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Theoretical calculations of kinetic isotope effects

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Treating the activated complex for unimolecular dissociation as uncoupled fragments simplifies the calculation of transition-state frequencies in the quasi-equilibrium-theory formulation of an isotopic rate-constant ratio. The general method is applied to the specific case of the intramolecular kinetic isotope effect in decarboxylation of malonic acid. The fragment models are further simplified by means of the "cut-off" approximation of Sterm and Wolfsberg. These model calculations are in agreement with the presently available experimental results. Applicability to reactions involving simultaneous multiple bond rupture or formation is noted.

THEORETICAL CALCULATIONS OF
KINETIC ISOTOPE EFFECTS

by

Paul Chien-Wei Chang

THESIS

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This thesis is dedicated to my parents

Wen-Yin Chang

and

Hoo-Lin Chang

CONTENTS

Chapter I - Introduction

Chapter I - Introduction

I. General Discussion

The explosively expanding system of human knowledge
of "Nature", if time is a partition factor, is composed of
two subsystems; "time-variant" and "time-invariant". In
the "time-variant" system there lies the major domain of
"Chemical Kinetics".

In nearly all areas of scientific research, whenever
a given system is brought under investigation, analysis
normally involves the isolation and definition of what-
ever elements or subsystems appear to contribute in some
essential way to the whole system. There is, in other
words, a tendency toward fundamentality. An extension
of this tendency might appear to suggest that only when
some basic building block of matter is defined will there
be a truly adequate understanding of natural phenomena.
The fact is that if such a substance exists, it has thus
far eluded the best effort at detection or definition.
Moreover, it is only because of the measurable interaction
of organized matter that we attempt to define the proper-
ties of matter at all.

Thus while we strive to explain the objects of our
research in the most fundamental terms possible, it may
well be that even at the prime level of fundamentality,
we may still be forced to deal with matter in terms of the
relationships among organized and particulate entities.

Indeed, attempts to explain the properties of matter at
this level tend, if anything, away from fundamentality.
Investigation of interparticle relationships, histori-
cally, has contributed more to a general understanding of
matter than has preoccupation with the intrinsic proper-
ties of the particles themselves.

Among those attempts to probe the behavior of parti-
culate matter is the investigation of the mechanism of
chemical reaction. A better understanding of the reaction
mechanism is one of the immediate goals which may lead to
the understanding of the general principles of reactivity.
Through a study of the rate of production of a certain
substance as a function of the concentrations of reactants,
it is frequently possible to find out how many entities of
each kind have to come together. And information about
the energy threshhold which must be surmounted before any
cluster of reactants may pass into the product, is general-
ly provided by the temperature coefficient of the reaction
rate.

It has been concluded that, even with sufficient
energy, not every molecule can pass through the energy
barrier. Hence the conformation theory of the transition
state enters here. In order to obtain a clear view of the
structures of the molecules during the course of reaction,
we demand a set of definitely defined functions of each
individual particle involved. Unfortunately, because of
the lack of exactness of the functions stated by Heisenberg's

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uncertainty principle[1] and the incompleteness of our know-
ledge, we would be, in general, satisfied if we had an
approximate idea of the structure and conformation of the
transition state.

Theoretical predictions thus play a vital role in the
game. In order to set up such a system which would produce
accurate enough results for a significant comparison with
the experimental date, the physical parameters have to be
known with a great accuracy. Because of the cancellation
effects of the errors during the computing process, the
ratio of kinetic rates is a much better method to examine
the validity of the theoretical model than others. By
varying the internal or external conditions of certain
reactions to study the influence on the relative kinetic
rate ratio, isotopic substitution has been suggested as
an easier method to test the assumptions made for a great
number of reactions. The superiority of the isotope method
lies mainly in the possibility of making the substitution
within the very reacting center and with a minimum of
change in parameters.

2. Brief History of the Study of Isotope Effects

In the year 1919 Lindemann initiated the study of isotope effects with a calculation of the difference in vapor pressures of lead isotopes.[2] The real interest of the investigators was not attracted until 1933 when Urey and Rittenberg published the result of their calculations of the equilibrium constants for the reactions[3]

$$H_2 + 2DCl = D_2 + HCl$$

$$H_2 + 2DI = D_2 + 2HI.$$

Thereafter, the investigations of equilibrium isotope exchange reactions was extended to many systems, mostly involving isotopes of hydrogen, carbon, oxygen and nitrogen.

