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T H E O R E T I C A L A S P E C T S O F

U N I M O L E C U L A R G A S R E A C T I O N S

by

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PREFACE

The theory of unimolecular gas reactions is of interest because of its intimate connection with the fundamental problems of inter- and intramolecular energy transfer as well as the other basic principles of chemistry. In the past, several theories varying in their degree of empiricism have been advanced but the most rigorous and detailed is the recent treatment by N. B. Slater in which calculations are based upon the normal coordinates of vibration of the reacting molecule. However, prior to the present work there had been very few test cases for the Slater theory (only one in complete detail) owing to the fact that only a small number of molecules exhibited unimolecular behaviour and at the same time were simple enough for the necessary vibrational analysis. With the appearance of more kinetic and spectroscopic data as well as the development of more powerful mathematical methods of analysis, it has been possible to apply the Slater theory, either rigorously or in an approximate fashion, to about five new reactions. Comparison of these calculations with experiment along with a similar comparison based upon the older theories has afforded a critical evaluation of the respective models assumed and indicated the postulates necessary for an ultimately satisfactory theory.

Much of the work contained here, with the exception of the chapter on ethyl chloride, has already been published by the author and his research director (1)(2)(3)(4). The thesis standardizes the notation and mathematical approach used in the various reactions under consideration and then discusses the Slater and older theories in the light of the collective results of all previous calculations.

The author is greatly indebted to Dr. H. J. Bernstein of the National Research Council for his advice and constant readiness to discuss and assist with the problems of normal mode analysis.

Throughout the course of the work, Dr. N. B. Slater of Leeds University has provided many valuable suggestions which are gratefully acknowledged. Thanks are also due to Dr. G. Herzberg and Dr. D. A. Ramsay, both of the National Research Council, for discussions which have served to deepen the author's understanding of vibrational spectroscopy. His sincere gratitude must further be conveyed to the entire staff of the Computing Centre at the University of Ottawa without whose assistance the calculations by digital computer could not have been begun, while more recently Dr. S. Baxter and his staff at the N.R.C. Structures Laboratory have been unstinting with their time and efforts devoted to the solution of the matrix problem by Ferranti computer. These studies were made possible financially by the National

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Finally, the author owes his most profound debt of thanks to his teacher and research supervisor, Prof. K. J. Laidler, whose unremitting encouragement and inexhaustible patience during periods of difficulty were the determining factors in bringing this work to conclusion.

C O N T E N T S

TABLES

FIGURES

A B S T R A C T

A brief review is made of the various older theories of unimolecular reactions and then the present situation is examined with particular attention to the theory of N. B. Slater. The assumptions implicit in the different reaction models are made clear and the model of Hinshelwood, Kassel, Rice and Ramsperger (HKRR) is contrasted with that of Slater. Molecular vibration theory is sketched and it is shown how the Wilson FG matrix method may be conveniently adapted to the calculation of the Slater parameters.

Both the HKRR and Slater theories are tested on the experimental data for the decompositions of N_2O, O_3, H_2O_2, CH_3CH_2Cl and more approximately in the case of N_2O_5 and C_2H_6. Slater's calculations on the isomerization of cyclopropane are discussed. From the results of these calculations certain deductions are made regarding the nature of a reacting species and especially the possibilities for energy transfer between normal modes. At the same time, a number of inadequacies in the Slater theory, hitherto not appreciated, have become evident and these lead to a critical evaluation of the entire theory.

Through the use of an electronic computer in the ethyl chloride calculations there has evolved a systematic approach to the standard problem of adjusting potential constants to produce a desired set of frequencies. Certain considerations in the choice of program and the form in which the problem is submitted to the computer have become apparent and are fully discussed.

GLOSSARY OF SYMBOLS

A	General molecule undergoing reaction
A^*	Molecule with sufficient energy to react
$A^\ddagger$	Activated complex
$[A]$	Concentration of the species A
A_k	Amplitude factor doefficient. See [26] and [104] (Slater)
a_{ij}	Coefficient of kinetic energy. See [66]
$[B]$	Matrix of elements B_{ij}
$[B]'$	Transpose of [B]
$[B]^{-1}$	Inverse of [B]
$\|B\|$	Determinant of elements B_{ij}
$[B_h]$	See [203]
b	$\epsilon^*/kT = E_o/RT$. See [10]
b_{ij}	Coefficient of potential energy. See [64]
D , d	Molecular bond distances
d_k	Generalized internal coordinate. See a[99].
$[E]$	Unit matrix
E_a	Experimental activation energy.
E_o	High-pressure activation energy. See [60] et seq.
exp	Exponential
$[F]$	Potential energy matrix in symmetry coordinates. Elements F_{jl} . See [76].
$[f]$	Potential energy matrix in internal coordinates. Elements f_{ik} . See [75].
f_n	Generalized potential energy force constant in internal coordinates. See [203].
$[G]$	Inverse kinetic energy matrix in symmetry coordinates. Elements G_{jl} . See [78]
$[g]$	Inverse kinetic energy matrix in internal coordinates. Elements g_{ik} . See [82]
$[H]$	$[G][F]$. See [180].
$I_n(\theta)$	See [34]. (Slater).
$[J]$	Jacobian matrix of elements J_{ah} . See [207]
K^1	First-order rate coefficient. See [5].
$k_1, k_{-1}, k_2, k_{-2}, k$	Rate constants as defined on pages 19 and 22.

$k^{\ddagger}$	Kassel frequency factor. See [14] and [15].
k_{∞}	Second-order, high-pressure frequency factor. See [3].
k	Boltzmann constant
L	Specific dissociation probability. See [28] et seq. (Slater)
[L]	Matrix of transformation from symmetry to normal coordinates. See [90].
$[L_a]$	a-th column of [L] or a-th eigenvector of [GF]. See [92].
[l]	Matrix of transformation from internal to normal coordinates. [r] = [l][Q] .
$[l_a]$	a-th column of [l]. See [97].
M	Molecular weight
m	Number of internal coordinates in molecule
N	Number of atoms in molecule; Avogadro's number
n	Number of vibrational degrees of freedom in molecule; number of modes contributing to the critical coordinate (Slater).
P	Pressure; critical distance in molecule. See [100]. (Slater)
$P_{1/2}$	Pressure at which $K^1/k_{\infty} = 1/2$
p	Critical coordinate in molecule. (Slater)
[Q]	Column matrix of normal coordinates
Q_i	Normal coordinate of the i-th mode.
q	Generalized molecular coordinate
$\dot{q}$	First time derivative of q
R	gas constant
[R]	Column matrix of symmetry coordinates R_j
R,r	Molecular bond distances.
[r]	Column matrix of internal coordinates r_k
$\bar{S}_j^{(t)}$	Symmetry vector for atom t and coordinate R_j . See [79].
$\bar{s}_k(t)$	Vector quantity for atom t and coordinate r_k . See Table 1.
s	Number of effective "oscillators" in molecule. (Hinshelwood and Kassel)

T	Temperature; kinetic energy.
t	Time; generalized atom of molecule.
$[U]$	Matrix of transformation from internal to symmetry coordinates. See [72].
V	Potential energy
$\overline{V}$	Unit vector. See Table 1.
$\overline{V}_1 \cdot \overline{V}_2$	Scalar product of vectors
$\overline{V}_1 \times \overline{V}_2$	Vector product
v	Reaction rate
x	See [35]; generalized vector
Z, Z_{-1}	Gas collision number
a_i	Amplitude factor for i-th normal mode. See [26]. (Slater)
α, β, γ	Molecular interbond angles
$\Gamma(z)$	Gamma function of z
γ_{ki}	See [24] and [98], (Slater)
	Internal energy of molecule
ϵ^*	Molecular internal energy necessary for reaction
ϵ_i	Energy in the i-th mode of vibration. See [95].
$[\Lambda]$	Diagonal matrix of λ_i . See [91]
λ_i	$4\pi\nu_i^2$. See [69].
μ_i	Normalized amplitude factor for i-th normal mode. See[117]
μ_p	Reciprocal mass of p-th atom. See [81]
ν	Frequency factor. See [33] (Slater)
ν_i	Frequency of i-th mode of vibration
ω	Collision frequency per molecule. See [29]
σ	Molecular collision diameter
θ	See [36]. (Slater)
ϕ	Dihedral angle of molecule
$\phi(s,b)$	Function of s and b . See [9].

CHAPTER 1

I N T R O D U C T I O N

This work professes to be a study of the nature of unimolecular processes in the gas phase and in particular a critical evaluation of the recent theory of N. B. Slater as compared to its predecessors. The basic postulates and assumed model of each of the existing theories are examined and, whenever possible, compared to experimental data in an effort to judge their validity and construct a more realistic picture of the phenomenon.

A unimolecular reaction is defined as one in which the activated complex consists of a single, activated, reactant molecule. As soon as the existence of certain elementary unimolecular reactions was definitely established, difficulties arose in accounting for the manner in which the molecules became activated. For if activation occurred by collision it was thought that the kinetics should be second-order whereas in fact such reactions exhibited first-order kinetics over a broad range of pressures. Perrin (5) postulated an activation by the absorption of radiation but this idea was abandoned when it was realized that these reactions did indeed change over from first to second-order at sufficiently low pressures. In 1922 Lindemann (6) showed how activation by collision could give rise to first-order kinetics under certain circumstances and his postulates remain the basis of all modern theories of unimolecular

reactions.

LINDEMANN THEORY

Postulates

By means of inter-molecular collisions, energy of translation is converted into internal forms of energy producing "activated" molecules A^*, i.e. molecules possessing sufficient energy to undergo reaction:

$$A + A \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} A^* + A$$

The activated species subsequently react at a rate k_2 :

$$A^* \xrightarrow{k_2} \text{products}$$

If the activated molecules are converted into products slowly compared to the rate with which they are deactivated by collision, and if they are in equilibrium with the normal molecules, then a stationary concentration of the former may be built up. If concentrations are denoted by square brackets this steady-state postulate for $[A^*]$ may be written:

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

from which it follows that the rate of formation of products, v, is given by:

$$v = k_2[A^*] = \frac{k_1 k_2 [A]^2}{k_{-1}[A] + k_2} \qquad [2]$$

Then at sufficiently high pressures $k_{-1}[A] \gg k_2$

and

$$v \doteq \frac{k_1 k_2}{k_{-1}} [A] \equiv k_\infty [A] \qquad [3]$$

so that the reaction is first-order with respect to [A].

On the other hand, at low pressures, $k_{-1}[A] \ll k_2$ and

$$v \doteq k_1 [A]^2 \qquad [4]$$

where the reaction is now of the second order. Notice that this second-order rate constant k_1 is simply the rate of energization which occurs in the first step of the reaction.

If a first-order rate coefficient K^1 is defined by

$$v = K^1[A] \qquad [5]$$

then from [2] and [5] :

$$\frac{K^1}{k_\infty} = \frac{1}{1 + \frac{k_2}{k_{-1}[A]}} \qquad [6]$$

k_∞ is computed from the high-pressure measurements and K^1 from [5] over the entire pressure range. If the theory is correct a plot of K^1/k_∞ against [A] should yield a curve passing through the origin and rising asymptotically to unity for large [A]. Such curves have been observed experimentally in a number of instances, confirming that the theory is qualitatively correct, but quantitatively the deviations are too large to make the theory acceptable without modification.

Criticism

From [6] it is found that $K^1/k_\infty = 1/2$ when $[A] = [A]_{1/2} = k_2/k_{-1} = k_\infty/k_1$. k_∞ is measured experimentally but if k_1 is estimated from simple collision theory as

$$k_1 = Z_1 \exp (- \epsilon^*/kT) \qquad [7]$$

where Z_1 = gas collision number

k = Boltzmann constant

ϵ^* = minimum energy required by the molecule in order to react,

it is found that the values of $[A]_{1/2}$ which result are much higher than those observed. This would indicate that k_1 is in fact greater than the value given by the simple function [7].

Furthermore, it follows from [6] that

$$\frac{1}{K^1} = \frac{k_{-1}}{k_1 k_2} + \frac{1}{k_1 [A]} \qquad [8]$$

which predicts $1/K^1$ to be a linear function of $1/[A]$. The curved function which is found in practice would imply that k_2 may not be a simple constant as the theory assumes.

HINSHELWOOD THEORY

Hinshelwood was able to overcome the first defect of the Lindemann theory mentioned above by recognizing that the rate constant for the energization process, k_1, may be greater for a complex molecule than for a simple one.

Postulates

The energy ϵ that a molecule possesses may be distributed in any fashion among its n total number of degrees of vibrational freedom but it is assumed that the

molecule is capable of reacting only when the requisite energy ϵ^*, or greater, is confined to s specified degrees of freedom. The reaction scheme is thought of as having an additional step:

$$A + A \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} A^* + A$$

$$A^* \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} A^{\ddagger} \xrightarrow{k^{\ddagger}} \text{products}$$

where A^* = "energized molecule" having energy ϵ^* or greater distributed among a specified s of its n degrees of vibrational freedom.

$A^{\ddagger}$ = "activated molecule" having ϵ^* or greater concentrated in the bond or bonds to be broken.

It is also assumed that a complete redistribution of energy occurs on each collision so that virtually every impact suffered by an A^* molecule will be de-energizing. Consequently k_{-1} is set equal to the collision number Z_{-1}. Now with the classical approximation of continuous energy to allow integration over all states, Hinshelwood (7) derives that the fraction of molecules with energy ϵ^* or greater distributed among s specified degrees of freedom is:

$$\left[\frac{1}{(s-1)!}\left(\frac{\epsilon^*}{kT}\right)^{s-1} + \frac{1}{(s-2)!}\left(\frac{\epsilon^*}{kT}\right)^{s-2} + \ldots + 1\right]\exp\left(-\frac{\epsilon^*}{kT}\right)$$

$$\equiv \phi(s,b)\exp(-b) \quad [9]$$

where $b \equiv \epsilon^*/kT = E_o/RT$ [10]

Under the assumption of a steady-state concentration of $[A^*]$, this fraction [9] is equal to k_1/k_{-1}. The resulting expression for k_1 is then:

$$k_1 = Z_{-1} \phi (s,b) \exp (-b) \quad [11]$$

Criticism

Although the Hinshelwood modification will indeed predict much larger values for k_1 and smaller pressures $[A]_{1/2}$ there are certain other difficulties. The most obvious is the absence of any a priori knowledge of the value of s or its relationship to n (other than $s \leq n$).

Secondly, the theory would predict k_∞ to be given by:

$$k_\infty = k_2 \phi (s,b) \exp (-b) \quad [12]$$

and since k_2 is considered constant the pre-exponential term should be strongly temperature dependent as seen from the definition [9] of $\phi (s,b)$. However such temperature dependence has not been observed.

Finally, the second objection to the Lindemann theory, relating to k_2, has in no way been removed. From these considerations it would appear that k_2 may no longer be considered constant.

KASSEL THEORY

A theory of unimolecular reactions developed by

Kassel (8)(9) and very similar work by Rice and Ramsperger (10) make the more realistic postulate that the coefficient k_2 increases with the energy possessed by the molecule. The greater the energy of the excited molecule the sooner will ϵ^* pass into the bond that is to be broken.

Postulates

Kassel considers the molecule as a system of loosely coupled harmonic oscillators of equal frequencies and makes a statistical calculation on the number of ways in which energy quanta may be distributed among these oscillators. Passing to the classical model as an approximation it is deduced that the probability that a molecule which contains energy ϵ in s of its oscillators will have at least ϵ^* in one oscillator is:

$$\left(\frac{\epsilon - \epsilon^*}{\epsilon}\right)^{s-1} \qquad [13]$$

The rate constant k_2, the rate with which the required energy passes into the particular oscillator, is proportional to this quantity and so

$$k_2 = k^{\ddagger} \left(\frac{\epsilon - \epsilon^*}{\epsilon}\right)^{s-1} \qquad [14]$$

This is combined with [11] from Hinshelwood to obtain k_∞:

$$k_\infty = \frac{k_1 k_2}{k_{-1}} = k^{\ddagger} \int_{\epsilon^*}^{\infty} \left(\frac{\epsilon - \epsilon^*}{\epsilon}\right)^{s-1} \phi\,(s,b)\, \exp\,(-b)\, d\epsilon$$

$$= k^{\ddagger} \exp\,(-b) \qquad [15]$$

An expression which will predict the variation of the first-order rate coefficient K^1 with pressure is obtained from

$$K^1 = \int_{\epsilon^*}^{\infty} \frac{k_1 k_2 / k_{-1}}{1 + k_2/(k_{-1}[A])} \, d\epsilon \qquad [16]$$

in which k_1 and k_2 are now functions of ϵ, [11] and [14], and k_{-1} is taken as the collision number Z_{-1}. This integration will reduce to

$$\frac{K^1}{k_\infty} = \frac{1}{(s-1)!} \int_0^{\infty} \frac{x^{s-1} \exp(-x)}{1 + B\left(\frac{x}{b+x}\right)^{s-1}} \, dx \qquad [17]$$

where

$$B = k^{\ddagger}/(Z_{-1}[A]) \qquad [18]$$

$$x = (\epsilon - \epsilon^*)/kT \qquad [19]$$

Criticism

The application of Kassel's expressions to a number of reactions has been extremely satisfactory but there remains the empiricism in the choice of s, the value required frequently being about half the total number of degrees of freedom in the molecule. Moreover, the physical significance of s in the Kassel formulation is quite vague. The s "oscillators" to which this author refers seem to have a status somewhere between that of a normal mode of vibration and of an interatomic distance in the molecule. For purposes of comparison with later theories it will be considered that

an "oscillator" is a normal mode of vibration the principal motion of which is the extension of the bond to be broken. (A more explicit account of "normal modes" is given in the next chapter.) $k^{\ddagger}$ may be regarded as an adjustable parameter in [17] or a measurable quantity found from k_{∞}.

GENERAL FEATURES OF HINSHELWOOD-KASSEL THEORIES

In the foregoing theories, beginning with that of Hinshelwood, a molecule is considered to be energized if amongst its vibrational degrees of freedom there is distributed sufficient energy for the molecule to undergo reaction when this energy eventually finds its way into one particular normal mode. An essential feature of these theories is that the energy is able to flow freely between a number s of the modes, and indeed an estimation of Kassel's $k^{\ddagger}$ leads to the conclusion that a redistribution of energy takes place on approximately every vibration. In the Kassel and Rice-Ramsperger modifications the rate with which the energy passes into the critical normal mode is considered to be greater the more energy that is present in the energized molecule. This is the form of the theory that will be considered below; for convenience it will be referred to as the HKRR theory.

SLATER THEORY

Only a summary of Slater's theory of unimolecular

reactions (11)(12)(13)(14) will be presented here, adhering closely to that author's notation, and a more explicit account of its application will be given in chapter 2 following the section on normal coordinate analysis.

Postulates

A molecule with n distinct normal modes of harmonic vibration is considered as a classical dynamical system which maintains its harmonicity up to the point of dissociation and which may be described by a set of n coordinates. These coordinates are generally the changes in bond lengths or angles between bonds so that the time-variation of a coordinate is the sum of n harmonic terms contributed by the normal modes, with amplitudes and phases determined by the last collision of the molecule. It is assumed that a molecule dissociates when one particular coordinate attains a certain critical length. This length will be attained only when the energies in the normal modes are sufficiently large, and only if the harmonic terms comprising the extension of the particular coordinate come sufficiently into phase before a further collision removes the high energies.

If the chosen molecular coordinates $q_1, q_2, \ldots q_m$ ($m \geq n$) are extensions from equilibrium distances or angles then it is a good approximation to write the kinetic and potential energies as

$$T = 1/2 \sum_{h,j=1}^{m} \sum a_{hj} \dot{q}_h \dot{q}_j \qquad [20]$$

and $$V = 1/2 \sum_{h,j=1}^{m} \sum b_{hj} q_h q_j \qquad [21]$$

which are the forms used in the vibrational analysis. Solution of the equations of motion gives q_h as a sum of vibrations in the n normal modes:

$$q_h = \sum_{i=1}^{n} U_{hi} \cos 2\pi (\nu_i t + \phi_i) \qquad [22]$$

where U_{hi} is the amplitude of q_h in the normal mode of frequency ν_i and phase ϕ_i .

If the reaction coordinate or critical coordinate, p (not necessarily one of the q's), is also an extension from an equilibrium value then it may be expressed in a form similar to [22] or

$$p = \sum_{1}^{n} a_i \sqrt{\epsilon_i} \cos 2\pi (\nu_i t + \phi_i) \qquad [23]$$

where a_i is the "amplitude factor" of the i-th mode (to be defined later) and ϵ_i is the energy in that mode.

A quantity γ_{ki} is calculated for each coordinate and made as follows:

$$\gamma_{ki} = U_{ki} / \sqrt{\epsilon_i} \qquad [24]$$

As all displacements are assumed small, the reaction

coordinate can be expressed as a sum of the contributions from each of the q's:

$$p = \sum_{1}^{n} A_k q_k \qquad [25]$$

where the coefficients A_k are calculable from the geometry of the molecule. For example, if p coincides with, say, q_3 then A_3 is unity and the other A's are fractional or zero depending upon the extent to which the motions in the other coordinates affect q_3. The amplitude factors α_i of p are defined by

$$\alpha_i = \sum_{1}^{m} A_k \gamma_{ki} \qquad [26]$$

and are found from [24] and [26]. Finally, a set of normalized amplitude factors μ_i are computed by

$$\mu_i = |\alpha_i| \Big/ \sqrt{\sum_i \alpha_i^2} \qquad [27]$$

Slater obtains for the first-order rate coefficient K^1 the expression (13)

$$K^1 = -\frac{1}{[A]}\frac{d[A]}{dt} = \int \cdots \int_0^{\infty} \frac{L \exp(-b)}{1 + L/\omega} \prod_1^n \left(\frac{d\epsilon_i}{kT}\right) \qquad [28]$$

where ω = collision frequency per molecule

$$= \left(4\sigma^2 \sqrt{\pi RT/M}\right) [A] \qquad [29]$$

σ = molecular collision diameter

M = molecular weight

L = "dissociation frequency" per molecule.

From [23] it is seen that the reaction coordinate p which is to attain a critical value p_o at dissociation is a function of time:

$$p = F(t) \qquad [30]$$

The fraction of activated molecules for which p rises to p_o in a short time δt is assumed to be $L\delta t$. A formula by Kac (15) is used to find the asymptotic frequency 2L of the zeros of $F(t) - p_o$ in the case where the frequencies ν_i are linearly independent and the ϕ_i's, after collision, are randomly distributed over the range (0, 1). Hence K^1 is obtained as an average of L over an equilibrium distribution of the energies ϵ_i within the molecule (12).

In the high-pressure region $L/\omega \gg 1$ and [28] becomes

$$K^1 \longrightarrow k_\infty = \int \cdots \int L \exp(-b) \prod_i (d\epsilon_i/kT) \qquad [31]$$

The substitution of Kac's formula for L and integration yields

$$k_\infty = \nu \exp(-b) \qquad [32]$$

where

$$\nu = \sqrt{\sum_i (\mu_i \nu_i)^2} \qquad [33]$$

Since the frequency factor ν is this "weighted" root-mean-square of the ν_i's it must always lie between the least and the greatest of the fundamental frequencies (16). If there are several equivalent critical coordinates in the molecule then [32] is multiplied by this factor. An example would be the twelve hydrogen to remote carbon distances in cyclopropane.

The expression for K^1 at general pressures is found by integrating [28] and when k_∞ is divided out the result is

$$\frac{K^1}{k_\infty} \equiv I_n(\theta) = \frac{1}{\Gamma(n+1)/2} \int_0^\infty \frac{x^{(n-1)/2} \exp(-x)}{1 + x^{(n-1)/2}\, \theta^{-1}}\, dx \qquad [34]$$

$$x = (\epsilon - \epsilon^*)/kT = (E - E_0)/RT \qquad [35]$$

$$\theta = (\omega/\nu)[4\pi b]^{(n-1)/2} \Gamma\tfrac{1}{2}(n+1) \prod_1^n \mu_i \qquad [36]$$

and as before $b = E_0/RT$. $\Gamma(z)$ denotes the gamma function, equal to $(z-1)!$ for integral values of z; for half-integral values it may be calculated from the relationship

$$\Gamma(z)\,\Gamma(z + 1/2) = 2^{1-2z} \sqrt{\pi}\, \Gamma(2z) \qquad [37]$$

μ_i is the continued product of the μ factors.

It should be mentioned that in [34] and [36] n is no longer the total number of degrees of vibrational

freedom in the molecule, but now the number of modes effectively contributing to the coordinate p ; that is, the number of modes for which a_i is not zero.

If degenerate modes are present giving, say, the three equal frequencies ν_{ia} , ν_{ib} , ν_{ic} , these are grouped together (13) so that n is only the number of distinct frequencies in the contributing modes and the amplitude factor for the ν_i's is

$$a_i = \sqrt{a_{ia}^2 + a_{ib}^2 + a_{ic}^2} \qquad [38]$$

At a specified temperature, [A] and consequently ω and θ , are functions of the pressure. If, for a given reaction, the number of contributing modes of vibration n is determined, and the activation energy measured experimentally, then $K^1/k_\infty = I_n(\theta)$ will be a function of the pressure. Numerical values of $I_n(\theta)$ have been calculated from [34] and tabulated by Slater (13) as a function of $\log \theta$ for a number of different n values. These functions are plotted in Figure 1 and will be utilized in the subsequent sections.

General Features of Slater Theory

It is seen that the basic assumptions of Slater's theory are entirely different from those of HKRR. In the former case energization of the molecule by collision causes the energy to be distributed statistically among the degrees

of freedom available and during subsequent vibration of the molecule this energy is assumed incapable of passing from one mode to another. Attention is fixed on a critical coordinate in the molecule and reaction occurs when this coordinate, due to in-phase contributions from the various vibrational modes, exceeds a limiting extension.

Criticism

Although Slater's theory is the most explicit and in some ways the most satisfactory to appear so far, the approximations involved should be clearly understood at the outset. These may be summarized as follows:

(a) The system is considered to be a classical one with continuous energy states, a feature common to previous theories as well. The quantum harmonic oscillator model has been discussed by Slater (16) who draws the conclusions: (i) The frequency factor ν is still given by [33] but the μ_i are now temperature dependent. The two models tend to coincide in this respect as $T \longrightarrow \infty$ or the ν_i tend to a common value. This effect is found to be small for practical tempebature ranges. (ii) E_o is a complicated function of temperature. The form of the function $I_n(\theta)$ will be the same as for the classical case [34] but owing to the different value of b the curve will be shifted laterally along the log P scale (P = pressure). In particular the predicted pressures at which the rate declines from the first order will differ from those of

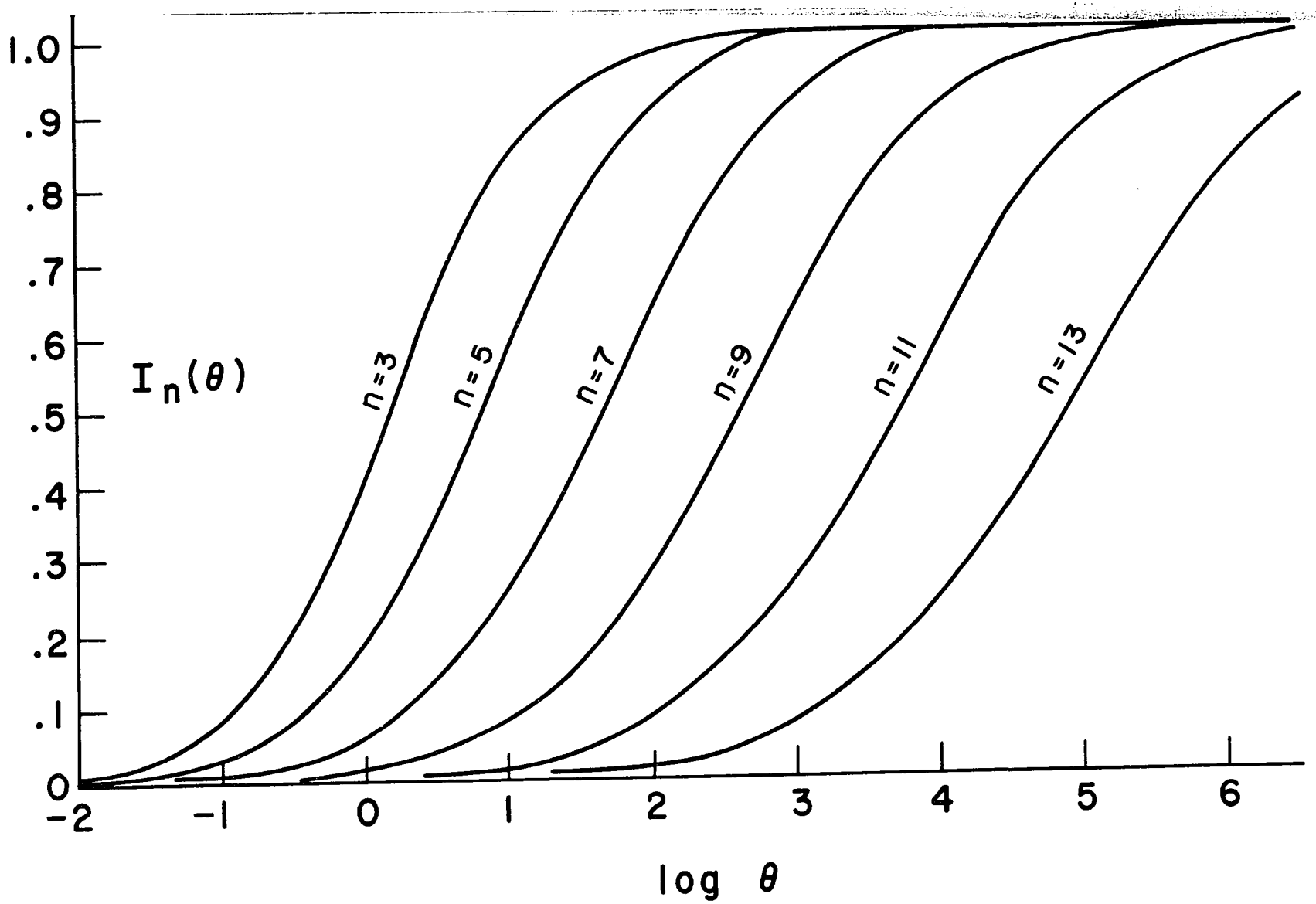


Figure 1. Plot of $I_n(\theta)$ as a function of log θ for various values of n .

the classical model. Slater gives no estimate of the magnitude of this effect but from his expression for E_o it is assumed to be fairly slight.

(b) Vibrations are harmonic. Although this is a good assumption for low-lying vibrational levels, a significant degree of anharmonicity is known to exist in the case of more energetic vibrations which are important in the dissociating molecule. The anharmonicity is represented mathematically by cubic and higher order terms in the potential function which is usually taken as a sum of quadratic terms only. Slater has considered certain more general potential functions (17) and has concluded that the anharmonicity will have a small effect on the predicted rates, at the most a reduction of about 2% in k_∞.

(c) Certain mathematical approximations are made in the evaluation of L and the integral [31]. These are fully discussed by Slater (13) and may be considered negligible for the purposes of the subsequent discussion.

(d) There is no a priori knowledge of which critical coordinate should be used in the calculations. A disturbing degree of empiricism seems to exist in the choice of p which is not always the most obvious of reaction coordinates.

(e) There is no passage of energy between normal modes during vibration. This may be the most drastic of the various approximations made and since it is here that the theory exhibits an essential difference from the

earlier ideas of HKRR a final discussion of this and the preceding criticism will be reserved for a later chapter.

NATURE OF COLLISIONAL PROCESSES

One assumption which first appears in [11] and has prevailed throughout the foregoing theories is that practically every collision between an A^* molecule and a non-energized one will serve to remove considerable energy from A^* returning the latter to a "normal" state A . For this reason the rate constant k_{-1} is set equal to the collision number Z_{-1} . However the proposition of of deactivation on every collision has recently been questioned by several authors (18)(19)(20). Forst points out (21) that if the reaction is taking place within a medium of foreign gas M the constant k_{-1} may be dependent upon the nature of M since different foreign gases exhibit different "quenching" efficiencies. Even in a medium of pure A it might be less than Z_{-1} because of the variety of molecular states available to act as collision partners.

This question is discussed by Mahan (20) in terms of an expression given by Schwartz and Herzfeld (22) which shows that the probability of translational-vibrational energy exchange decreases sharply as the amount of energy transferred increases. This tends to rule out the assumption of a statistical redistribution of energy on every collision

leaving the deactivating process to consist of small energy exchanges. Rice has shown (23) that this ought to lead to a different type of pressure dependence for the rate constant than that previously derived. Mahan estimates that k_{-1} should be in the neighbourhood of 0.1 Z_{-1}. However the Herzfeld theory was derived to predict the small transition probabilities found in sonic velocity experiments where the molecules reside principally in their lower energy levels, whereas for highly excited molecules the equation is only approximate. It may be mentioned also that Mahan's experimental evidence is very indirect.

One is only able to conclude that although there is a distinct possibility of k_{-1} being significantly different from Z_{-1} the evidence is by no means conclusive nor has it yet produced a reliable estimate of the former.

RECENT CONTRIBUTIONS TO THE THEORY

The theory of unimolecular reactions has been approached from many different points of view with varying degrees of success. In this section reference is made to the work of Benson, Marcus and Eyring and where possible the equivalence of their ideas to the preceding theories is discussed.

