied is shown in Table 5.96.

TABLE 5.96 - Deviation of k_{uni}/k_{∞} from Unity at Very High Pressures

	M o d e l I		M o d e l II	
	I ^a	II ^b	I ^a	II ^b
C ₂ H ₆ (T=873 ^o K)	30%	30%	20%	23%
C ₂ H ₂ F ₄ (T=1350 ^o K)	3%	3%	2%	2%
C ₂ HF ₅ (T=1400 ^o K)	1%	1%	1%	1%
C ₂ F ₆ (T=1450 ^o K)	1%	1%	1%	1%

^a Neglecting centrifugal effects.

^b Including centrifugal effects.

The deviation from unity observed for the ethane molecule may be attributed to the Whitten-Rabinovitch approximation. At low energies, the nature of the vibrational energy levels assures discontinuous energy-level sums which are approximated here by a smooth representation.

4. The Experimental A_{∞} and E_{∞} Values

The fall-off curves are sensitive to the values taken for the experimental A_{∞} and E_{∞} which the model is adjusted to fit. The effect of these changes is to produce a displacement of the fall-off curves to higher pressures.

$$\Delta \log P = (1 - \theta) \log A_{\infty} / A'$$

where

$$\theta = (s + \frac{1}{2}r - 1)kT / (E_0 + E_z + \langle E^+ \rangle)$$

The features of the model can be varied without any significant effect on the results, provided the model reproduces correctly the required high-pressure Arrhenius parameters. The changes which are likely to affect the results significantly are relaxation of the strong collision assumption and alteration of the numerical values of the Arrhenius parameters which the model is made to fit.

5. Centrifugal Effects

The results of the computation of the fall-off behaviour for C_2H_6 , $C_2H_2F_4$, C_2HF_5 , C_2F_6 corrected for the centrifugal effects are listed in Tables 5.58, 5.71, 5.80, 5.93, 5.13, 5.37, 5.51. As expected the looser Model I enters the fall-off region at higher pressures than Model II. The centrifugal effect allows part of the adiabatic rotational energy to be used for overcoming the potential energy barrier, thus reducing E_0 and the density of states $N^*(E^*)$, increasing the rate constant $k_a(E^*)$. All the results for Models I and II confirm this prediction. The value of k_{uni} , being inversely proportional to $k_a(E^*)$, decreases when the centrifugal effects are included. Some discrepancies are observed in the calculations with Model II. Since in this case the search for r^+ is made at different energies when centrifugal effects are included or not, a healthy evaluation of this effect is not possible.

Besides the values for k_{uni} are also calculated by considering the values of $k_{\text{uni}}/k_{\infty}$ at the pressure at which the integration is done [$k_{\text{uni}}^* = (k_{\text{uni}}/k_{\infty})k_{\infty}$]. The results computed by the two methods agree to within a factor of 1 or 2. This accuracy justifies the use of RRKM.

TABLE 5.97 - Contribution of Centrifugal Effects and Anharmonicity to $k_a(E^*)$ (Model I)

Model I	$k_a(E_0 + E^+)$ (sec^{-1})	$k_a(E_0 + E^+ + \langle \Delta E_J \rangle)$ (sec^{-1})	$k_a(E_0 + E^+)_{\text{anh}}$ (sec^{-1})	$k_a(E_0 + E^+ + \langle \Delta E_J \rangle)_{\text{anh}}$ (sec^{-1})
C_2H_6 ($T=873^{\circ}\text{K}$)	0.7576×10^9	0.2740×10^{10}	0.2546×10^9	0.1032×10^{10}
$\text{C}_2\text{H}_2\text{F}_4$ ($T=1350^{\circ}\text{K}$)	0.3277×10^{10}	0.9550×10^{10}	0.1157×10^{10}	0.3708×10^{10}
C_2HF_5 ($T=1400^{\circ}\text{K}$)	0.2469×10^{10}	0.2562×10^{11}	0.9118×10^9	0.1143×10^{11}
C_2F_6 ($T=1450^{\circ}\text{K}$)	0.3637×10^{10}	0.4506×10^{11}	0.1346×10^{10}	0.2037×10^{11}

TABLE 5. 98 - Contribution of Centrifugal Effects and Anharmonicity to $k_a(E^*)$ (Model II)

Model II	$k_a(E_0 + E^+)$ (sec ⁻¹)	$k_a(E_0 + E^+ + <\Delta E_{J>})$ (sec ⁻¹)	$k_a(E_0 + E^+)_{anh}$ (sec ⁻¹)	$k_a(E_0 + E^+ + <\Delta E_{J>})_{anh}$ (sec ⁻¹)
C ₂ H ₆	0.3278x10 ⁹	0.1433x10 ⁹	0.3405x10 ⁷	0.1740x10 ⁸
C ₂ H ₂ F ₄	0.1343x10 ¹⁰	0.5667x10 ¹⁰	0.2007x10 ⁹	0.9761x10 ⁹
C ₂ HF ₅	0.4688x10 ⁹	0.1741x10 ¹⁰	0.7820x10 ⁸	0.3230x10 ⁹
C ₂ F ₆	0.5740x10 ⁹	0.1610x10 ¹⁰	0.1354x10 ⁹	0.4073x10 ⁹

 TABLE 5. 99 - Contribution of Centrifugal Effects and Anharmonicity to k_{uni} (Model I)

Model I	k_{uni} (sec ⁻¹)	$k_{uni}(+C.E.)$ (sec ⁻¹)	$k_{uni}(anh)$ (sec ⁻¹)	$k_{uni}(anh)$ (+C.E.)(sec ⁻¹)	k_{uni}^* (sec ⁻¹)	$k_{uni}^*(+C.E.)$ (sec ⁻¹)
C ₂ H ₆	2.7194x10 ⁻⁵	2.2943x10 ⁻⁵	3.0290x10 ⁻⁵	2.8011x10 ⁻⁵	2.4325x10 ⁻⁵	2.0324x10 ⁻⁵
C ₂ H ₂ F ₄	5.61x10 ²	4.29x10 ²	6.55x10 ²	5.34x10 ²	5.18x10 ²	3.62x10 ²
C ₂ HF ₅	5.47x10 ²	3.08x10 ²	6.29x10 ²	3.95x10 ²	4.88x10 ²	3.19x10 ²
C ₂ F ₆	1.61x10 ³	7.70x10 ²	1.91x10 ³	1.02x10 ³	1.42x10 ³	7.91x10 ²

* $k_{uni} = k_{\infty, th} (k_{uni}/k_{\infty})$ at the appropriate pressure.