In 1947, H. C. Urey published "The Thermodynamic Properties of Isotopic Substances",[4] which contains vibrational data and partition function ratios for many of the simpler isotopic molecules, and Bigeleisen and Mayer[5] obtained general expression for a ratio of partition functions for isotope fractionation in equilibrium exchange reactions. During the following two years Beeck[6] discovered a large carbon isotope fractionation in the dissociation of propane upon electron impact, and Bigeleisen[7] combined the absolute rate theory with his previous work.

In later years Polanyi[8], Weston[9], and Shavitt[10] proceeded by arriving at the best potential-energy surfaces for the reactions, and making absolute calculations of the rates of the reactions that are to be compared. Although

the results of their investigations have thrown light on the question of obtaining the best methods for arriving at potential-energy surfaces, the actual computation of potential energy surface is impossibly complex for all but the simplest systems.

3.   Statement and General Purpose of the Investigation

Recent theoretical work has centered upon a search
for approximated computable models that, if the calculated
isotope effects are in agreement with experimental data,
may provide some valuable information about reaction
mechanisms. Different theoretical models have been inves-
tigated, but the results are somewhat disappointing. In
addition to the extreme compexity involved in actual com-
putation, the crudest models have often given predictions
at least as good as those of more refined calculations.
It is hoped that in developing a certain general method
for calculating the kinetic isotope effects, the actual
computation may be simplified and the accuracy may be
improved.

In order to examine the validity of the investigated
method, the decarboxylation of malonic acid is chosen to
be a trial, since this particular reaction has already
been thoroughly investigated. The calculated kinetic
isotope effects will be compared with the presently avail-
able experimental data[12] of this reaction in the vapor
phase.

Chapter II - Reaction Rate Theory

Chapter II - Reaction Rate Theory

I. Arrhenius Equation

Qualitative observations of the rate of chemical reactions were recorded by early writers, but the first significant kinetic measurements may be said to have been those of Wilhelmy[13], who in 1850 measured the rate of inversion of sucrose and investigated the influence of concentration upon the rate. He came to the conclusion:

$$C = C_o \exp(-kT) \tag{II-1}$$

where C_o = initial concentration of sugar

C = concentration of sugar at time t

k = rate constant.

Later workers have obtained the same result. The important paper of Guldberg and Waage[14] pointed out that the laws of chemical equilibrium can be derived from the kinetic laws by assuming that at equilibrium the rates of forward and reverse reactions are the same.

In 1889 the Arrhenius law[15] was formulated.

$$k = A \exp (E_a/RT) \tag{II-2}$$

where k is the kinetic rate constant, E_a is the molar activation energy of the reaction, R(cal/mole deg.) is the gas constant, T is the absolute temperature, and A is called the pre-exponential factor or frequency factor. According to Arrhenius, Eq. (II-2) indicated that molecules must acquire a certain critical energy, E_a, before they can react, the Boltzmann factor, $\exp (E_a/RT)$, being

the fraction of molecules that possess the necessary energy. From the standpoint of the Arrhenius law, a complete understanding of the factors determining the rate constant of a reaction involves an understanding of the activation energy and the pre-exponential factor. Although the quantum-mechanical theories of molecular structures have been formulated in detail, the evaluation of activation energy still remains as an unsolved problem. The problem of calculating frequency factors on the basis of fundamental principles has been attacked in two ways, namely, the kinetic theory of collisions and the statistical mechanics approach. The latter approach will be introduced in this Chapter.

2. Potential Energy Surface

The activation energies of chemical reactions are most conveniently considered using the method of potential-energy surfaces. The electronic potential energy for a system of n atoms undergoing "adiabatic" reaction can be considered by means of the Born-Oppenheimer[16] approximation as a continuous and single-valued function of the nuclear motion. In general, the interaction between two (n + 1)-dimensional systems is an n-dimensional vector space. The behavior of nuclei thus can be described by motion on the surface.

The three-dimensional diagram in Fig. II-1 is employed to introduce this concept briefly. The potential-energy surface for the reaction would possess low valleys corresponding to the energy states of reactant and product, and the valleys would be separated by regions of higher potential energy. The family of parabolas in the X-Z plane represents all the possible reactant paths. The minimum of the trajectory of the maximum of all the reaction paths is defined as an activation point. The reacting system at this point is defined as "activated complex" or transition state.

It is easily seen from Fig. II-1 that if a system at an activation point moves along the direction of the reaction path (X-axis), the value of its image in the range of the function, potential energy, decreases. And any change

Fig. II-1

of value along the direction of the Y-axis would increase
the potential energy. This specific member of the family
is in general the reaction path, and the direction of
steepest descent is defined as the reaction coordinate.