Benson

In Slater's theory the "specific dissociation probability" L, which corresponds to k_2 , is a function

of the energies $\epsilon_1, \epsilon_2, \ldots \epsilon_n$ residing in each of the n normal modes of vibration. In the high-pressure region where there is an equilibrium concentration of energetic A^* molecules Slater has shown (12) that L may be averaged over all distributions $(\epsilon_1, \ldots \epsilon_n)$ of a total energy ϵ to give an expression for k_2:

$$k_2 = \nu \left(\frac{\epsilon - \epsilon^*}{\epsilon} \right) \qquad (\epsilon > \epsilon^*) \qquad [39]$$

where ν has its previous significance [33]. (It is to be noted that this is formally equivalent to the Kassel expression [14], as must be any model of harmonic oscillators which yields a k_∞ of the form [32] (24).)

Benson (25) has used this result [39] of Slater's in an attempt to calculate mean reaction rates and the pressures $[A]_{1/2}$ for unimolecular processes. When the figures for $[A]_{1/2}$ are compared to those predicted by the Slater theory for corresponding values of n the difference is very large (nearly an atmosphere for the worst case of $n = 9$). The discrepancy results from the erroneous assumption by Benson that the expression [39] may be extended to pressures below those of the first-order region to $[A]_{1/2}$. Slater (12) has warned that, at low pressures where the concentration $[A^*]$ is depleted by dissociation, for a given total energy ϵ those distributions $(\epsilon_1, \ldots \epsilon_n)$ giving the largest values of L are the most depleted so that a use of an average k_2 of L is incorrect. At these

pressures there is no longer an "equal density of occupation of all regions of the (energy) hypersurface ϵ ", - to use Benson's terminology, - and Figure 1 of his paper (25) ceases to be valid.

Absolute Rate Theory

Slater has shown (12) that the quantity ν which appears in his formulation may be equated to the expression:

$$\nu = \frac{\nu_1 \nu_2 \cdots \nu_n}{\nu_2' \nu_3' \cdots \nu_n'} \qquad [40]$$

where the ν_i' are the normal frequencies of the system constrained to have the reaction coordinate p fixed at zero. The first-order, high-pressure rate constant was seen to be

$$k_\infty = \nu \exp(-b) \qquad [41]$$

The absolute rate theory of Eyring (26)(27) formulates the same constant as

$$k_\infty = \frac{kT}{h} \frac{f^*}{f} \exp(-b) \qquad [42]$$

in which k = Boltzmann constant

f = partition function of a normal A molecule

f^* = partition function of the activated complex

Under the assumptions that (a) the molecular species is composed of classical harmonic oscillators, (b) there can be no bond extension so as to affect rotational partition

functions, Giddings and Eyring (28) show that [42] reduces to

$$k_\infty = \frac{\nu_1 \nu_2 \cdots \nu_n}{\nu_2' \nu_3' \cdots \nu_n'} \exp(-b) = \nu \exp(-b) \qquad [43]$$

The interpretation of the ν_i' here is close enough to that of Slater in [40] to make the two theories equivalent at high pressures (12). Giddings and Eyring then give an integral for a general rate constant at any pressure using the total energy as parameter. In principle there is no contradiction between this expression and the theory of Slater.

Marcus

An integral for K^1/k_∞, which is of the same form as Slater's function $I_n(\theta)$ [34], has been derived by Marcus (29):

$$\frac{K^1}{k_\infty} = \frac{1}{\Gamma(1 + r/2)} \int_0^\infty \frac{\omega^{r/2} \exp(-\omega)}{1 + a\,\omega^{r/2}}\, d\omega \qquad [44]$$

in which the parameter "a" is inversely proportional to the pressure. Comparing [44] with $I_n(\theta)$ of Slater [34] there is the equivalence,

$$r + 1 = n \qquad [45]$$

Since θ varies as the pressure but appears as θ^{-1} in the denominator of [34], the two expressions for K^1/k_∞ will

have the same pressure dependence. However, despite this close formal resemblance the interpretations are quite different. The r of [44] represents the number of "non-adiabatic rotations of the activated complex" and is not related to the vibrational degrees of freedom. As with Eyring's theory, Marcus' approach is to make calculations from an assumed form of the activated complex as well as for the "normal" molecule. In a second paper (30) the theory is applied to the dissociation of ethane into ethyl radicals under the assumption of both a "loose" and a "rigid" activated complex, the latter giving reasonably good agreement with experiment. Such an approach has the advantage of being able to consider internal rotations and an increased entropy in the activated complex of which the Slater theory takes no account, and for this reason it may be useful in obtaining some knowledge of the molecular state just prior to reaction as in the ethane case. However, the large number of assumptions which must be made about the nature of this activated complex in order to begin calculations is a disadvantage when compared to the Slater theory which deals with a concrete and easily visualized model.

EQUILIBRIUM POSTULATES

All the well-known theories of chemical kinetics are equilibrium theories in which a Maxwell-Boltzmann

energy distribution of reactants is postulated to persist during a reaction. This postulate has been recognized as an approximation, since the process of reaction will disturb the equilibrium, but it is generally assumed to be a good one. Montroll and Shuler (31) have examined various models of chemical reactions to estimate then extent of departure from equilibrium and to develop techniques for analyzing reactions in which the departure is significant.

The calculations of Montroll and Shuler and previous work reviewed by them are in essential agreement on the point that the perturbation of the equilibrium distribution and the corresponding deviation from the equilibrium rate is quite small when $E_o/RT = b \geq 5$. Under this condition the use of equilibrium theory is justified. Detailed calculations for the case of a diatomic molecule have also been carried out by Nikitin (32).

COMPARISON OF HKRR AND SLATER THEORIES

Attention is now returned to the HKRR and Slater theories and their comparison. Qualitative differences in the assumed models are discussed with reference to a potential energy surface for an imaginary system, and then methods by which the theories may be quantitatively compared to experiment are discussed.

Potential Energy Diagram

Some of the basic differences between the HKRR and Slater theories are most easily visualized by means of

a potential energy diagram. Figure 2 represents the potential energy surface over which the linear triatomic system ABC would move during the course of its axial vibrations ν_1 and ν_2, (n = 2). The bending mode of vibration would require a different set of axes for its representation. To simplify discussion the atomic masses are assumed to be such that $\Delta(A - B) = \Delta(A - C)$ in ν_1 and $\Delta(A - b) = -\Delta(A - C)$ in ν_2. The equipotential contours of the diagram show valleys parallel to each of the axes which correspond to dissociation of ABC into A + BC or AB + C. The elliptical contours represent an energy basin in which the normal molecule resides. A cross-section of this basin would show it to be parabolic near its bottom (harmonic vibrations) but tending to level out to a saddle point or col as the upper extremities are approached in the directions of the two valleys. The assumption of purely harmonic oscillations in both the HKRR and Slater theories would have the basin retain its parabolic character right up to the level of the col and then flatten out abruptly in these directions.

The two normal modes shown at the top of the figure consist of oscillations in the energy basin along the lines of the heavy arrows. The first mode is motion along the 45 degree dashed line with frequency ν_1 and the second is perpendicular to the former in this case with frequency ν_2. Dissociation of the molecule will be chiefly to the products AB + C since the col at "a"

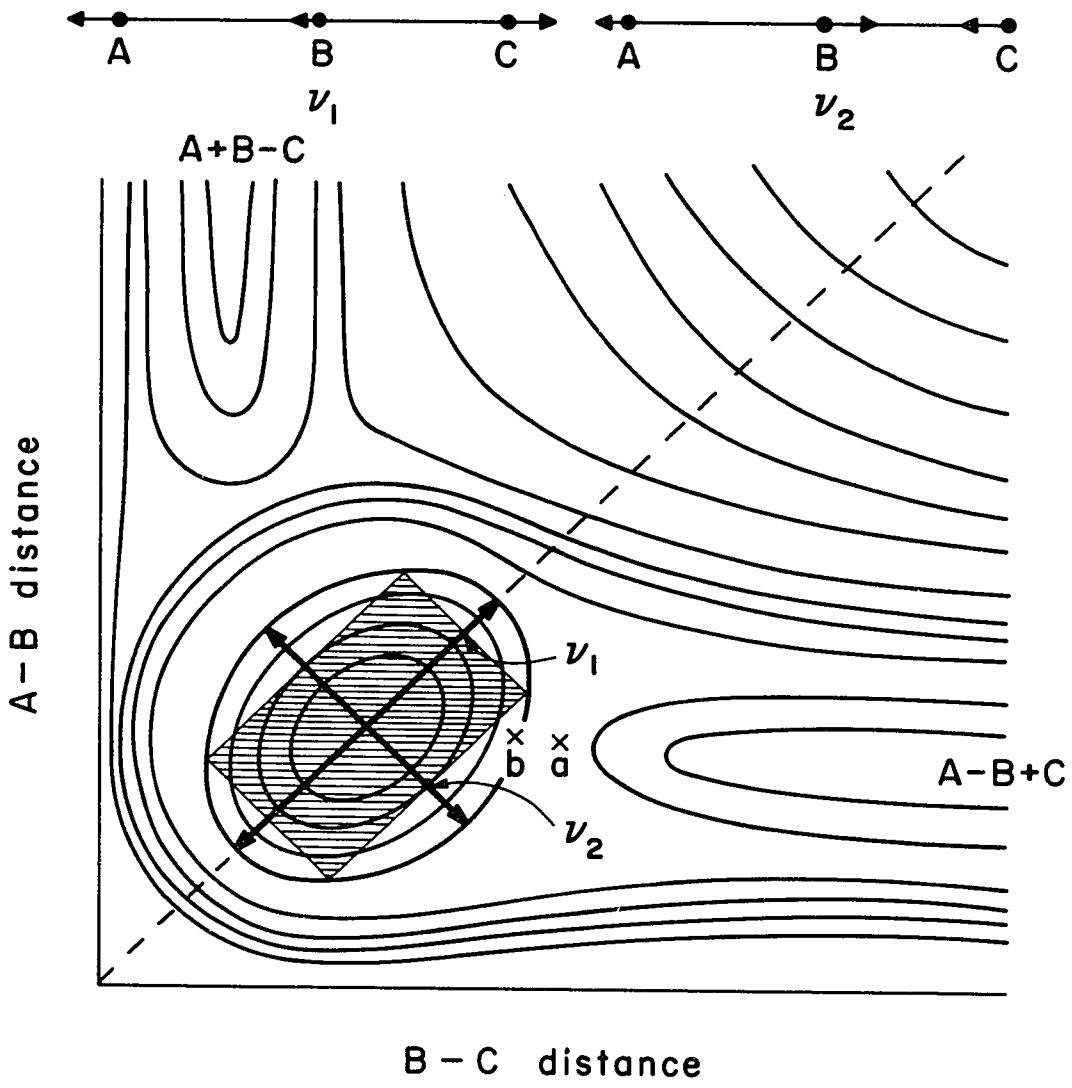


Figure 2. Schematic potential energy surface for the linear molecule ABC indicating the axial modes of vibration.

over which the system must pass to reach this (horizonatal) valley is the lower of the two.

Now the vibrational energy (in these two modes) acquired by the molecule from collision may be divided in any proportion between the two degrees of freedom. Suppose that in the first mode ϵ_1 is such as to produce an amplitude indicated by ν_1 on the diagram while ϵ_2 produces an amplitude extending to the point ν_2. These points define the shaded rectangle. If the two modes are independent with no possibility of energy transfer between them, as assumed in the Slater theory, then the system will be constrained to move within the rectangle. Because of the different frequencies and phases of the two modes, their superposition will generally result in a complicated Lissajous figure which, if ν_1 and ν_2 are linearly independent, will eventually cover the rectangle, but at no time is the system allowed to leave these confines. The molecular configuration represented by the point "b", for example, although its potential energy would be less than $\epsilon_1 + \epsilon_2$ (which is the height of the outermost elliptical contour in this case) will not be realized by the system since it lies outside the rectangle defined by the original partition of energy between the modes.

On the other hand, if the modes are considered to be "coupled", as the HKRR theory assumes, this implies the possibility of energy flow between them. And if this flow is completely unrestricted, as the theory also assumes,

then the system will no longer be confined to the rectangular area. Instead, given time, all configurations of energy $\epsilon_1 + \epsilon_2$ are available to it and every point within the outermost elliptical curve, including "b", may be realized.

For dissociation to occur, the system must achieve the configuration "a" at the energy col. The direction from the centre of the basin to "a" is the reaction coordinate p. Now the same remarks apply to "a" as well as to "b"; if the system has sufficient total energy in $\epsilon_1 + \epsilon_2$ and if the coupling between modes is assumed then dissociation will eventually occur provided another collision does not intervene to remove some of the energy. But under Slater's restriction of no coupling, dissociation will only occur if the total energy is partitioned in such a particular manner as to define a rectangle which encloses "a". That is, the molecule is only energized in the Slater sense when the components of ν_1 and ν_2 along p, taken at their maximum values and added together, exceed the point "a". Consequently, Slater's definition of energization is a more stringent one than that of HKRR and, in the Slater view, not all molecules energized in the HKRR sense are capable of undergoing reaction.

Rates of Energization

It has been seen previously in [11] that the rate of energization to the state A^* is given by the HKRR theory to be

$$k_1 = Z_{-1}\, \phi\,(s,b)\, \exp\,(-b) \qquad [46]$$

If $^*/kT \gg 1$ only the first term of the series need be considered giving

$$k_1 \doteq Z_{-1}\, \frac{1}{(s-1)!}\, b^{s-1}\, \exp\,(-b) \qquad [47]$$

The Slater model, being based upon quite different assumptions, would be expected to give a different expression for k_1. The general rate expression of this theory was seen in [34] to be

$$\frac{K^1}{k_\infty} = \frac{1}{\Gamma\frac{1}{2}(n+1)} \int_0^\infty \frac{x^{(n-1)/2}\, \exp\,(-x)}{1 + x^{(n-1)/2}\, \theta^{-1}}\, dx \qquad [48]$$

It can be shown that as $[A] \longrightarrow 0$ one obtains:

$$\lim_{P \longrightarrow 0} \left(\frac{K^1}{k_\infty} \right) = \frac{K^1(\text{low } P)}{k_\infty} = \frac{\theta}{\Gamma\frac{1}{2}(n+1)} \qquad [49]$$

Now from the Lindemann expression [2]:

$$v = \frac{k_1 k_2 [A]^2}{k_{-1}[A] + k_2} \qquad [50]$$

and the definition [5]:

$$v = K^1[A] \qquad [51]$$

it is seen that

$$K^1 = \frac{k_1 k_2 [A]}{k_{-1}[A] + k_2} \qquad [52]$$

From the latter, as $[A] \longrightarrow 0$, it follows that

$$K^1 \text{ (low P)} = k_1 [A] \qquad [53]$$

From [49] and [53]:

$$\frac{k_1 [A]}{k_\infty} = \frac{\theta}{\Gamma \frac{1}{2} (n + 1)} \qquad [54]$$

and

$$k_1 = \frac{(\theta/[A])\, k_\infty}{\Gamma \frac{1}{2} (n + 1)} \qquad [55]$$

Inserting the expressions for θ and k_∞ from [36] and [32] the result is

$$k_1 = Z_{-1} [4\pi b]^{(n-1)/2} \exp(-b) \prod_{i=1}^{n} \mu_i \qquad [56]$$

where again [56] is to be multiplied by the number of equivalent critical coordinates in the molecule.

The expressions [47] and [56] for the two theories are to be compared. As Slater has pointed out (13) the rate given by [56] is, for a given ϵ^* and s or n ,

always less than that given by [47]. As discussed in the preceding section this is so because whereas according to the HKRR theory a molecule is capable of reaction provided only that is has acquired the energy *, this is a necessary but not a sufficient condition for reaction according to the Slater assumptions. For reaction to occur by Slater's mechanism the energy * must be distributed in a particular manner among the normal modes so that, when the vibrations come suitably into phase, the critical coordinate p is extended to the point of reaction. If, for example, one of the μ's in [56] is small it indicates that the motion of the corresponding mode contributes very little to the extension of p and hence energy here is "trapped", unable to contribute much to the reaction rate.

Relation of E_o to Activation Energy

The experimental activation energy E_a of a reaction is defined by

$$\frac{d \ln k}{dT} = \frac{E_a}{RT^2} \qquad [57]$$

Now if the pre-exponential term in the expression for a rate constant k is a function of temperature then the E_a found from the usual plot of ln k against 1/T is not strictly the E_o which appears in b .

In the HKRR and Slater theories the pre-exponential term of k_1 involves the temperature to a simple power

(see [47] and [56])and so is of the form

$$k_1 = aT^n \exp\ (-E_o / RT\ ) \qquad [58]$$

From this

$$\frac{d \ln k_1}{dT} = \frac{n}{T} + \frac{E_o}{RT^2} = \frac{E_o + nRT}{RT^2} \qquad [59]$$

Comparing [57] and [59] it is seen that

$$E_o = E_a - nRT \qquad [60]$$

In the high-pressure, first-order region where one is measuring k_∞, both the HKRR and Slater theories predict that $n = 0$ so that $E_o = E_a$ (high P).

However, in the low-pressure range, from [47] it is seen that the HKRR theory gives $n = 1/2 - (s - 1)$ since Z_{-1} contains $T^{1/2}$. Consequently,

$$E_o\ (\text{HKRR}) = E_a + (s - 1)RT - (1/2)RT \qquad [61]$$

Similarly for the Slater theory, [56] gives $n = 1/2 - (n-1)/2$ so that

$$E_o\ (\text{Slater}) = E_a + (1/2)(n-1)RT - (1/2)RT \qquad [62]$$

Bases for Testing the Two Theories

As far as the high-pressure first-order behaviour is concerned, it has now been shown that all modern theories of unimolecular reactions lead to approximately

the same conclusions (eq. [15], [32] and [43]).

There are much wider divergences between the different theories in the low-pressure, second-order region however, corresponding to the two fundamentally different definitions of energization. Slater (13) has referred to the possibility that his assumptions might be valid at low pressures, but that at very low pressures the rate of energization might be as predicted by [46] rather than [56]; this might be the case if there is a slow flow of energy between the normal modes, this flow being rapid enough to contribute to reaction provided that the time between collisions is sufficiently long. Until recently there have been no data available to allow this hypothesis to be tested. What are needed for this purpose are low-pressure second-order rate constants, and these are most likely to be found with small molecules.

In a very few cases reaction rates have been measured at both pressure extremes including the transition range between them in which the reaction order changes from second to first. With such extensive data the HKRR theory may best be tested and compared with the Slater theory by seeing which of the two expressions [17] or [34] give the better fit with the experimental curve over the entire pressure range.

Following chapter 2 which is devoted to theory, the unimolecular reactions of several molecules of increasing complexity have been considered in the succeeding chapters

with a view to testing and comparing the existing theories as indicated above. Wherever possible the application of the theories has been carried out with complete rigour —— preceeded by a normal coordinate analysis in the case of the Slater theory —— and compared with the best experimental data available.

CHAPTER 2

APPLICATION OF VIBRATIONAL ANALYSIS TO SLATER THEORY

In this chapter the general principles of the theory of molecular vibrations will first be sketched and then the Wilson FG matrix method (33)(34) discussed in some detail, since it is this method which has been used in most cases to follow. It is shown how the Wilson analysis is extended to obtain the normal coordinates of vibration, and finally, how these are used in the calculation of the Slater amplitude factors.

As well as the original papers there are several standard texts on the subject of molecular vibrations (35) (36).

GENERAL VIBRATIONAL THEORY

A molecule of N atoms possesses $n = 3N - 6$ (or $3N - 5$ if linear) degrees of vibrational freedom and consequently the system will require a minimum of n coordinates to describe its vibrational motion. With each degree of freedom is associated a fundamental frequency ν_i. These frequencies of motion are observed in the infrared and Raman spectra and the usual problem is that

of calculating the potential field or certain other structural parameters of the molecule from these experimental data. In discussing the underlying theory however, it is simpler to consider the reverse problem, — the calculation of the ν_i from a knowledge of the molecule in its equilibrium configuration. It is sometimes required to extend the analysis to determine the amplitudes of motion of the constituent atoms in vibration and it is this information that is required for the Slater theory of unimolecular reactions.

Since it is just the fundamental frequencies which are to be determined the system considered is a purely classical one of N point masses, each one having an equilibrium position. The system as a whole possesses no motion of translation or rotation since the vibrational problem may be treated as distinct from these. Displacement from its equilibrium position in any direction causes an atom to be acted upon by restoring forces which are assumed to be linearly related to the displacement:

$$F_r = -k_r q_r \qquad [63]$$

This approximation is found to be a very good one for small vibrations. The force law [63] gives rise to simple harmonic motion in which q_r will be expressible as a periodic sine or cosine function.

Now when all N atoms are displaced simultaneously, each of the three components of force acting on a given

atom is a function of the three displacement components of each of the other (N-1) atoms, and so the resulting motion will be very complicated. However, it is possible to resolve such a motion into n "normal modes of vibration" each having a characteristic frequency ν_i and possessing certain other properties. In any one normal mode, the atoms execute straight-line simple harmonic motions, all passing through their origins simultaneously and with the relative amplitudes of the various atoms in a fixed ratio. The amplitude of the mode as a whole and its phase relationship to the other normal modes are quantities which, in the gas phase, are determined by the nature of the last collision suffered.

Suppose $q_1, q_2, \ldots q_m$ (m n) are the coordinates in which the system is to be analysed. If these are defined as <u>deviations</u> from equilibrium values and if the potential energy zero of the system is taken to be the equilibrium configuration (all the q's zero) then by neglecting cubic and higher order terms in the potential function one can write:

$$2V = \sum_{i,j=1}^{m} b_{ij} q_i q_j \qquad [64]$$

where

$$b_{ij} = b_{ji} = \left(\frac{\partial^2 V}{\partial q_i \partial q_j} \right)_o \qquad [65]$$

A similar expression results for the kinetic energy T :

$$2T = \sum_{i,j=1}^{m} a_{ij}\dot{q}_i\dot{q}_j \qquad (a_{ij} = a_{ji}) \qquad [66]$$

in which $\dot{q}_r$ signifies the time derivative of q_r and the a_{ij} are functions of the atomic masses and molecular geometry.

The equations of motion in Lagrange form are

$$\frac{d}{dt}\left(\frac{\partial T}{\partial \dot{q}_r}\right) - \frac{\partial T}{\partial q_r} + \frac{\partial V}{\partial q_r} = 0 \qquad (r = 1,2,\ldots m) \quad [67]$$

These are applied to [64] and [66] and wherever a second time derivative $\ddot{q}_r$ of q_r appears it is replaced by

$$\ddot{q}_r = -\lambda q_r \qquad [68]$$

where

$$\lambda = 4\pi^2\nu^2 \qquad [69]$$

which is the condition for simple harmonic motion. The result is m linear, homogeneous equations in the q's. According to a well-known theorem of such equations, the determinant of the coefficients must equal zero. This takes the form

$$\begin{vmatrix} (b_{11} - \lambda a_{11}) & (b_{12} - \lambda a_{12}) & \cdots \\ (b_{21} - \lambda a_{21}) & (b_{22} - \lambda a_{22}) & \cdots \\ \cdots & \cdots & \cdots \\ \cdots & \cdots & (b_{mm} - \lambda a_{mm}) \end{vmatrix} = 0 \qquad [70]$$

[70] is known as the "secular determinant". Its expansion yields an m-th order equation in λ which is the "secular equation". Of this equation n roots are real and non-zero and these give the n characteristic or normal mode frequencies of vibration of the molecule.

FG MATRIX METHOD

In practice only the very simplest systems would be treated in accordance with the above considerations for the problem rapidly becomes unmanageable with any degree of complexity in the molecule. Through the application of group theory a great simplification may be effected by making use of the symmetry properties of the molecule in its equilibrium comfiguration. Depending upon the symmetry elements in the molecule, it has been shown that the normal mode motions have certain symmetry properties as well, (ref. 35 page 82). These properties serve to categorize the modes into symmetry "classes" or "species" of vibration. By choosing the q's with reference to the various symmetry elements present ("symmetry coordinates") the secular determinant will factor into a number of smaller determinants, one for each symmetry species, and each of the order of the number of modes in that species.

The Wilson FG matrix method (33)(34), of which an account will now be given, avails itself of this factoring property and reduces the volume of calculation through the use of matrix and vector algebra.

Symmetry Coordinates

The first step in any calculation is to determine the point group to which the molecule belongs and the number of fundamental vibrations of each symmetry species within the group. This may be worked out very easily from tabulated relationships (35)(37) as soon as the equilibrium configuration of the system is known. Symmetry coordinates R_j are then constructed from the m "internal coordinates" r_k (bond distances and angles) of the molecule (m n):

$$R_j = \sum_{k=1}^{m} U_{jk} r_k \qquad (j = 1,2,\ldots n) \qquad [71]$$

or, in matrix notation,

$$[R] = [U][r] \qquad [72]$$

where [R] and [r] are column matrices. This construction may be undertaken in a systematic fashion (36)(38) or simply by considering that the resulting coordinates must have the following properties:

(a) Normalized such that

$$\sum_{k=1}^{m} (U_{jk})^2 = 1 \qquad [73]$$

(b) Mutually orthogonal such that for any two symmetry coordinates R_j and R_l

$$\sum_{k=1}^{m} U_{jk} U_{lk} = 0 \qquad [74]$$

(c) Transformable under the symmetry operations of the point group such that if there are f_1 vibrations of the first species, f_2 of the second, etc. then f_1 of the coordinates transform according to the first species, f_2 according to the second, and so on. This is well illustrated by Meister and Cleveland (39) including the case of degenerate vibrations.

[F] Matrix

As seen in [64] the potential energy may be expressed in terms of the internal coordinates:

$$2V = \sum_{i,k=1}^{m} f_{ik}\, r_i\, r_k = [r]'\,[f]\,[r] \qquad [75]$$

In order to have a similar expression in the symmetry coordinates R,

$$2V = \sum_{j,l=1}^{n} F_{jl}\, R_j\, R_l = [R]'\,[F]\,[R] \qquad [76]$$

it is easily shown (39) that the matrix of the F_{jl} elements is found from

$$[F] = [U][f][U]' \qquad [77]$$

where [f] has been defined in [75]. Although [F] is a square matrix of order n it is composed of smaller factors, one identified with each symmetry class of vibration.

[G] Matrix

In order to arrive at a secular determinant it is next necessary to formulate a matrix [G] which is related, through its inverse, to the kinetic energy of the system:

$$2T = [\dot{R}]' \; [G]^{-1} \; [\dot{R}] \qquad [78]$$

If the matrix $[G]^{-1}$ is required, reference should be made to Polo (40).

As this is perhaps the most laborious part of the calculation, various attempts have been made at its simplification. Wilson, Decius and Cross (36) carried out their calculations in terms of the r's whereas Brodersen (41) discusses the advantages in using symmetry coordinates constructed as linear combinations of cartesian displacement coordinates differently oriented for each atom. Wilson's method (34), which utilizes certain vector quantities $\bar{s}_k(t)$, will be used in subsequent calculations and developed here.

The physical meaning of $\bar{s}_k(t)$ is the following: If all atoms except atom t are in their equilibrium positions, then $\bar{s}_k(t)$ is the direction in which a given displacement of atom t will produce the greatest increase in the coordinate r_k (36). Now Decius (42) has given a detailed discussion of the four types of internal coordinates which are sufficient to describe all the vibrational degrees of freedom for any molecule. These are (i) bond stretching, (ii) interbond bending, (iii) bond

torsion, (iv) out of plane bending. It is then possible to tabulate the various $\bar{s}$ vectors which can arise for each of these four types of coordinates. The expressions used by different authors (36)(43) have been collected and the notation changed so that all formulae are in terms of unit vectors $\bar{r}$ directed along the chemical bonds in the molecule. These expressions, which are now perfectly general, are presented in Table 1. They cover every case except that for interbond bending in a linear arrangement of atoms for which reference should be made to Ferigle and Meister(44). There are N x m vectors $\bar{s}_k(t)$, one defined for each atom t and internal coordinate r_k. However in practice it is only necessary to consider one atom from each set of "equivalent atoms". The atoms equivalent to any arbitrarily selected one are all those into which the given atom can be sent by operations of the symmetry group.

Vector quantities $\bar{S}_j^{(t)}$ are next formed (39) from

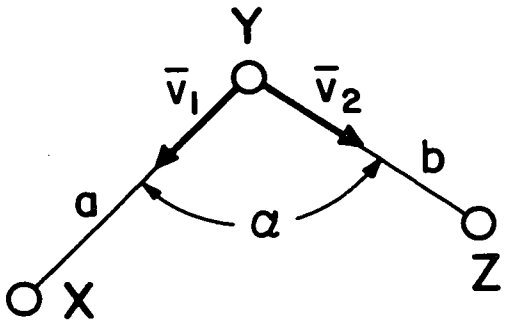
$$\bar{S}_j^{(t)} = \sum_{k=1}^{m} U_{jk}\bar{s}_k(t) \qquad [79]$$

These might be called "symmetry vectors" by their analogy with the formation of the symmetry coordinates in [71]. Again, symmetry vectors are formed only for one atom of each equivalent set.

Finally, the elements of [G] are obtained from the scalar products:

Table 1

Generalized $\bar{s}$ vectors.



(i) Bond stretching

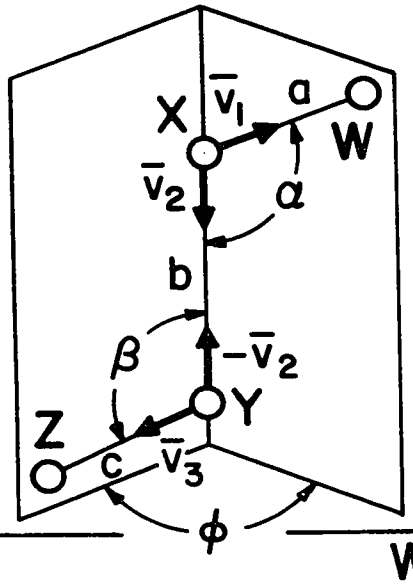
$$\bar{s}_a(X) = \bar{V}_1$$

$$\bar{s}_a(Y) = -\bar{V}_1$$

(ii) Interbond bending

$$\bar{s}_\alpha(X) = (\cos\alpha\,\bar{V}_1 - \bar{V}_2)/a\sin\alpha$$

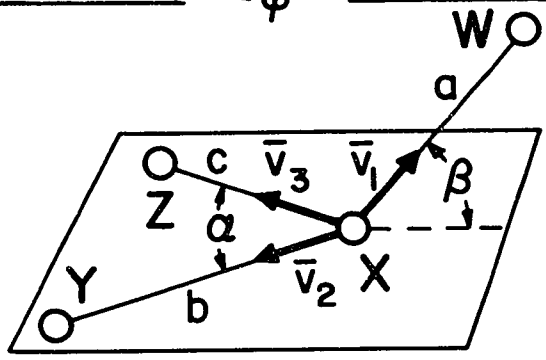
$$\bar{s}_\alpha(Y) = [(a - b\cos\alpha)\bar{V}_1 + (b - a\cos\alpha)\bar{V}_2] / ab\sin\alpha$$



(iii) Bond torsion

$$\bar{s}_\phi(W) = (1/a)\csc^2(\bar{V}_1 \times \bar{V}_2)$$

$$\bar{s}_\phi(X) = -\csc\alpha\left(\frac{\csc\alpha}{a} - \frac{\cot\alpha}{b} - \frac{\cot\beta\cos\phi}{b}\right)(\bar{V}_1 \times \bar{V}_2) + \frac{\cot\beta\sin\phi}{b\sin\alpha}(\bar{V}_1 - \cos\alpha\,\bar{V}_2)$$



(iv) Out of plane bending

$$\bar{s}_\beta(W) = \frac{1}{a}\left(\frac{\bar{V}_3 \times \bar{V}_2}{\cos\beta\sin\alpha} - \tan\beta\,\bar{V}_1\right)$$

$$\bar{s}_\beta(Y) = -\frac{1}{b}\csc^3\alpha\sec\beta\,[(\bar{V}_1\cdot\bar{V}_2) - (\bar{V}_2\cdot\bar{V}_3)(\bar{V}_1\cdot\bar{V}_3)]\,(\bar{V}_2\cdot\bar{V}_3)$$

$$\bar{s}_\beta(X) = \sec\beta\left(\frac{\sin\beta}{a}\bar{V}_1 - \left\{\frac{\sin^2\alpha}{a} + (\bar{V}_2\cdot\bar{V}_3)\left[\frac{(\bar{V}_1\cdot\bar{V}_3)}{b} + \frac{(\bar{V}_1\cdot\bar{V}_2)}{c}\right] - \frac{(\bar{V}_1\cdot\bar{V}_2)}{b} - \frac{(\bar{V}_1\cdot\bar{V}_3)}{c}\right\}\csc^3\alpha\,(\bar{V}_2 \times \bar{V}_3)\right)$$

$$G_{jl} = \sum_p \mu_p \eta_p \bar{S}_j^{(t)} \cdot \bar{S}_l^{(t)} \qquad [80]$$

where p refers to one set of equivalent atoms and

$$\mu_p = 1/m_p \qquad [81]$$

m_p = mass of an atom in the p-th set

η_p = number of atoms in the p-th set

In the case of degenerate modes the procedure is a simple extension of the above and is outlined explicitly by Meister and Cleveland (39).

Alternatively to steps [79] and [80] the same result is obtained by forming a matrix [g] from :

$$g_{ik} = \sum_{t=1}^{n} \mu_t \bar{s}_i(t) \cdot \bar{s}_k(t) \qquad [82]$$

and then, similar to [77],

$$[G] = [U]\,[g]\,[U]' \qquad [83]$$

As in the case of the [F] matrix, [G] will be factored by symmetry classes.