 TABLE 5.100 - Contribution of Centrifugal Effects and Anharmonicity to k_{uni} (Model II)

Model II	k_{uni} (sec ⁻¹)	$k_{uni}(+C.E.)$ (sec ⁻¹)	$k_{uni}(anh)$ (sec ⁻¹)	$k_{uni}(anh)$ (+C.E.)(sec ⁻¹)	k_{uni}^* (sec ⁻¹)	$k_{uni}^*(+C.E.)$ (sec ⁻¹)
C ₂ H ₆	4.0196x10 ⁻⁶	3.2735x10 ⁻⁶	4.0269x10 ⁻⁶	3.2963x10 ⁻⁶	3.86x10 ⁻⁶	3.05x10 ⁻⁶
C ₂ H ₂ F ₄	3.90x10 ²	3.67x10 ²	4.70x10 ²	5.12x10 ²	3.86x10 ²	3.84x10 ²
C ₂ HF ₅	2.76x10 ²	2.85x10 ²	3.05x10 ²	3.43x10 ²	2.69x10 ²	2.66x10 ²
C ₂ F ₆	6.51x10 ²	6.15x10 ²	7.23x10 ²	7.26x10 ²	6.09x10 ²	5.63x10 ²

As mentioned previously in Chapter III, an approximation formula for the evaluation of the centrifugal effects has been given by Waage and Rabinovitch [45] (Eq. (3.39)). The effect of the factor F is to shift the fall-off curve to higher pressures by the constant- $\log F$ along the $\log P$ axis. Results for Model I including the centrifugal effects computed by the direct method and by using the Waage-Rabinovitch approximation are given in Table 5.100. As seen in this table the approximation gives better results for lower values of I^+/I .

TABLE 5.101 - Illustration of the $P^{1/2}$ Pressure for C_2H_6 , $C_2H_2F_4$, C_2HF_5 , C_2F_6 .

Model I	$P^{1/2}$ (Torr)	$P^{1/2}$ (Torr) (+C.E.)	$P^{1/2*}$ (Torr) (+C.E.)
C_2H_6 (T=873 ⁰ K)	12	43	28
$C_2H_2F_4$ (T=1350 ⁰ K)	610	4800	2125
C_2HF_5 (T=1400 ⁰ K)	560	6000	2074
C_2F_6 (T=1450 ⁰ K)	950	16000	3770

* This pressure is calculated by using the Waage-Rabinovitch [45] approximation for the centrifugal effects.

6. Anharmonicity

When anharmonicity of vibrations is taken into account, the density of vibrational energy levels is increased, particularly at high energies. As a result of this increase there is a decrease in $k_a(E^*)$ and an increase in the value of k_{uni} . All the results including anharmonicity effects satisfy (Tables 5.97, 5.98, 5.99, 5.100) this expectation.

Two different values for the dissociation energy have been used in the anharmonicity calculations of the ethane molecule. D^* has been obtained from the tabulated anharmonicity constants whereas D is the mean of the dissociation energies calculated from the relationship of Hershbach and Laurie [85]. The disagreement between D and D^* is appreciable. The relation $D_e = h\nu/2x$ is valid only for a diatomic molecule so that the x of each vibration has been adjusted to fit an independent Morse oscillator. On the other hand, the Morse function may not be a particularly good representation even for a diatomic molecule. The big difference between D and D^* does not affect the calculated rates too much. The effect of anharmonicity on k_{uni} is less than a factor of two, so that the results are insensitive to even gross errors in D_e 's. The term $\exp(-E^+/kT)$ in the rate constant integral predominates at high energies even though the correction is appreciable. The small effect of anharmonicity in thermal reactions is due more to the smearing out effect of the thermal distribution of energies rather than to the small value of the anharmonic correction factor itself.

In the fall-off region anharmonicity is thought to cause decreased curvature of the fall-off plot relative to the harmonic case. Since while $N^*(E^*)$ increases $P(E^+)$ is much less affected, the net result would be a shift of the fall-off curve toward lower pressure.

TABLE 5.102- The Effect of Different Mean Dissociation Energies on the Rate Constants of Ethane (Model I)

	$D^* = 62.06 \text{ kcal mole}^{-1}$	$D = 43.69 \text{ kcal mole}^{-1}$
$k_a(E^+ + E_0)$	$0.7576 \times 10^9 \text{ sec}^{-1}$	$0.7576 \times 10^9 \text{ sec}^{-1}$
$k_a(E^+ + E_0)_{\text{anh}}$	$0.2546 \times 10^9 \text{ sec}^{-1}$	$0.1348 \times 10^9 \text{ sec}^{-1}$
$k_a(E^+ + E_0 + \langle \Delta E_J \rangle)$	$0.2740 \times 10^{10} \text{ sec}^{-1}$	$0.2740 \times 10^{10} \text{ sec}^{-1}$
$k_a(E^+ + E_0 + \langle \Delta E_J \rangle)_{\text{anh}}$	$0.1032 \times 10^{10} \text{ sec}^{-1}$	$0.5854 \times 10^9 \text{ sec}^{-1}$
k_{uni}	$2.7194 \times 10^{-5} \text{ sec}^{-1}$	$2.7194 \times 10^{-5} \text{ sec}^{-1}$
$k_{\text{uni}}(\text{anh})$	$2.9455 \times 10^{-5} \text{ sec}^{-1}$	$3.0290 \times 10^{-5} \text{ sec}^{-1}$
$k_{\text{uni}}(+\text{C.E.})$	$2.2943 \times 10^{-5} \text{ sec}^{-1}$	$2.2943 \times 10^{-5} \text{ sec}^{-1}$
$k_{\text{uni}}(+\text{C.E.})_{\text{anh}}$	$2.6433 \times 10^{-5} \text{ sec}^{-1}$	$2.8011 \times 10^{-5} \text{ sec}^{-1}$

* D^* is calculated from known anharmonicity constants. D is calculated using Herschbach and Laurie's approximation.