 This type of potential-energy surface would provide
detailed information about the reacting system in the
transition-state. But, in transforming the real physical
system to the mathematical system, the actual computation
is extremely complex for even the simplest systems.
Hence the transition-state approach of the absolute rate
theory has become a general method for calculating reac-
tion rates from simple structural parameters by means of
the principles of statistical mechanics.

3. Quasi-Equilibrium Theory

During the course of chemical reactions it is important to distinguish clearly between two aspects of the problem: one is concerned with the direction and extent of chemical change, the other with the rate with which it takes place. These two systems, "time-invariant" and "time-variant", have no simple connections. A chemical reaction between two substances may occur almost to completion, but the time for even a very small fraction of the molecules to react may be extremely long. Although the theory of equilibria and the theory of kinetic rates are non-parametric, there is a close relationship between the two. This is so because the molecules undergoing reaction and passing through activated states which can be regarded as in equilibrium with the molecules in their normal states. The concentration of activated molecules can therefore be calculated by ordinary equilibrium theory, so that if the probability of the decomposition of activated molecules is known, the rate of reaction can be calculated. In general, this is called quasi-equilibrium theory.

The problem of calculating rates therefore resolves itself into two parts: the calculation of the concentrations of activated molecules and the calculation of the rates of reaction of the activated molecules.

Consider a reaction

$$A + B = X \; \rightleftharpoons C + D$$

which has proceeded to equilibrium. Then, according to
our assumption, the activated complex X will also be in
equilibrium with the reactants and products, and their
concentration may be calculated accurately by the methods
of statistical mechanics in terms of the concentrations
of A and B.

The theory involves the hypothesis, however, that
even when the reactants and products are not at equili-
brium with each other, the activated complexes are at
equilibrium with the reactants. When we state that the
activated complexes are in equilibrium with the reactants,
we refer only to those complexes that in the immediate
past were reactant molecules.

It is to be emphasized that there is no assumption
that there is a classical type of equilibrium between
initial and activated states; addition to the system of
activated complexes moving from the initial to the final
state would not disturb the equilibrium, as would be
required if the equilibrium were classical.

The quasi-equilibrium theory is supported by the
derivations made by Bishop and Laidler[18]. They concluded
that reactions are satisfactorily interpreted on the basis
of the quasi-equilibrium assumption, provided that E_a/RT
for the reaction has a value of 5 or larger. If the
value of E_a/RT is smaller than 5, the reaction will occur

so rapidly that there can no longer be equilibrium even among the reactant molecules; the more energetic species will be removed more rapidly than the supply of them can be replenished, and there will not be a Boltzmann distribution of reactant molecules.

4. Statistical Treatment

The single molecule partition function Q is defined
as

$$Q = \Sigma \ q_i \exp[-E_i/KT] \qquad (II-3)$$

where K is the Boltzmann constant, E_i is the total energy
of a molecule in the ith energy level and q_i is a statis-
tical weight equal to the number of different molecular
states that have the same energy E_i. The individual pro-
ducts $q_i \exp[-E_i/KT]$ represent the relative probability of
finding a molecule in the ith energy level, with energy
E_i, and so

$$P(E_i) = q_i \exp[-E_i/KT] \qquad (II-4)$$

represents a discrete energy distribution function for
molecules restricted to quantized energy states.

To a good approximation, the total energy of a mole-
cule can be separated into independent terms,

$$E_t = E_e + E_v + E_{rot} + E_{tr} \qquad (II-5)$$

where E_t is the total energy of a molecule, E_e is the
electronic energy, E_v is the vibrational energy arising
from the internal motions of the nuclei, E_{rot} is the rota-
tional energy of the molecule as a whole, and E_{tr} is the
translational energy.

According to the Boltzmann formulation for the distri-
bution function of a set of molecules among various energy
states we have

$$P(E) \propto \exp[-E/KT] \qquad (II-6)$$

Since E is separable,

$$P(E) \propto \exp[(-E_e-E_v-E_{rot}-E_{tr})/KT] \qquad (II-7)$$

and for the partition function we can write

$$Q = [\Sigma q_e \exp(-E_e/KT)][\Sigma q_v \exp(-E_v/KT)]$$
$$\times [\Sigma q_{rot} \exp(-E_{rot}/KT)][\Sigma q_{tr} \exp(-E_{tr}/KT)]$$
$$\qquad (II-8)$$
$$= Q_e Q_v Q_{rot} Q_{tr} \qquad (II-9)$$

since the individual sums are independent. Thus for energies which are separable in this manner we can say that the partition function Q will be a product of individual partition functions for the different kinds of energy.