Secular Determinant and Equation

It can be shown that the secular determinant is of the form:

$$\| [F] - [G]^{-1} \lambda \| = 0 \qquad [84]$$

or

$$\| [G] [F] - [E] \lambda \| = 0 \qquad [85]$$

where [E] is the unit matrix. In the language of matrix algebra it is required to find the characteristic roots or eigenvalues λ_i of the matrix [GF] ≡ [H] . Expansion of [85] yields the secular equation in λ which is of the n-th order, or less in the case of symmetry factoring:

$$\lambda^n - C_1\lambda^{n-1} + C_2\lambda^{n-2} - C_3\lambda^{n-3} + \ldots = 0 \qquad [86]$$

Wilson (33) has shown that the coefficients of the equation may be derived directly from the matrices as

$$C_s = \sum \| G \|^{(s)} \| F \|^{(s)} \qquad [87]$$

where $\| G \|^{(s)}$ is any s-rowed minor of $\| G \|$, $\| F \|^{(s)}$ is the corresponding minor of $\| F \|$ and the sum is to be taken over all such minors. This procedure applies to the symmetry classes separately and the roots of [86] give the normal frequencies of the class. The solution by digital computer of factors which are too large to be calculated by hand is discussed at the start of chapter 7.

Normal Coordinates

With each normal mode can be associated a "normal coordinate", Q_i , and in terms of these the potential and kinetic energies of the molecule take the forms:

$$2V = \sum_{i=1}^{n} \lambda_i Q_i^2 \qquad [88]$$

$$2T = \sum_{i=1}^{n} \dot{Q}_i^2 \qquad [89]$$

The normal coordinates (column matrix [Q]) are linearly related to the coordinates in which the vibrational analysis has been carried out, —— in this case the R's, —— by a transformation:

$$[R] = [L]\,[Q] \qquad [90]$$

in which the constant coefficients [L] are to be found.

It is easily shown (36) that

$$[GF]\,[L] = [L]\,[\Lambda] \qquad [91]$$

where $[\Lambda]$ is the diagonal matrix $(\lambda_1, \lambda_2, \ldots \lambda_n)$. This relationship is a set of simultaneous equations which determine the transformation [L] (except for normalization). In matrix terminology, with each eigenvalue λ_a of [H] = [GF] is associated an eigenvector $[L_a]$ which is the a-th column of the square matrix [L].

$$[H]\,[L_a] = [L_a]\,\lambda_a \qquad [92]$$

Physically, the vector $[L_a]$ is a column of n numbers whose ratios are the ratios of the n coordinates $R_1 : R_2 : R_3 : \ldots : R_n$ in the normal mode of vibration

whose frequency is given by λ_a .

As with any matrix vector, $[L_a]$ can be found from the ratios of any row of first minors of the determinant $\| [H] - [E]\lambda_a \|$. This is what is implied in [91]. But it is only the ratio of the vector components that can be determined and in order to satisfy [88] and [89] the $[L_a]$'s must be normalized according to:

$$[L]' [F] [L] = [\Lambda] \qquad [93]$$

and

$$[L]' [G]^{-1} [L] = [E] \qquad [94]$$

However it will be seen that this normalizing is unnecessary for the purposes of the Slater theory and the vectors $[L_a]$ may be accepted with any internal scaling.

CALCULATION OF SLATER AMPLITUDE FACTORS

Once the matrix of eigenvectors [L] has been obtained it is a relatively straightforward matter to apply this information to the Slater expressions.

Calculation of γ_{ki}

The quantities γ_{ki} of [24], one for each coordinate k and mode i , are calculated as follows:

(a) For a given mode with eigenvector $[L_a] = (L_{1a}, L_{2a}, L_{3a} \ldots L_{na})$ the energy ϵ_a in the

mode may be found from any of [75], [76] or [78] of which the simplest is [76]:

$$\epsilon_a = 1/2 \sum_{j,l=1}^{n} F_{jl} R_j R_l = 1/2 \sum_{j,l=1}^{n} F_{jl} L_{ja} L_{la} \quad [95]$$

(b) In general it will be simpler to express the critical coordinate p in terms of the internal coordinates r_k rather than the R_j. The reverse transformation of [72] is

$$[r] = [U]^{-1} [R] \quad [96]$$

or

$$[l_a] = [U]^{-1} [L_a] \quad [97]$$

Consequently, when the ratios of the R's in the various modes are determined by [L], the corresponding ratios of the internal coordinates r_k are given by [l]. Now γ_{ki} may be found for each internal coordinate r_k by:

$$\gamma_{ka} = \frac{l_{ka}}{\sqrt{\epsilon_a}} \quad [98]$$

in which l_{ka} is the k-th component of $[l_a]$. From the form of [98] it will be seen that γ_{ka} is independent of any scaling factors in the vectors since these will cancel.

The Critical Coordinate

In practice the critical coordinate p will be the deviation of some distance within the molecule, either of a bond length, the distance between two non-bonded atoms, or some other parameter which, it will be assumed, can be simply expressed as a function of the internal coordinates r_k .

Coordinates d_k are defined as the molecular parameters of which the r_k are deviations:

$$\Delta d_k = r_k \qquad [99]$$

and similarly the distance P :

$$\Delta P = p \qquad [100]$$

Then P is a function of the d's:

$$P = F(d_1 , d_2 , \ldots d_m) \qquad [101]$$

and

$$\Delta P = \sum_{k=1}^{m} \frac{\partial P}{\partial d_k} \Delta d_k \qquad [102]$$

or

$$p = \sum_{k=1}^{m} \frac{\partial P}{\partial d_k} r_k \qquad [103]$$

Comparing this with Slater's expression [25] it is seen that

$$A_k = \frac{\partial P}{\partial d_k} \qquad [104]$$

The simplest case arises when P coincides with one of the d_k. Two other general cases of frequent interest will be discussed:

(a) Distance between atoms two bonds removed: See Figure 3 (a). Here P is the distance XZ and angle XYZ = α as shown. Now

$$P = (a^2 + b^2 - 2ab \cos \alpha)^{1/2} \qquad [105]$$

so that if $d_1 = a$, $d_2 = b$ and $d_3 = \alpha$ one finds:

$$A_1 = \frac{\partial P}{\partial a} = (a - b \cos \alpha)/P \qquad [106]$$

$$A_2 = \frac{\partial P}{\partial b} = (b - a \cos \alpha)/P \qquad [107]$$

$$A_3 = \frac{\partial P}{\partial \alpha} = (ab \sin \alpha)/P \qquad [108]$$

(b) Distance between atoms three bonds removed: See Figure 3 (b). The most general case is considered in which atoms WXY define a plane which is at an angle ϕ to that of atoms XYZ. P is the distance WZ; the other parameters are indicated in the figure. In this case it can be shown that

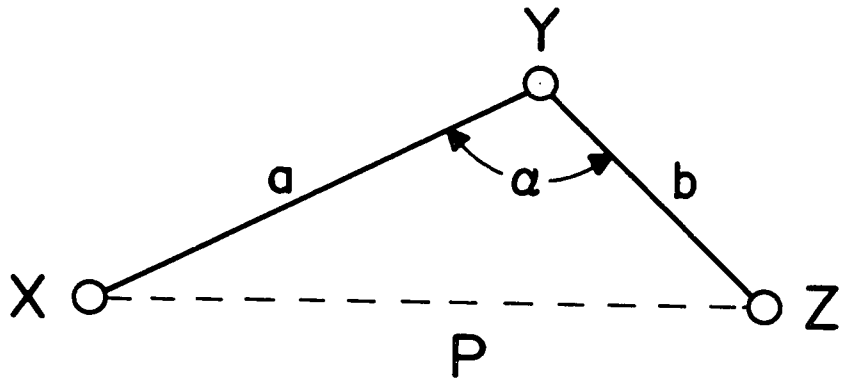


Figure 3(b).

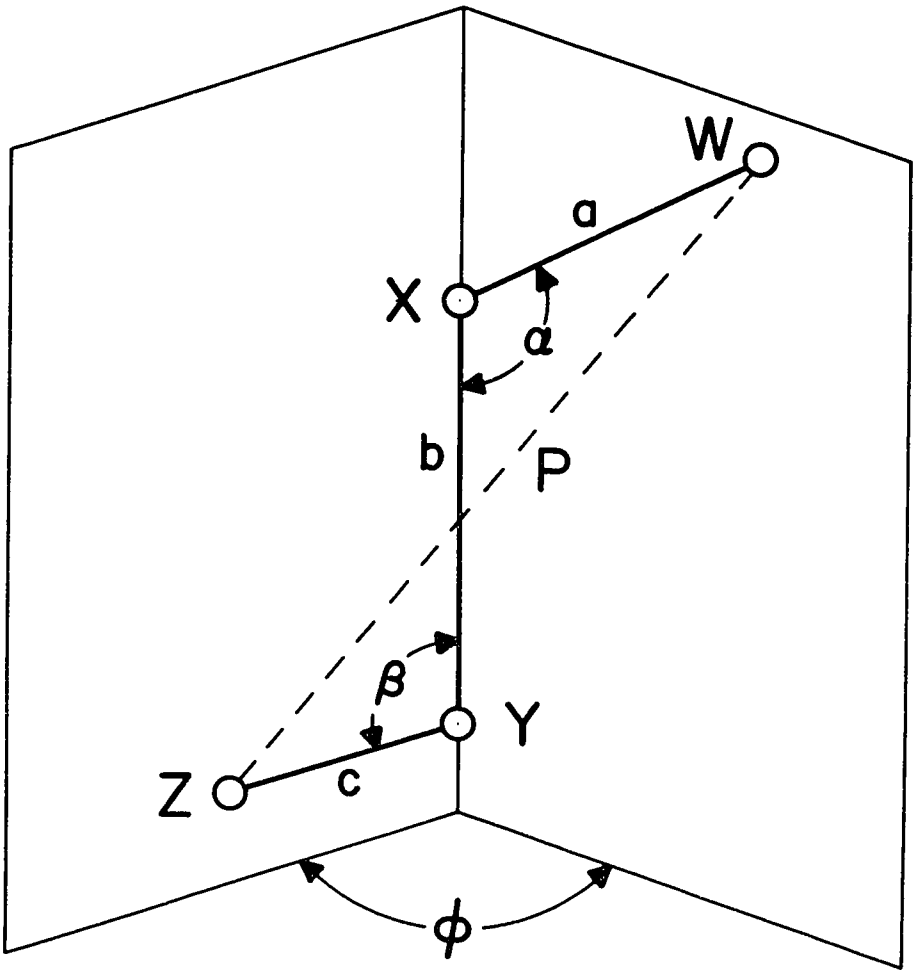


Figure 3(a).

Figure 3. Two possible choices of critical coordinate in a molecule, (a) distance between atoms two bonds removed; (b) distance between atoms three bonds removed.

$$P = \left\{ a^2 + b^2 + c^2 - 2b\,[a \cos \alpha + c \cos \beta] + 2ac\,[\cos(\alpha-\beta) - 2 \sin \alpha \sin \beta \cos^2(\phi/2)] \right\}^{1/2} \quad [109]$$

which reduces to simpler forms for the special cases in which $\alpha = \beta$, $a = c$, or $\phi = 0$. Now if $d_1 = a$, $d_2 = b$, $d_3 = c$, $d_4 = \alpha$, $d_5 = \beta$, $d_6 = \phi$, then

$$A_1 = \frac{\partial P}{\partial a} = (1/P)\,[a - b \cos \alpha + c \cos(\alpha - \beta) - 2c \sin \alpha \sin \beta \cos^2(\phi/2)] \quad [110]$$

$$A_2 = \frac{\partial P}{\partial b} = (1/P)\,[b - a \cos \alpha - c \cos \alpha] \quad [111]$$

$$A_3 = \frac{\partial P}{\partial c} = (1/P)\,[c - b \cos \beta + a \cos(\alpha - \beta) - 2a \sin \alpha \sin \beta \cos^2(\phi/2)] \quad [112]$$

$$A_4 = \frac{\partial P}{\partial \alpha} = (1/P)\,[a(b - c \cos \beta) \sin \alpha - ac \cos \alpha \sin \beta \cos \phi] \quad [113]$$

$$A_5 = \frac{\partial P}{\partial \beta} = (1/P)\,[c(b - a \cos \alpha) \sin \beta - ac \sin \alpha \cos \beta \cos \phi\,] \quad [114]$$

$$A_6 = \frac{\partial P}{\partial \phi} = (1/P)\ ac \sin\alpha \sin\beta \sin\phi \qquad [115]$$

Amplitude Factors

Having computed the γ_{ki} and A_k the amplitude factors a_i for each mode are found simply from [26]:

$$a_i = \sum_{k=1}^{m} A_k \gamma_{ki} \qquad [116]$$

which in turn are normalized according to [27]:

$$\mu_i = \| a_i \| \Big/ \sqrt{\sum_i a_i^2} \qquad [117]$$

CHAPTER 3

DECOMPOSITION OF NITROUS OXIDE

The thermal decomposition of nitrous oxide is of very special interest, since the molecule is one of the simplest capable of undergoing unimolecular breakdown. The reaction is therefore particularly suitable for testing the various theories of unimolecular reactions that have been proposed. Until recently the experimental results for the reaction have been somewhat confusing, owing to various complications such as the existence of surface effects. However, Johnston (45) has recently carried out a detailed critical analysis of the various results and has shown that when the complications are eliminated the reaction represents an excellent example of a straightforward unimolecular decomposition. It is possible that Johnston slightly oversimplifies the situation (46), but it seems likely that the rate constants he deduces for the high and low-pressure reaction are close to the true ones. They should certainly be sufficiently reliable to permit a careful test of the theories, and this is what has been done in the present chapter.

EXPERIMENTAL DATA

Only the bare results will be stated here; for a more detailed discussion of the experimental work reference should be made to Johnston's paper (45). The rate-controlling step is believed to be

$$N_2O = N_2 + O ,$$

a reaction that is endothermic by 39.5 kcal. The high-pressure activation energy ($E_a = E_o$) of the reaction is close to 60.0 kcal. At 880°K the high-pressure first-order rate constant is

$$k_\infty = 7.47 \times 10^{-4} \text{ sec}^{-1}$$

and this corresponds to a frequency factor of

$$8.134 \times 10^{11} \text{ sec}^{-1}$$

(The term "frequency factor" is a general one applied to the pre-exponential part of k_∞. In Kassel's theory it is $k^{\ddagger}$; in Slater's ν, and in less detailed descriptions it is frequently designated as A.) By extrapolation of Johnston's second-order rate coefficients to zero pressure the rate of energization is estimated to be

$$k_1 = 14.0 \text{ cc mole}^{-1} \text{ sec}^{-1}$$

The pressure at which the first-order rate coefficient falls to one-half of its limiting value is approximately

$$P_{1/2} = 1.3 \times 10^{4} \text{ mm.}$$

THEORY OF THE HIGH-PRESSURE RATE

The experimental frequency factor at high pressure, 8.134×10^{11} sec^{-1}, is significantly below what would be expected on the basis of equations [15], [31] and [43] above. The frequencies of vibration of the molecule are of the order of 10^{13} sec^{-1}, so that $k^{\dagger}$ in Kassel's theory is of this magnitude. Slater's average vibrational frequency, weighted using the μ values derived below, is

$$\nu = 4.98 \times 10^{13} \text{ sec}^{-1}$$

The value of kT/h at 888°K is equal to 1.85×10^{13} sec^{-1}. It is therefore seen that the experimental value is too low by between one and two powers of 10.

The reason for this lies in the fact that the rate-controlling step involves a change of multiplicity:

$$N_2O(^1\Sigma) \longrightarrow N_2(^1\Sigma) + O(^3P)$$

Since a triplet and a singlet can only give a triplet it follows that the reaction must involve a transition from one potential-energy curve to another, as represented

schematically in Figure 4. The ground state of N_2O correlates with $N_2(^1\Sigma)$ and $O(^1D)$, and the curve for this crosses the repulsive curve for $N_2(^1\Sigma) + O(^3P)$. The forms of these curves have been discussed by Stearn and Eyring (47). At the time their paper was published, however, the experimental evidence pointed to an activation energy as low as 52 kcal and a transmission coefficient of about 10^{-4}. This suggested a resonance splitting of as little as 5 cal per mole, and difficulty was experienced in explaining such a small value. The value of 10^{-1} to 10^{-2} obtained above leads to a resonance separation of the order of 500 cal per mole and this is what might reasonably be expected on the basis of spin-orbit interactions (47).

THEORY OF THE LOW-PRESSURE RATE

The low-pressure second-order rate constant, found experimentally to be about 14.0 cc mole^{-1} sec^{-1}, is, according to all theories, the rate of energization of the molecule. This value must be explained in terms of the distribution of energy of activation amongst the four normal modes of vibration, with or without flow of energy between the normal modes. In the calculations the collision diameter has been taken as 3.31×10^{-8} cm, as employed by Johnston (45). At 888°K, the temperature at which the experimental data were obtained, this corresponds to a

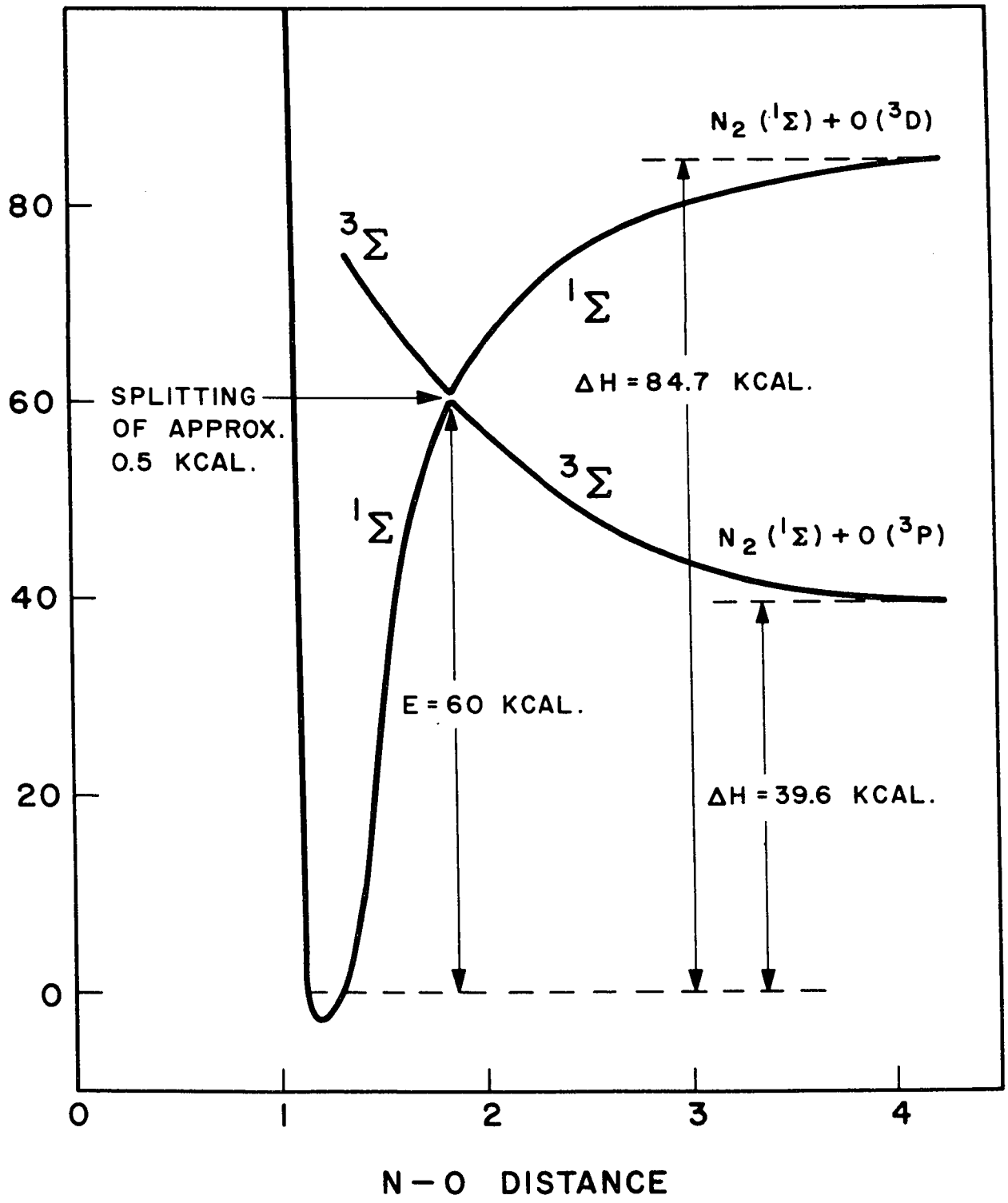


Figure 4. Schematic potential energy curves for the decomposition of nitrous oxide. The curves are based on those calculated by Stearn and Eyring, but are modified to accomodate the latest thermochemical and kinetic values.

collision number of

$$Z_{-1} = 3.182 \times 10^{-10} \text{ cc molecule}^{-1} \text{ sec}^{-1}$$
$$= 1.916 \times 10^{14} \text{ cc mole}^{-1} \text{ sec}^{-1}$$

HKRR Theory

Taking $E_o = 60.0$ kcal per mole and $T = 888^{\circ}K$, the value of b from [10] is 33.95 . With $s = 2$, the value of k_1 from [46] is

$$k_1 = 6.09 \text{ cc mole}^{-1} \text{ sec}^{-1}$$

which is reasonably close to the experimental value of $14.0 \text{ cc mole}^{-1} \text{ sec}^{-1}$. This choice of s gives the best agreement; $s = 4$, for example, leads to $1.22 \times 10^3 \text{cc mole}^{-1} \text{ sec}^{-1}$. The reason that $s = 3$ and $s = 4$ lead to rates that are too high is presumably that there is little flow of energy between the two axial and the two bending modes (see below).

Slater Theory

The vibrational analysis for the N_2O molecule has been carried out and the calculations along with the determination of the Slater parameters are given at the end of the chapter to avoid loss of coherence. The molecule is linear and the normal modes of vibration are shown in Figure 5. Two of the frequencies, ν_1 and ν_3 in the conventional notation, correspond to axial vibrations,

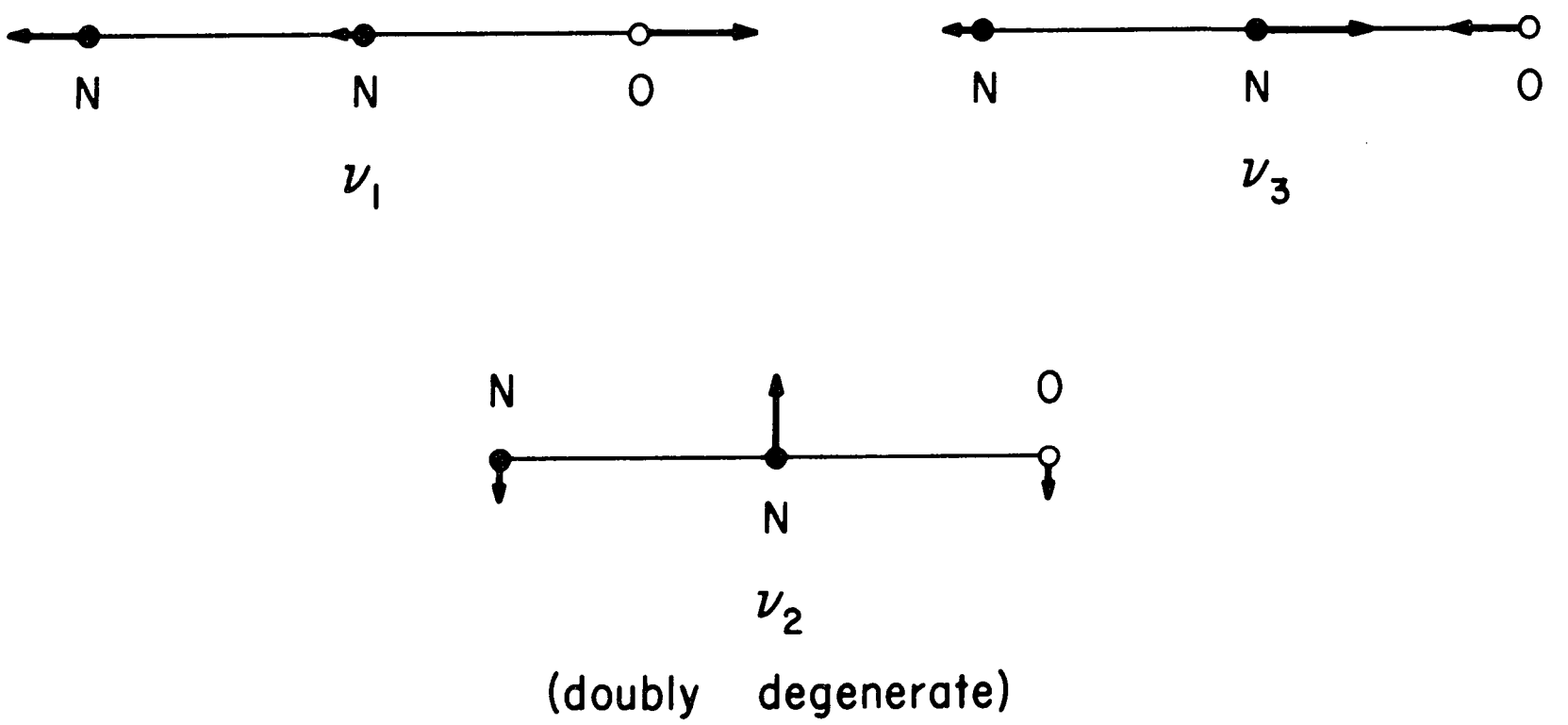


Figure 5. The normal modes of vibration of nitrous oxide.

and one frequency, ν_2, corresponds to the doubly degenerate vibrations perpendicular to the axis. The motion of the molecule may be described in terms of three co-ordinates w, x, and y, of which w denotes the mutual displacement of the nitrogen atoms and x and y the components of the displacement of the oxygen atom relative to the center of the N-N distance; x is along the axis of the molecule and y perpendicular to it. The analysis below gives the desired matrix [1] to which reference is made in [97].

In applying Slater's theory the critical coordinate for the dissociation into N_2 + O has been taken as the distance from the O atom to the centre of mass of N-N. The variation, p, in this coordinate, is equal simply to x and does not involve w and y. Since the bending vibrations involve only y it follows that they do not contribute to the decomposition so that n must be taken equal to 2. (It is readily shown that Slater's A_y of [25] or [104] is zero so that the bending vibrations do not make a contribution to any choice of axial coordinate.) The amplitude factors α and μ corresponding to the two axial vibrations are shown in Table 2, along with the frequencies (48) used in the calculation.

Table 2

Frequencies and amplitude factors
of the two axial modes of N_2O

i	ν_i ($sec^{-1} \times 10^{-13}$)	a_i ($\times 10^3$)	μ_i
1	3.864	1.236	0.8201
3	6.709	0.8625	0.5723

The product of the μ's is given by

$$\prod_{i=1,3} \mu_i = \mu_1 \mu_3 = 0.4693$$

Using Slater's equation [56] with $n = 2$ the value of k_1 is then found to be

$$k_1 = 1.72 \text{ cc mole}^{-1} \text{ sec}^{-1}$$

which is below the experimental value by a factor of 8.

THE FALLING-OFF OF THE HIGH-PRESSURE RATE COEFFICIENT

Figure 6 is a plot of the experimental first-order rate coefficients as a function of pressure (45). The two lines to the left show the theoretical behavior based on Kassel's theory with s equal to 2 and to 4. These curves were constructed by numerical integration of

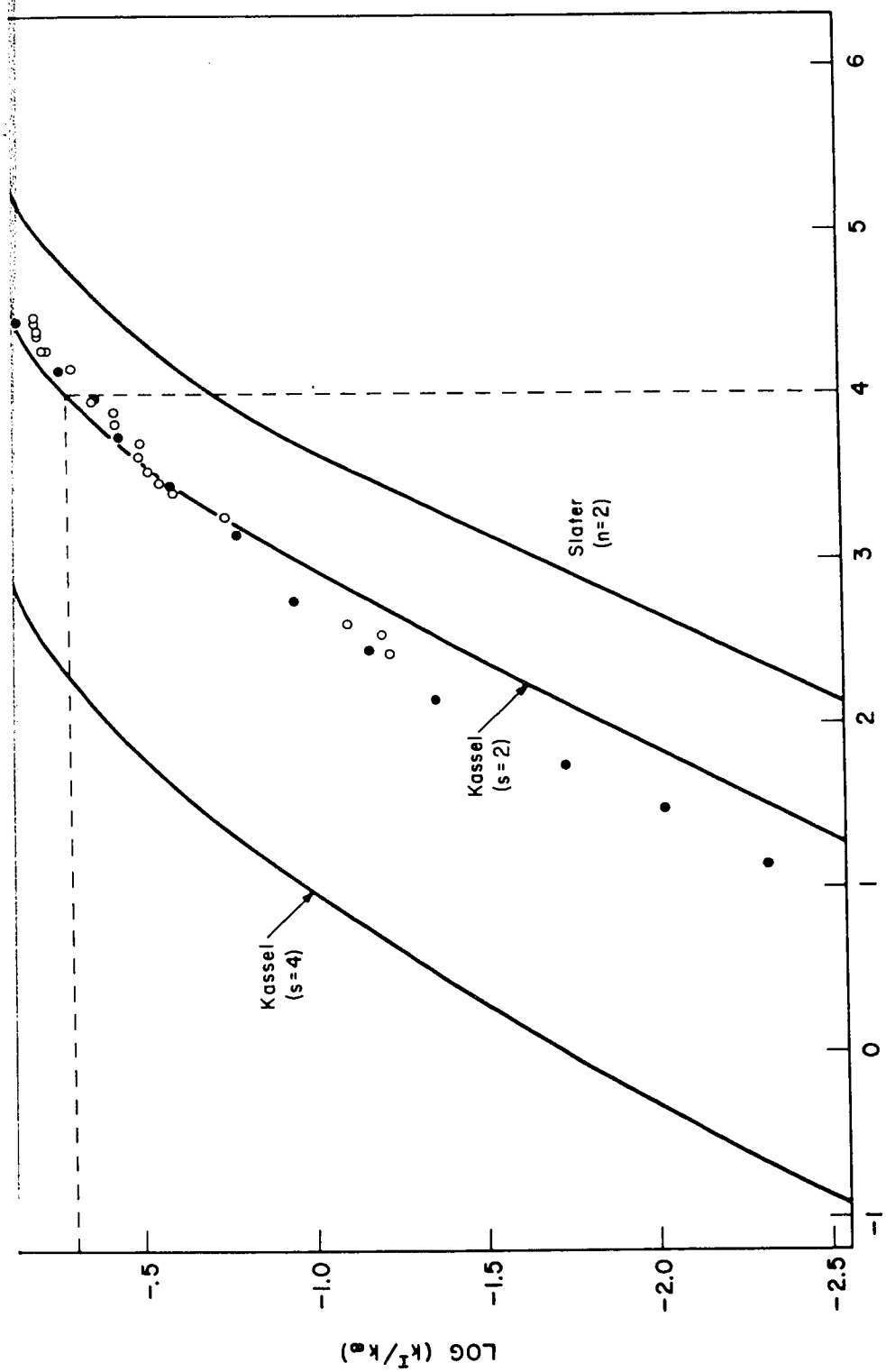


Figure 6. Plot of the logarithm of the first-order rate coefficient against the logarithm of the pressure for N_2O decomposition. The data is that given by Johnston (45); the full-line curves are theoretical predictions.

Kassel's general rate equation [17] using the values

$$k^* = 8.134 \times 10^{11} \text{ sec}^{-1} \text{ (experimental)}$$

$$Z_{-1} = 3.182 \times 10^{10} \text{ cc molecule}^{-1} \text{ sec}^{-1}$$

The curve for $s = 4$ is seen to lead to rates that are much higher than the experimental ones, but that for $s = 2$ falls very close to the experimental values. The pressure for $s = 2$ at which K^1 reaches one half its limiting rate is 1.3×10^4 mm., and this is essentially the same as the experimental value. It is of interest that the approximate relationship

$$[A]_{1/2} \doteq k_\infty / k_1 \qquad [118]$$

for the half-pressure leads to a value of 6.78×10^3 mm.

Slater's curve is of the same shape as Kassel's but is displaced to the right as shown in Figure 6. The predicted half-pressure is 6.3×10^4 mm in this case, which is significantly larger than the observed value.

DISCUSSION

The main conclusion of this study is that the Kassel treatment with s equal to 2 leads to satisfactory rates over the entire pressure range, and to a reliable estimate of the half-pressure $P_{1/2}$. The Slater expression however, leads to rates that are significantly too low

except in the high-pressure region, and to too high a value for $P_{1/2}$. It may be concluded then that for this simple molecule there appears to be a flow of energy between the normal modes, as envisaged by the HKRR theory but not by Slater's theory.

As mentioned in chapter 1, this treatment involves the assumption that deactivation occurs on every collision. If this is not the case the Slater and Kassel rates of energization are correspondingly reduced. The conclusion that Slater's rate of energization is too low is then true a fortiori; Kassel's rates with $s = 2$ would be too low as well but agreement might be obtained with s equal to 3 or 4.

VIBRATIONAL ANALYSIS

The theory of vibrations in asymmetric linear triatomic molecules, and of N_2O in particular, has been discussed by Rosenthal (49). The potential and kinetic energy functions and molecular parameters employed in that paper, along with the calculated force constants, have been used in the present investigation to compute the amplitude factors and other quantities required for Slater's treatment of unimolecular reactions.

The vibrational modes are shown in Figure 5. The mutual displacement of the nitrogen atoms is denoted by w, while x and y are the components of the displanement

of the oxygen atom relative to the centre of the two nitrogen atoms; x is the displacement along the axis and y that perpendicular to it.