Gorin Model/Critical Configuration

The critical configuration provides an actual boundary between reactants and products. The RRKM theory assumes a transmission coefficient of unity. If the critical configuration is located in the reactant region there will be a kinematic equilibrium between reactants and the critical configuration, but there is no assurance that crossing the critical configuration toward products would lead to products. If the critical configuration is chosen in the product region, there will not be a kinematic equilibrium between reactants and critical configurations. Therefore, in choosing the critical configuration the two criteria of kinematic equilibrium and a transmission of unity should be fulfilled.

Since in this study the potential energy of the reaction coordinate is represented by a Morse function, the r^\ddagger value given by the criterion of minimum state density is less than the value given by the Gorin model at the rotational barrier. Choosing the critical configuration at the rotational barrier (Gorin model) located in the product region gives an overestimate of the unimolecular rate. In fact, the k_{uni} values calculated for Model I are higher than the ones calculated for Model II.

One of the results of the criterion of minimum state density is a prediction of both an internal energy and external rotational energy dependence on the critical configuration study. The dependence of R^\ddagger on both E^* and E_J^* is significant. As these energies are increased the value for R^\ddagger is decreased. The location of the bottle-neck in the molecular phase space is dependent on both energies E^* and E_J^* . In this work, the value of E^* , where the search for the minimum density is made, is chosen in such a way that it is an average of the total energies at which the integration is performed. A fit to a rate constant does not provide a unique critical configuration which may be used for rate calculations at all energies.

On the other hand, the free rotor postulated in Model I has an increased value of $N^*(E^*)$ at all energies, thereby decreasing the specific rate constant $k_a(E^*)$ and increasing k_{uni} .

Although E. Tschuikow-Roux and coworkers have dealt with the experimental decomposition of fluoroethanes, a complete theoretical treatment of the carbon-carbon bond fission in these molecules has not been given before. Both the effects of adiabatic rotations and anharmonicity

of vibrations together on the rate constant have been taken into account. Furthermore, the results obtained in this dissertation allow us to compare the two different Models applied to the critical configuration for an RRKM treatment as well as the relative behaviour of the above mentioned molecules at different pressures. The fact that the results obtained with the Gorin Model are higher than those obtained by the minimization of the number of states and the experimental ones, should not exclude completely the use of the Gorin Model for a loose transition state since it permits an estimation of the rate constant.

APPENDIX I

APPENDIX I

THE GAMMA FUNCTION $\Gamma(n)$

The gamma function $\Gamma(n)$ is defined, for $n > 0$, by the integral;

$$\Gamma(n) = \int_{x=0}^{\infty} x^{n-1} \exp(-x) dx \quad (n > 0)$$

n is restricted in this work to positive integral or half-integral values.

$$\Gamma(n + 1) = n\Gamma(n)$$

$$\Gamma(1) = 1$$

$$\Gamma(1/2) = \sqrt{\pi}$$

If n is integral,

$$\Gamma(n) = (n - 1)\Gamma(n - 1)$$

$$= (n - 1)!$$

If n is half-integral

$$\Gamma(n) = (n - 1)(n - 2) \dots 5/2, 3/2, 1/2, \Gamma(1/2).$$

APPENDIX II

EVALUATION OF $k_a(E^*)$ and k_{uni}

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TRKM PROGRAM CODED BY W.L. HASE AND D.L. BUNKER (OCPE 234) AND
MODIFIED BY V. AVITYENTE FOR C2H2F4
ARRAYS OF INFORMATION READ IN
WH* FREQUENCIES IN MOLECULE
TRM* REDUCED MOMENTS OF INERTIA IN MOLECULE
SYMM* SYMMETRY NUMBERS FOR INTERNAL ROTORS IN MOLECULE
TM* PRINCIPAL MOMENTS OF INERTIA FOR MOLECULE
TC* PRINCIPAL MOMENTS OF INERTIA FOR MOLECULE
WC* FREQUENCIES IN THE CRIT. CONFIG.
TRC* REDUCED MOMENTS OF INERTIA FOR CRIT. CONFIG.
SYMC* SYMMETRY NUMBERS FOR INTERNAL ROTORS IN CRIT. CONFIG.
ARRAYS READ IN FOR DETERMINING THE CRIT. CONFIG. BY MINIMUM STATE
DENSITY
WCC(I,J)* FREQUENCY CHANGES AS R+ INCREASES, I IS THE NUMBER OF
MODES WHICH VARY WITH R+. J IS THE NUMBER OF REACTION
COORDINATE INTERVALS+1.
TRCC(I,J)* REDUCED MOMENTS OF INERTIA AS R+ INCREASES, I IS THE
NUMBER OF REDUCED MOMENTS OF INERTIA WHICH VARY WITH R+
J AS BEFORE
TCC(I,J)* PRINCIPAL MOMENTS OF INERTIA CHANGES AS R+ IS INCREASED,
I AND J AS BEFORE, MAXIMUM VALUE FOR I IS 3.
VRDAG* VALUES OF POTENTIAL ENERGY OF CRITICAL COORDINATE
ARRAYS PRODUCED BY THE MAIN PROGRAM