A. Electronic Partition Function

The partition function for electronic energy is calculated directly from the observed electronic levels of the atom or molecule, using the relationship

$$Q_e = \Sigma q_e \exp[-E_e/KT] \qquad (II-10)$$

At ordinary temperatures the excited electronic levels of an atom or molecule are usually too high to make a significant contribution to the partition function. If the lowest state is a singlet state, the statistical weight q_e is unity, so that if the lowest state is taken as the zero level and all other levels are sufficiently high, the partition function is approximately unity. In general, it may be assumed that excited electronic levels may be

neglected if their energy is more than 4KT.

B. Translational Partition Function

The partition function per unit volume (1 cc) for the translational motion of a molecule of mass m having three degrees of translational freedom can be shown[19] to be

$$Q_{tr} = \frac{(2\pi mKT)^{3/2}}{h^3} \qquad (II-11)$$

where h is Planck's constant.

C. Vibrational Partition Function

The vibrational partition function for a diatomic molecule that has only a single internal vibration is approximated by the expression

$$E_V = (n + 1/2)\ h\nu_0 \qquad (II-12)$$

where n is an integer and $n \geq 0$. The vibrational partition function can be approximated as

$$Q_V = \exp[-E_0/KT] \qquad (II-13)$$

when $h\nu_0 >> KT$, and where

$$E_0 = (1/2)h\nu_0 \qquad (II-14)$$

represents the lowest vibrational energy possible for the molecule and is referred to as the zero-point energy, because it represents the residual energy of the molecule at 0° K.

For more complex molecules, assuming harmonic vibrations, the vibrational energy is

$$E_v = \sum_{i=1}^{J} \sum_{n=0}^{\infty} (n + 1/2)h\nu_i \qquad (II-15)$$

where ν_i is the fundamental frequency of the ith vibrational degree of freedom and there are J vibrational degrees of freedom. For the ith degree of freedom

$$\sum_{n=0}^{\infty} \exp[-(n + 1/2)h\nu_i/KT]$$

$$= \exp[-h\nu_i/2KT] \sum_{n=0}^{\infty} \exp[-nh\nu_i/KT]$$

$$= \exp[-h\nu_i/2KT][1-\exp(-h\nu_i/KT)]^{-1} \qquad (II-16)$$

so that the vibrational partition function for a polyatomic molecule, to the harmonic oscillator approximation, is

$$Q_v = \prod_{i=1}^{J} [\exp(-h\nu_i/2KT)][1-\exp(-h\nu_i/KT)]^{-1} \qquad (II-17)$$

This can be written as

$$Q_v = \exp(-E_0/KT) \prod_{i=1}^{J} [1-\exp(-h\nu_i/KT)]^{-1} \qquad (II-18)$$

However since the zero-point energy is not independent of isotopic substitution, it is convenient for our purpose to write the vibrational partition in the form

$$Q_v = \prod_{i=1}^{J} [\exp(h\nu_i/2KT) - \exp(-h\nu_i/2KT)]^{-1}$$

$$= \prod_{i=1}^{J} [2\sinh(h\nu_i/2KT)]^{-1} \qquad (II-19)$$

D. Rotational Partition Function

The allowed rotational states, for a diatomic mole-
cule, will depend on whether or not the two nuclei are
identical. At temperatures at which the energy differ-
ence of adjacent rotational states is small compared to
KT we can write an approximate molecular partition
function

$$Q_{rot} = (\frac{8\pi^2 IKT}{\sigma h^2})$$

where I is the moment of inertia perpendicular to the
axis,

$$I = (\frac{m_1 m_2}{m_1 + m_2})r^2 = \mu r^2$$

and σ, the symmetry number, equals 2 if the nuclei are
identical and is otherwise equal to 1.

For polyatomic molecules, for comparatively high
temperature, the rotational partition function is

$$Q_{rot} = \frac{8\pi^2 (8\pi^3 ABC)^{1/2} (KT)^{3/2}}{\sigma h^3} \prod_i (2S_i + 1)$$

where A, B, C are the principal moments of inertia, σ is
equal to the number of indistinguishable ways of orienting
the molecule in space, and $\prod_i (2S_i + 1)$ is the statistical
spin factor for the nuclei.