The most general quadratic potential function consistent with geometrical symmetry may be written in terms of four force constants:

$$2V = Ax^2 + Bw^2 + Cy^2 + 2Dxw \qquad [119]$$

If q_{NN} and q_{NO} denote the N-N and N-O distances we may define q and β by

$$q \equiv q_{NN} + q_{NO} \qquad [120]$$

$$\beta \equiv q_{NN}/(2q_{NO} + q_{NN}) \qquad [121]$$

and

$$M \equiv m_1/(m_1 + 2m_2) \qquad [122]$$

where m_1 and m_2 are the masses of the oxygen and nitrogen atoms respectively. The kinetic energy is then

$$2T = m_2 \left\{ 2M\dot{x}^2 + \dot{w}^2/2 + 2\beta^2\dot{y}^2 \left[1 + (\beta^2/M)\right]^{-1} \right\} \qquad [123]$$

Applying the Lagrange equations of motion [67] to [119] and [123] and using the definitions:

$$E \equiv 2M \qquad [124]$$

$$F \equiv 1/2 \qquad [125]$$

$$G \equiv 2\beta^2 \left[1 + (\beta^2/M)\right]^{-1} \qquad [126]$$

the secular determinant is

$$\begin{vmatrix} A - m_2 E\lambda & D & 0 \\ D & B - m_2 F\lambda & 0 \\ 0 & 0 & C - m_2 G\lambda \end{vmatrix} = 0 \qquad [127]$$

The values of the constants derived by Rosenthal (49) are:

$$A = 14.72 \times 10^5 \text{ dynes cm}^{-1}$$
$$B = 17.20 \times 10^5 \text{ dynes cm}^{-1}$$
$$D = -7.08 \times 10^5 \text{ dynes cm}^{-1}$$

while the observed frequencies employed in the calculation (48) are:

$$\nu_1 = 1288.7 \text{ cm}^{-1}$$
$$\nu_2 = 588.3 \text{ cm}^{-1}$$
$$\nu_3 = 2237.9 \text{ cm}^{-1}$$

The required vectors $[l_a]$ are found by taking first minors of the determinant [127]. Recalling that $\lambda \equiv 4\pi^2\nu^2$ the result is that

for ν_1, $x:w:y = (B-m_2F\lambda_1):-D:0 = (1.00):(0.685):0$;

for ν_2, $x:w:y = 0:0:(C-m_2G\lambda_2) = 0:0:k$;

for ν_3, $x:w:y = D:-(A-m_2E\lambda_3):0 = (-0.462):(1.00):0$.

Retaining the conventional numbering of the modes, which is confusing from the point of view of symmetry classes, the matrix [1] of the vectors is :

$$[1] = \begin{array}{c|ccc} & \nu_1 & \nu_2 & \nu_3 \\ \hline x & 1.00 & 0 & -0.462 \\ w & 0.685 & 0 & 1.00 \\ y & 0 & k & 0 \end{array} \qquad [128]$$

Because the critical coordinate is simply

$$p = x \qquad [129]$$

the quantities A_k of [25] are $A_x = 1$, $A_w = 0$, $A_y = 0$. From [116] and [98] the amplitude factors a_i are

$$a_i = \gamma_{xi} = l_{xi}/\sqrt{\epsilon_i} \qquad [130]$$

The l_{xi} are of course the elements of the first row of

[1] while ϵ_i are calculated (for i = 1 and 3) from [119] using the l_{ik} for the x , w and y . These a_i along with the normalized amplitude factors μ_i calculated from [117] are listed in Table 2 above.

CHAPTER 4

DECOMPOSITION OF OZONE

The pyrolysis of ozone has been reviewed and reinvestigated experimentally by Benson and Axworthy (50) who show that most of the known data are quantitatively explained on the basis of a simple mechanism, the first step of which is:

$$M + O_3 = M + O_2 + O$$

There was no evidence for a direct bimolecular reaction of ozone to produce O_2 nor for important surface effects or energy chains. The data with which theory will be compared is that for the above reaction with $M = O_3$.

EXPERIMENTAL DATA

The experimental data for ozone are concerned entirely with the low-pressure region in which the kinetics are second-order. Attention will therefore be confined to this region where, all theories agree, the measured rate is the rate of energization.

Benson and Axworthy report (50) that the low-pressure activation energy E_a for this reaction is

24.0 kcal and that the rate of energization is given by

$$k_1 = 4.61 \pm 0.25 \times 10^{12} \exp(-24000/RT) \text{ l mole}^{-1} \text{ sec}^{-1}$$

At 372.8°K this gives

$$k_1 = 44.1 \text{ cc mole}^{-1} \text{ sec}^{-1} .$$

THEORETICAL RATES OF ENERGIZATION

HKRR Theory

Using a collision diameter of 3.35×10^{-8} cm the collision number Z_{-1} at 372.8°K is found to be 2.021×10^{-10} cc molecule^{-1} sec^{-1}. Since $E_a = 24.0$ kcal, E_o is found from [61] and at 372.8°K $b = 33.85$. Taking $s = 3$, the total number of vibrational modes in the molecule, k_1 is calculated from [46] to be :

$$k_1 = 148 \text{ cc mole}^{-1} \text{ sec}^{-1}$$

and with $s = 2$,

$$k_1 = 22.4 \text{ cc molecule}^{-1} \text{ sec}^{-1}$$

Slater Theory

(a) Critical coordinate as an O-O distance: By taking the critical coordinate as the extension of the O-O bond it is found that all three normal modes contribute to the dissociation. Consequently, with $n = 3$, the Slater

value of b, obtaining E_o from [62], is 32.85. The amplitude factors a_i and μ_i for this critical coordinate have been calculated in the section devoted to the vibrational analysis at the end of the chapter and are presented in Table 3 along with the assignment of fundamentals due to Wilson and Badger (51) which has been employed.

Table 3

Frequencies and amplitude factors for the 0-0 stretch in O_3

i	ν_i (cm^{-1})	a_i ($x10^4$)	μ_i
1	1110	7.98	0.578
2	705	2.68	0.194
3	1043	10.94	0.793

The product $\prod_i \mu_i$ is :

$$\mu_1\mu_2\mu_3 = 0.0888$$

The weighted vibrational frequency ν, defined by [33] is found to be 3.164×10^{13} sec^{-1}. According to the Slater theory this is equal to the high-pressure frequency factor, for which no experimental value is available.

The rate constant k_1, on the Slater model, may now be calculated from [56] to give

$$k_1 = 48.6 \text{ cc mole}^{-1} \text{ sec}^{-1}$$

which is very close to the experimental rate.

(b) Hypothetical critical coordinate giving maximum rate: Because of the arbitrariness which frequently arises in the choice of the critical coordinate, it is always possible to calculate the maximum possible rate based upon some hypothetical coordinate which makes $\prod_i \mu_i$ a maximum. Since $\sum_i \mu_i^2 = 1$, the quantity $\prod_i \mu_i$ is a maximum when each μ equals $1/\sqrt{n}$ for which

$$\prod_i \mu_i \text{ (max.)} = n^{-n/2}$$

In this case $\prod_i \mu_i \text{ (max.)} = 0.192$ and from [56] again,

$$k_1 \text{ (max.)} = 105 \text{ cc mole}^{-1} \text{ sec}^{-1}$$

which is double the value calculated above.

DISCUSSION

The most interesting result of these calculations is that equation [56], with the most reasonable choice of reaction coordinate, gives rise to a rate of energization that agrees closely with the experimental value. The maximum rate allowed by the Slater theory and the rate calculated using the HKRR expression with $s = 3$ are

somewhat too high. It is to be noted, however, that the discrepancies are not very great and that the results for this reaction do not permit a firm conclusion to be drawn as to whether the Slater or HKRR assumptions are applicable. A slightly different collision number or activation energy could give good agreement using the HKRR expression.

VIBRATIONAL ANALYSIS

A vibrational assignment and calculation of the force constants for ozone has been carried out by Penney and Sutherland (52)(53). There are, however, certain mathematical errors in this treatment, and it proved impossible, using Penney and Sutherland's procedure, to arrive at a satisfactory set of force constants for the molecule. Dr. N. B. Slater is gratefully acknowledged for pointing out that the original calculations, based upon the Penney-Sutherland assignment, were not self-consistent; this led to a re-examination of the problem and the formulation of a more satisfactory treatment.

Normal Coordinates

In the present work use has been made of the more recent vibrational assignment of Wilson and Badger (51) and of the following values of the apex angle and the interatomic (bonded) distance:

$$\theta = 116^{\circ}49'$$

$$d_1 = d_2 \equiv d = 1.278 \times 10^{-8} \text{ cm}$$

The latter values were obtained by Trambarulo, Ghosh, Burrus and Gordy (54) and confirmed by subsequent workers (55)(56). This microwave work supports the assignment of Wilson and Badger, and the agreement of independent determinations allows confidence in these parameters. The angle quoted above differs somewhat from the earlier electron-diffraction value (57) of 127°.

By re-analysing the rotational spectrum of O_3 to include the effect of centrifugal distortion (using the Kivelson-Wilson energy expression (58) for a semirigid rotator) Pierce (59) was able to make a sensitive determination of the potential function that is compatible with both the distortion frequency shifts and the observed infrared spectrum. In the general potential function,

$$2V = f_d[(\Delta d_1)^2 + (\Delta d_2)^2] + f_\delta(\Delta\delta)^2 + 2f_{dd}(\Delta d_1)(\Delta d_2) + f_{d\delta}(\Delta\delta)[(\Delta d_1) + (\Delta d_2)] \qquad [131]$$

the constants are:

$$f_d = 5.7007 \times 10^5 \text{ dynes cm}^{-1}$$

$$f_\delta = 2.0983 \times 10^{-11} \text{ dynes cm}$$

$$f_{dd} = 1.5233 \times 10^5 \text{ dynes cm}^{-1}$$

$$f_{d\delta} = 0.4248 \times 10^{-3} \text{ dynes}$$

These values can be used to reproduce the frequencies of Wilson and Badger (51) to within o.2%.

Following the FG matrix treatment outlined in chapter 2, the internal coordinates are designated as $r_1 = \Delta d_1$, $r_2 = \Delta d_2$, $r_3 = \Delta\delta$, so that

$$2V = [r]' [f] [r] \qquad [132]$$

The molecule belongs to the symmetry point group C_{2v} for which the character table is presented in table 4. The number of modes of each species is easily worked out (35) and the last column of Table 4 shows the manner in which the three degrees of vibrational freedom are divided among the various symmetry species in the case of ozone. The symmetry coordinates, chosen so as to satisfy conditions (a), (b) and (c) on pages 58-9, are:

$$R_1 = (\Delta d_1 + \Delta d_2)/\sqrt{2} \qquad [133]$$

$$R_2 = \Delta\delta \qquad [134]$$

$$R_3 = (\Delta d_1 - \Delta d_2)/\sqrt{2} \qquad [135]$$

These expressions define the matrix [U] of [72].

Formation of the matrices [F] and [G] yields the numerical elements:

Table 4

Character table for the point group C_{2v} with the number of vibrations of each symmetry species for O_3.

C_{2v}	I	$C_2(z)$	$_v(xz)$	(yz)	Number of genuine vibrations
A_1	+1	+1	+1	+1	2
A_2	+1	+1	-1	-1	0
B_1	+1	-1	+1	-1	1
B_2	+1	-1	-1	+1	0

$F_{11} = 7.2240$ $\quad$ $G_{11} = 0.58354$

$F_{12} = F_{21} = 2.0983$ $\quad$ $G_{12} = G_{21} = -0.37199$

$F_{22} = 0.60077$ $\quad$ $G_{22} = 1.1296$

$F_{33} = 4.1774$ $\quad$ $G_{33} = 0.92246$

in which the basic units are gm , sec , and angstroms. All other elements are zero.

The matrix [L] found from [91] is

$$[L] = \begin{array}{c|ccc} & \nu_1 & \nu_2 & \nu_3 \\ \hline R_1 & 1.000 & 0.193 & 0 \\ R_2 & -0.903 & 1.000 & 0 \\ R_3 & 0 & 0 & k \end{array} \qquad [136]$$

in which the unit of distance is the angstrom and angles are in radians. The matrix [1] is obtained from [97] and since

$$[U]^{-1} = [U]' \qquad [137]$$

the result is

$$[l] = \begin{array}{c|ccc} & \nu_1 & \nu_2 & \nu_3 \\ \hline r_1 & 0.707 & 0.136 & (0.707)k \\ r_2 & 0.707 & 0.136 & -(0.707)k \\ r_3 & -0.903 & 1.00 & 0 \end{array} \qquad [138]$$

From these figures it is a simple matter to depict the form of the normal coordinates as shown in Figure 7.

Amplitude Factors

The critical coordinate p is taken simply as the variation in the O-O bond:

$$p = r_1 = \Delta d_1 \qquad [139]$$

It is recognized that there are now two critical coordinates present. Then, by [104], $A_1 = 1$, $A_2 = 0$ and $A_3 = 0$. Consequently, the only γ_{ki} required are those for which $k = 1$ and it is seen from [116] that $a_i = \gamma_{1i}$.

ϵ_i is most easily computed from [95] and then the $\gamma_{1i} = a_i$ are obtained from [98] and [138]. Finally, the normalized amplitude factors μ_i are calculated according to [117]. These amplitude factors are presented above in Table 3.

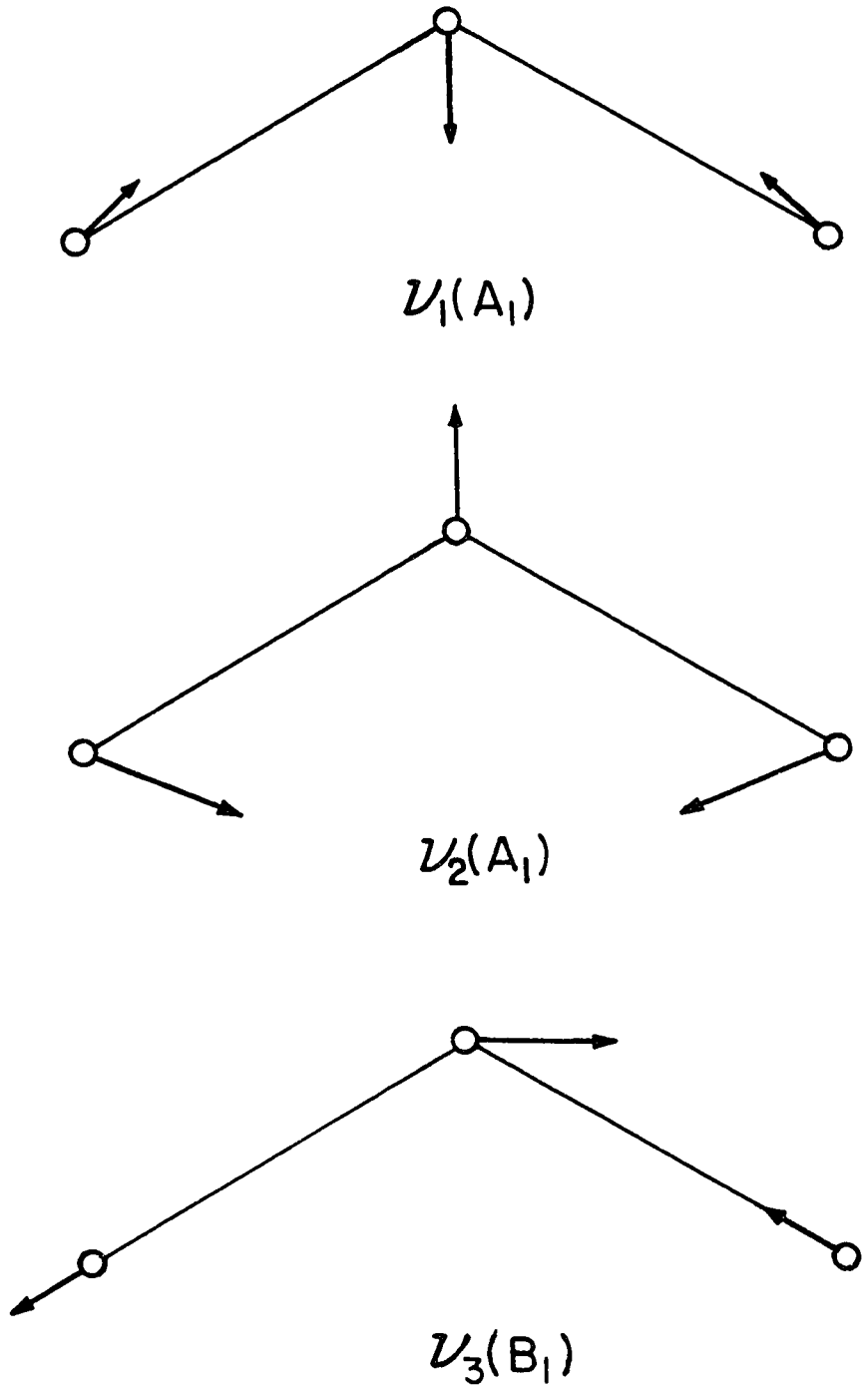


Figure 7. The normal modes of vibration of the ozone molecule.

CHAPTER 5

DECOMPOSITION OF HYDROGEN PEROXIDE

Measurements have recently been made on the rates of the homogeneous thermal decomposition of hydrogen peroxide (21)(60)(61) and suitable spectroscopic information is available for the molecule (62) enabling the Slater parameters to be calculated. As in the case of ozone, experimental data are confined to the low-pressure region in which the kinetics are of the second order (the transition pressure being too high for convenient study). Nevertheless, the results provide sufficient information for a partial test of the theories.

EXPERIMENTAL DATA

Since the theoretical considerations and the more recent kinetic results have indicated the reaction to be of the second order under the actual conditions of the experiments, we have calculated a second-order constant from the data of Giguère and Liu (60). The result at $723^{\circ}K$ is

$$k_1 = 1.5 \times 10^4 \text{ cc mole}^{-1} \text{ sec}^{-1}$$

and the activation energy is 48.0 kcal per mole. Hoare, Protheroe and Walsh (61) also obtain an activation energy of 48.0 kcal, and find the reaction to be second-order; from their results at 723°K the second-order constant is calculated to be

$$k_1 = 7.6 \times 10^3 \text{ cc mole}^{-1} \text{ sec}^{-1} .$$

Forst (21) also obtains second-order kinetics and his activation energy is 48.1 kcal. His rate constant at 723°K is

$$k_1 = 2.82 \times 10^4 \text{ cc mole}^{-1} \text{ sec}^{-1}.$$

The rate constants are seen to be in good agreement.

The assignment of the fundamental frequencies of vibration, according to Giguère and Bain (62), is given in Table 6.

THEORETICAL CALCULATION OF RATES

The rates of energixation predicted by both the HKRR and Slater theories are computed. In the latter case calculations have been carried out with different choices of the critical coordinate.

HKRR Theory

In the following calculations the experimental activation energy (60) has been taken as

$$E_a = 48.0 \text{ kcal mole}^{-1} .$$

The molecular collision diameter σ is assumed to be

$$\sigma = 2.93 \times 10^{-8} \text{ cm}$$

which is the same as for oxygen (63). The resulting collision number at 723^0K is found from [29]:

$$Z_{-1} = \omega/[A] = 2.56 \times 10^{-10} \text{ cc molecule}^{-1} \text{ sec}^{-1}$$

Then taking $s = 6$, the parameter b is calculated from [10] and [61], and using [46] to obtain k_1 it is found that

$$k_1 = 1.97 \times 10^5 \text{ cc mole}^{-1} \text{ sec}^{-1}$$

which is somewhat larger than the experimental value of 1.5×10^4 cc mole^{-1} sec^{-1}. The use of $s = 5$ gives better agreement, the calculated value being

$$k_1 = 2.66 \times 10^4 \text{ cc mole}^{-1} \text{ sec}^{-1}$$

In order to find the half-pressure predicted by Kassel's general rate equation, the expression [17] was integrated numerically taking $s = 5$ and $k = 3 \times 10^{13}$ sec^{-1}.

The pressure obtained was

$$P_{1/2} = 3.5 \times 10^3 \text{ mm.}$$

This high value supports the conclusion that the rates measured so far (21)(60)(61), in the region of a few millimeters pressure, are in fact second-order rates. Since this predicted $P_{1/2}$ is not experimentally inaccessible (as opposed to that given by Slater's treatment below) it would be of interest to carry out measurements in this region,

Slater Theory

The rate predicted by the Slater treatment depends upon the choice of critical coordinate p. Since the rate determining step in the hydrogen peroxide decomposition is the rupture of the O-O bond (60), the deviation of the length of this bond from its equilibrium value, ΔD, is the most obvious choice for p. The structure of the molecule is shown in Figure 8.

(a) O-O distance as critical: The vibrational analysis and determination of Slater parameters are again relegated to the final section of the chapter. The normal modes of vibration are represented in Figure 9. With the present choice of p it is found that only the four symmetric modes, $\nu_1 - \nu_4$, contribute to its extension. The amplitude factors α_i and μ_i for this case have been calculated below and are presented in Table 5.

Equations [10] and [62] with $n = 4$ are used to

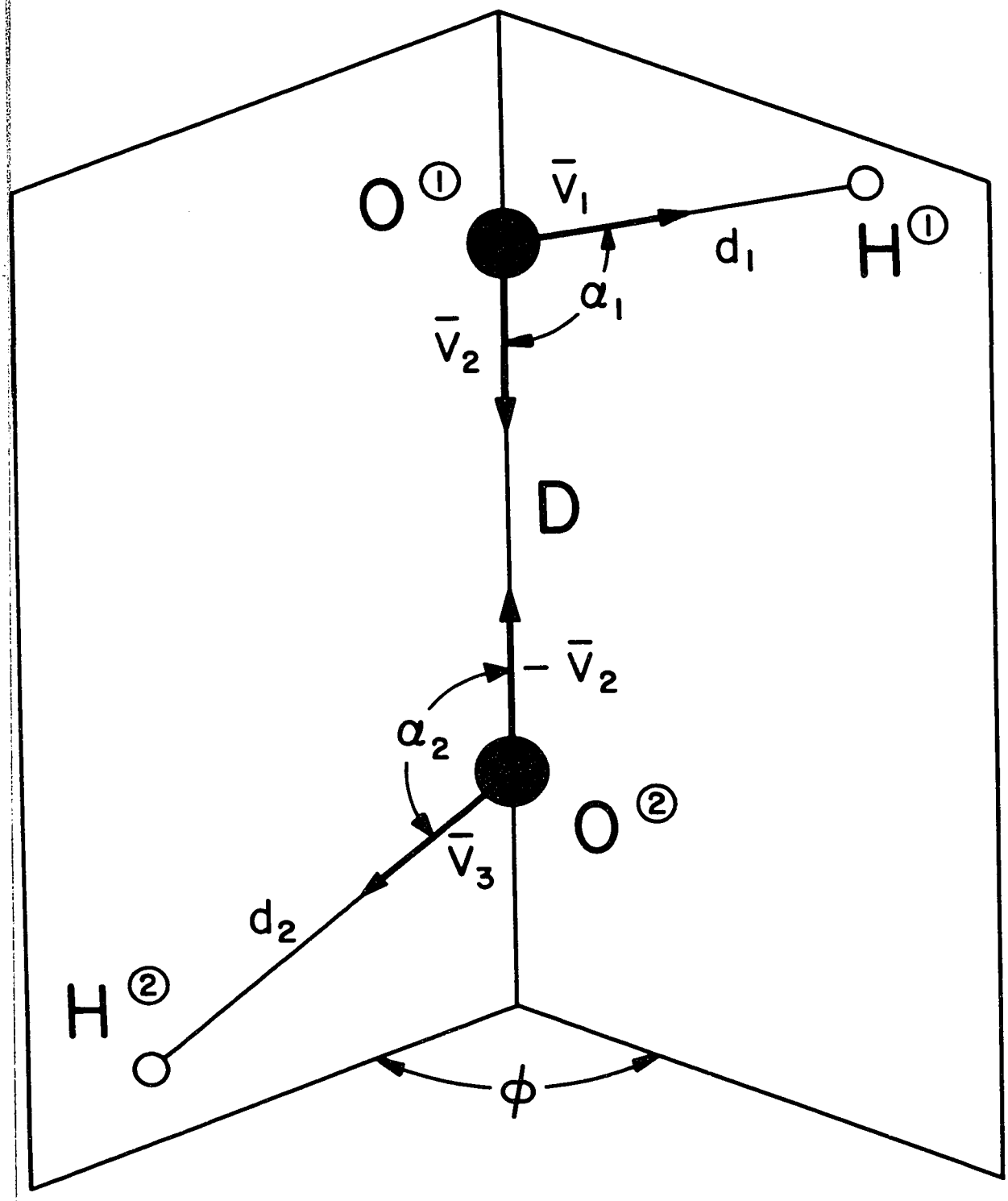


Figure 8. Schematic representation of the hydrogen peroxide molecule, showing the internal coordinates and unit vectors employed in the treatment.

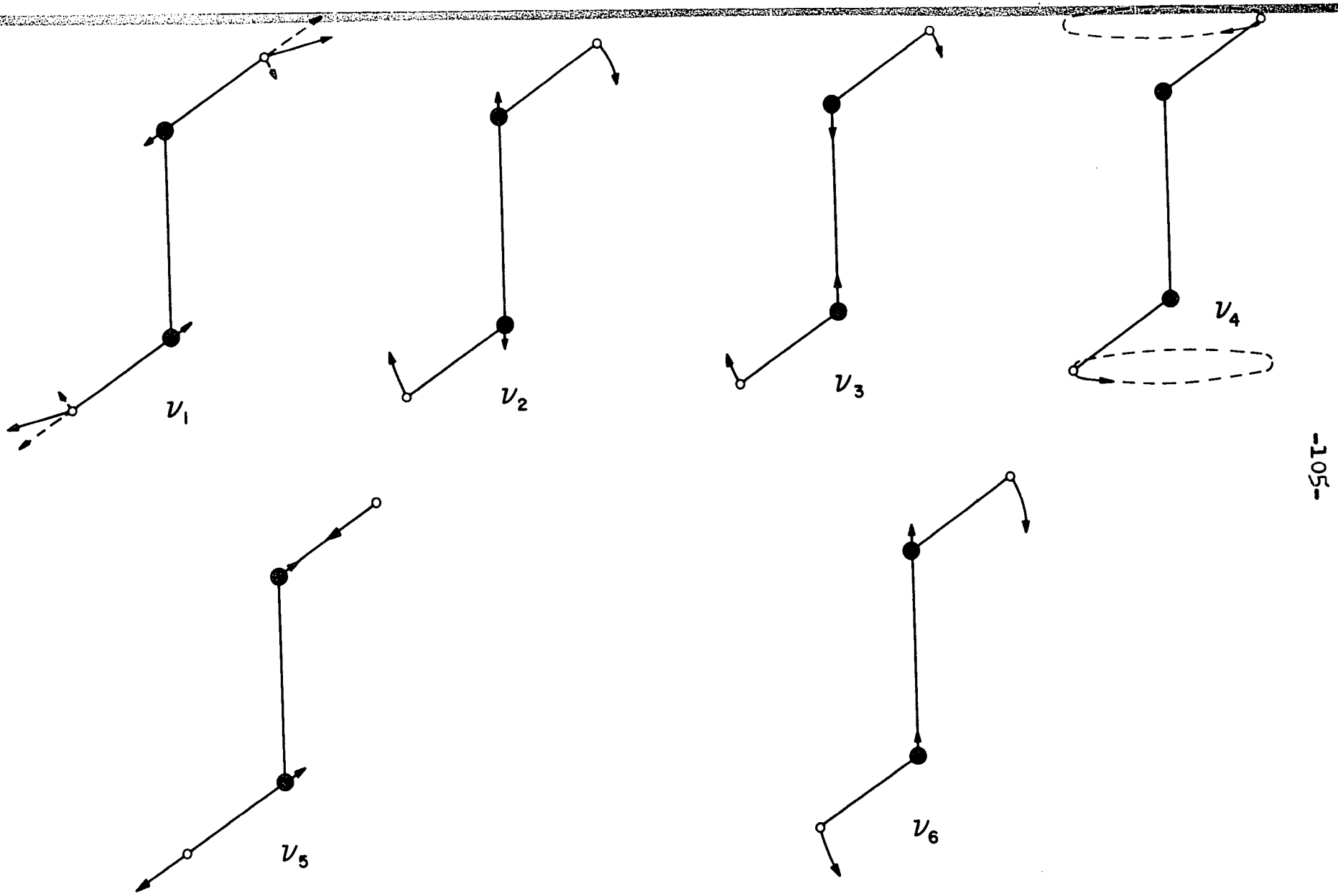


Figure 9. The normal modes of vibration of the hydrogen peroxide molecule.

Table 5

Amplitude factors for the 0-0 stretch in H_2 .

i	$a_i (x10^4)$	μ_i
1	0.299	0.0131
2	6.630	0.291
3	21.82	0.956
4	0.829	0.0363

calculated b . The weighted root-mean-square frequency, defined by [33], is equal to

$$\nu = 923.1 \text{ cm}^{-1} = 2.767 \times 10^{13} \text{ sec}^{-1} .$$

From [32] the Slater theory would predict a high-pressure first-order rate constant of

$$k_\infty = 8.74 \times 10^{-2} \text{ sec}^{-1} ,$$

The Slater rate of energization is computed from [56], using the same value for Z_{-1} as in the HKRR theory and is found to be

$$k_1 = 0.553 \text{ cc mole}^{-1} \text{ sec}^{-1}$$

which is below the experimental value by a factor of 3×10^4.

(b) <u>O-H distance as critical</u>: As mentioned earlier, when the molecule under consideration contains atoms of widely differing mass, such as hydrogen and carbon or oxygen, the Slater theory usually gives better results if the critical coordinate can be chosen so as to involve one of the light atoms. This section describes the results of calculations based on the assumption that p is the change in the distance between a hydrogen atom and the remote oxygen atom. There are two equivalent p coordinates, and the two antisymmetric modes will contribute as well as the other four.

The new amplitude factors for this case have been calculated and are listed in Table 6 along with the fundamental frequencies employed in the treatment (62). From these factors:

$$\prod_i \mu_i = 1.336 \times 10^{-4}$$

$$\nu = 3.989 \times 10^{13} \text{ sec}^{-1}$$

With this p coordinate k_∞ becomes

$$k_\infty = 0.252 \text{ sec}^{-1} .$$

A new value of b is calculated from [10] and [62] using $n = 6$. The rate constant k_1 is then found from [56] to be

$$k_1 = 4.71 \times 10^2 \text{ cc mole}^{-1} \text{ sec}^{-1}$$

which is still far below the experimental value.

The relationship between the Slater parameter θ and the pressure in this case is:

$$\theta = 5.12 \times 10^{-21} N \qquad [140]$$

in which N is the concentration in molecules per cc. With $n = 6$ it can be estimated from the curves of Figure 1 that $K^1/k_\infty = 0.5$ when θ is about 17.6. From [140] this leads to a half-pressure of

Table 6

Frequencies and amplitude factors for the O-H distance in H_2O_2.

i	ν_i (cm^{-1})	a_i ($\times 10^4$)	μ_i
1	3610	-4.14	0.0996
2	1315	-17.8	0.429
3	877	25.8	0.620
4	660	1.91	0.0460
5	3614	7.30	0.176
6	1266	25.9	0.623

$$P_{1/2} = 2.56 \times 10^{5} \text{ mm}$$

which is much greater than that predicted by the HKRR theory above.

(c) $\prod\mu$ maximized: Finally, it is possible to calculate the greatest possible value of k_1 (and minimum value of $P_{1/2}$) that the Slater theory can give, by taking the maximum value of $\prod\mu_i$ with $n = 6$. This would occur when all six μ factors were equal to $1/\sqrt{6}$, since the sum of their squares must be unity. Under these conditions it can be shown that

$$\nu = 3.271 \times 10^{13} \text{ sec}^{-1},$$

$$\prod_i \mu_i = 4.630 \times 10^{-3},$$

$$P_{1/2} = 6.06 \times 10^{3} \text{ mm}$$

and calculation of k_1 yields

$$k_1 = 1.63 \times 10^{3} \text{ cc mole}^{-1} \text{ sec}^{-1}$$

which is still too low.

DISCUSSION

The main conclusion to be drawn from these calculations is that whereas the HKRR formula gives a satisfactory interpretation of the low-pressure rate, taking $s = 5$,

the Slater treatment leads to rates that are significantly too low regardless of the choice of reaction coordinate. This suggests that in hydrogen peroxide there can be an appreciable flow of energy between at least five of the six normal modes as proposed in the HKRR theory. In chapter 3, a similar situation was seen to exist in the case of N_2O .

VIBRATIONAL ANALYSIS

The analysis of the vibrational spectrum has been carried out using the FG matrix method of Howard and Wilson (64)(33)(34) but with the more recent notation laid out in the section on vibrational theory. The force constants employed are those derived by Giguère and Bain (62).

Symmetry and Coordinates

The structure and internal coordinates r_k of the hydrogen peroxide molecule are shown schematically in Figure 8. The molecule is of C_2 symmetry, and the appropriate character table with number of vibrations of each species is shown in Table 7.

Normalized and orthogonal symmetry coordinates R_j for the two classes of vibrations are formed from the r_k as discussed earlier and are defined:

A vibrations

$$R_1 = \Delta D \qquad [141]$$

$$R_2 = (\Delta d_1 + \Delta d_2)/\sqrt{2} \qquad [142]$$

Table 7

Character table for the point group C_2 with the number of vibrations of each symmetry species for H_2O_2 .