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SUMM* SUMS OF VIBRATIONAL-INTERNAL ROTATIONAL STATES
DENN* DENSITIES OF VIBRATIONAL-INTERNAL ROTATIONAL STATES
CH* ANHARMONIC CORRECTION FACTOR FOR DENSITY OF STATES
CC* ANHARMONIC CORRECTION FACTOR FOR SUM OF STATES
RDAG* VALUES OF CRITICAL COORDINATE
RK* RATE CONSTANT FOR THE FORMATION OF ACTIVATED COMPLEXES
FROM ENERGIZED MOLECULES WITH NON-FIXED ENERGY E*
RKU* THE VALUE OF THE INTEGRAL IN THE OVERALL FIRST ORDER
RATE CONSTANT KUNI (SEE P. J. ROBINSON AND K.A. HOLBROOK,
'UNIMOLECULAR REACTIONS', WILEY-INTERSCIENCE, NEW YORK,
1972)
RKAN* SAME AS RK WITH ANHARMONIC CORRECTION
RKUAN* SAME AS RKU WITH ANHARMONIC CORRECTION

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IF CENTRIFUGAL EFFECTS ARE INCLUDED CEF=1, IF NOT CEF=0

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DIMENSION TH(3), TC(3), TRC(3), RK(2000), VRDAG(100), RDAG(100), EROT(3)
DIMENSION SYMC(5), TRM(3), SYMM(3), SUMM(2000), WH(50), WC(50)
DIMENSION DENN(2000), CH(2000), CC(2000), RKUAN(2000)
DIMENSION WCC(5,50), TRCC(3,50), TCC(3,50), RKU(2000), RKAN(2000)

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1 FORMAT(3F10,3I5,F10.0)
2 FORMAT(9F6.2)
3 FORMAT(9F6.3)
4 FORMAT(//,'ZERO=',F7.2,'KCAL/MOLE ESTAR=',F7.2,'KCAL/MOLE
* EINC=',F6.2,'KCAL/MOLE REACTION PATH DEGENERACY=',F4.1,/,',RATE
* CONSTANTS TO BE CALCULATED',I5)
5 FORMAT(7I10)
6 FORMAT(7F10.0)
7 FORMAT(7F10.3)
8 FORMAT(I20,I25)
9 FORMAT(78F12.1)
10 FORMAT(//,'OVERALL FIRST ORDER RATE CONSTANT=',E10.4,'OVERALL
* FIRST ORDER RATE CONSTANT WITH ANHARMONIC CORRECTION=',E10.4)
11 FORMAT(//,'REDUCED MOMENT OF INERTIA=',E8.3,5X,'SYMMETRY NUMBER=',F
*4.1/)
12 FORMAT(9F6.2)
15 FORMAT(//,'FREQUENCIES IN MOLECULE',/)
16 FORMAT(//,'MOMENTS OF INERTIA FOR MOLECULE',/3F12.3///)
17 FORMAT(//,'NUMBER OF OSCILLATORS IN MOLECULE NUMBER OF INTERNAL
* ROTORS IN MOLECULE',/)
18 FORMAT(//,'MOMENTS OF INERTIA FOR COMPLEX',/3F12.3///)
19 FORMAT(//,'NUMBER OF OSCILLATORS IN COMPLEX NUMBER OF INTERNAL ROT
* ORS IN COMPLEX',/)
20 FORMAT(//,'FREQUENCIES IN COMPLEX',/)
21 FORMAT(//,'SYMMETRY NUMBER IN COMPLEX',/)
22 FORMAT(//,'REDUCED MOMENT IN COMPLEX',/)
23 FORMAT(//,'REDUCED MOMENT IN MOLECULE',/F9.3)
28 FORMAT(//,'ANHARMONIC CORRECTION FOR MOLECULES AVERAGE BOND ENERGY
* ',F7.2,'KCAL/MOLE',/)
29 FORMAT(//,'ANHARMONIC CORRECTION FOR COMPLEX AVERAGE BOND ENERGY
* ',F7.2,'KCAL/MOLE',/)
30 FORMAT(//,'SYMMETRY NUMBER IN MOLECULE',/)
31 FORMAT(//,'TEMP=',F10.0,'KELVIN',/)
35 FORMAT(1HU,'ESTAR',14X,'RDAG',13X,'HARMONIC',10X,'ANHARMONIC',11X,
* 'HARMONIC',11X,'ANHARMONIC',7X,'ANHARMONIC',3X,'ANHARMONIC')
35 FORMAT(1HU,'KCAL/MOLE',10X,'KCAL/MOLE',7X,'DENSITY',13X,'SUM',
* 15X,'K(E*)',15X,'KUNI',10X,'K(E*)',5Y,'KUNI',1
37 FORMAT(1H,F7.2,F19.2,E18.4,E18.4,2F20.4,2E13.4)
38 FORMAT(//,'TM PRIN MOMENT OF INERTIA=',3F10.3)
39 FORMAT(//,'STRUCTURE OF CRITICAL CONFIGURATION IS CALCULATED USING
* THE CRITERION OF MINIMUM STATE DENSITY',/,'VIBRATION ENERGY OF AC
* TIVATED MOLECULE=',F7.2,'KCAL/MOLE',13X,'NUMBER OF REACTION COOR
* DINATE INTERVALS=',I3)
40 FORMAT(1H,F25.2,25X,F20.2)
41 FORMAT(//,'ROTATIONAL ENERGY IN COO,1=',F5.3,'KCAL/MOLE',/,'ROTAT
* IONAL ENERGY IN COO,2=',F6.3,'KCAL/MOLE',/,'ROTATIONAL ENERGY IN
* COO,3=',F6.3)
42 FORMAT(1H,I,J,Y,'VALUE OF REACTION COO=',10X,'POTENTIAL EN. OF REAC
* TION COO=',10X,'KCAL/MOLE')
43 FORMAT(1H,'A MIN WAS NOT FOUND')
44 FORMAT(1H,'A MIN WAS FOUND')
45 FORMAT(1H,'REAC. COO=',F7.3,10X,'ZERO=',F7.3,'KCAL/MOLE')
46 FORMAT(//,'WCC=VIB FREQ CHANGING WITH R+',/)
47 FORMAT(//,'TC=PRIN MOMENT OF INERTIA=',3F10.3)
49 FORMAT(//,'TCC=PRIN MOM OF INERTIA CHANGING WITH R+',/)