E. Rate of Chemical Reaction

The rate of chemical reaction can be written as
$$rate = k\ C_F \tag{II-20}$$

where k is the specific rate constant, and C_r is a function of reactant concentrations as experimentally observed. Then,

$$C_r = K_1 \prod_r Q_r \qquad \text{(II-21)}$$

where Q_r is the total partition function for the rth reactant, and K_1 is a constant which depends on stable and metastable configurations, which may or may not be reaction intermediates. The value of K_1 can be calculated statistically if structural parameters are known, by assuming these structures are in equilibrium with the reactants. It is assumed that K_1 is independent of isotopic substitution; therefore, in the kinetic rate ratio formulation it would be cancelled out.

3. Absolute Reaction Rate Theory

In Eq. (II-21) Q_r is the total molecular partition function per unit volume, which for a nonlinear reactant is

$$Q_r = (\frac{2\pi M_r KT}{h^3}) \quad [\frac{8\pi^2 (8\pi^3 ABC)^{1/2} (KT)^{3/2}}{\sigma_r h^3}] \quad \prod_i^{3n-6} \frac{1}{2 \sinh(\frac{U_i}{2})}$$

$$(II-22)$$

where $U_i = hc\omega_i/KT$, ω_i = fundamental frequencies of vibration. Eq. II-22 is evaluated by summing over all the energy states by allowing vibrational motions about the stable configuration.

Since the activated complex is unstable in one coordinate, the reaction coordinate, Eq. II-22 is invalid for the activated complex. This difficulty is avoided by Eyring [19] by restricting the activated complex by definition to a narrow range δ about the activation point.

Fig. II-2
δ-range of transition state.

The transition state thus comprises all systems on the potential energy surface within a distance $\pm \delta/2$ from a surface orthogonal to the reaction coordinate at the activation point. If we let x be the reaction coordinate, the specific reaction rate constant is

$$k = \mathcal{K}(\nu_x Q / \underset{r}{\Pi} Q_r)\exp(-\Delta E_0/RT) \qquad (II-23)$$

where $\mathcal{K}$, the probability of reflection at the energy barrier of systems which have sufficient energy to surmount it, is the transmission coefficient; ν_x is the frequency of motion in x; and Q is the partition function of activated complex.

If motion in x corresponds to a normal mode of vibration for the activated complex, then the 3n-7 other normal modes comprise motions within the transition state configuration, and the rate constant can be written as

$$k = \mathcal{K}\left(\frac{\nu_x Q_x^{\ddagger}}{\underset{r}{\Pi} Q_r}\right)\left(\frac{2\pi M^{\ddagger} KT}{h^2}\right)^{3/2}\left[\frac{8\pi^2(8\pi^3 A^{\ddagger} B^{\ddagger} C^{\ddagger})^{1/2}(KT)^{3/2}}{\sigma h^3}\right]x$$

$$\left[\overset{3n-7}{\underset{i}{\Pi}}\frac{1}{2\sinh(\frac{U_i}{2})}\right]\exp(-\Delta E_0/RT) \qquad (II-24)$$

where $Q_x^{\ddagger}$ is the translational partition function corresponding to the motion of a particle in one-dimensional space.

Since we have assumed that all systems lying in the length δ shown in Fig. II-2 are activated complexes, we

can further assume that the concentration of activated complexes depends only upon the potential energy within the activated state. Therefore the calculated rate will be unchanged if the partition function which has a maximum in x is replaced by one for which potential energy is constant in x or by one which has a minimum in x.

The translational motion of a particle of mass m is one-dimensional box of length δ can be described by the translational partition function

$$Q_{tr} = \frac{(2\pi mKT)^{1/2}}{h} \delta \qquad (II-25)$$

so if the "effective mass"* is m_o the partition function associated with motion in x of the activated complex is given by

$$Q_x^{\ddagger} = [\frac{2\pi m_o KT}{h^2}]^{1/2} \delta \qquad (II-26)$$

The frequency in x is

$$\nu_x = \frac{\bar{\dot{x}}}{\delta} \qquad (II-27)$$

$$= \frac{1}{\delta} \times [\frac{\int_0^{\infty} \exp(\frac{-m_o \dot{x}^2}{2KT}) \dot{x} d\dot{x}}{\int_{-\infty}^{+\infty} \exp(\frac{-m_o \dot{x}^2}{2KT}) d\dot{x}}] \qquad (II-28)$$

$$= \frac{1}{\delta} \times [\frac{KT}{2\pi m_o}] \qquad (II-29)$$

* In the case of two "oscillator" system, the effective mass is the reduced mass.