C_2	I	$C_2(2)$	Number of genuine vibrations
A (symmetric)	+1	+1	4
B (antisymmetric)	+1	-1	2

$$R_3 = (\Delta\alpha_1 + \Delta\alpha_2)/\sqrt{2} \qquad [143]$$

$$R_4 = \Delta\phi \qquad [144]$$

B vibrations

$$R_5 = (\Delta d_1 - \Delta d_2)/\sqrt{2} \qquad [145]$$

$$R_6 = (\Delta\alpha_1 - \Delta\alpha_2)/\sqrt{2} \qquad [146]$$

These expressions define the [U] matrix of [72].

[F] Matrix

The complete [f] matrix in which force constants relating to every pair of internal coordinates are recognized would be the following:

$$[f] = \begin{array}{c|cccccc} & \Delta D & \Delta d_1 & \Delta d_2 & \Delta\alpha_1 & \Delta\alpha_2 & \Delta\phi \\ \hline \Delta D & f_D & f_{Dd} & f_{Dd} & df_{D\alpha} & df_{D\alpha} & d^2f_{D\phi} \\ \Delta d_1 & & f_d & f_{dd} & df_{d\alpha} & df'_{d\alpha} & df_{d\phi} \\ \Delta d_2 & & & f_d & df'_{d\alpha} & df_{d\alpha} & df_{d\phi} \\ \Delta\alpha & & & & d^2f_\alpha & d^2f_{\alpha\alpha} & d^2f_{\alpha\phi} \\ \Delta\alpha & (f_{ik} = f_{ki}) & & & & d^2f_\alpha & d^2f_{\alpha\phi} \\ \Delta\phi & & & & & & d^2f_\phi \end{array} \qquad [147]$$

However, adoption of the simple potential function used by Giguère and Bain (62) gives $f_{Dd} = f_{D\alpha} = f_{D\phi} = f_{d\alpha} = f'_{d\alpha} = f_{d\phi} = f_{\alpha\phi} = 0$. From this and the [U] matrix formed

from the coefficients of the symmetry coordinates, the following [F] elements are obtained from [77], in which $d_1 = d_2 \equiv d$:

A vibrations

$$F_{11} = f_d \qquad [148]$$

$$F_{22} = f_d + f_{dd} \qquad [149]$$

$$F_{33} = d^2(f_\alpha + f_{\alpha\alpha}) \qquad [150]$$

$$F_{44} = d^2 f_\phi \qquad [151]$$

B vibrations

$$F_{55} = f_d - f_{dd} \qquad [152]$$

$$F_{66} = d^2(f_\alpha - f_{\alpha\alpha}) \qquad [153]$$

where

$$F_{j1} = 0 \quad \text{for} \quad j \neq 1$$

[G] Matrix

The matrix [G] is computed as discussed in chapter 2. Figure 8 shows the unit vectors $\bar{V}$ in terms of which the vectors $\bar{s}_k(t)$ are defined. The latter are combined to form the symmetry vectors $\bar{S}_j(t)$ according to [79] and these in turn are multiplied in pairs to give the [G] elements by [80]:

A vibrations

$$G_{11} = 2\mu_0 \qquad [154]$$

$$G_{22} = \mu_H + \mu_0 \qquad [155]$$

$$G_{33} = \mu_H/d^2 + [\mu_0/\sin^2\alpha][1/D^2 + B^2 + H^2 + 2H(B + 1/D)\cos\alpha - 2aB/D] \qquad [156]$$

$$G_{44} = 2\mu_H/d^2\sin^2\alpha + 2\mu_0(C^2 + E^2)\sin^2\alpha \qquad [157]$$

$$G_{12} = 2\mu_0 \cos\alpha \qquad [158]$$

$$G_{13} = -[\sqrt{2}\mu_0/\sin\alpha][A - B\cos\alpha] \qquad [159]$$

$$G_{14} = 0 \qquad [160]$$

$$G_{23} = -[\mu_0/\sin\alpha][B + H\cos\alpha - a/D] \qquad [161]$$

$$G_{24} = \sqrt{2}\mu_0 E \sin^2\alpha \qquad [162]$$

$$G_{34} = [\sqrt{2}\mu_0/\sin\alpha][E(a + \cos^2\alpha)/D - (EB - C/D)\sin^2\alpha] \qquad [163]$$

B vibrations

$$G_{55} = \mu_H + \mu_0 \qquad [164]$$

$$G_{66} = \mu_H/d^2 + [\mu_0/\sin^2\alpha][1/d^2 + 1/D^2 + B^2 + (2/d)(B - 1/D)\cos\alpha + 2aB/D] \qquad [165]$$

$$G_{56} = -[\mu_0/D\sin\alpha][1 + a] \qquad [166]$$

$$G_{jl} = G_{lj}$$

in which $\alpha_1 = \alpha_2 \equiv \alpha$ and $\mu_0 = 3.764 \times 10^{22}$, $\mu_H = 5.974 \times 10^{23}$ gm^{-1} are the reciprocals of the masses of the O and H atoms respectively. Further,

$$A = (1/d) - (\cos\alpha)/D \qquad [167]$$

$$B = (1/D) - (\cos\alpha)/d \qquad [168]$$

$$C = \csc\alpha[(\csc\alpha)/d - \cot\alpha(1 - \cos\phi)/D] \quad [169]$$

$$E = \cos\alpha \sin\phi/D \sin^2\alpha \quad [170]$$

$$H = (1/d) - (2\cos\alpha)/D \quad [171]$$

$$a = 0.08947 = \cos 84^\circ 52' = (\bar{V}_1 \cdot \bar{V}_3) \text{ (see Figure 8)} \quad [172]$$

The approximation $\bar{V}_3 \cdot (\bar{V}_1 \times \bar{V}_2) = -\sin^2\alpha$ was made since $\phi \pm 90^\circ$.

Numerical Evaluation

The force constants given by Giguère and Bain (62) are, in units of 10^5 dyne cm^{-1} ,

$f_D = 3.84$ $\quad$ $f_\alpha = 0.89$

$f_d = 7.28$ $\quad$ $f_{\alpha\alpha} = 0.04$

$f_{dd} = -0.01$ $\quad$ $f_\phi = 0.11$

The molecular parameters (62) are

$$D = 1.49 \times 10^{-8} \text{ cm} ,$$

$$d_1 = d_2 \equiv d = 0.97 \times 10^{-8} \text{ cm} ,$$

$$\alpha_1 = \alpha_2 \equiv \alpha = 102^\circ ,$$

$$\phi = 82^\circ (\pm 20^\circ) .$$

The [F] and [G] elements were evaluated using these figures and are given below. The basic units are grams, seconds and angstroms.

[F] elements ($\times 10^{-5}$)

$F_{11} = 3.84$ $F_{44} = 0.104$

$F_{22} = 7.27$ $F_{55} = 7.29$

$F_{33} = 0.875$ $F_{66} = 0.800$

[G] elements ($\times 10^{-23}$)

$G_{11} = 0.7528$ $G_{12} = G_{21} = -0.1107$

$G_{22} = 6.350$ $G_{13} = G_{31} = -0.5366$

$G_{33} = 7.134$ $G_{14} = G_{41} = 0$

$G_{44} = 14.401$ $G_{23} = G_{32} = -0.2128$

$G_{55} = 6.350$ $G_{24} = G_{42} = -0.07353$

$G_{66} = 7.258$ $G_{34} = G_{43} = -0.4941$

$G_{56} = G_{65} = -0.2813$

As an approximate check on the work, the secular equation was expanded by [85]-[87] and solved by successive approximations. The roots yielded values for the fundamental frequencies that were within 3% of the observed value for the lowest frequency and within 1% for the highest. The observed frequencies are listed in Table 6 above.

Normal Coordinates

The product matrix [GF] has been formed and the matrix [L] calculated from [91]. The result is presented in Table 8. From this [l] is calculated by first forming $[U]^{-1}$ simply as

$$[U]^{-1} = [U]' \qquad [173]$$

Table 8

[L] matrix for H_2O_2 in units of angstroms and radians.

	ν_1	ν_2	ν_3	ν_4	ν_5	ν_6
R_1	0.0182	0.145	1.00	0.00599	0	0
R_2	-1.00	-0.00292	0.0119	-0.00182	0	0
R_3	0.386	-1.00	0.589	0.0183	0	0
R_4	0.0166	0.0934	-0.211	1.00	0	0
R_5	0	0	0	0	1.00	0.00554
R_6	0	0	0	0	-0.0506	1.00

Table 9

[1] matrix for H_2O_2 in units of angstroms and radians.

	ν_1	ν_2	ν_3	ν_4	ν_5	ν_6
ΔD	0.0182	0.145	1.00	0.00599	0	0
Δd_1	-0.707	-0.00206	0.00841	-0.00129	0.707	0.00392
Δd_2	-0.707	-0.00206	0.00841	-0.00129	-0.707	-0.00392
$\Delta \alpha_1$	0.293	-0.707	0.416	0.0129	-0.0358	0.707
$\Delta \alpha_2$	0.293	-0.707	0.416	0.0129	0.0358	-0.707
$\Delta \phi$	0.0166	0.0934	-0.211	1.00	0	0

since [U] is unitary, and then using [97]. This matrix is given in Table 9. Having obtained [l], the six normal coordinates of vibration of H_2O_2 are easily represented pictorially as shown in Figure 9.

Amplitude Factors

(a) O-O distance as critical: Since the rate-determining step in the hydrogen peroxide decomposition is the rupture of the O-O bond (60), calculations are first carried out on the assumption that

$$p = \Delta D = r \qquad [174]$$

Consequently, from the definition [104] of A_k it is seen that $A_1 = 1$ and the other A's are zero. Hence, from [98] and [116] the amplitude factors a_i are simply

$$a_i = \gamma_{1i} = l_{1i} / \sqrt{\epsilon_i} \qquad [175]$$

in which the l_{1i} are in the first row of Table 9 and ϵ_i is most readily calculated from [95] using the numerical elements of [F] and [L] above. The a_i are normalized to the μ_i by [117] and both are listed in Table 5 above.

(b) O-H distance as critical: Here $p = \Delta P$ in which P is the distance from $H^{(1)}$ to $O^{(2)}$ in the molecule, (see Figure 8). In this case all six of the normal modes will contribute to p. This choice of reaction coordinate is illustrated in Figure 3(a) and the A_k are found from [105]-[108]. In terms of the internal coordinates

of this molecule they are:

$$A_1 = \frac{\partial P}{\partial D} = \frac{1}{P}(D - d\cos\alpha) = 0.87217 \qquad [176]$$

$$A_2 = \frac{\partial P}{\partial d_1} = \frac{1}{P}(d - D\cos\alpha) = 0.65982 \qquad [177]$$

$$A_4 = \frac{\partial P}{\partial \alpha_1} = \frac{Dd\sin\alpha}{P} = 0.72887 \qquad [178]$$

$A_3 = A_5 = A_6 = 0$ since variations in d_2, α_2 and ϕ do not affect p. Of course now there are the two equivalent critical coordinates. The number of significant figures given here is unjustified but they are carried forward to the calculation of the amplitude factors.

The γ_{ki} are not affected by the choice of p but now γ_{2i} and γ_{4i} will be required as well as the γ_{1i} found above. The new α_i and μ_i are computed from [116] and [117] and are presented in Table 6 above.

CHAPTER 6

ISOMERIZATION OF CYCLOPROPANE

The thermal isomerization of cyclopropane to propylene has been discussed in detail by Slater (65) and will only be summarized here. Slater's calculation, carried out with complete rigour and compared to the experimental results of Pritchard, Sowden and Trotman-Dickenson (66), was the first, and before the present work, the only test case for the Slater theory. The satisfactory agreement that was obtained over the wide pressure range of .01 - 100 cm has earned considerable prestige for the theory but there remain certain difficulties which will be mentioned below. Pritchard *et al* (66) have calculated the rates theoretically predicted by the Hinshelwood and Kassel theories as well and compared these with their own experimental data and those of Chambers and Kistiakowsky (67).

HKRR THEORY

A plot of $\log K^1/k_\infty$ against $\log P$ is made by Pritchard *et al* (66) of the data. This curve is compared with that predicted by the HKRR theory in which

$$s = 13$$

$\sigma = 3.9 \times 10^{-8}$ cm

$E_o = 65$ kcal mole^{-1} (experimental)

The agreement is extremely good over most of the pressure range but the measured points fall a little below the theoretical curve in the low-pressure region. The authors admit that a more convex curve which would be a better fit could have been obtained by taking $s = 12$ and a correspondingly larger value for the collision diameter σ.

SLATER THEORY

Slater (65) has calculated the rate curve predicted by his own theory. The vibrational analysis was based upon a set of force constants obtained by Saksena (68). Symmetry coordinates were composed from the atomic cartesian coordinates and amplitude factors were determined taking as critical coordinate the extension of the distance from a hydrogen to a remote carbon atom. Slater discusses the form of the calculation when degenerate vibrations and equivalent critical coordinates are involved and evaluates all the necessary parameters. Taking the collision diameter $\sigma = 5 \times 10^{-8}$ cm, values of K^1/k_∞ were computed for the entire rate curve. The shape of this curve is an exact fit to the experimental one. However, the Slater pressures are all a factor of 3.6 larger than those measured for the corresponding rate constant; that is, Slater's curve

is shifted 0.56 units to the right, on the logarithmic scale, from the experimental curve.

DISCUSSION

The fact that the Slater theory, which involves no arbitrary parameters, predicts with a high degree of accuracy the shape of the curve of log K^1/k_∞ against log P is indeed strong support for the theory and its assumed model. As Slater points out (65), the absolute pressures predicted would be decreased by the factor 3.6 if either σ^2 or $\prod\mu$ were increased by this same factor. Although it is unlikely that σ is larger than the 5×10^{-8} cm used, the $\prod\mu$ might be sufficiently increased by use of the most recent force constants.

There is here an opportunity to emphasize once more the arbitrariness in the selection of the critical coordinate. When the reaction involves the rupture and creation of a number of bonds as in this case, a simple linear reaction coordinate is by no means obvious. Slater (65) also carried out the calculations on the assumption that p was the stretching of a C-C bond but the results gave no agreement whatever with experiment.

In this case, then, the experimental results are explained equally well by both the Slater model using a C-H as the critical coordinate, and the HKRR model in which s is taken as 12 or 13.

CHAPTER 7

OTHER REACTIONS

In this chapter certain additional unimolecular reactions which have been treated in a more approximate fashion will be discussed. Although the results here are not conclusive, these considerations serve to define a region in which more detailed study might prove fruitful.

NITROGEN PENTOXIDE

Mills and Johnston (69) and Johnston and Perrine (70)(cf. ref. 46, page 74) have studied the decomposition of nitrogen pentoxide in the presence of nitric oxide, and have shown that values can be derived for both the rate of energization and the high-pressure first-order rate of splitting the molecule into NO_2 and NO_3. The rate of energization at 300°K is found to be

$$k_1 = 1.175 \times 10^5 \text{ cc mole}^{-1} \text{ sec}^{-1} .$$

Spectroscopic data are not available for a complete vibrational analysis so that only a brief discussion is given. When all fifteen normal modes are considered,

the HKRR theory gives a rate of energization

$$k_1 = 2.79 \times 10^9 \text{ cc mole}^{-1} \text{ sec}^{-1}$$

which is much too high. The best agreement is obtained with $s = 7$ for which

$$k_1 = 1.45 \times 10^5 \text{ cc mole}^{-1} \text{ sec}^{-1}.$$

With Slater's theory one can only calculate a maximum rate. For $n = 15$

$$\prod_{\mu(max)} = n^{-n/2} = 1.5 \times 10^{-9}$$

and the resulting rate at $300^\circ K$ is

$$k_1 = 4.01 \times 10^8 \text{ cc mole}^{-1} \text{ sec}^{-1} .$$

This is much higher than the experimental value and nearly as high as the HKRR rate taking $s = 15$. The calculated rate would, of course, be much reduced when the true μ values are employed and on the basis of past experience there is no reason to doubt that the final calculated rate will be reasonably close to the experimental value.

At the moment there are therefore two possible explanations for the observed behaviour. One is that the HKRR theory applies and an unrestricted flow of energy exists between seven of the normal modes, but that energy

from the remaining eight (perhaps because of certain symmetry restrictions) is not available to these seven. The second is that, in accordance with Slater's proposals, the energy must be distributed in a particular manner among all fifteen normal modes, and that reaction occurs when the vibrations come suitably into phase. If more detailed calculations show that the Slater rate agrees with the experimental one there will still be no simple way of deciding between the two alternatives; if, however, Slater's rate is too low the first must be accepted.

ETHANE

Kinetic values for the unimolecular dissociation of ethane into two methyl radicals may be deduced from the results of Dodd and Steacie (71)(cf. ref. 72) on the recombination of methyl radicals in the presence of acetone. At a temperature of 473°K and a pressure of 10 mm and above, the recombination is second-order and the rate coefficient is 3.7×10^{13} cc mole^{-1} sec^{-1}. This coefficient decreases by a factor of 4 as the pressure is lowered from 10 mm to 1 mm. Assuming the reaction to be essentially third-order at 1 mm, a third-order rate constant of 3×10^{20} cc mole^{-2} sec^{-1} corresponding to the process

$$CH_3 + CH_3 + CH_3COCH_3 \longrightarrow C_2H_6 + CH_3COCH_3$$

may be deduced. From the same data Hoare and Walsh (73)

estimate approximately 10^{-27} cc^2 $molecule^{-2}$ sec^{-1}, in satisfactory agreement.

Using a value of 85.0 kcal for the energy of dissociation of ethane into $2CH_3$, and of 16 e.u. for the standard entropy of the process, a value of 10^{-36} mole cc^{-1} is calculated for the equilibrium constant for the dissociation at 473°K. (The standard state is 1 mole per cc; the value for the entropy corresponds to a planar methyl radical and agrees with that quoted by Trotman-Dickenson, ref. 46.) These figures lead to a value of

$$k_1 = \sim 3 \times 10^{-16} \text{ cc mole}^{-1} \text{ sec}^{-1}$$

for the second-order rate of energization corresponding to the dissociation process.

The molecule possesses eighteen degrees of vibrational freedom. The HKRR theory, when s is taken as 18, gives

$$k_1 = \sim 5 \times 10^{-8} \text{ cc mole}^{-1} \text{ sec}^{-1}$$

which is much too large. However with s = 9 the result is

$$k_1 = \sim 2.5 \times 10^{-15} \text{ cc mole}^{-1} \text{ sec}^{-1}$$

and slightly better agreement might be achieved with s = 8 .

The eighteen normal modes of vibration of the

molecule, which is assumed to be of D_{3d} symmetry, are comprised of the following symmetry species:

$$3A_{1g} + A_{1u} + 2A_{2u} + 3E_u(2) + 3E_g(2) = 18 \qquad [179]$$

Inspection of the character table for the point group D_{3d} or a schematic representation of the normal coordinates (ref. 35, page 115) shows that the A_{1u}, A_{2u} and E_u vibrations bring about no change in the C-C bond distance. If the critical coordinate for the symmetrical splitting is the C-C bond distance, as would seem reasonable, it follows that only for the $3A_{1g}$ and $3E_g$ modes will the μ's of Slater be non-zero. The three E_g modes (doubly degenerate) are each counted once only (13) as shown in [38], so that only six modes in all have non-zero μ's for this choice of coordinate. The μ factors for the E_g modes will probably be small since these contribute very little to C-C stretching. However, a maximum rate for $n = 6$ may be calculated from the Slater equation [56] by taking $\prod \mu_i = n^{-n/2}$. The rate constant calculated in this way is

$$k_1 = \sim 10^{-20} \text{ cc mole}^{-1} \text{ sec}^{-1} ,$$

which is too small by a factor of about 10^4. The use of a larger value for n would give better agreement but it would then be necessary to potulate a reaction coordinate which would not appear to be consistent with a symmetrical

dissociation into methyl radicals. (See discussion below, however.)

It is seen that the HKRR theory gives too large a rate of energization when all eighteen modes are considered; the best agreement is obtained with eight or nine. The latter value is consistent with the hypothesis that there is a flow of energy possible between the nine normal modes of g symmetry, $3A_{1g} + 3E_g(2)$, but that energy cannot pass from the nine u modes into the former.

CYCLOBUTANE AND CYCLOBUTENE

In a recent communication Thiele and Wilson (74) have attempted to apply similar arguments, based on symmetry considerations of the reaction coordinate, to the unimolecular decomposition of cyclobutane and isomerization of cyclobutene. As in the discussion of ethane above, these authors determine the most probable symmetry of the distorted molecule just prior to reaction and then take as the Slater number n the number of modes which are of such symmetry species as to contribute to this distortion. The Slater parameter ν is taken as the experimental high-pressure frequency factor and $\prod \mu_i$ is calculated both at its maximum value, $n^{-n/2}$, and on the assumption of a "representative spread" of the μ_i as discussed by Slater (13). Having determined θ as a function of pressure from [36] and [29], a value for P_5, the pressure at which $K^1/k_\infty = 0.95$, is obtained from Slater's

tabulated figures (13) and compared to the experimental values. In both cases the theoretical value of P_5 is far above the experimental, leading the authors to conclude that the Slater theory may require some substantial modifications.

However, it may well be that the predictions of which modes will contribute to the reaction, based upon symmetry considerations, are greatly over-simplified in the last three examples. It is reasonable to assume that the displacement of <u>every</u> atom, regardless of the symmetry class to which the motion belongs, will alter the potential field so as to have <u>some</u> effect on the bonds which are to be broken or formed in the reaction. Consequently, the Slater theory does not hesitate to choose a critical coordinate which bears no relation to the symmetry of the reaction as a whole, and preference is for coordinates involving a light atom whose relatively large amplitude of motion will give rise to a greater $\prod \mu_i$ factor. With critical coordinates involving H atoms in the above cases, the values of n would be increased and much closer agreement to the experimental P_5 would result.

CHAPTER 8

DECOMPOSITION OF ETHYL CHLORIDE

The results of the calculations presented in chapters 3-7 seem to imply that the Slater theory is suited to predict the rates of reactions involving rather large molecules, such as cyclopropane, much better than it is for the reactions of simple molecules. Of course it is in the former case that the transition pressure region is most easily attained experimentally. As a final test case for the Slater theory, calculations on the thermal decomposition of ethyl chloride have been undertaken. It was hoped that the number of degrees of freedom in this molecule would be sufficient to render a satisfactory agreement between the Slater theory and the experimental data. Further, since the reaction is simply the removal of HCl to give ethylene, there would seem to be much less uncertainty in the choice of a critical coordinate, the most obvious one being the distance from Cl (on C_1) to one of the H atoms on C_2.

Because of its low degree of symmetry, the molecule has not previously been submitted to a normal coordinate analysis. The very laborious analysis, which includes the determination of a set of force constants, has been attempted with the aid of electronic computers. In

the course of this work a number of techniques and special considerations became evident, and for that reason sections dealing with the machine solution of the secular determinant and the adjustment of force constants have been inserted at the first of the chapter.

MACHINE SOLUTION OF THE EIGENVALUE PROBLEM

As in any vibrational analysis, the problem of determining the characteristic frequencies and amplitudes of motion may be reduced to the problem of determining the eigenvalues or roots, with the corresponding eigenvectors, of a matrix the order of which is the number of vibrational degrees of freedom in the system. As mentioned on pages 64 and 65, it is required to find the characteristic roots λ_i and vectors $[L_i]$ of an unsymmetric, real matrix $[H]$, where

$$[H] \equiv [G][F] \qquad [180]$$

and both $[G]$ and $[F]$ are symmetric and positive definite.

Most programs written for the solution of this problem by electronic digital computer (including the programs used in the present study) are based upon the familiar "power method" (ref. 75 page 231) which is summarized below.

Power Method of Solution

Suppose the matrix [H] to be solved is of order n with roots λ_1 , λ_2 , ... λ_n where

$$|\lambda_1| > |\lambda_2| > \ldots > |\lambda_n| \qquad \lambda_1 = \text{real}$$

and the eigenvectors associated with the roots are $[L_1]$, $[L_2]$, ... $[L_n]$. The method begins by choosing an arbitrary vector [v] of order n , - usually (1 , 1 , ... 1) in the absence of any previous knowledge of the solution, - and successively multiplying it by [H] , or "iterating" on it by [H] . It can then be shown that

$$[H]^m [v] \equiv [v]_m = \lambda_1^m \left\{ [L_1] + \left(\frac{\lambda_2}{\lambda_1}\right)^m [L_2] + \left(\frac{\lambda_3}{\lambda_1}\right)^m [L_3] + \ldots + \left(\frac{\lambda_n}{\lambda_1}\right)^m [L_n] \right\} \qquad [181]$$

Since λ_1 is the dominant root,

$$\lim_{m \to \infty} [v]_m = \lambda_1^m [L_1] = [L_1] \qquad [182]$$

because λ_1^m , as a constant, only scales $[L_1]$ and does not alter the ratios of its components. Further,

$$\lim_{m \to \infty} \left(\frac{[v]_m}{[v]_{m-1}} \right) = \lambda_1 \qquad [183]$$

Consequently, after a sufficient number of iterations n, the first root and vector are obtained. To calculate λ_2 and $[L_2]$, iteration may be carried out on a new vector $[v_1]$ which is orthogonal to $[L_1]$, or alternatively, λ_1 may be removed from $[H]$ by one of the "deflation" processes (75)(76) to give a new matrix $[H_1]$ whose dominant root is λ_2. This scheme is continued until all the latent roots and vectors have been calculated.

Modifications of the Power Method

Although the power method gives rapid results in many cases it cannot be denied that there are so many cases in which it does not, that it is seldom used by itself. It is seen from [181] that if the fractions λ_r/λ_1 are not appreciably less than unity, or if $[v]$ just happens to be nearly orthogonal to $[L_1]$, then convergence on λ_1 will be extremely slow. In matrices of the size that are being calculated in the present work (7 x 7 and 11 x 11) the former difficulty is almost sure to arise for some of the roots.

Modifications to the basic method are continually appearing (76)(77) in an effort to achieve a more powerful program. These incorporate a number of deflation procedures, some of which reduce the order of the matrix as each root is obtained, acceleration methods which achieve a more rapid convergence to the eigenvector, and methods for separating nearly equal roots.

In any of these cases there exists an optimum situation

which is attained by proper choice of "origin" for the matrix. If a constant β is added to the diagonal elements, this merely shifts the roots from λ_i to $\lambda_i + \beta$ and leaves the vectors unaffected. When approximate values for the λ_i are known, β may be so chosen as to distribute the roots fairly evenly about zero. Then in general (providing there are no pairs of roots with equal moduli) the ratios of successive eigenvalues will be the most satisfactory for convergence. Alternatively, β may first be chosen to make the r largest roots converge most rapidly and then a second value assigned to it so that the $(n-r)$ smallest roots are obtained.

Symmetrization of Matrix

The solution by computer of symmetric matrices is generally much simpler than for unsymmetric, one reason being that the roots of a symmetric matrix are always real. Consequently, instead of solving the matrix equation [91], some authors prefer to use an equivalent one in which the matrix to be calculated is symmetric rather than the unsymmetric [GF] .

Mann, Fano, Cahill and Shimanouchi (78) replace [91] by

$$([D]' [F] [D]) [Y] = [Y] [\Lambda] \qquad [184]$$

in which [D] is the matrix of transformation from the column matrix [x] of 3N mass-weighted cartesian coordinates to

the column matrix [r] of internal coordinates. [Y] relates the normal coordinates Q_i to [x] by

$$[x] = [Y]\,[Q] \qquad [185]$$

and in terms of the matrix [l] of [97] ,

$$[l] = [D]\,[Y] \qquad [186]$$

The product matrix $([D]'[F][D])$ of [184] is now symmetric and possesses the same eigenvalues as [GF]. The eigenvectors give the normal coordinates directly in mass-weighted cartesian form. As it stands, however, the matrix is of order 3N , although symmetry factoring can still be applied if symmetry coordinates are first constructed from the cartesian coordinates. This treatment has the advantage of avoiding calculation of [G] , but in some cases the calculation of [D] would be nearly as troublesome. Mann, Shimanouchi, Meal and Fano employ this method in the normal coordinate analysis of the halogenated ethylenes (79)(80).

Miyazawa (81) has shown how the roots and vectors of [H] may be obtained through the solution of symmetric matrices only. The process involves several steps:

(a) The eigenvalues t_i and vectors $[A_i]$ of [G] are found.

(b) A diagonal matrix [B] is formed from the square roots of the eigenvalues t_i .

(c) If [A] is the square matrix of the vectors $[A_i]$ found in (a), then the product [A][B] is formed.

(d) A matrix [K] is calculated, where

$$[K] \equiv [AB]' [F] [AB] \qquad [187]$$

(e) The eigenvalues λ_i and vectors $[C_i]$ of [K] (which is symmetric) are now computed. The λ_i are the desired roots of [H] .

(f) The vectors $[L_i]$ of [H] are obtained from

$$[L_i] = [AB] [C_i] \qquad [188]$$

Although solution of symmetric matrices is more rapid than that of unsymmetric matrices, the difficulty of nearly equal roots may still be encountered. Furthermore, each additional step in the symmetrization process contributes a round-off error which is carried forward. On small and medium sized machines such as the IBM 650, experience has shown this error to be appreciable after a few multiplications. If a sufficiently rapid program is available, it is much more preferable to work with the original, unsymmetric [H] matrix.

Method of Coordinate Rotation

Howland (82) has recently discussed the solution by a method of coordinate rotation of determinantal equations of the form

$$[V]\,[x] = \lambda\,[T]\,[x]\,, \qquad [189]$$

provided [V] and [T] are symmetric. This would apply to the present problem which may be written:

$$[F][L_a] = \lambda_a\,[G]^{-1}[L_a] \qquad [190]$$

where both [F] and $[G]^{-1}$ are symmetric. The method in this case is quite different from the power method and does not suffer from the defects of the latter, although computation time may be somewhat lengthy. A program based on this procedure has been compiled for the small Bendix computer, but for certain 10 x 10 matrices a complete solution required approximately sixty hours! (83)

SELECTION AND ADJUSTMENT OF FORCE CONSTANTS

In chapter 2 the solution of the secular determinant to obtain the normal frequencies and coordinates was described. This was discussed from the assumption that the potential field was completely specified through knowledge of all the constants b_{ij} of the potential energy expression [64]. However the more usual problem, as in the case of ethyl chloride below, is that of evaluating these "force constants" from a knowledge of the fundamental frequencies of vibration. This problem is much more difficult than the former for there are usually many more constants than

independent frequencies from which they are to be determined. Thus, if a molecule possesses n normal vibrations belonging to a particular symmetry class, there will be $n(n + 1)/2$ constants in the most general potential function.

One solution to this difficulty is to employ the normal frequencies of isotopic molecules if the data are available. Assuming that the force constants are the same in the isotopic species, it is only the [G] matrix which will be altered. This supplies additional equations by which the unknowns are determined.

Even when this information is at hand, in all but the simplest cases it is usual to approximate the form of the potential function, for example, by assuming valence type forces, and thus reduce the number of unknown constants. And finally, even some of these constants must be assumed zero in order to arrive at a determinable number of unknowns. It should be mentioned that one can frequently increase the number of terms considered in the potential function by setting certain force constants equal to corresponding constants in similar molecules and taking these as known.

With such approximations it is possible that more than one set of constants may give the same set of frequencies. Often a decision between the various sets of constants is possible merely from a common-sense analysis of the potential function, but unfortunately no rigorous method is available. In some cases a calculation of the amplitudes may be helpful,

and eventually a comparison with known constants from similar molecules may be taken into account. A satisfactory calculation of further frequencies, however, is by no means a proof of the correctness of the constants.

The usual practice, then, is to begin with the simplest possible set of force constants, the estimation of which is guided by considerations of other molecules, compose [F] and [G] matrices, calculate the frequencies and compare them with the experimental values. The discrepancies are noted, the force constants altered slightly to give a new [F], and the calculation repeated. In simple cases the adjustments to [F] may be made merely on a trial and error basis. However for larger matrices, as arise with ethyl chloride, it becomes necessary to have some guide whereby the alterations may be effected in a systematic fashion. The Jacobian method described in the following section has proved very useful in the present work.

Jacobian Method of Adjusting Force Constants

Literature dealing with the problem of adjusting force constants to produce a desired set of frequencies appears to be very scarce. A Japanese paper by Miyazawa (84) sketches the Jacobian method which employs perturbation theory, and more recently Howland (82) has discussed the same method applied to determinental equations generally. In what follows, Howland's derivation has been adapted to the molecular vibration problem.