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104 40 FORMAT(//,'TPCC=PLD MOMENT OF INERTIA CHANGING WITH D+',/)
105 51 FORMAT(5F12.0)
106 52 FORMAT(//,'PCSSURF=',1E10,'4','THE COLLISION NUMBER =',1E10,'4)
107 1000 READ(5,1)EZERO,ESTAR,INC,NEN,SIGMA
108 WRITE(6,4)EZERO,ESTAR,INC,SIGMA,NEN
109 KT=0.0
110 XKTD=0.0
111 COM1=J.3736E-10
112 READ(5,5)NSM,NRM
113 READ(5,6)(NM(I),I=1,NSM)
114 READ(5,7)(TM(I),I=1,3)
115 READ(5,7)(TRM(I),I=1,3)
116 READ(5,6)(SYMM(I),I=1,NRM)
117 WRITE(6,17)
118 WRITE(6,8)NSM,NRM
119 WRITE(6,15)
120 WRITE(6,9)(NM(I),I=1,NSM)
121 WRITE(6,38)(TM(I),I=1,3)
122 WRITE(6,23)(TRM(I),I=1,3)
123 WRITE(6,10)
124 READ(5,6)(SYMM(I),I=1,NRM)
125 READ(5,5)NSC,NPC
126 READ(5,6)(WC(I),I=1,NSC)
127 READ(5,6)TEMP
128 READ(5,6)(SYMC(I),I=1,NPC)
129 READ(5,7)(TRC(I),I=1,NPC)
130 READ(5,5)P,Z
131 WRITE(6,19)
132 WRITE(6,8)NSC,NRC
133 WRITE(6,20)
134 WRITE(6,9)(WC(I),I=1,NSC)
135 WRITE(6,21)
136 WRITE(6,6)(SYMC(I),I=1,NPC)
137 WRITE(6,22)
138 WRITE(6,7)(TRC(I),I=1,NRC)
139 WRITE(6,31)TEMP
140 WRITE(6,52)CEF
141 READ(5,1)RDAGI,RDAGF,ECC,NN
142 ANN=4
143 READ(5,7)(VRDAG(I),I=1,M)
144 ANN=FLOAT(NN)
145 DELRD=(RDAGF-RDAGI)/ANN
146 RDAGI1=RDAGI
147 DO 58 I=2,M
148 RDAG(I)=RDAG(I-1)+DELRD
149 PRINT 39,ECC,NN
150 READ(5,2)DAM,DAC
151 WRITE(6,28)DAM
152 WRITE(6,29)DAC
153 WRITE(6,51)P,Z
154 PRINT 42
155 DO 60 I=1,M
156 PRINT 40,RDAG(I),VRDAG(I)
157 JJ=0
158 IF(WC(NSC).GT.0) GO TO 66
159 I=1
160 IF(WC(I).LT.0) GO TO 64.
161 I=I+1
162 GO TO 63
163 JJ=NSC-I+1
164 DO 65 J=1,JJ
165 READ(5,2)(WCC(J,I),I=1,M)
166 KK=0
167 IF(NPC.EC.0) GO TO 70
168 IF(TRC(NPC).GT.0) GO TO 70
169 I=1
170 IF(TRC(I).LT.0) GO TO 68
171 I=I+1
172 GO TO 67
173 KK=NRC-I+1
174 DO 69 J=1,KK
175 READ(5,7)(TRCC(J,I),I=1,M)
176 LL=0
177 READ(5,7)(TC(I),I=1,3)
178 WRITE(6,47)(TC(I),I=1,3)
179 IF(TC(3).GT.0) GO TO 95
180 I=1
181 IF(TC(I).LT.0) GO TO 72
182 I=I+1
183 GO TO 71
184 LL=3-I+1
185 DO 73 J=1,LL
186 READ(5,12)(TCC(J,I),I=1,M)
187 WRITE(6,46)
188 DO 100 J=1,JJ
189 PRINT 2,(WCC(J,I),I=1,M)
190 WRITE(6,48)
191 DO 101 J=1,LL
192 WRITE(6,12)(TCC(J,I),I=1,M)
193 WRITE(6,49)
194 DO 102 J=1,KK
195 WRITE(6,21)(TRCC(J,I),I=1,M)
196 CALL CDETR(NSC,NPC,WCC,JC,WCC,TRC,SYMC,KK,TRCC,TC,LL,TCC,ECC,NN,
197 *RDAG,VRDAG,DELRD,EPOT,EZERO,JOKER,RDAGS,TM,DAC)
198 IF(JOKER.EC.0) GO TO 75
199 WRITE(6,43)
200 GO TO 77
201 75 WRITE(6,44)
202 77 WRITE(6,45)RDAG,EZERO
203 95 IF(CEF.EQ.1.0) GO TO 78
204 DELEJ='0'