In the numerator we take one-half of the integral

$$\int_{-\infty}^{+\infty} \exp\left(\frac{-m_0 \dot{x}^2}{2KT}\right) \dot{x} \, dx,$$

since we are interested only in those motions which lead toward product. From Eq.II-26 and Eq.II-29

$$\nu_x Q_x^{\ddagger} = \frac{1}{\delta} \left(\frac{KT}{2\pi m_0}\right)^{1/2} \left(\frac{2\pi m_0 KT}{h^2}\right)^{1/2} \qquad \delta = \frac{KT}{h} \qquad (II-30)$$

Thus we see that the actual value of δ is immaterial. Hence, the specific reaction rate can be written

$$k = \left(K\frac{KT}{h}\right)\left(\prod_r Q_r\right)^{-1} \left(\frac{2\pi MKT}{h^2}\right)^{3/2} \left[\frac{8\pi^2 (8\pi^3 A^{\ddagger} B^{\ddagger} C^{\ddagger})^{1/2} (KT)^{3/2}}{\sigma \, h^3}\right]$$

$$\times \left[\prod_1^{3n-7} \left(2 \sinh \frac{U_1}{2}\right)^{-1}\right] \exp(-E_0/RT)$$

$$(II-31)$$

The above expression can be derived by alternative methods.

As we have mentioned in the previous sections that the total partition function can be separated into contributions corresponding to translational, rotational, vibrational, and electronic energies. The partition function for vibrational motion per normal mode is given by

$$Q_v = [1-\exp(-h\nu/KT)]^{-1} \exp[h\nu/2KT] \qquad (II-32)$$

If one degree of the vibrational energy of the activated complexes corresponds to the very loose vibration, then it can be considered as the reaction coordinate and

$$\lim_{\nu \to 0} Q_\nu = \lim_{\nu \to 0} [1 - \exp(-h\nu/KT)]^{-1} \qquad (II-33)$$

According to Maclaurin series expansion

$$\exp(-h\nu/KT) = \sum_{n=0}^{\infty} \frac{(-h\nu/KT)^n}{n!} \qquad (II-34)$$

when $|\ h\nu/KT\ | < \infty$,

then $\lim_{\nu \to 0} [-\sum_{n=0}^{\infty} \frac{(-h\nu/KT)^n}{n!}] = [1 - \lim_{\nu \to 0} \sum_{n=0}^{\infty} \frac{(-h\nu/KT)^n}{n!}]^{-1}$

$$(II-35)$$

If we omit the square and higher terms in Eq. II-34,
Eq. II-27 becomes

$$\lim_{\nu \to 0} Q_\nu = [1 - (1 - \frac{h\nu}{KT})]^{-1} \exp(h\nu/2KT) = \frac{KT}{h\nu} \qquad (II-36)$$

Hence the equilibrium constant between the reactants and
the activated complexes can be written as

$$K^* = \frac{[x^*]}{\prod_r [r]} (\frac{KT}{h\nu}) [\frac{Q_\ddagger}{\prod_r Q_r} \exp(-\Delta E_0/RT)] \qquad (II-37)$$

where $Q_\ddagger$ is the partition function of activated complexes
less one degree of vibrational freedom, and $[r]$ is the
concentration of reactants. By rearranging Eq. II-37, we
have

$$\nu [x^*] = \prod_r [r] (\frac{KT}{h}) [\frac{Q_\ddagger}{\prod_r Q_r} \exp(-\Delta E_0/RT)] \qquad (II-38)$$

The left-hand side of Eq. II-40 can be divided by the
concentration of reactants to give the rate constant of
reaction

$$k = (\frac{KT}{h}) [\frac{Q^{\ddagger}}{\pi\, Q_r}\ exp(-\,\Delta E_o/RT)] \qquad\qquad (II\text{-}39)$$

Since not every activated complex reaching the top of the potential energy barrier is converted into reaction product we introduce the "transmission coefficient" $\varkappa$. Then Eq. II-39 can be written as

$$k = \varkappa\ \frac{KT}{h}\ [\frac{Q^{\ddagger}}{\pi\, Q_r}\ exp(-\,\Delta E_o/RT)]. \qquad\qquad (II\text{-}40)$$

This result is identical with that obtained by Eyring method in Eq. II-31.