(a) Formation of the Jacobian matrix: The matrix equation involving the force constants is:

$$[GF][L_a] = \lambda_a [L_a] \qquad a = 1,2,\ldots n \qquad [191]$$

or

$$[F][L_a] = \lambda_a [G]^{-1}[L_a] \qquad [192]$$

To simplify the notation, let the column vector $[L_a] \equiv x$ and drop the square brackets and subscript on λ temporarily. Then [192] becomes:

$$F x = \lambda G^{-1} x \qquad [193]$$

Altering the elements of F by ΔF produces variations in x and λ so that, from [193],

$$(F + \Delta F)(x + \Delta x) = (\lambda + \Delta\lambda) G^{-1} (x + \Delta x) \qquad [194]$$

Then, to the first order,

$$Fx + F(\Delta x) + (\Delta F)x = \lambda G^{-1}x + \lambda G^{-1}(\Delta x) + (\Delta\lambda)G^{-1}x \qquad [195]$$

But from [193] the first terms on each side of the equation may be eliminated. Hence

$$(F - \lambda G^{-1})\Delta x + (\Delta F)x - (\Delta\lambda)G^{-1}x = 0 \qquad [196]$$

Form the scalar product with x ; i.e. multiply by the row vector x' which is the transpose of x :

$$x'(F - \lambda G^{-1})\Delta x + x'(\Delta F)x - (\Delta \lambda)x'G^{-1}x = 0 \qquad [197]$$

But since $(F - \lambda G^{-1})$ is symmetric it is possible to write:

$$x'(F - \lambda G^{-1})\Delta x = \left\{(F - \lambda G^{-1})x\right\}' (\Delta x) = 0 \qquad [198]$$

From the last two equations,

$$x'(\Delta F)x - (\Delta \lambda)x'G^{-1}x = 0 \qquad [199]$$

or

$$\Delta \lambda = \frac{x'(\Delta F)\, x}{x'\, G^{-1}\, x} \qquad [200]$$

Since it is not usual to work with the matrix $[G]^{-1}$, one can replace $G^{-1}x$ by $\frac{1}{\lambda} Fx$ from [193]. Then [199] becomes

$$x'(\Delta F)x - \frac{(\Delta \lambda)}{\lambda}\, x'\, F\, x = 0 \qquad [201]$$

or, returning to the former notation in which the a-th root λ_a was considered ,

$$[L_a]'[\Delta F][L_a] - \frac{\Delta \lambda_a}{\lambda_a}\, [L_a]'[F][L_a] = 0 \qquad [202]$$

Now let f_h be the h-th force constant such as f_D, f_α, $f_{d\alpha}$, etc. Define a matrix $[B_h]$ associated with f_h by

$$[F] \equiv \sum_h f_h [B_h] \qquad [203]$$

$[B_h]$ will be a square matrix of the same order as $[F]$, with every element zero except at the locations at which f_h appears in $[F]$. These elements of $[B_h]$ will be the factors by which the f_h are multiplied in the corresponding elements of $[F]$. With the type of symmetry coordinates that have been described in chapter 2, sample elements of $[B_h]$ would be 1, $-1/\sqrt{2}$, $d^2/\sqrt{6}$, and so forth. It follows from [203] that

$$[\Delta F] = \sum_h (\Delta f_h) [B_h] \qquad [204]$$

Inserting [204] in [202] gives

$$[L_a]' \left\{ \sum_h (\Delta f_h)[B_h] \right\} [L_a] = \frac{\Delta \lambda_a}{\lambda_a} [L_a]'[F][L_a] \qquad [205]$$

Now if only the h-th force constant changes, [205] can be written:

$$(\Delta f_h)[L_a]'[B_h][L_a] = \frac{\Delta \lambda_a}{\lambda_a} [L_a]'[F][L_a] \qquad [206]$$

from which

$$J_{ah} \equiv \frac{\Delta \lambda_a}{\Delta f_h} \doteqdot \frac{\partial \lambda_a}{\partial f_h} = \frac{[L_a]' [B_h] [L_a]}{[L_a]' [F] [L_a]} \lambda_a \qquad [207]$$

This defines the elements of the Jacobian matrix [J] .

[207] is a very useful relationship since the quantity J_{ah} is the increment of change in the a-th root that will be produced by a unit change in the h-th force constant. It is to be noted that the relationship is not exact for large variations because of the approximation involved in passing to the partial derivative, but becomes more exact the smaller the variation. Such a calculation is a vast improvement over the empirical method of obtaining [J] as used by Mann et al. (79). These authors took each force constant in turn, arbitrarily increased it by a small increment, and then solved the [GF] matrix to find the variations produced in the roots, thus obtaining the elements $\Delta \lambda_a / \Delta f_h$.

Miyazawa (84) gives the simple relationship:

$$J_{ah} = [L_a]' [B_h] [L_a] \qquad [208]$$

which, of course, is only true if the eigenvectors are scaled such that

$$[L_a]' [F] [L_a] = \lambda_a \qquad [209]$$

However such scaling requires that

$$\sum_{i,j} L_{ia} L_{ja} F_{ih} = \lambda_a \qquad [210]$$

and can only be accomplished by actually performing the multiplication of [209]. Consequently it is preferable to take the vectors $[L_a]$ with any internal scaling (many computer programs produce the vectors scaled so that the largest element is +1.0) and use these numbers directly in [207].

The condition [210] is simple enough if $[F]$ is diagonal for it then becomes

$$\sum_{i} L_{ia}^2 F_{ii} = \lambda_a \qquad [211]$$

This seems to be the case for the acids studied by Miyazawa (84).

(b) Adjustment of force constants: Once the initial choice of potential constants has been made the problem is worked through to obtain a set of roots λ_i and vectors $[L_i]$. These values are used in [207] to obtain a Jacobian element J_{ah} for each root and each of the unknown force constants. The calculated roots are then compared to the experimental data. If the a-th root must be altered to make it equal the observed value, then the a-th row of $[J]$ gives the variations in λ_a produced by each force constant f_h. From these considerations, certain adjustments are made to the constants, the problem

is worked through again and the adjustment procedure repeated. Although [J] changes slightly with each modification to [F] it is usually sufficient to calculate the former once and use it unchanged in subsequent estimations. This adjustment cycle is repeated until all the calculated roots agree with the experimental values to the desired degree of accuracy.

Mann et al. (79) describe a method of force constant adjustment which uses a least-squares criterion to ensure that the constants finally established are such as to give the best possible agreement between calculated and observed frequencies. The method is easily adapted for matrix operations on a digital computer. The Jacobian matrix must first be calculated (empirically, by these workers) and then a series of matrix multiplications and inversions are performed using [J] and the vector $(\Delta\lambda_1 , \Delta\lambda_2 , \ldots \Delta\lambda_n)$ to obtain a vector of the force constant adjustments, $(\Delta f_1, \Delta f_2, \ldots)$. These adjustments are applied and the cycle repeated. This calculation was performed for the 7 x 7 matrix in the ethyl chloride analysis, but without advantage. It appeared that the calculated roots must be within about 1% of the observed values before the method can be applied, and this accuracy was sufficient for the purposes of the present work in any case. However, it is also possible that the error accumulated through the several matrix operations required on the computer (IBM 650) was enough to invalidate the results.

EXPERIMENTAL KINETIC DATA FOR THE ETHYL CHLORIDE DECOMPOSITION

The thermal decomposition of ethyl chloride has been studied in high-pressure range 20-200 mm by Barton and Howlett (85) who find the reaction to be homogeneous and first order giving, stoicheiometrically, ethylene and hydrogen chloride. More recently, Howlett (86) investigated the reaction at lower pressures where the same unimolecular decomposition occurs homogeneously but below 20 mm the rate constant becomes pressure-dependent.

In the high-pressure region the unvarying first order constant was found to be expressed by

$$k_\infty = 10^{14.6} \exp(-60800/RT) \text{ sec}^{-1}$$

which, at 729°K, gives

$$k_\infty = 2.36 \times 10^{-4} \text{ sec}^{-1}$$

with $$E_a = 60.8 \text{ kcal mole}^{-1}$$

Below about 8 mm K^1 drops rapidly with the initial pressure, falling to half the limiting value at 1.2 mm. The experimental points of Howlett (86) have been taken from Figure 1 of that paper, the pressure scale converted to logarithmic form, and these points plotted in Figure 12 in the following section.

Unfortunately there is a rather large degree of scattering.

The most recent spectroscopic data for the molecule are those of Allen and Bernstein (87) and of Daasch, Liang and Nielsen (88)(89) which propose two alternative but only slightly different assignments of the fundamental frequencies. This is discussed in the vibrational analysis below.

THEORETICAL CALCULATION OF RATES

No attempt has been made to fit a curve based on the HKRR theory to the experimental points. It will only be pointed out that Howlett (86), using an expression by Hinshelwood (ref. 7, page 81), estimates that $s = 13\text{-}14$ as the number of vibrational degrees of freedom contributing to the reaction and between which energy is assumed to flow.

Slater Theory

The equilibrium configuration of the ethyl chloride molecule, along with the designation of internal coordinates, is shown schematically in Figure 10. Since the reaction is simply HCl abstraction to give ethylene, the most likely linear reaction coordinate is the variation in the distance $Cl\text{-}H_1$ and it is upon this assumption that subsequent calculations have been based. Of course an equivalent critical coordinate would be $\Delta(Cl\text{-}H_2)$.

The very lengthy vibrational analysis, which involves the deduction of a set of potential constants, has

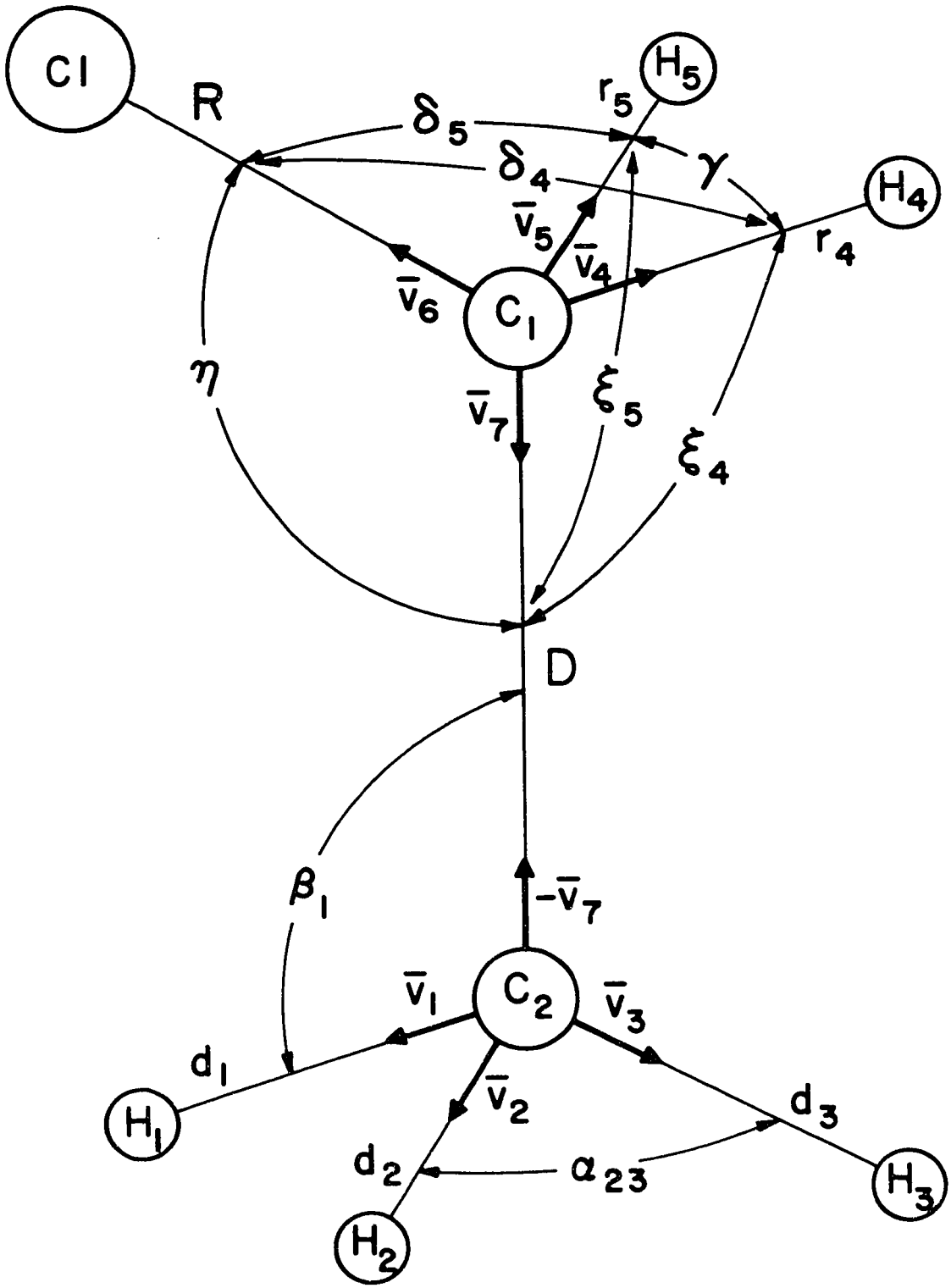


Figure 10. Schematic representation of the ethyl chloride molecule, showing the internal coordinates and unit vectors employed in the treatment.

been carried out to a degree of accuracy sufficient for the present application and the details are presented in the final section of the chapter. The molecule has a total of eighteen vibrational degrees of freedom and the eighteen normal coordinates have been represented approximately in Figure 11. In the numbering of the modes employed here $\nu_1 - \nu_{11}$ are vibrations symmetric with respect to a plane passing through Cl, C_1, C_2, and H_3, while modes $\nu_{12} - \nu_{18}$ are antisymmetric with respect to this plane.

Howlett (86) estimates the effective molecular diameter σ of the molecule to be 5.5×10^{-8} cm which is the value used here. At a temperature of 729°K, at which the kinetic runs were performed, the collision frequency per molecule, ω, may be calculated from [29]. In this formula [A] is the gas concentration in molecules per cc. Converting this to conventional pressure units at 729°K the resulting expression is

$$\omega = 8.704 \times 10^6 \, P \, \text{sec}^{-1} \qquad [212]$$

where P = pressure in mm of H_g.

The amplitude factors a_i and μ_i have been calculated in a manner similar to that in preceding chapters and are presented in Table 10 along with the assignment of fundamental frequencies assumed. Since the chosen critical coordinate bears no simple relationship to any element of symmetry in the molecule, it would be expected that every one of the eighteen modes would have some effect on its

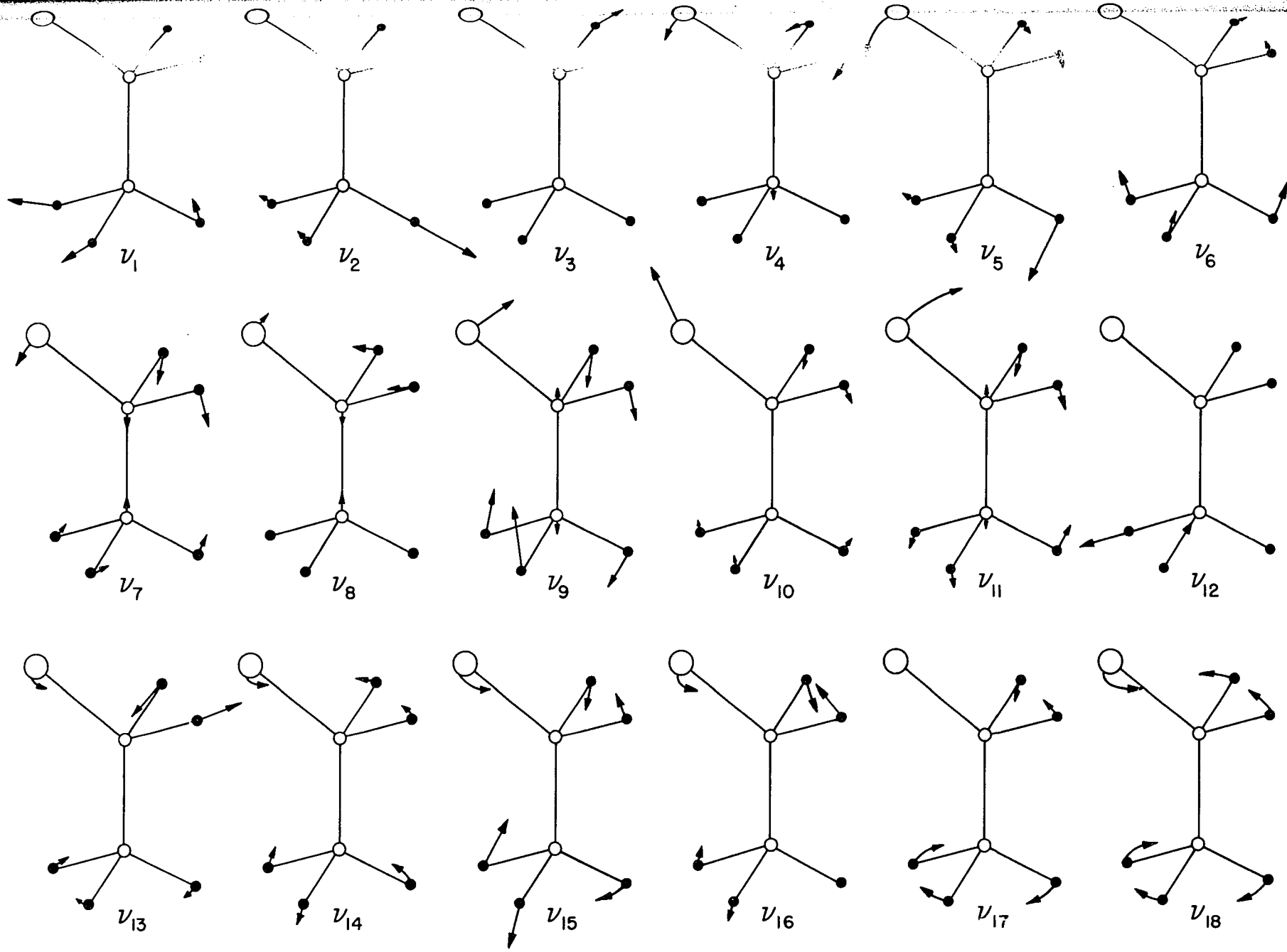


Figure 11. The normal modes of vibration of the ethyl chloride molecule.

Table 10

Frequencies and amplitude factors for the H-Cl distance in $CH_3\ CH_2\ Cl$

i	ν_i (cm^{-1})	a_i ($\times 10^4$)	μ_i
1	2983	1.24	.00539
2	2940	-0.475	.00207
3	2890	-2.26	.00985
4	1456	-2.41	.0105
5	1450	-18.1	.0790
6	1383	-8.94	.0391
7	1287	-23.9	.105
8	1080	-7.41	.0323
9	972	-4.65	.0203
10	676	21.8	.0951
11	336	52.4	.229
12	3012	4.58	.0200
13	2878	0.331	.00144
14	1452	21.5	.0937
15	1245	36.9	.161
16	972	-19.7	.0860
17	785	24.0	.105
18	242.5	213	.930

extension, (i.e. have non-zero a_i). This is indeed the case although certain of the vibrations are seen to contribute very little. The fact which complicates the calculations is the very large value of a_{18} which corresponds to the "torsional" mode ν_{18}. This anomaly first appears in the [1] matrix of Table 18 in the vibrational analysis. The last column of the matrix, corresponding to ν_{18}, shows that the only internal coordinate which undergoes appreciable change in this mode is the angle ϕ, where $\Delta\phi$ is a measure of the "torsion" or internal rotation of the CH_2Cl group with respect to the CH_3 group. The preponderantly large value of $\gamma_{20.18}$ in the Table 19 of γ_{ki} indicates that a great portion of the total energy in this mode is devoted to the torsional motion. Finally, the fact that such motion has a considerable effect on the critical coordinate ($A_\phi = 0.5$) leads to the unusually large value of a_{18}. As a result, the μ_i show a very uneven distribution, μ_{18} being 0.930 while the next largest is $\mu_{11} = 0.229$ and only three others are greater than 0.10. This has a marked effect on the statistics of the Slater calculations, as will be seen presently, for the continued product $\prod_i \mu_i$ will now be much smaller than for a normal distribution of the μ_i.

In order to compute the theoretical rate curve it is necessary to obtain the Slater parameter θ of [36] as a function of pressure. In this expression, ω has already been related to P in [212]; ν is calculated

from [33]; $b = E_o / RT$ where E_o is obtained from [62]; $\Gamma(z)$ equals $(z-1)!$ for integral values of z or may be computed from [37] for half-integral values; The $\prod \mu_i$ term is found from Table 10. Now as Slater discusses (13), it is permissible to omit the normal coordinates with very small μ_i (thereby reducing the number of effective modes) if such an omission will increase the calculated rate constant. On the other hand, since K^1 increases rapidly with n it is uncertain how small the μ_i should be before it is discarded. In his cyclopropane calculations (65) Slater omits $\mu_5 = 0.015$ when all the other μ's are greater than 0.10. Preliminary calculations, in which all eighteen μ factors were retained, resulted in the theoretical curve being far removed to the right (on the pressure scale) from the experimental points. The relationship between θ and P which must be obtained is of the form

$$\theta_n = f(n)\, P \qquad [213]$$

as seen from [36], and since K^1/k_∞ is itself a function of θ, $f(n)$ must be much larger in order that $P = \theta_n / f(n)$ be sufficiently reduced to coincide with experiment.

In an effort to find the curve which best approximates the observed rates, the function θ_n has been calculated for the various assumptions:

(a) $n = 18$; all μ_i considered.

(b) $n = 13$; omitting all $\mu_i < 0.015$

(c) $n = 13$; omitting all $\mu_i < 0.025$

(d) $n = 9$; omitting all $\mu_i < 0.05$

(e) $n = 5$; omitting all $\mu_i < 0.10$

The results of these calculations are seen in Table 11.

Of the five determinations made of $f(n)$, the function attains a maximum at $f(13)$. This was calculated by omitting from $\prod \mu_i$ the factors μ_1 , μ_2 , μ_3 , μ_4 , and μ_{13} , all of which are smaller than 0.015 . It is noticed that $n = 13$ is in agreement with the value for s given by the HKRR theory (86) which is also the case for cyclopropane (66). For $n = 13$ the weighted root-mean-square frequency ν , found from [33], is calculated to be 1.24×10^{13} sec^{-1} . The high-pressure, first-order rate constant is then given by

$$k_\infty = 2\nu \exp(-60800/RT) = 1.46 \times 10^{-5} \text{ sec}^{-1}$$

The factor of 2 arises from the two equivalent critical coordinates.

Slater (13) has tabulated values of K^1/k_∞ as a function of $\log \theta$, for various n , determined from the general integral [34]. Using these figures, along with [213] and $f(13)$, the theoretical curve of K^1/k_∞ against $\log P$ may now be drawn and compared with experiment. This is shown in Figure 12, where the calculated curve for $f(13)$ is that furthest to the right.

Table 11

f(n) at various n

for CH_3CH_2Cl at 729°K.

	n	f(n)
(a)	18	9.83×10^{-4}
(b)	13	2.66×10^{-1}
(c)	11	1.64×10^{-1}
(d)	9	4.18×10^{-2}
(e)	5	1.87×10^{-4}

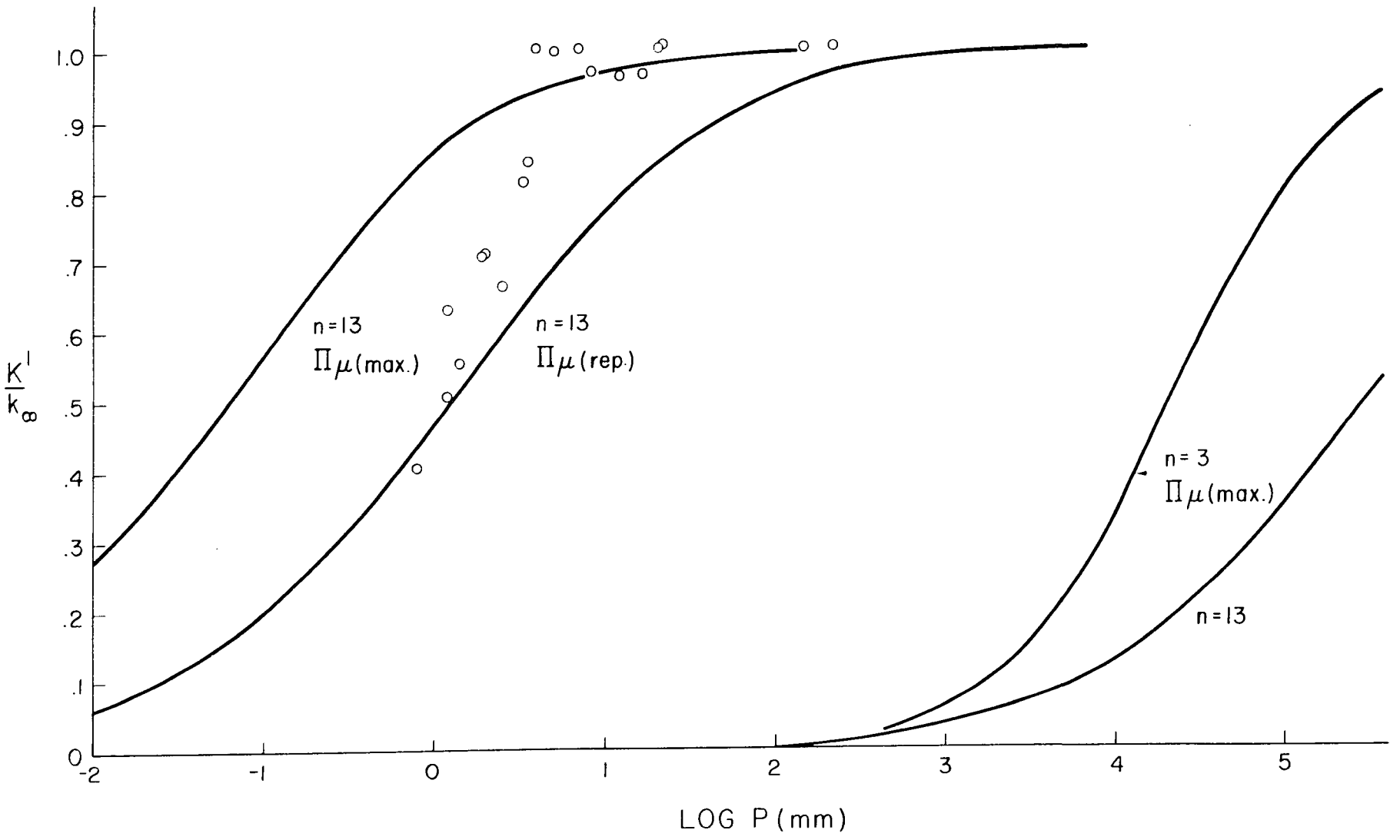


Figure 12. Experimental and theoretical plots of K^1/k_∞ against log P for CH_3CH_2Cl decomposition.

As a maximum, f(13) brings the theoretical curve the furthest to the left (the smallest values of P) of any f(n) , and yet the pressures given by this curve are still about $10^{5.4}$ greater than those measured experimentally. As already suspected, the reason for this lies in the uneven distribution of the μ_i factors which makes $\prod \mu_i$ abnormally small. Retaining n = 13 as a reasonable value, another curve may be drawn based upon a hypothetical critical coordinate which gives the μ_i factors a normal, or "representative" distribution. From experience with a few molecules involving a hydrogen in the critical coordinate, Slater (13) refers to a "representative" distribution of μ_i as one in which the largest is about five times the least and, on the assumption that the μ_i are in a geometrical progression with $\mu_1 = 5\mu_n$, it is deduced that

$$\prod_{i=1}^{13} \mu_i \text{ (rep)} = 0.050(13)^{-6.5} = 2.87 \times 10^{-9}$$

Using this value, the f(13) of [213] is found to be

$$f(13)(\text{rep}) = 6.54 \times 10^{4}$$

which is far larger than any of the f(n) listed in Table 11. The curve based on $\prod \mu_i(\text{rep})$ along with one for $\prod \mu_i(\text{max}) = n^{-n/2}$ are shown in Figure 12 as well. The latter is seen to lie below the experimental pressures, while that for $\prod \mu_i(\text{rep})$

is approximately in the correct region.

The difficulty with the three curves discussed so far is that they are much flatter than the experimental trend. But the shape of the Slater curve, for a fixed value of n, is invariant; changing such parameters as the critical coordinate, E_o or σ merely has the effect of shifting the curve laterally to the right or left. It can be seen from Figure 1, however, that decreasing the value of n makes the curve slightly steeper, which is necessary in the present case if agreement with experiment is to be achieved. The final curve to be constructed was for the case of $n = 3$ (to obtain a maximum steepness) and $\prod_{i=1}^{3} \mu_i\,(max) = 0.192$ (to bring the curve as far as possible to the left). For this case $f(3)(max) = 7.19 \times 10^{-5}$. The result, shown in Figure 12, is indeed an excellent approximation to the trend followed by the experimental points but it is removed too far to the right to be meaningful.

DISCUSSION

The Slater value of k_∞, calculated for $n = 13$ is somewhat lower than the experimental value of 2.36×10^{-4} sec^{-1}. This is due to the high pre-exponential term of $10^{14.6}$ found experimentally and of which the unmodified Slater theory can take no account. The pre-exponential term of k_∞ in this theory is ν, which is always about 10^{13} and it is only when there are several equivalent critical coordinates in the molecule that ν is increased by this

factor.

With regard to the application of the Slater theory to the experimental data in the transition pressure region, it may only be said that with an alternative choice of critical coordinate for which the μ_i are more evenly distributed and for which n is slightly less than thirteen (to increase the slope) a reasonable agreement between theory and experiment might be expected. At any rate, because of the scattering of the experimental points, exact agreement for any chosen set of molecular parameters could not be realized. The main conclusion to be drawn from these calculations is the somewhat negative result that one of the chief inadequacies of the Slater theory, - perhaps more so for larger molecules than for simple ones, - is the assumption that the critical coordinate in a reacting molecule may be considered as a simple, linear distance. It is quite conceivable that if the critical "coordinate" in the present example were multi-dimensional, involving the variations in C-H and H-H distances as well as the H-Cl distance, the μ_i would all have comparable magnitudes with the result that the predicted curve would fall in the region of the experimental points. Admittedly the shape of the Slater curve for large n is not close to that of the observed points but in this case variations in the data make the objection much less serious than if the points all fell along a smooth curve.

VIBRATIONAL ANALYSIS

When the molecules N_2O, O_3 and H_2O_2 were considered in the preceding chapters, the vibrational analysis simply consisted of setting up the secular determinant using previously determined force constants and obtaining the normal coordinates of vibration which were then used to calculate the Slater amplitude factors. In the case of ethyl chloride, however, because of the low degree of symmetry in the molecule, calculations become very laborious even with the aid of an electronic computer and for this reason no determination of force constants has been undertaken, prior to this work, although reliable spectroscopic data have been available since 1954 (87)(88)(89). As will be seen, the force constants deduced in this section must be considered as approximate only, for although they may be used to reproduce the seven "antisymmetric" frequencies very closely, the adjustment process was not carried on long enough to obtain more than rough agreement with the eleven "symmetric" frequencies. To achieve agreement throughout would have required very prolonged calculations and it was felt that the normal coordinates obtained from the set of constants eventually used were sufficiently accurate to provide a test for the Slater theory.

Molecular Structure

The structure of the ethyl chloride molecule has

been represented schematically in Figure 10. From microwave studies of the normal and deuterated molecule, Wagner and Dailey (90) could unambiguously establish the equilibrium configuration as the staggered rather than the eclipsed form. The internal coordinates used in the analysis are indicated in Figure 10 and will be numbered as follows: $r_1 = \Delta D$, $r_2 = \Delta d_1$, $r_3 = \Delta d_2$, $r_4 = \Delta d_3$, $r_5 = \Delta r_4$, $r_6 = \Delta r_5$, $r_7 = \Delta R$, $r_8 = \Delta\beta_1$, $r_9 = \Delta\beta_2$, $r_{10} = \Delta\beta_3$, $r_{11} = \Delta\beta_4$, $r_{12} = \Delta\beta_5$, $r_{13} = \Delta\beta_6$, $r_{14} = \Delta\alpha_{12}$, $r_{15} = \Delta\alpha_{23}$, $r_{16} = \Delta\alpha_{13}$, $r_{17} = \Delta\gamma$, $r_{18} = \Delta\delta_4$, $r_{19} = \Delta\delta_5$, $r_{20} = \Delta\phi$. The coordinate ϕ measures the internal rotation about the C-C bond, $\Delta\phi$ being the angle through which the CH_2Cl group turns relative to the CH_3 group, measured from the equilibrium position.

The structural parameters of the molecule have been determined by electron diffraction and more recently by microwave measurements. Some of these results along with the parameters assumed for this analysis are presented in Table 12. Further results from electron diffraction experiments are quoted by Allen and Sutton (94) in which R ranges from 1.76 to 1.81 x 10^{-8} cm and α between 110° and 111°30'. The set of parameters chosen for the present work were assumed to be sufficiently reliable for the determination of normal coordinates.

Symmetry and Coordinates

The molecule is of C_s symmetry and vibrations are either symmetric (A') or antisymmetric (A'') with respect to a plane passing through Cl, C_1, C_2 and H_3.

Table 12

Structural data for ethyl chloride. Distances are given in angstrom units.

Parameter	Ref.(91) Electron diff'n	Ref.(92) Micro-wave	Ref.(93) Micro-wave	Ref.(93) alternative Micro-wave	Ref.(90) Micro-wave	Values used in present analysis
D	1.54	1.54	1.54	1.55	1.5495	1.55
d	1.09	1.103	1.09	1.09	1.101	1.101
r	1.09	1.103	1.09	1.09	1.101	1.101
R	1.76	1.78	1.780	1.771	1.7785	1.78
α	$109^\circ 28'$	$109^\circ 28'$	$109^\circ 28'$	$109^\circ 28'$	$110^\circ 00'$	$109^\circ 28'$
β	$109^\circ 28'$	$109^\circ 28'$	$109^\circ 28'$	$109^\circ 28'$		$109^\circ 28'$
γ	$109^\circ 28'$	$110^\circ 20'$	$109^\circ 28'$	$109^\circ 28'$	$110^\circ 00'$	$109^\circ 28'$
ξ	$109^\circ 28'$		$109^\circ 28'$	$109^\circ 28'$		$109^\circ 28'$
η	$111^\circ 30'$	$111^\circ 30'$	$111^\circ 6'$	$111^\circ 16'$	$110^\circ 30'$	$111^\circ 30'$

The character table for this point group, along with the number of vibrations of each species for the case of $CH_3 CH_2 Cl$, is presented in Table 13 below. There are $3N-6 = 18$ degrees of vibrational freedom in the molecule. It is noticed that because of the single element of symmetry present the degree of symmetry factoring is very slight.