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08 30 TO 79
09 DELEJ = (1.987*TEMP/1000)*(1.0 - (TC(1)/TM(1)*TC(2)/TM(2)*TC(3)/TM(3)
10 *1**J.5)+1.5
11
12 79 EDAG = (ESTAR - EZERO + DELEJ)*(0.5)
13 IF (EDAG, LE, 0.) GO TO 107
14
15 A=0
16 AK=D.0
17 DO 89 I=1, NEN
18 CALL WRSEMI(NSM, NRM, WM, TRM, SYMM, F, K, AK, DEN)
19 DEN(I)=DEN
20
21 89 E=E+INC
22 EDAG
23 A=1
24 AK=D.0
25 DO 97 I=1, NEN
26 CALL WRSEMI(NSC, NRC, WC, TRC, SYMC, E, K, AK, SUM)
27 SUM(I)=SUM
28
29 E=E+INC
30 EDAG
31 A=1
32 DO 103 I=1, NEN
33 CALL ANHARM(NSM, NRM, WM, DAM, K, E, C)
34 CH(I)=C
35
36 103 E=E+INC
37 EDAG
38 A=1
39 DO 104 I=1, NEN
40 CALL ANHARM(NSC, NRC, WC, DAC, K, E, C)
41 CC(I)=C
42
43 104 E=E+INC
44 WRITE(6, 35)
45 WRITE(6, 36)
46 DO 106 I=1, NEN
47 RK(I) = SIGMA * SUMH(I) / DEN(I) / CON1
48 RKU(I) = (SUMH(I) * EXP(-EDAG / (0.001987 * TEMP))) / (1. + ((RK(I) / Z / P)))
49 RKAN(I) = PK(I) * CC(I) / CH(I)
50 RKUAN(I) = (SUMH(I) * EXP(-EDAG / (0.001987 * TEMP))) / (1. + ((PKAN(I) / Z / P)))
51 WRITE(6, 37) ESTAR, EDAG, DEN(I), SUMH(I), RK(I), PKU(I), RKAN(I), RKUAN(I)
52
53 SUMH(I) = SUMH(I) * CC(I)
54 DEN(I) = DEN(I) * CH(I)
55 ESTAP = ESTAP + EINC
56 106 EDAG = EDAG + EINC
57 DO 110 I=1, NFN
58 RKTD = RKTD + (RKUAN(I) / 1000000.)
59 RKT = RKT + (RKU(I) / 1000000.)
60 WRITE(6, 10) RKT, RKTD
61 GO TO 999
62
63 107 ESTAR = ESTAR + EINC
64 GO TO 95
65
66 999 STOP
67
68 END

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263 C SUBROUTINE WOSEMI(NS,NR,W,TR,SYM,E,K,AK,DS)
264 SAGINOVITCH SEMI CLASSICAL TECHNIQUE
265 DIMENSION W(SU),TR(S),SYM(S)
266 PFR=1.0
267 R=FLOAT(NR)
268 S=FLOAT(NS)
269 EN=E*349.8
270 IF(INP.EQ.0) GO TO 2
271 C CALCULATE PART.FUNC.FOR INT.ROTOPS/(KT)**R/2
272 DO 1 I=1,NP
273 PFIR=0.4316*(TR(I))*U.5/SYM(I)
274 PFR=PFR*PFIR
275 C CALCULATE B
276 SWS=0.0
277 SWS=0.0
278 DO 3 I=1,NS
279 SWS=SWS+W(I)*W(I)
280 SWS=SW+W(I)
281 SWS=SW**2
282 C BETA=(S-1.0)*(S+R/2.0)/S*SWS/SSW
283 CALCULATE ZERO POINT ENERGY
284 EZ=0.0
285 DO 4 I=1,NS
286 EZ=EZ+W(I)/2.0
287 C CALCULATION OF GAMMA FUNCTIONS
288 NRT=(NP/2)*2
289 IF(NR-NRT)5,5,7
290 NDUM=NS+NR/2
291 GAMA=0.0
292 DO 6 I=1,NDUM
293 GAMA=GAMA+ALOG10(FLOAT(I))
294 GO TO 9
295 7 VZ=NS+NR/2+1
296 GAMAT=0.0
297 MAX=2*NZ
298 DO 8 I=1,MAX,2
299 GAMAT=GAMAT+ALOG10(FLOAT(I))
300 GAMA=GAMAT+ALOG10(1.7725/2.0**NZ)
301 C CALCULATION OF PRODUCT OF FREQUENCIES
302 APRD=0.0
303 DO 10 I=1,NS
304 APRD=APRD+ALOG10(W(I))
305 IF(K.EQ.0) GO TO 14
306 XP=S+R/2.0-AK
307 EP4=EN/EZ
308 IF(EP4=1.0)1,12,12
309 W=-1.0/(5.0*EP4+2.73*EP4**0.5+3.51)
310 GO TO 13
311 XXX=-1.0506*EP4**0.25+2.3026
312 W=EXP(XXX)
313 AA=1.0-BETA*W
314 ASU=ALOG10(PFR)*GAMA-APRD+(XP*ALOG10(EN+AA*EZ))
315 JS=10.0**ASU
316 GO TO 18
317 C CALCULATION OF DENSITY
318 XP=S+R/2.0-1.0
319 EP4=EN/EZ
320 IF(EP4=1.0)15,16,16
321 JPPER=-1.0*(5.0/EZ+0.5*2.73/EN**0.5/EZ**0.5)
322 DENOM=(5.0*EP4+2.73*EP4**0.5+3.51)**2.0
323 DELW=UPPER/DENOM
324 W=-1.0/(5.0*EP4+2.73*EP4**0.5+3.51)
325 GO TO 17
326 JPPER=-1.0506+0.25/EN**0.75+2.3026
327 DENOM=EZ**0.25
328 XXX=-1.0506*EP4**0.25+2.3026
329 DELW=UPPER/DENOM*EXP(XXX)
330 W=EXP(XXX)
331 AA=1.0-BETA*W
332 ADUM=ALOG10(PFR)+ALOG10(S+R/2.0)-GAMA-APRD
333 ADEN=ADUM+(XP*ALOG10(EN+AA*EZ))+ALOG10(1.0-EZ*BETA*DELW)
334 JS=10.0**ADEN
335 18 RETURN
336 END