In the quantum mechanical treatment of reaction vibration, a slightly different expression from Eq. II-18 was obtained:

$$\nu_q Q_q = \nu_q [2\ sinh\ (\frac{U_q}{2})]^{-1} \qquad\qquad (II\text{-}41)$$

However, if we assume $\nu_q = |\nu_x|$ and $\frac{h\nu_q}{KT} < 1$, then

$$\nu_q Q_q = (\frac{KT}{h})\ [1 + \frac{U_q^2}{24}]^{-1} \qquad\qquad (II\text{-}42)$$

The difference between the two is approximately the quantum mechanical tunneling factor.[20]

The expression for the specific rate constant, which will be employed through the rest of this discussion, is obtained.

$$k = \left(\not{k} \frac{KT}{h} \right) \left\{ \prod_r \left(\frac{2\pi M_r KT}{h^2} \right)^{3/2} \frac{8\pi^2 (8\pi^3 A_r B_r C_r)^{1/2} \ (KT)^{3/2}}{\sigma_r h^3} \right.$$

$$\left. \times \prod_1^{3n-6} \frac{1}{2 \sinh(\frac{U_1}{2})} \right\}^{-1} \left(\frac{2\pi M^{\ddagger} KT}{h^3} \right)^{3/2} \left[\frac{8\pi^2 (8\pi^3 A^{\ddagger} B^{\ddagger} C^{\ddagger})^{1/2} (KT)^{3/2}}{\sigma_r^{\ddagger} h^3} \right]$$

$$\times \prod_1^{3n-7} \frac{1}{2 \sinh(\frac{U_1}{2})} \qquad\qquad (II\text{-}43)$$

6. Isotope Effects

A. Isotope Effects on Potential-Energy Surfaces

The calculation of the influence of isotopic mass on the rate of reaction, it is clear, requires a set of very detailed descriptions of the roles of the individual atoms and the forces exerted by the electron cloud. It is also clear that in order to predict the reaction rate and the isotope effect of a certain reaction accurately, detailed information about the transition state is required. The absolute reaction rate theory thus has proved to be a better method than others for this purpose at the present stage. However, in practical cases, this theory is limited by our incomplete knowledge of the actual transition state and the impossibility, at present, of making a quantum-mechanical calculation accurate enough for any but the simplest systems. A qualitative agreement between the theoretical prediction and experimental data is, there-fore, generally sufficient.

Theoretical models, in general, are based upon the presently available knowledge about stable molecules. Most bonds which are not directly involved in the reac-tion will behave normally as to length and force constant. For bonds which are ruptured in the reaction, the length will generally be increased and the force constant weakened if the corresponding mode of vibration has not disappeared completely as a consequence of the

transformation of the corresponding vibrational coordinate
into the coordinate of decomposition. In general, as a
result of the weakening of the corresponding vibrational
coordinate, we assume that the frequency of this vibration
is zero.

In ordinary calculation of the reaction rates we
know very little about the transmission coefficient and
the amount of tunneling through the potential energy
barrier. However, in the absolute rate theory the tunnel-
ing contribution is generally negligible. And the trans-
mission coefficient is not very sensitive to isotopic
mass and will consequently cancel in the kinetic isotope
rate ratio.

By definition, the isotopes are two forms of an ele-
ment differing only in the number of neutrons in the
nucleus but not in any ordinary chemical properties.
Since the electronic structures of two isotopes of the
same element are identical, the mass of the nucleus enters
the calculations only via the "effective mass" of the
system of nucleus plus electrons. Hence the forces
which hold the atoms together will be nearly independent
of changes in the masses of the atomic nuclei caused by
isotopic substitution. Then we can say that the poten-
tial-energy surface and hence the interatomic distances
and the vibrational force constants could be treated as
invariant under isotopic substitution, with an accuracy

which is sufficient for our present purpose. But
zero-point energy (and thus activation energy) and ν_x
depend upon vibrational frequencies and thus on masses.
A potential-energy diagram for the isotopic substitution
of light molecules by heavier molecules is shown in
Fig. III-I.

Fig. III-I Potential-Energy diagram for isotope effect.