Symmetry coordinates R_j are constructed as outlined in chapter 2. When the number of internal coordinates m exceeds the number of degrees of freedom n, it is necessary to form m symmetry coordinates of which $(m - n)$ are "redundant", (i.e. identically zero) and to which the other n coordinates must be orthogonal as defined by [74]. Since $m = 20$ and $n = 18$ in this case, the two symmetry coordinates R_{19} and R_{20}, placed in the A' class, are redundant:

A' vibrations

$$R_1 = (\Delta d_1 + \Delta d_2)/\sqrt{2} \qquad [214]$$

$$R_2 = (\Delta r_4 + \Delta r_5)/\sqrt{2} \qquad [215]$$

$$R_3 = (2\Delta\beta_3 - \Delta\beta_1 - \Delta\beta_2)/\sqrt{6} \qquad [216]$$

$$R_4 = (2\Delta\eta - \Delta\xi_4 - \Delta\xi_5)/\sqrt{6} \qquad [217]$$

$$R_5 = (2\Delta\alpha_{12} - \Delta\alpha_{23} - \Delta\alpha_{13})/\sqrt{6} \qquad [218]$$

$$R_6 = (2\Delta\gamma - \Delta\delta_4 - \Delta\delta_5)/\sqrt{6} \qquad [219]$$

$$R_7 = \Delta D \qquad [220]$$

$$R_8 = \Delta d_3 \qquad [221]$$

$$R_9 = \Delta R \qquad [222]$$

$$R_{10} = (\Delta\alpha_{12} + \Delta\alpha_{23} + \Delta\alpha_{13} - \Delta\beta_1 - \Delta\beta_2 - \Delta\beta_3)/\sqrt{6} \qquad [223]$$

$$R_{11} = (\Delta\gamma + \Delta\delta_4 + \Delta\delta_5 - \Delta\xi_4 - \Delta\xi_5 - \Delta\eta)/\sqrt{6} \qquad [224]$$

Table 13

Character table for the point group C_s with the number of vibrations of each symmetry species of CH_3CH_2Cl.

C_s	I	σ	Number of genuine vibrations
A'	+1	+1	11
A''	+1	-1	7

$$R_{19} = (\Delta\alpha_{12} + \Delta\alpha_{23} + \Delta\alpha_{13} + \Delta\beta_1 + \Delta\beta_2 + \Delta\beta_3)/\sqrt{6} \equiv 0 \quad [225]$$

$$R_{20} = (\Delta\gamma + \Delta\delta_4 + \Delta\delta_5 + \Delta\zeta_4 + \Delta\zeta_5 + \Delta\eta)/\sqrt{6} \equiv 0 \quad [226]$$

A'' vibrations

$$R_{12} = (\Delta d_1 - \Delta d_2)/\sqrt{2} \quad [227]$$

$$R_{13} = (\Delta r_4 - \Delta r_5)/\sqrt{2} \quad [228]$$

$$R_{14} = (\Delta\beta_1 - \Delta\beta_2)/\sqrt{2} \quad [229]$$

$$R_{15} = (\Delta\zeta_4 - \Delta\zeta_5)/\sqrt{2} \quad [230]$$

$$R_{16} = (\Delta\alpha_{23} - \Delta\alpha_{13})/\sqrt{2} \quad [231]$$

$$R_{17} = (\Delta\delta_4 - \Delta\delta_5)/\sqrt{2} \quad [232]$$

$$R_{18} = \Delta\phi \quad [233]$$

These expressions define the [U] matrix of [72].

Potential Function and [F] Matrix

The choice of a potential function in terms of the internal coordinates was influenced by the force constants calculated for 1, 1, 1-trichloroethane by El-Sabban, Meister and Cleveland (95). Guided by the results of these workers, it was decided that the cross terms in the potential function that could be neglected were those which expressed interactions between:

(a) ϕ and the other internal coordinates,

(b) CH_2Cl and CH_3 groups,

(c) angles having no bond or atom in common,

(d) D and the d's or r's.

The resulting [f] matrix which contains all the remaining force constants is given in Table 14. In this matrix f'

	ΔD	Δd_1	Δd_2	Δd_3	Δr_4	Δr_5	ΔR	$\Delta\beta_1$	$\Delta\beta_2$	$\Delta\beta_3$	$\Delta\xi_4$	$\Delta\xi_5$	$\Delta\eta$	$\Delta\alpha_{12}$	$\Delta\alpha_{23}$	$\Delta\alpha_{13}$	$\Delta\gamma$	$\Delta\delta_4$	$\Delta\delta_5$	$\Delta\phi$
ΔD	f_D						f_{DR}	$df_{D\beta}$	$df_{D\beta}$	$df_{D\beta}$	$df_{D\xi}$	$df_{D\xi}$	$Rf_{D\eta}$							
Δd_1		f_d	f_{dd}	f_{dd}				$df_{d\beta}$	$df'_{d\beta}$	$df'_{d\beta}$				$df_{d\alpha}$	$df''_{d\alpha}$	$df_{d\alpha}$				
Δd_2			f_d	f_{dd}				$df'_{d\beta}$	$df_{d\beta}$	$df'_{d\beta}$				$df_{d\alpha}$	$df_{d\alpha}$	$df'_{d\alpha}$				
Δd_3				f_d				$df'_{d\beta}$	$df'_{d\beta}$	$df_{d\beta}$				$df'_{d\alpha}$	$df_{d\alpha}$	$df_{d\alpha}$				
Δr_4					f_r	f_{rr}	f_{rR}				$df_{r\xi}$	$df'_{r\xi}$	$df_{r\eta}$				$df_{r\gamma}$	$df_{r\delta}$	$df'_{r\delta}$	
Δr_5						f_r	f_{rR}				$df'_{r\xi}$	$df_{r\xi}$	$df_{r\eta}$				$df_{r\gamma}$	$df'_{r\delta}$	$df_{r\delta}$	
ΔR							f_R				$df_{R\xi}$	$df_{R\xi}$	$Rf_{R\eta}$				$df_{R\gamma}$	$df_{R\delta}$	$df_{R\delta}$	
$\Delta\beta_1$								d^2f_β	$d^2f_{\beta\beta}$	$d^2f_{\beta\beta}$				$d^2f_{\beta\alpha}$	$d^2f''_{\beta\alpha}$	$d^2f_{\beta\alpha}$				
$\Delta\beta_2$									d^2f_β	$d^2f_{\beta\beta}$				$d^2f_{\beta\alpha}$	$d^2f_{\beta\alpha}$	$d^2f'_{\beta\alpha}$				
$\Delta\beta_3$										d^2f_β				$d^2f'_{\beta\alpha}$	$d^2f_{\beta\alpha}$	$d^2f_{\beta\alpha}$				
$\Delta\xi_4$											d^2f_ξ	$d^2f_{\xi\xi}$	$d^2f_{\xi\eta}$				$d^2f_{\xi\gamma}$	$d^2f_{\xi\delta}$	$d^2f'_{\xi\delta}$	
$\Delta\xi_5$												d^2f_ξ	$d^2f_{\xi\eta}$				$d^2f_{\xi\gamma}$	$d^2f'_{\xi\delta}$	$d^2f_{\xi\delta}$	
$\Delta\eta$													R^2f_η				$d^2f_{\eta\gamma}$	$d^2f_{\eta\delta}$	$d^2f_{\eta\delta}$	
$\Delta\alpha_{12}$					$(f_{ik}=f_{ki})$									d^2f_α	$d^2f_{\alpha\alpha}$	$d^2f_{\alpha\alpha}$				
$\Delta\alpha_{23}$															d^2f_α	$d^2f_{\alpha\alpha}$				
$\Delta\alpha_{13}$																d^2f_α				
$\Delta\gamma$																	d^2f_γ	$d^2f_{\gamma\delta}$	$d^2f_{\gamma\delta}$	
$\Delta\delta_4$																		d^2f_δ	$d^2f_{\delta\delta}$	
$\Delta\delta_5$																			d^2f_δ	
$\Delta\phi$																				d^2f_ϕ

is a force constant expressing the interaction between two internal coordinates which have one atom but no bond in common.

With this [f] matrix and the [U] matrix, formed from the coefficients in the symmetry coordinates, the elements of the [F] matrix are obtained from [77]:

A' vibrations

$$F_{1.1} = f_d + f_{dd} \quad [234]$$

$$F_{1.3} = d(f'_{d\beta} - f_{d\beta})/\sqrt{3} \quad [235]$$

$$F_{1.5} = d(f_{d\alpha} - f'_{d\alpha})/\sqrt{3} \quad [236]$$

$$F_{1.8} = \sqrt{2}\, f_{dd} \quad [237]$$

$$F_{1.10} = d(2f_{d\alpha} + f'_{d\alpha} - f_{d\beta} - 2f'_{d\beta})/\sqrt{3} \quad [238]$$

$$F_{2.2} = f_r + f_{rr} \quad [239]$$

$$F_{2.4} = d(2f_{r\eta} - f_{r\xi} - f'_{r\xi})/\sqrt{3} \quad [240]$$

$$F_{2.6} = d(2f_{r\gamma} - f_{r\delta} - f'_{r\delta})/\sqrt{3} \quad [241]$$

$$F_{2.9} = \sqrt{2}\, f_{rR} \quad [242]$$

$$F_{2.11} = d(f_{r\gamma} + f_{r\delta} + f'_{r\delta} - f_{r\xi} - f'_{r\xi} - f_{r\eta})/\sqrt{3} \quad [243]$$

$$F_{3.3} = d^2(f_\beta - f_{\beta\beta}) \quad [244]$$

$$F_{3.5} = d^2(f'_{\beta\alpha} - f_{\beta\alpha}) \quad [245]$$

$$F_{3.8} = 2d(f_{d\beta} - f'_{d\beta})/\sqrt{6} \quad [246]$$

$$F_{4.4} = [d^2(f_\xi + f_{\xi\xi} - 4f_{\xi\eta}) + 2R^2 f_\eta]/3 \quad [247]$$

$$F_{4.6} = d^2(f_{\xi\delta} + f'_{\xi\delta} - 2f_{\xi\gamma} + 2f_{\eta\gamma} - 2f_{\eta\delta})/3 \quad [248]$$

$$F_{4.7} = 2(Rf_{D\eta} - df_{D\xi})/\sqrt{6} \quad [249]$$

$$F_{4.9} = 2(Rf_{R\eta} - df_{R\xi})/\sqrt{6} \quad [250]$$

$$F_{4.11} = [d^2(f_\xi + f_{\xi\xi} - f_{\xi\gamma} - f_{\xi\delta} - f'_{\xi\delta} + f_{\eta\gamma} + 2f_{\eta\delta} - f_{\xi\eta}) - R^2 f_\eta]/3 \quad [251]$$

$$F_{5.5} = d^2(f_\alpha - f_{\alpha\alpha}) \quad [252]$$

$$F_{5.8} = 2d(f'_{d\alpha} - f_{d\alpha})/\sqrt{6} \quad [253]$$

$$F_{6.6} = d^2(2f_\gamma - 4f_{\gamma\delta} + f_\delta + f_{\delta\delta})/3 \quad [254]$$

$$F_{6.9} = 2d(f_{R\gamma} - f_{R\delta})/\sqrt{6} \quad [255]$$

$$F_{6.11} = d^2(f_\gamma - 2f_{\xi\gamma} - f_{\eta\gamma} + f_{\gamma\delta} - f_\delta - f_{\delta\delta} + f_{\xi\delta} + f'_{\xi\delta} + f_{\eta\delta})/3 \quad [256]$$

$$F_{7.7} = f_D \quad [257]$$

$$F_{7.9} = f_{DR} \quad [258]$$

$$F_{7.10} = -3df_{D\beta}/\sqrt{6} \quad [259]$$

$$F_{7.11} = -(2df_{D\xi} + Rf_{D\eta})/\sqrt{6} \quad [260]$$

$$F_{8.8} = f_d \quad [261]$$

$$F_{8.10} = d(2f_{d\alpha} + f'_{d\alpha} - f_{d\beta} - 2f'_{d\beta})/\sqrt{6} \quad [262]$$

$$F_{9.9} = f_R \quad [263]$$

$$F_{9.11} = [d(f_{R\gamma} + 2f_{R\delta} - 2f_{R\xi}) - Rf_{R\eta}]/\sqrt{6} \quad [264]$$

$$F_{10.10} = d^2(f_\alpha + 2f_{\alpha\beta} + f_\beta + 2f_{\beta\beta} - 2f'_{\beta\alpha} - 4f_{\beta\alpha})/2 \quad [265]$$

$$F_{11.11} = [2d^2(2f_{\gamma\delta} - 2f_{\xi\gamma} - f_{\eta\gamma} + f_\delta + f_{\delta\delta} - 2f_{\xi\delta} - 2f'_{\xi\delta} + f_\xi + f_{\xi\xi} + 2f_{\xi\eta} - 2f_{\eta\delta}) + d^2f_\gamma + R^2f_\eta]/6 \quad [266]$$

A'' vibrations

$$F_{12.12} = f_d - f_{dd} \quad [267]$$

$$F_{12.14} = d(f_{d\beta} - f'_{d\beta}) \quad [268]$$

$$F_{12.16} = d(f'_{d\alpha} - f_{d\alpha}) \quad [269]$$

$$F_{13.13} = f_r - f_{rr} \quad [270]$$

$$F_{13.15} = d(f_{r\xi} - f'_{r\xi}) \quad [271]$$

$$F_{13.17} = d(f_{r\delta} - f'_{r\delta}) \quad [272]$$

$$F_{14.14} = d^2(f_{\beta} - f_{\beta\beta}) \quad [273]$$

$$F_{14.16} = d^2(f'_{\beta\alpha} - f_{\beta\alpha}) \quad [274]$$

$$F_{15.15} = d^2(f_{\varsigma} - f_{\varsigma\varsigma}) \quad [275]$$

$$F_{15.17} = d^2(f_{\varsigma\delta} - f'_{\varsigma\delta}) \quad [276]$$

$$F_{16.16} = d^2(f_{\alpha} - f_{\alpha\alpha}) \quad [277]$$

$$F_{17.17} = d^2(f_{\delta} - f_{\delta\delta}) \quad [278]$$

$$F_{18.18} = d^2 f_{\phi} \quad [279]$$

in which $F_{jl} = F_{lj}$ and all other elements are zero.

[G] Matrix

The [G] elements were composed in exactly the same manner as for the H_2O_2 molecule, using the relationships [79], [80], Table 1, and the unit vectors indicated in Figure 10. This process becomes rather complex with the large number of internal coordinates involved and the algebraic expressions for the elements are much too lengthy to be given here. The expressions were evaluated using the parameters listed in Table 12 and $\mu_C = 0.5018$, $\mu_{Cl} = 0.1698$ and $\mu_H = 5.974 \times 10^{23}$ gm^{-1} as the reciprocals of the masses of the C, Cl and H atoms respectively. These numerical values are given below. The basic units are grams, seconds and angstroms, and each element is to be multiplied by the factor 10^{23}.

A' vibrations

$G_{1.1} = 6.309$

$G_{1.2} = 0$

$G_{1.3} = 0.3883$

$G_{1.4} = 0.2041$

$G_{1.5} = -0.4961$

$G_{1.6} = 0$

$G_{1.7} = -0.2365$

$G_{1.8} = -0.2365$

$G_{1.9} = 0$

$G_{1.10} = 2.409$

$G_{1.11} = 0.003328$

$G_{2.2} = 6.309$

$G_{2.3} = 0.2643$

$G_{2.4} = 0.2975$

$G_{2.5} = 0$

$G_{2.6} = -0.5443$

$G_{2.7} = -0.2365$

$G_{2.8} = 0$

$G_{2.9} = -0.2246$

$G_{2.10} = \sim 0$

$G_{2.11} = 0.5859$

$G_{3.3} = 5.917$

$G_{3.4} = 0.8968$

$G_{3.5} = 3.327$

$G_{3.6} = -0.6048$

$G_{3.7} = -0.1869$

$G_{3.8} = -0.5492$

$G_{3.9} = -0.3738$

$G_{3.10} = -3.285$

$G_{3.11} = -0.1992$

$G_{4.4} = 2.616$

$G_{4.5} = -0.5931$

$G_{4.6} = -0.8870$

$G_{4.7} = 0.1367$

$G_{4.8} = -0.1871$

$G_{4.9} = -0.2949$

$G_{4.10} = -0.01979$

$G_{4.11} = 1.895$

$G_{5.5} = 13.42$

$G_{5.6} = 0$

$G_{5.7} = 0$

$G_{5.8} = 0.7016$

$G_{5.9} = 0$

$G_{5.10} = -1.642$

$G_{5.11} = 0.001291$

$G_{6.6} = 10.83$

$G_{6.7} = 0.05657$

$G_{6.8} = 0$

$G_{6.9} = 0.6976$

$G_{6.10} = \sim 0$

$G_{6.11} = 8.026$

$G_{7.7} = 1.004$

$G_{7.8} = -0.1672$

$G_{7.9} = -0.1839$

$G_{7.10} = 1.052$

$G_{7.11} = 0.8890$

$G_{8.8} = 6.476$

$G_{8.9} = 0$

$G_{8.10} = 0.1372$

$G_{8.11} = 0.0001104$

$G_{9.9} = 0.6716$

$G_{9.10} = 0.1027$

$G_{9.11} = -0.09306$

$G_{10.10} = 12.17$

$G_{10.11} = 0.002865$

$G_{11.11} = 12.02$

A'' vibrations

$G_{12.12} = 6.643$

$G_{12.13} = 0$

$G_{12.14} = -0.6726$

$G_{12.15} = -0.4578$

$G_{12.16} = 0.8593$

$G_{12.17} = 0$

$G_{12.18} = 0.4188$

$G_{13.13} = 6.643$

$G_{13.14} = -0.4578$

$G_{13.15} = -0.6726$

$G_{13.16} = 0$

$G_{13.17} = -0.5989$

$G_{13.18} = 0.4310$

$G_{14.14} = 5.918$

$G_{14.15} = 0.9205$

$G_{14.16} = 1.599$

$G_{14.17} = 0.4098$ $G_{16.16} = 13.42$

$G_{14.18} = 3.831$ $G_{16.17} = 0$

$G_{15.15} = 5.918$ $G_{16.18} = 0.5378$

$G_{15.16} = -0.5880$ $G_{17.17} = 5.484$

$G_{15.17} = -1.245$ $G_{17.18} = 5.822$

$G_{15.18} = -0.7199$ $G_{18.18} = 28.67$

Fundamental Frequencies

The most recent spectral analyses available are those of Allen and Bernstein (87) and of Daasch, Liang and Nielsen (88)(89). The assignments proposed by these two groups are very similar but Daasch et al. assign two A' and one A'' species in the 1450 cm^{-1} region and consider 1242 cm^{-1} to be of species A''; the former group assign one A' and two A'' species in the 1450 cm^{-1} region and the 1242 cm^{-1} band is taken as A'. Allen and Bernstein (87) observe an additional band in the Raman spectrum which aids in their assignment and, as discussed by these authors, this assignment is preferred because the discrepancies between corresponding bands in the Raman and infrared spectra which exist in the scheme of Daasch et al. are now removed. However, when calculations were begun with the 7 x 7 matrices corresponding to the antisymmetric modes of vibration it was found that, with reasonable values for the force constants, the frequencies of Daasch et al. could be reproduced, whereas it would require an impossibly large value for f_ζ to obtain a ν_{15} of

1440 cm^{-1} as proposed by Allen and Bernstein. As a result, calculations were continued in an attempt to reproduce the assignment of Daasch, Liang and Nielsen (88) whose frequencies are listed in Table 17. It should be pointed out, however, that the subsequent difficulty in obtaining agreement with the symmetric frequencies may have been the result of an erroneous assignment by Daasch et al.

One modification has been made to this latter assignment. These authors report a value of 276 cm^{-1} for ν_{18} which corresponds to the torsional mode of vibration. More recent studies of the microwave spectrum indicate that ν_{18} is somewhat lower. Lide (96) finds that ν_{18} = 242.5 cm^{-1} from the potential barrier to rotation and this is supported by the work of Wagner and Dailey (90) who obtain a frequency of 236±40 cm^{-1}. The value of 242.5 cm^{-1} has been adopted for the torsional frequency (in place of 276 cm^{-1}) in the subsequent calculations.

Adjustment of Force Constants

The problem of deducing a set of potential constants was begun for the case of the seven antisymmetric A'' vibrations for which the IBM 650 digital computer at the University of Ottawa was used. A program for matrix multiplication was required to compute the 7 x 7 product matrix [GF] but when difficulties were encountered in the use of the library programs of the Computing Centre, Mr. S. Villanyi kindly undertook to write a program which was used in all

subsequent multiplications. This program required about five minutes to compute a 7 x 7 product and about nine minutes for one of dimensions 11 x 11 .

Having determined the 7 x 7 product [GF], it was necessary to find its eigenvalues and associated eigenvectors. The only IBM library program that was available for this purpose, number 5.2.016, was not particularly rapid nor flexible. It combines Weilandt's deflation (ref. 75 page 306) with the power method but has no provision for changing origin at will. The difficulty of nearly equal roots which prevents rapid convergence, as discussed earlier, was continually being encountered. Eventually convergence of all seven eigenvalues with their corresponding vectors was achieved by the two-stage procedure mentioned above in which the four largest roots were calculated by a suitable choice of origin, and then the origin shifted to obtain the three smallest roots.

It is usually possible to identify one diagonal element of the [GF] matrix with each root sought. The two are of comparable magnitude since the off-diagonal elements, arising from the interaction terms between different coordinates, are generally much smaller that the diagonal elements. The first rough adjustments to the force constants can then be made simply by altering the elements of [F] which affect the diagonal element of [GF] corresponding to a given root, bringing the diagonal element more in line with the desired value of the root.

Once a set of frequencies approximately agreeing with the observed values has been calculated, it is possible to make the more refined adjustments through the use of the Jacobian matrix [J] whose elements are derived from [207]. Perhaps the simplest method of obtaining the scalar quantities $[L_a]'[F][L_a]$ is to form the complete matrix [L] whose columns are the eigenvectors $[L_a]$ most recently calculated from [GF], and perform the multiplication $[L]'[F][L]$ by computer. The diagonal elements of this triple product are then the numbers $[L_a]'[F][L_a]$ required for [207]. The matrices $[B_h]$ are very simply formed from the definition [203]. The elements J_{ah} thus calculated will then serve as a quantitative guide for further adjustments to the constants.

The Jacobian matrix for the seven A'' vibrations was determined and is presented in the two pages of Table 15. Rather than consider the force constants separately in this case, the Jacobian elements are given for the thirteen (different) non-zero [F] elements as a whole. Since these are very simple functions of the f_h here, corrections to the latter are easily deduced. After about six adjustments the seven A'' frequencies were obtained, all within 1% of the observed values (88)(96) with the exception of ν_{15} which differed by 2.3%.

When the same IBM program was used in an attempt to solve the 11 x 11 matrix [GF] of the symmetric vibrations, convergence of the roots could not be effected although several different choices of origin were made. This program

Table 15

[J] matrix for the A'' vibrations of CH_3CH_2Cl .

i	$\frac{\partial \lambda_i}{\partial F_{12.12}}$	$\frac{\partial \lambda_i}{\partial F_{13.13}}$	$\frac{\partial \lambda_i}{\partial F_{14.14}}$	$\frac{\partial \lambda_i}{\partial F_{15.15}}$	$\frac{\partial \lambda_i}{\partial F_{16.16}}$	$\frac{\partial \lambda_i}{\partial F_{17.17}}$
12	6.57	0.017	0.050	0.026	0	0
13	0.017	6.60	0.038	0.047	0	0.016
14	0.040	0	0.951	0.020	12.7	0.008
15	0.004	0	4.60	1.94	0.008	0.026
16	0.003	0	0.941	3.15	0.005	2.34
17	0.001	0.021	0.182	0.787	0.001	3.19
18	0	0	0.001	0	0	0.012

Elements have been reduced by the factor 10^{23} .

Table 15 (continued)

i	$\frac{\partial \lambda_1}{\partial F_{18.18}}$	$\frac{\partial \lambda_1}{\partial F_{12.14}}$	$\frac{\partial \lambda_1}{\partial F_{12.16}}$	$\frac{\partial \lambda_1}{\partial F_{13.15}}$	$\frac{\partial \lambda_1}{\partial F_{13.17}}$	$\frac{\partial \lambda_1}{\partial F_{14.16}}$	$\frac{\partial \lambda_1}{\partial F_{15.17}}$
12	0.035	-1.15	0.086	0.042	-0.004	-0.007	-0.052
13	0.083	-0.050	-0.005	-1.11	-0.645	0.007	0.055
14	0.337	0.390	1.43	-0.003	0.002	6.95	-0.025
15	1.69	-0.285	0.012	-0.054	0.006	-0.374	-0.452
16	4.91	-0.104	0.008	0.040	0.034	-0.143	-5.31
17	3.20	-0.020	0.002	-0.257	-0.519	-0.027	3.17
18	18.9	0	0	0	-0.001	0	0

Elements have been reduced by the factor 10^{23} .

was eventually abandoned and computation was continued on the larger Ferranti computer at the Structures Laboratory of the National Research Council. The program used with this machine bears the title "EIG:NSM" and has all the characteristics desirable in such a program. In addition to the deflation which progressively reduces the size of the matrix, it is possible to achieve a more rapid convergence through "acceleration" of the iterations or a change in origin, each of which may be introduced simply by a setting on the hand-switches without interrupting the program. With merely one change of origin it was possible to obtain a complete solution of the 11 x 11 matrix within 45 minutes. Unfortunately these advantages were somewhat offset by the very delicate nature of the computer itself for, as frequently occurred, only a minor electronic difficulty was enough to halt the program entirely.

After several adjustments to the data it was decided to use the eigenvectors calculated at that stage without further modifications. The calculated frequencies for both A' and A'' vibrations are given in Table 17 and compared to the observed values of Daasch, Liang and Nielsen (88). Seven of the A' frequencies obtained are in fairly good agreement with experiment, but the remaining four, ν_4, ν_5, ν_7 and ν_{11}, show larger differences.

Because of these differences the force constants deduced,—at least those which appear in the A' and not the A'' calculations,— must be considered as only approximate,

although they were assumed sufficient for the Slater calculations. These constants are listed in Table 16. Comparison with similar molecules such as ethane (97) and 1, 1, 1-trichloroethane (95) show that the magnitudes of the constants do not exceed reasonable limits.

Normal Coordinates

Both of the eigenvalue programs employed on the [GF] matrix yielded the corresponding vector with each root. These vectors are the $[L_a]$ of [92] and together make up the [L] matrix. The matrix [1] is now obtained from

$$[1] = [U]'[L] \qquad [280]$$

as indicated in [97], and is presented in the three pages of Table 18. These figures give the relative variations in each of the twenty internal coordinates for each mode of vibration. From this data the eighteen normal coordinates are represented approximately in Figure 11, of the preceding section.

Amplitude Factors

(a) A_k coefficients: The Slater coefficients A_k are defined by [104] and express the effects of variations in the internal coordinates on the chosen critical coordinate. Taking $p = \Delta P$ as the variation in the $Cl\text{-}H_1$ distance, it is seen that the only internal coordinates for which the A_k are non-zero are $r_1 = \Delta D$, $r_2 = \Delta d_1$, $r_7 = \Delta R$, $r_8 = \Delta\beta_1$,

Table 16

Force constants for CH_3CH_2Cl.

(10^5 dynes/cm)

Type	Value	Type	Value
f_D	5.300	$f_{r\xi}$	0.2000
f_d	4.917	$f'_{r\xi}$	0.0000
f_r	4.557	$f_{r\eta}$	0.0000
f_R	2.980	$f_{r\gamma}$	0.2937
f_β	0.7660	$f_{r\delta}$	0.2660
f_ξ	0.4774	$f'_{r\delta}$	0.0010
f_η	0.3900	$f_{R\xi}$	0.0030
f_α	0.4390	$f_{R\eta}$	0.1500
f_γ	0.2800	$f_{R\gamma}$	0.0000
f_δ	0.3477	$f_{R\delta}$	0.0000
f_ϕ	0.00883	$f_{R\delta}$	0.0000
f_{DR}	0.3758	$f_{\beta\beta}$	-0.0200
$f_{D\beta}$	0.2500	$f_{\beta\alpha}$	0.0141
$f_{D\xi}$	0.2500	$f'_{\beta\alpha}$	0.0000
$f_{D\eta}$	-0.3000	$f_{\xi\xi}$	-0.0200
f_{dd}	0.0000	$f_{\xi\eta}$	0.0000
$f_{d\beta}$	0.1817	$f_{\xi\gamma}$	0.0200
$f'_{d\beta}$	0.0000	$f_{\xi\delta}$	0.0141
$f_{d\alpha}$	0.2337	$f'_{\xi\delta}$	-0.0079
$f'_{d\alpha}$	-0.0600	$f_{\eta\gamma}$	0.0030
f_{rr}	0.0400	$f_{\eta\delta}$	0.0050
f_{rR}	0.1000	$f_{\gamma\delta}$	0.0200
$f_{\alpha\alpha}$	0.0100	$f_{\delta\delta}$	-0.0400

Table 17

Observed and calculated fundamental frequencies of CH_3CH_2Cl.

	Observed (88) (cm^{-1})	Calculated (cm^{-1})	% diff.	Species
ν_{12}	3012	3013	0.03	A''
ν_1	2983	3056	2.4	A'
ν_2	2940	2989	1.7	A'
ν_3	2890	2888	0.1	A'
ν_{13}	2878	2881	0.1	A''
ν_4	1456	1914	31.5	A'
ν_{14}	1452	1467	1.0	A''
ν_5	1450	1698	17.1	A'
ν_6	1383	1320	4.6	A'
ν_7	1287	1161	9.8	A'
ν_{15}	1245	1216	2.3	A''
ν_8	1080	1050	2.8	A'
ν_9	972	974	0.2	A'
ν_{16}	972	974	0.2	A''
ν_{17}	785	791	0.8	A''
ν_{10}	676	723	7.0	A'
ν_{11}	336 (276)	648	92.9	A'
ν_{18}	242.5 (ref.96)	242.7	0.08	A''

Table 18

[l] matrix for CH_3CH_2Cl.

(Distances are in angstroms and angles in radians)

k		ν_1	ν_2	ν_3	ν_4	ν_5
1	ΔD	-.033	-.035	.023	.255	.023
2	Δd_1	.707	.143	.018	-.002	.073
3	Δd_2	.707	.143	.018	-.002	.073
4	Δd_3	-.104	1.00	-.007	-.004	.099
5	Δr_4	-.012	.004	.707	-.065	-.029
6	Δr_5	-.012	.004	.707	-.065	-.029
7	ΔR	.005	.001	-.029	.012	-.034
8	$\Delta\beta_1$	-.229	-.038	-.019	-.023	.036
9	$\Delta\beta_2$	-.229	-.038	-.019	-.023	.036
10	$\Delta\beta_3$	-.209	-.011	.027	-.034	.937
11	$\Delta\xi_4$	-.002	.011	-.149	-.157	-.101
12	$\Delta\xi_5$	-.002	.011	-.149	-.157	-.101
13	$\Delta\eta$	.032	-.010	-.085	-.216	-.479
14	$\Delta\alpha_{12}$	.185	.072	.135	.035	.480
15	$\Delta\alpha_{23}$	.241	.095	.000	.104	-.072
16	$\Delta\alpha_{13}$	.241	.095	.000	.104	-.072
17	$\Delta\gamma$	-.071	-.045	.236	.993	.358
18	$\Delta\delta_4$	.022	.017	.074	-.232	-.054
19	$\Delta\delta_5$	.022	.017	.074	-.232	-.054
20	$\Delta\phi$	0	0	0	0	0

Table 18 (continued)

k	ν_6	ν_7	ν_8	ν_9	ν_{10}	ν_{11}
1	.055	-.113	-.191	.196	-.024	.178
2	-.094	-.033	-.013	-.046	-.009	.001
3	-.094	-.033	-.013	-.046	-.009	.001
4	.013	.000	-.006	-.081	-.001	.032
5	.022	-.042	-.024	-.002	-.018	.016
6	.022	-.042	-.024	-.002	-.018	.016
7	.019	-.003	-.059	-.260	1.00	-.062
8	-.294	-.046	-.021	-.761	-.090	.212
9	-.294	-.046	-.021	-.761	-.090	.212
10	-.351	-.159	-.019	.463	.106	-.279
11	.211	-.700	.046	-.422	-.284	-.453
12	.211	-.700	.046	-.422	-.284	-.453
13	.022	-.248	.087	.447	.349	.772
14	.504	.626	-.041	-.320	.081	.271
15	-.095	-.026	.011	.579	.021	-.162
16	-.095	-.026	.011	.579	.021	-.162
17	-.240	.157	.757	.126	.382	.111
18	-.102	.534	-.468	.136	-.082	.012
19	-.102	.534	-.468	.136	-.082	.012
20	0	0	0	0	0	0

Table 18 (continued)

k	ν_{12}	ν_{13}	ν_{14}	ν_{15}	ν_{16}	ν_{17}	ν_{18}
1	0	0	0	0	0	0	0
2	.707	.028	.040	.045	.018	.009	.000
3	-.707	-.028	-.040	-.045	-.018	-.009	.000
4	0	0	0	0	0	0	0
5	-.029	.707	.004	-.006	-.001	-.054	.001
6	.029	-.707	-.004	.006	.001	.054	-.001
7	0	0	0	0	0	0	0
8	-.069	-.056	.279	.707	-.165	-.113	-.005
9	.069	.056	-.279	-.707	.165	.113	.005
10	0	0	0	0	0	0	0
11	-.046	-.060	-.001	.387	.707	.273	.001
12	.046	.060	.001	-.387	-.707	-.273	-.001
13	0	0	0	0	0	0	0
14	0	0	0	0	0	0	0
15	.003	-.007	.707	-.505	.130	.058	.000
16	-.003	.007	-.707	.505	-.130	-.058	.000
17	0	0	0	0	0	0	0
18	.003	-.035	.021	.036	-.479	.702	-.019
19	-.003	.035	-.021	-.036	.479	-.702	.019
20	.068	.108	.249	.730	-.531	1.00	1.00

$r_{13} = \Delta\eta$ and $r_{20} = \Delta\phi$. This type of critical coordinate, which is the distance between atoms three bonds removed, is illustrated in Figure 3(b). The equilibrium distance $P = Cl\text{-}H_1$ may be determined from [109] which, in terms of the internal coordinates here, becomes

$$P = \left\{ R^2 + D^2 + d_1^2 - 2D\,[R\cos\eta + d_1\cos\beta_1] + 2Rd_1[\cos(\eta - \beta_1) - 2\sin\eta\sin\beta_1\cos^2 30^0] \right\}^{1/2} \quad [281]$$

Similarly, the six A_k coefficients are found from [110]-[115] with the substitutions: $a = R$, $b = D$, $c = d$, $\alpha = \eta$, $\beta = \beta_1$ and $\phi = 60^0$. Inserting the values of these parameters, the numerical results are:

$$P = 2.950 \times 10^{-8} \text{ cm}$$
$$A_1 = \partial P/\partial D = 0.8709$$
$$A_2 = \partial P/\partial d_1 = 0.3574$$
$$A_7 = \partial P/\partial R = 0.6521$$
$$A_8 = \partial P/\partial \beta_1 = 0.8780$$
$$A_{13} = \partial P/\partial \eta = 1.191$$
$$A_{20} = \partial P/\partial \phi = 0.5047$$

(b) γ_{ki} factors: The quantities γ_{ki} are readily computed from the elements of [F], [L] and [1]. The energy ϵ_i in each mode is found from [95] using [F] and [L] and then γ_{ki} obtained by [98]. The γ_{ki} need not be

calculated for every coordinate but only for $k = 1,2,7,8,13$ and 20 which are those having non-zero A_k as seen above. These factors are listed in Table 19.