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337- SUBROUTINE CCDETR(NSC,NRC,WC,JJ,WCC,TRC,SYMC,KK,TRCC,TC,LL,TCC,ECC
338- ,NN,PDAG,VRDAS,DELRO,EROT,EZERO,JOKE,PDAS,TD,DAC)
339- DIMENSION WC(50),WCC(5,5),TRCC(5,5),SYMC(5),TRCC(3,5),VRDAG(30),RDA
340- *C(2),TRCC(2),C1TRCC(2),C2TRCC(2),C3WCC(5),C2WCC(5),C1WCC(5),C1TRCC(2),
341- *C2TRCC(2),C2WCC(5),C1WCC(5)
342- *THE FLAGGED FREQUENCIES DIM IS 5
343- *FITTING THE FLAGGED REDUCED CONSTANTS IN THE QUADRATIC EQ.FOR
344- *DIMENSION IS SET FOR A MAX.OF 2 FLAGGED REDUCED MOMENTS OF INERTIA
345- *C1TRCC,C2TRCC,C1WCC THE CONSTANTS IN THE QUADRATIC EQ.FOR FITTING
346- *DIMENSION IS SET FOR A MAX.OF 2 FLAGGED REDUCED MOMENTS OF INERTIA
347- *C2TRCC,C2TCC,C1TCC THE CONSTANTS IN THE QUADRATIC EQ.FOR FITTING
348- *TCC(I,J) *PRINCIPAL MOMENTS OF INERTIA, DIM IS SET TO 3
349- *VRDAG * VALUES OF POTENTIAL ENERGY OF CRITICAL CO-ORDINATE
350- *EROT * ROTATIONAL ENERGY IN X,Y,Z CO-ORDINATES FOR DETERMINING THE
351- *ERTVIB=U.O
352- *KDUH=NN+1
353- *MARKER=0
354- *JOKER=0
355- *
356- 99 DO 8 K=1,KDUH
357- IF (JJ.EQ.0) GO TO 2
358- DO 1 I=1,JJ
359- L=NSC-JJ+1
360- 1 C(L)=WCC(I,K)
361- 2 IF (KK.EQ.0) GO TO 4
362- DO 3 I=1,KK
363- 3 W=NRC-KK+1
364- TRC(M)=TRCC(I,K)
365- 4 IF (LL.EQ.0) GO TO 6
366- DO 5 I=1,LL
367- 5 V=3-LL+I
368- TC(N)=TCC(I,K)
369- IF ((TH(1)-N,00005).GT.0,0) GO TO 33
370- TH(1)=1.0
371- TC(1)=1.0
372- IF (CEF.LT.1,0) GO TO 7
373- 33 ERTVIB=(1.287*TEMP/1000)*1.70*(TC(1)/TH(1)+TC(2)/TH(2)+TC(3)/TH(3)
374- *1)**0.5
375- 7 E=ECC*VRDAG(K)+ERTVIB
376- JAN=1
377- AK=0.5
378- CALL WRSEMI(NSC,NRC,WC,TRC,SYMC,E,JAN,AK,DEN)
379- DENN(K)=DEN
380- JAN=0
381- CALL ANHARM(NSC,NRC,WC,DAC,JAN,E,C)
382- DENN(K)=DENN(K)*C
383- 8 CONTINUE
384- 4=1
385- DO 9 K=2,KDUH
386- IF (DENN(K).GT.DENN(4)) GO TO 9
387- 4=K
388- 9 CONTINUE
389- IF (MARKER.EQ.1) GO TO 24
390- IF (M.EQ.1) GO TO 23
391- IF (M.EQ.KDUH) GO TO 23
392- 4=M
393- DENOM=PDAG(K+1)**2-J**2-U*RDAS(K)**2-V*RDAS(K-1)**2-U
394- UPPER=RDAG(K+1)**2-U*RDAG(K)**2,0
395- C3=(VRDAG(K+1)-2*VRDAG(K)+VRDAG(K-1))/DENOM
396- C2=(VRDAG(K+1)-VRDAG(K)-C3*UPPER)/DELRO
397- C1=VRDAG(K-1)-C2*RDAG(K-1)-C3*PDAG(K-1)**2-U
398- IF (JJ.EQ.0) GO TO 11
399- DO 10 I=1,JJ
400- C3WCC(I)=WCC(I,K+1)-2*WCC(I,K)+WCC(I,K-1)/DENOM
401- C2WCC(I)=(WCC(I,K+1)-WCC(I,K)-C3WCC(I)*UPPER)/DELRO
402- C1WCC(I)=WCC(I,K-1)-C2WCC(I)*RDAG(K-1)-C3WCC(I)*RDAG(K-1)**2-U
403- 10 IF (KK.EQ.0) GO TO 13
404- DO 12 I=1,KK
405- C3TRCC(I)=(TRCC(I,K+1)-2*TRCC(I,K)+TRCC(I,K-1))/DENOM
406- C2TRCC(I)=(TRCC(I,K+1)-TRCC(I,K)-C3TRCC(I)*UPPER)/DELRO
407- C1TRCC(I)=TRCC(I,K-1)-C2TRCC(I)*PDAG(K-1)-C3TRCC(I)*RDAG(K-1)**2-U
408- 12 IF (LL.EQ.0) GO TO 15
409- DO 14 I=1,LL
410- C3TCC(I)=(TCC(I,K+1)-2*TCC(I,K)+TCC(I,K-1))/DENOM
411- C2TCC(I)=(TCC(I,K+1)-TCC(I,K)-C3TCC(I)*UPPER)/DELRO
412- C1TCC(I)=TCC(I,K-1)-C2TCC(I)*RDAG(K-1)-C3TCC(I)*RDAG(K-1)**2-U
413- 14 DELRO=DELRO/10.0
414- RDAG(I)=PDAG(K-1)
415- VRDAG(I)=VRDAG(K-1)
416- DO 16 I=2,21
417- RDAG(I)=PDAG(I-1)+DELRO
418- 16 VRDAG(I)=C1+C2*RDAG(I)+C3*RDAG(I)**2-U
419- IF (JJ.EQ.0) GO TO 19
420- DO 17 I=1,JJ
421- DO 17 J=1,21
422- WCC(I,J)=C1WCC(I)+C2WCC(I)*RDAG(J)+C3WCC(I)*RDAG(J)**2-U
423- 17 IF (KK.EQ.0) GO TO 20
424- DO 19 I=1,KK
425- DO 19 J=1,21
426- 19 TRCC(I,J)=C1TRCC(I)+C2TRCC(I)*PDAG(J)+C3TRCC(I)*PDAG(J)**2-U
427- 20 IF (LL.EQ.0) GO TO 22
428- DO 21 I=1,LL
429- DO 21 J=1,21
430- 21 TCC(I,J)=C1TCC(I)+C2TCC(I)*RDAG(J)+C3TCC(I)*RDAG(J)**2-U
431- 22 KDUH=21
432- MARKER=1
433- GO TO 99
434- 23 JOKER=1
435- 24 4=M
436- IF (JJ.EQ.0) GO TO 25
437- DO 25 I=1,JJ
438- L=NSC-JJ+1
439- 25 WC(L)=WCC(I,K)
440- 26 IF (KK.EQ.0) GO TO 28
441- DO 27 I=1,KK
442- 27 W=NRC-KK+1
443- TRC(M)=TRCC(I,K)
444- 28 IF (LL.EQ.0) GO TO 30
445- DO 29 I=1,LL
446- 29 V=3-LL+I
447- TC(N)=TCC(I,K)
448- EZERO=VRDAG(K)
449- PDAGG=PDAG(K)
450- RETURN
451- END