(c) The α_i and μ_i : The amplitude factors α_i are obtained as the sum of products designated in [116] and are normalized to give the μ_i factors by [117]. These are listed, along with the frequencies employed, in Table 10 of the preceding section.

Although the normal coordinates represented in Figure 11 are only approximate, it is seen that they may be correlated with the μ_i factors; the largest μ_i belonging to modes in which the Cl-H_1 distance is changing the most.

Table 19

Factors γ_{ki} for the H-Cl distance in CH_3CH_2Cl .

$\gamma_{ki} \times 10^4$

	A_k =	.8709	.3574	.6521	.8780	1.191	.5047
	k / i	1	2	7	8	13	20
$\sqrt{\epsilon_i}$							
516	1	-0.637	13.7	0.093	-4.45	0.622	0
510	2	-0.686	2.80	0.0261	-0.752	-0.197	0
492	3	0.476	0.359	-0.598	-0.389	-1.74	0
202	4	12.6	-0.116	-0.579	-1.15	-10.7	0
286	5	0.808	2.56	-1.28	1.25	-16.8	0
229	6	2.42	-4.12	0.835	-12.8	0.949	0
187	7	-6.05	-1.79	-0.145	-2.43	-13.3	0
168	8	-11.4	-0.756	-3.52	-1.26	5.20	0
326	9	6.01	-1.42	-7.97	-23.4	13.7	0
443	10	-0.541	-0.193	22.6	-2.04	7.87	0
233	11	7.64	0.025	-2.67	9.11	33.2	0
495	12	0	14.3	0	-1.39	0	1.37
473	13	0	0.602	0	-1.18	0	2.29
180	14	0	2.24	0	15.5	0	13.9
264	15	0	-1.70	0	26.8	0	27.7
206	16	0	0.857	0	-8.00	0	-25.7
170	17	0	0.505	0	-6.64	0	58.7
23.5	18	0	0	0	-2.12	0	425

CHAPTER 9

DISCUSSION OF RESULTS AND EVALUATION OF SLATER THEORY

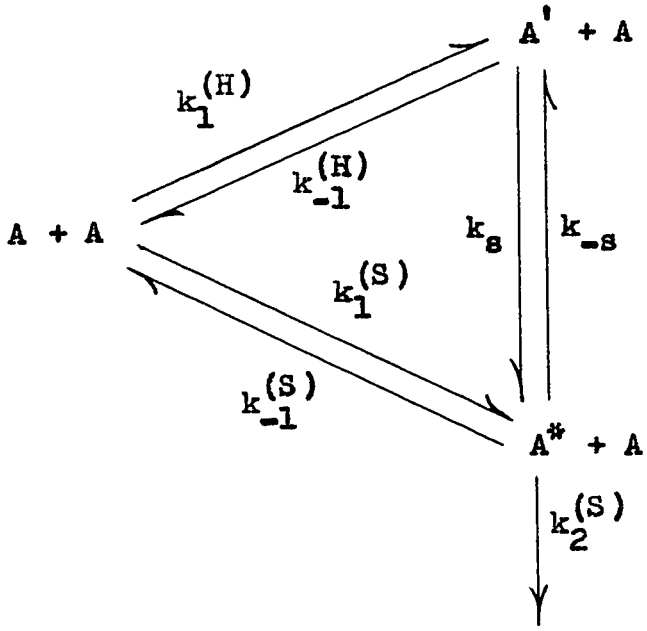
The intention of this chapter is to point out the various merits and inadequacies of the Slater theory that have become apparent from the present and previous work, and, where possible, to indicate the regions of certain necessary modifications.

ENERGY COUPLING BETWEEN MODES

For the decomposition reactions of both N_2O and H_2O_2 (and perhaps ethane) it was found that equation [56] based on the Slater model and employing the most reasonable critical coordinate gave a rate of energization k_1 that was substantially lower than that observed experimentally. In each of these cases, however, equation [46] based on the HKRR model was able to predict the observed value using a plausible value for s. Ozone was a border-line case in which the experimental rate was given equally well by both the HKRR theory with $s = 2$ and by Slater's theory in which all three normal modes contributed to the reaction coordinate. For larger molecules, on the other hand, such

as cyclopropane, nitrogen pentoxide and ethyl chloride (with a suitable choice of critical coordinate) it appears that the Slater theory is adequate to explain the measured rates.

These results may be discussed in terms of the following mechanism, which represents an extension of the original proposal of Lindemann(6):



In this scheme a distinction has been made between two types of energized molecules, represented by A' and A^*. The A^* molecules are those that are energized in the Slater sense; they not only contain ϵ^* or more of energy but have it distributed among the normal modes in such a way that, when the vibrations come suitably into phase, there can be a sufficient extension of the critical coordinate. The A' molecules are those that contain the critical energy ϵ^*, but do not have it suitably distributed for reaction to

occur without flow of energy. Slater's condition is a more stringent one than HKRR's and the rate constant $k_1^{(S)}$ will generally be considerably smaller than $k_1^{(H)}$.

If there can be no flow of energy between the modes the rate constants k_s and k_{-s} are both equal to zero, and reaction can therefore only occur by direct energization to A^*; Slater's treatment then applies. If, on the other hand, k_s is not very small, A^* can be formed not only directly but also from A'. At very low pressures, in fact, most of the A^* may be formed from A', since A' may be formed from $A + A$ much more rapidly than A^*, and at very low pressures practically every A' produced will eventually become an A^*. At intermediate pressures, on the other hand, more of the A^* may be produced directly from $A + A$, and Slater's treatment will then apply. On the basis of this mechanism one would therefore expect three regions of kinetic behaviour:

(a) A high-pressure region where the kinetics will be first order; here both A' and A^* will be essentially at equilibrium, and the rate of reaction is controlled by the rate of breakdown of A^*. Slater's formula for high-pressure rates [33] (suitably modified by an entropy factor) should therefore apply in this region.

(b) An intermediate-pressure region, where there is predominantly a direct energization to form A^*; Slater's low-pressure formula [56] should apply here.

(c) A low-pressure region, where A^* will be formed predominantly from A', and the HKRR formula [46]

will apply. In some cases, when k_s is sufficiently large, the intermediate region will effectively disapeear, and it would seem that this is the case with H_2O_2 and N_2O. The circumstances under which k_s will be large are discussed later.

Application of the steady-state method to the above reaction scheme gives, for the overall rate of reaction,

$$v = \frac{k_2^{(S)}[A]^2\left\{k_1^{(S)}k_{-1}^{(H)}[A]+k_s(k_1^{(S)}+k_1^{(H)})\right\}}{k_{-1}^{(H)}(k_{-1}^{(S)}[A]+k_2^{(S)})[A]+(k_sk_{-1}^{(S)}+k_{-s}k_{-1}^{(H)})[A]+k_sk_2^{(S)}} \quad . \quad [281]$$

In the event that k_s and k_{-s} are small this equation reduces to the form of [2]:

$$v = \frac{k_2^{(S)}\ k_1^{(S)}\ [A]^2}{k_{-1}^{(S)}\ [A] + k_2^{(S)}} \qquad [282]$$

and Slater's treatment therefore applies. At high pressures under all conditions, [281] becomes

$$v = \frac{k_2^{(S)}\ k_1^{(S)}}{k_{-1}^{(S)}}\ [A] \qquad [283]$$

so that Slater's expression for the high-pressure rate will always apply, even if k_s is large. At very low pressures [281] reduces to

$$v = (k_1^{(S)} + k_1^{(H)})\,[A]^2 ,$$

which, since $k_1^{(H)}$ is probably always much greater than $k_1^{(S)}$, becomes

$$v = k_1^{(H)}\,[A]^2 \qquad [284]$$

At very low pressures the rate should therefore be given by the HKRR formula for the rate of energization.

Some of the rate constants appearing in [281] are functions of energy; $k_1^{(H)}$ and $k_1^{(S)}$ are given by [46] and [56], and $k_2^{(S)}$ is given by Slater's treatment. The overall rate must therefore be obtained by a suitable integration of [281]; in view of the algebraic complexity, however, it would seem to be impossible to obtain a solution in a convenient form.

The factors which influence the rate of flow of energy between modes may now be considered. From the foregoing results it appears that this energy flow is more pronounced in N_2O and H_2O than in N_2O_5, C_3H_6 and C_2H_5Cl. These figures suggest that flow can occur more readily in small molecules with fewer normal modes than in the larger systems where there are more degrees of freedom. The reason for this may be seen from both the classical and quantum points of view.

On a classical model, it is known that the

passage of energy between normal modes increases with the anharmonicity of the vibrations and with the total energy content of the modes. If the vibrations are all of sufficiently low energy that the behaviour is strictly harmonic there is no coupling between the oscillators and no flow of energy. The greater the deviation from harmonic behaviour, however, the greater the coupling. Now if a given amount of energy is distributed amongst a small number of normal modes the average amount in each may be sufficiently large that there is a significant amount of coupling. Energy may then flow readily between the modes, and the HKRR formula for energization will apply. If the number of modes is large, however, each vibration will be occurring mainly in the harmonic region; there will then be little coupling, and reaction can only occur if the vibrations come suitably into phase, as visualized by Slater.

In terms of quantum concepts, flow is to be regarded as occurring as a result of Fermi resonance between closely spaced levels corresponding to different modes of vibration. If the molecules are in the lower energy states of each normal mode the probability of a transition to another mode through Fermi resonance may be small, owing to a small probability that levels in different modes, or their overtones, are close to one another. The probability is much greater, however, if higher levels of each normal mode are excited; these levels are more numerous and more closely spaced, and there is a much greater probability of

higher levels resonating with levels in other modes or with their overtones.

For molecules whose reaction rates are most satisfactorily described by the HKRR theory with a value of s which is less than the total number of degrees of freedom, it may be concluded that there are restrictions to flow throughout all the normal modes of the molecule. This may well arise as a result of symmetry; the possibilities of Fermi resonance are, for example, much reduced when the modes correspond to different symmetries. There can be no resonance between the fundamentals of normal modes of different species; however, the possibility of overtones, which may be of different symmetry from their fundamentals, allows resonance to occur provided that the energies are closely matched.

The fact that the Slater theory does not allow for the passage of energy between modes, which is known to occur, has for some time been recognized as a weakness in the theory. However the theory had not previously been tested by calculations of the second-order rate constant k_1 ; and it was not until the present work that the seriousness of this defect, in the case of small molecules, was appreciated. It appears, therefore, that this is one region in which the theory must be modified if it is to have general applicability.

It is of interest to note that Slater has recently contributed to a modification which proposes a slightly more realistic model for the HKRR theory. As that theory assumes an unrestricted flow of energy between the s modes but

considers only one of them to be involved in the reaction coordinate, it would be desirable to allow for the participation of several modes while retaining the notion of energy flow. In a paper by Steel (98), $G_{s,z}$ designates the probability that the energy in an s-oscillator system lies in the range $(\epsilon, d\epsilon)$ when there is at least ϵ^* in z of the oscillators (rather than only one). Then if λ is the specific dissociation probability of molecules containing $\epsilon \geqq \epsilon^*$ localized within the z "critical" oscillators, the expression for k_∞ is

$$k_\infty = \int_{\epsilon^*}^{\infty} \lambda \, G_{s,z}(\epsilon, \epsilon^*) \, d\epsilon \qquad [285]$$

With the help of Slater, [285] was integrated for the case in which λ is considered constant, the result being:

$$k_\infty = \frac{\lambda}{(z-1)!}\left[1 + (z-1)b^{-1} + \ldots + (z-1)!\, b^{1-z}\right]b^{s-1}\exp(-b) \qquad [286]$$

where b has its usual significance of [10].

HIGH-PRESSURE FREQUENCY FACTOR

Experimental first-order rates k_∞ of dissociation or isomerization are usually represented by the Arrhenius form

$$k_\infty = A \exp(-b) \qquad [287]$$

Slater has shown (99) that if a molecule has quantized energy and can dissociate if it has more than a critical energy, then the only molecular model giving the Arrhenius form of first-order reaction rate is that of a system of degenerate harmonic oscillators, similar to the model of HKRR. The HKRR expression for k_∞ has been seen in [15]. If the molecular energies are effectively classical and continuous, the Arrhenius form determines the specific rate, for molecules of given total energies, as a simple function of the classical weights of the states; and specific rates of this form arise naturally in several reaction rate theories. In the Slater theory $A = c\nu$, where ν is an average frequency always lying between the greatest and the least of the normal frequencies of the molecule (16) and c is the number of equivalent critical coordinates in the molecule. Since c is generally unity or a small integer, the Slater high-pressure frequency factor A is always of the order of 10^{13} sec^{-1}.

Although a value of 10^{13} sec^{-1} is considered a normal frequency factor, unusually large values of A, between 10^{14} and 10^{17} sec^{-1}, have been observed in the thermal decompositions of metal alkyls (100), carbonyl compounds (101) and azo compounds (102)(103). Following a suggestion by Peard, Stubbs and Hinshelwood (104), Pritchard (100)(101) has interpreted the high frequency factors in terms of the simultaneous rupture of more than one bond.

The compounds, represented by R_2X, may decompose

either by

$$(a)\quad R\,X\,R \longrightarrow R\,X + R$$
$$R\,X \longrightarrow R + X$$

or

$$(b)\quad R\,X\,R \longrightarrow R + X + R$$

In many cases the two schemes are of comparable activation energies. Consequently, if one may speak of vibrational modes which are symmetric or antisymmetric with respect to X , the former will contribute to process (b) while the latter will promote (a). In the torsional mode, the larger the R groups the greater their interaction and contribution to the symmetric type of reaction (b). Since it is found that A is normal when R is a small group, but increases with the size of R , Pritchard proposes that reaction occurs by (a) in the first instance, but in addition (b) becomes increasingly frequent with the increasing complexity of R . This is explained theoretically in terms of the Hinshelwood expression [12] for k_∞ in which ϕ (s,b) increases with s and the latter is assumed to be greater for the larger molecules.

It is the point of Steel's paper (98) that the pre-exponential factor of [12] is similarly increased by the use of his model in which z = 2 or 3 .

Another way of considering the high frequency factors is from the point of view of the entropy contribution to A . Since it is really a <u>free</u> energy barrier over which the reactant molecules must pass, the expression [287] is

more correctly written

$$k_{\infty} = B \exp (\Delta S^*/R) \exp (-\Delta H^*/RT) \qquad [288]$$

where ΔS^* and ΔH^* are the entropy and heat of activation respectively. Since ΔS^* varies only slightly with temperature, the experimental activation energy obtained from the usual plot of $\ln k$ against $1/T$ is ΔH^* where now

$$A = B \exp (\Delta S^*/R) \qquad [289]$$

Although ΔS^* is apparently small for the reactions with normal frequency factors, it may assume significant proportions for reactions in which the activated complex has a very distorted of "loose" structure, possibly due to internal rotations. This may be the case, for example, in ethyl chloride where the frequency factor is $10^{14.6}$ (86). An interesting discussion of these possibilities has been given by Hinshelwood (105).

The models of both the HKRR and Slater theories, by assuming purely harmonic oscillations up to the point of reaction, artificially constrain the system in configuration but not in energy. Evans and Rushbrooke (106) show that with the HKRR theory this actually leads to a negative entropy of activation. To correct the theory it is suggested that the $k^{\ddagger}$ of [14] and [15] be replaced by $k^{\ddagger} \exp(\Delta S^*/R)$ so that this entropy term now appears explicitly in the

frequency factor.

Returning to the Slater theory, it is recognized that a second deficiency in the theory (though less serious than the first) is that the purely harmonic model does not allow for the appreciable entropies of activation that exist in certain reactions. Of course there are cases of unusually low frequency factors as well, such as in the decomposition of nitrous oxide (chapter 3), and here the Slater theory is equally inadequate in its prediction of k_∞.

CHOICE OF CRITICAL COORDINATE

It has been pointed out on several occasions in the preceding chapters that there remains a fair degree of empiricism in the choice of the Slater critical coordinate p. Although there may be only a limited number of possibilities for this choice, it has become evident that <u>any</u> simple linear reaction coordinate is probably an over-simplification of the truth. Whereas the restriction on energy flow was seen to be an approximation most serious for small molecules, this assumption of a linear p is probably most serious for large molecules in which the displacements of the many constituent atoms will all have some effect on the potential field and reaction "coordinate". The shape of the Slater curve remains unchanged for a given value of n, and altering the molecular parameters merely shifts it laterally along the pressure axis. However, various critical coordinates alter the number of contributing modes n and consequently the shape of the curve as well. It might be expected that the

objection here would be stronger for very unsymmetrical molecules (such as ethyl chloride) than for more symmetrical ones (such as cyclopropane); for despite the earlier remark about symmetry considerations being an unsafe guide to the choice of n, a linear reaction coordinate might be slightly more realistic where the form of vibrations is governed by the presence of many symmetry elements. In the worst cases, however, the theory approaches the arbitrariness of the HKRR theory in the matter of deciding upon the number of effective degrees of freedom.

MERITS OF SLATER THEORY

Although the Slater theory fails to be completely general, in many respects it is the most satisfactory theory of unimolecular reactions to appear so far. There are undoubtedly many cases for which the deficiencies mentioned above are not serious and it is felt that the basic physical model is a highly realistic one for all but very small molecules, in spite of itsapproximations. The model has the advantage of being easily visualized, of containing only one experimentally determined parameter, E_o, and of being concrete where the earlier HKRR theory was vague and indefinite.

C O N C L U D I N G R E M A R K S

Although the HKRR theory, the Slater theory, and others are known to contain certain approximations, they are nevertheless very useful in yielding knowledge of reaction mechanisms. If the unmodified theory cannot be made to fit the experimental data one may draw the conclusion that the implicit assumptions of the theory are too drastic for the case at hand; if agreement is obtained with, say, the HKRR but not the Slater model it may be assumed that the former approximates the truth more closely than the latter. With the accumulation of experimental data and more test cases, the areas in which the various theories are most applicable should become apparent. With this knowledge it may eventually be possible to formulate a general theory which satisfactorily accounts for all observed rates and which will form the basis of a much deeper understanding of kinetic phenomena.

With regard to future calculations based on the Slater theory, it is suggested that considerable aid may be derived and perhaps labour avoided by referring to the field of electron diffraction studies. These studies give, not only accurate information regarding interatomic distances but also data on the amplitude of vibration of the various

atoms (107). Since these experiments yield the mean amplitudes $\left\langle \bar{l}_{ij}^{2} \right\rangle^{1/2}$ of vibration between any pair of atoms i and j this knowledge might be used either directly in the Slater theory or as an approximate check on independent calculations. For this purpose it would seem advisable to adopt a type of potential field first proposed by Urey and Bradley (108)(109) in which the coordinates used are the distances between atoms, both bonded and non-bonded. These mean amplitudes $\left\langle \bar{l}_{ij}^{2} \right\rangle^{1/2}$ may be calculated theoretically as well. Although the exact treatment is laborious (110), Morino, Kuchitsu, Takahashi and Maeda (111) have worked out an approximate method for their calculation in which the enumeration of the [L] matrix, the most time-consuming procedure, is replaced by the calculation of $[F]^{-1}$. The formulae obtained are applicable with about 4% accuracy to almost all cases except atom pairs having frequencies above 1200 cm^{-1} and for these certain modified formulae are presented. Ainsworth and Karle (112) have compared theoretical with experimental values of $\left\langle \bar{l}_{ij}^{2} \right\rangle^{1/2}$ for the case of 1,2-dichloroethane.

C L A I M S T O O R I G I N A L R E S E A R C H

1. Derivation of a standard method for obtaining the Slater parameters, based upon the Wilson FG matrix method of normal coordinate analysis.

2. Comparison of the Slater and previous theories of unimolecular reactions with the experimental data for the thermal decompositions of N_2O , O_3 , H_2O_2 , C_2H_5Cl , N_2O_5 and C_2H_6 .

3. Discovery of evidence suggesting that the reaction of small molecules involves a considerable flow of energy between normal modes as opposed to the reaction of larger systems which depends upon independent contributions to the molecular deformation from each mode separately.

4. Critical evaluation of the Slater theory of unimolecular reactions.

5. Derivation of a systematic method for the standard problem of adjusting force constants to produce a desired set of frequencies of molecular vibration. The method is particularly adapted to calculations

carried out by high-speed electronic computers.

6. Calculation of approximate values for the eighteen normal coordinates of ethyl chloride.

REFERENCES

1 E. K. Gill and K. J. Laidler, Can. J. Chem. 36, 1570 (1958).

2 E. K. Gill and K. J. Laidler, Trans. Faraday Soc. 55, 753 (1959).

3 E. K. Gill and K. J. Laidler, Proc. Roy. Soc. A251, 66 (1959).

4 E. K. Gill and K. J. Laidler, Proc. Roy. Soc. A250, 123 (1959).

5 J. Perrin, Ann. phys. (9), 11, 1 (1919).

6 F. A. Lindemann, Trans. Faraday Soc. 17, 598 (1922).

7 C. N. Hinshelwood, The Kinetics of Chemical Change, Oxford, 1940.

8 L. S. Kassel, J. Phys. Chem. 32, 225 (1928).

9 L. S. Kassel, Kinetics of Homogeneous Gas Reactions, Reinhold, New York, 1932.

10 O. K. Rice and H. C. Ramsperger, J. Am. Chem. Soc. 49, 1617 (1927); 50, 617 (1928).

11 N. B. Slater, Proc. Camb. Phil. Soc. 35, 36 (1939).

12 N. B. Slater, Proc. Roy. Soc. A194, 112 (1948).

13 N. B. Slater, Phil. Trans. A246, 57 (1953).

14 N. B. Slater, Proc. Roy. Soc. A218, 224 (1953).

15 M. Kac, Amer. J. Math. 65, 609 (1943).

16 N. B. Slater, Proc. Roy. Soc. Edinburgh A64, 161 (1955).

17 N. B. Slater, Proc. Leeds Phil. Soc. 6, 268 (1955).

18 D. J. Wilson and H. S. Johnston, J. Am. Chem. Soc. 75, 5763 (1953).

19 M. Volpe and H. S. Johnston, J. Am. Chem. Soc. 78, 3903 (1956).

20 B. H. Mahan, J. Phys. Chem. 62, 100 (1958).

21 W. Forst, Can. J. Chem. 36, 1308 (1958).

22 R. N. Schwartz and K. F. Herzfeld, J. Chem. Phys. 22, 767 (1954).

23 O. K. Rice, J. Chem. Phys. 4, 242 (1936).

24 N. B. Slater, Proc. Leeds Phil. Soc. 6, 259 (1955).

25 S. W. Benson, J. Chem. Phys. 20, 1064 (1952).

26 H. Eyring, J. Chem. Phys. 3, 107 (1935).

27 S. Glasstone, K. J. Laidler and H. Eyring, The Theory of Rate Processes, McGraw-Hill, New York, 1941.

28 J. C. Giddings and H. Eyring, J. Chem. Phys. 22, 538 (1954).

29 R. A. Marcus, J. Chem. Phys. 20, 359 (1952).

30 R. A. Marcus, J. Chem. Phys. 20, 364 (1952).

31 E. W. Montroll and K. E. Shuler, Advances in Chem. Phys. 1, 361 (1958).

32 E. E. Nikitin, Doklady Akad. Nauk. S.S.S.R. 119, 526 (1958).

33 E. B. Wilson, J. Chem. Phys. 7, 1047 (1939).

34 E. B. Wilson, J. Chem. Phys, 9, 76 (1941).

35 G. Herzberg, Infrared and Raman Spectra, Van Nostrand, New York, 1945.

36 E. B. Wilson, J. C. Decius and P. C. Cross, Molecular Vibrations, McGraw-Hill, New York, 1955.

37 A. G. Meister, F. F. Cleveland and M. J. Murray, Amer. J. Phys. 11, 239 (1943).

38 J. R. Nielsen and L. H. Berryman, J. Chem. Phys. 17, 659 (1949).

39 A. G. Meister and F. F. Cleveland, Amer. J. Phys. 14, 13 (1946).

40 S. R. Polo, J. Chem. Phys. 24, 1133 (1956).

41 S. Brodersen, Mat. Fys. Skr. Dan. Vid. Selsk. 1, no. 4 (1957).

42 J. C. Decius, J. Chem. Phys. 17, 1315 (1949).

43 R. J. Malhiot and S. M. Ferigle, J. Chem. Phys. 23, 30 (1955).

44 S. M. Ferigle and A. G. Meister, J. Chem. Phys. 19, 982 (1951).

45 H. S. Johnston, J. Chem. Phys. 19, 663 (1951).

46 A. F. Trotman-Dickenson, Gas Kinetics, Butterworth Scientific Publications, London, 1955, p. 72.

47 A. E. Stearn and H. Eyring, J. Chem. Phys. 3 778 (1935).

48 E. F. Barker, Phys. Rev. 41, 369 (1932).

49 J. E. Rosenthal, J. Chem. Phys. 5, 465 (1937).

50 S. W. Benson and A. E. Axworthy, J. Chem. Phys. 26, 1718 (1957).

51 M. K. Wilson and R. M. Badger, J. Chem. Phys. 16, 741 (1948).

52 W. G. Penney and G.B.B.M. Sutherland, Proc. Roy. Soc.

A156, 654 (1936).

53 G.B.B.M. Sutherland and W. G. Penney, Proc. Roy. Soc. A156, 678 (1936).

54 R. Trambarulo, S. N. Ghosh, C. A. Burrus and W. Gordy, J. Chem. Phys. 21, 851 (1953).

55 P. N. Wolfe and D. Williams, Phys. Rev. 93, 360 (1954).

56 R. H. Hughes, J. Chem. Phys. 24, 131 (1956).

57 W. Shand and R. A. Spurr, J. Am. Chem. Soc. 65, 179 (1943).

58 D. Kivelson and E. B. Wilson, J. Chem. Phys. 20, 1575 (1952); 21, 1229 (1953).

59 L. Pierce, J. Chem. Phys. 24, 139 (1956).

60 P. A. Giguere,and I. D. Liu, Can. J. Chem. 35, 283 (1957).

61 D. E. Hoare, J. B. Protheroe and A. D. Walsh, Nature 182, 654 (1958).

62 P. A. Giguere and O. Bain, J. Phys. Chem. 56, 340 (1952).

63 S. Chapman, Phil. Trans. A216, 347 (1916).

64 J. B. Howard and E. B. Wilson, J. Chem. Phys. 2,620 (1934).

65 N. B. Slater, Proc. Roy. Soc. A218, 224 (1953).

66 H. O. Pritchard, R. G. Sowden and A. F. Trotman - Dickenson, Proc. Roy. Soc. A217, 563 (1953).

67 T. S. Chambers and G. B. Kistiakowsky, J. Am. Chem. Soc. 56, 399 (1934).

68 B. D. Saksena, Proc. Indian Acad. Sci. 10, 449 (1939).

69 R. L. Mills and H. S. Johnston, J. Am. Chem. Soc. 73, 938 (1951).

70 H. S. Johnston and R. L. Perrine, J. Am. Chem. Soc. 73, 4782 (1951).

71 R. E. Dodd and E. W. R. Steacie, Proc. Roy. Soc. A233, 283 (1954).

72 E. W. R. Steacie, J. Chem. Soc., 3986 (1956).

73 D. E. Hoare and A. D. Walsh, Trans. Faraday Soc. 53, 1102, (1957).

74 E. Thiele and D. J. Wilson, Can. J. Chem. 37, 1035 (1959).

75 E. Bodewig, Matrix Calculus, North-Holland Publishing Co., Amsterdam, 1956.

76 J. H. Wilkinson, Proc. Camb. Phil. Soc. 50, 536 (1954).

77 E. E. Osborne, J. Soc. Indust. Appl. Math. 6, 279 (1958).

78 D. E. Mann, L. Fano, W. F. Cahill and T. Shimanouchi, J. Chem. Phys. 22, 764 (1954).

79 D. E. Mann, T. Shimanouchi, J. H. Meal and L. Fano, J. Chem. Phys. 27, 43 (1957).

80 D. E. Mann, L. Fano, J. H. Meal and T. Shimanouchi, J. Chem. Phys. 27, 51 (1957).

81 T. Miyazawa, J. Chem. Phys. 29, 246 (1958).

82 J. L. Howland, Determinantal Equations, a paper read at the Mathematical Colloquium, McGill University, March 18, 1959.

83 J. L. Howland, private communication.

84 T. Miyazawa, J. Chem. Soc. Japan 76, 1132 (1955).

85 D. H. R. Barton and K. E. Howlett, J. Chem. Soc., 165 (1949).

86 K. E. Howlett, J. Chem. Soc., 3695 (1952).

87 G. Allen and H. J. Bernstein, Can. J. Chem. 32, 1124 (1954).

88 L. W. Daasch, C. Y. Liang, and J. R. Nielsen, Third Progress Report to the U.S.A.E.C., submitted June 15, 1953.

89 L. W. Daasch, C. Y. Liang and J. R. Nielsen, J. Chem. Phys. 22, 1293 (1954).

90 R. S. Wagner and B. P. Dailey, J. Chem. Phys. 26, 1588 (1957).

91 J. Y. Beach and D. P. Stevenson, J. Am. Chem. Soc. 61, 2643 (1939).

92 R. S. Wagner and B. P. Dailey, J. Chem. Phys. 22, 1459 (1954).

93 R. N. Dixon, Spectrochimica Acta 9, 59 (1957).

94 P. W. Allen and L. E. Sutton, Acta Cryst. 3, 46 (1950).

95 M. Z. El-Sabban, A. G. Meister and F. F. Cleveland, J. Chem. Phys. 19, 855 (1951).

96 D. R. Lide, J. Chem. Phys. 30, 37 (1959).

97 G. E. Hansen and D. M. Dennison, J. Chem. Phys. 20, 313 (1952).

98 C. Steel, private communication (to be published).

99 N. B. Slater, Trans. Faraday Soc. 55, 5 (1959).

100 H. O. Pritchard, J. Chem. Phys. 25, 267 (1956).

101 D. Clark and H. O. Pritchard, J. Chem. Soc., 2136 (1956).

102 C. Steel and A. F. Trotman-Dickenson, J. Chem. Soc., 975 (1959).

103 H. C. Ramsperger, J. Am. Chem. Soc. 51, 2134 (1929).

104 M. G. Peard, F. J. Stubbs and C. N. Hinshelwood, Proc. Roy. Soc. A214, 471 (1952).

105 C. N. Hinshelwood, Nature 180, 1233 (1957).

106 M. G. Evans and G. S. Rushbrooke, Trans Faraday Soc. 41, 621 (1945).

107 I. L. Karle and J. Karle, J. Chem. Phys. 17 1052 (1949).

108 H. C. Urey and C. A. Bradley, Phys. Rev. 38, 1969 (1930).

109 T. Shimanouchi, J. Chem. Phys. 17, 245, 734, 848 (1949).

110 Y. Morino, K. Kuchitsu and T. Shimanouchi, J. Chem. Phys. 20, 726 (1952).

111 Y. Morino, K. Kuchitsu, A. Takahashi and K. Maeda, J. Chem. Phys. 21, 1927 (1953).

112 J. Ainsworth and J. Karle, J. Chem. Phys. 20, 425 (1952).