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.CIT.CON

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452 SUBROUTINE ANHARM(INS,NR,W,DA,K,E,C)
453 DIMENSION W(E,C)
454 S=FLOAT(NS)
455 AK=FLOAT(K)
456 EN=E*349.8
457 J=DA*349.8
458 AN=S*AK-1.0+R/2.0
459 EZ=U*0
460 DO 1 I=1,NS
461 EZ=EZ+W(I)/2.0
462 EPH=EN/EZ
463 SW=U*U
464 SWS=N*0
465 DO 2 I=1,NS
466 SWS=SWS+W(I)*W(I)
467 SW=SW+W(I)
468 AM=(SWS/S1)/(SW/S)**2.0
469 AM2=S*(4.0*S+2.5*(R+2.0*AK))/(R.0*(AN+1.0)**2.0*(AN+2.0))
470 AM3=S*(24.0*S**2.0+29.5*S*(R+2.0*AK)+9.25*(R+2.0*AK)**2.0)/(24.0*(
471 *AN+1.0)**3.0*(AN+2.0)*(AN+3.0))
472 F1=(1.0+2.0/EPH)**1*(EPH/2.0)**1*(1.0+EPH/2.0)
473 F2=EXP(-1.0)/(3.0*(1.0*EPH))
474 F3=(F1*F2)**(S*EZ/((AN+1.0)*0))
475 F4=AM2*(1.0*EPH)**2.0*(EZ/D)**2.0
476 F5=AM3*(1.0*EPH)**3.0*(EZ/D)**3.0
477 C=F3*EXP(F4+F5)
478 RETURN
479 END
480

```

EVALUATION OF k_{uni}/k_{∞}

```

1* REAL K,M
2* CCCCCC
3* DETERMINATION OF THE FALL-OFF REGION
4* CALCULATION OF THE INTEGRAL FOR KUNT/KINF ACCORDING TO E.TSCHITKOW
5* HOIX, J. CHEM. PHYS. 49, 1115 (1969)
6* THIS PROGRAM IS CODED BY T.L. ISENHOUR, T.L. ISENHOUR, INTRODUCTION
7* TO COMPUTED PROGRAMMING, ALLYN AND BACON, INC., BOSTON, 1972.)
8* AND MODIFIED BY V. AVTYATE
9* THE EXPRESSION FOR THE INTEGRAND CHANGES ACCORDING TO THE LIMITS
10* CONSIDERED.
11* INTEGRAL I IS EVALUATED BETWEEN 0 AND THETA
12* INTEGRAL II IS EVALUATED BETWEEN THETA AND 1
13* INTEGRAL III IS EVALUATED BETWEEN 1 AND 2
14* THETA* (MINIMUM FREQUENCY OF THE COMPLEX)/FZ
15* K* THE PRESSURE AT WHICH THE INTEGRAL IS EVALUATED
16*
17* C
18* INTEGRAL FOR CASE I WITHOUT C.E.
19* FUNC(Z7,K) = (EXP(-22.41*Z7)*Z7**0.5)/(1+(1.070300F6/K)*Z7**0.5)/(1
20* *Z7+3.3291**17))
21*
22* DIMENSION M(20)
23* I=0
24* READ(5,30) (V(I), I=1,11)
25* READ(5,9) X1, X2, N, ACC
26* 3 I=I+1
27* N=N
28* K=M(I)
29* WRITE(6,19) X1, X2, N, ACC, K
30* FA=0.0
31* CON=FUNC(X1,K)+FUNC(X2,K)
32* 2 DX=(X2-X1)/FLOCAT(N)
33* SUM1=0.
34* SUM2=0.
35* L=N/2-1
36* X=X1
37* DO 10 I=1,L
38* X=X+DX
39* SUM1=SUM1+FUNC(X,K)
40* X=X+DX
41* 10 SUM2=SUM2+FUNC(X,K)
42* F=(CON+4.*SUM1+2.*SUM2)*DX/3
43* WRITE(6,29) N, F
44* IF (ABS(F-FA)-ACC*ABS(FA)) 13,13,12
45* 12 N=2*N
46* FA=F
47* GO TO 2
48* 13 CONTINUE
49* 9 FORMAT(2F10.4,110,F10.3)
50* 10 FORMAT(///,2F10.4,110,1PE15.4,1E5.0)
29* 16 FORMAT(, ,110,1F15.5)
30* 30 FORMAT(11E5.0)
31* IF(I,GT,11) GO TO 4
32* GO TO 3
33* 4 STOP
34* END
56*

```

Introduction

Gas

propene

1959

of

pressure

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