B. Application of Rate Theory to Isotope Effects

Consider the unimolecular decomposition

$$X = X^{\ddagger} = \text{Products},$$

in which the validity of QET is assumed, then the rate constant for this reaction can be written in the form of Eq. II-45:

$$k = (\varkappa\,\frac{KT}{h})\;\left[\left(\frac{2\pi M_r KT}{h^2}\right)^{3/2}\;\frac{8\pi^2(8\pi^3 A_r B_r C_r)^{1/2}\,(KT)^{3/2}}{\sigma h^3}\right.$$

$$\times\;\prod_{1}^{3n-6}\frac{1}{2\sinh(\frac{U_i}{2})}\;\right]^{-1}$$

$$\times\;\left(\frac{2\pi M^{\ddagger}KT}{h^2}\right)^{3/2}\;\frac{8\pi^2(8\pi^3 A^{\ddagger}B^{\ddagger}C^{\ddagger})^{1/2}\,(KT)^{3/2}}{\sigma^{\ddagger}h^3}\;\prod_{1}^{3n-7}\frac{1}{2\sinh(\frac{U_i}{2})}$$

<div align="right">(II-44)</div>

If we replace one atom in X by a lighter isotope, the reaction is written as:

$$X' = X'^{\ddagger} = \text{Products},$$

and the rate constant is

$$k' = (\varkappa'\frac{KT}{h})\;\left[\left(\frac{2\pi M_r'KT}{h^2}\right)^{3/2}\;\frac{8\pi^2(8\pi^3 A_r'B_r'C_r')^{1/2}\,(KT)^{3/2}}{\sigma_r'h^3}\right.$$

$$\times\;\prod_{1}^{3n-6}\frac{1}{2\sinh(\frac{U_i'}{2})}\;\right]^{-1}\;\left(\frac{2\pi M^{\ddagger}{}'KT}{h^2}\right)^{3/2}\;\frac{8\pi^2(8\pi^3 A^{\ddagger}{}'B^{\ddagger}{}'C^{\ddagger}{}')^{1/2}\,(KT)^{3/2}}{\sigma^{\ddagger}{}'h^3}$$

$$\times\;\prod_{1}^{3n-7}\frac{1}{2\sinh(\frac{U_i'}{2})}$$

<div align="right">(II-45)</div>

By comparing Eq. II-44 and Eq. II-45, we have,

$$\frac{k'}{k} = \left(\frac{K'}{K}\right) \left[\left(\frac{M'_r}{M_r}\right)^{3/2} \left(\frac{\sigma_r}{\sigma'_r}\right) \left(\frac{A'_r B'_r C'_r}{A_r B_r C_r}\right)^{1/2} \prod_i^{3n-6} \frac{\sinh\left(\frac{U_i}{2}\right)}{\sinh\left(\frac{U'_i}{2}\right)}\right]^{-1}$$

$$\times \left(\frac{M^{\ddagger'}}{M^{\ddagger}}\right)^{3/2} \left(\frac{\sigma^{\ddagger}}{\sigma^{\ddagger'}}\right) \left(\frac{A^{\ddagger'} B^{\ddagger'} C^{\ddagger'}}{A^{\ddagger} B^{\ddagger} C^{\ddagger}}\right)^{1/2} \prod_i^{3n-7} \frac{\sinh\left(\frac{U^{\ddagger}_i}{2}\right)}{\sinh\left(\frac{U^{\ddagger'}_i}{2}\right)}$$

(II-46)

If we rearrange Eq. II-46 and assume that the transmission-coefficient cancel out, we get

$$\frac{k'}{k} = \left(\frac{M_r}{M'_r} \times \frac{M^{\ddagger'}}{M^{\ddagger}}\right)^{3/2} \left(\frac{\sigma'_r}{\sigma_r} \times \frac{\sigma^{\ddagger}}{\sigma^{\ddagger'}}\right) \left(\frac{A_r B_r C_r}{A'_r B'_r C'_r} \times \frac{A^{\ddagger'} B^{\ddagger'} C^{\ddagger'}}{A^{\ddagger} B^{\ddagger} C^{\ddagger}}\right)^{1/2}$$

$$\times \prod_i^{3n-6} \frac{\sinh\left(\frac{U_i}{2}\right)}{\sinh\left(\frac{U'_i}{2}\right)} \prod_i^{3n-7} \frac{\sinh\left(\frac{U^{\ddagger}_i}{2}\right)}{\sinh\left(\frac{U^{\ddagger'}_i}{2}\right)}$$

(II-47)

By multiplying both sides of Eq. II-47 by $(\sigma^{\ddagger'}\sigma'_r)/(\sigma^{\ddagger}\sigma'_r)$ we arrive our general expression:

$$\left(\frac{k'}{k}\right)\left[\frac{\sigma_r \sigma^{\ddagger'}}{\sigma'_r \sigma^{\ddagger}}\right] = \left(\frac{M_r}{M'_r} \times \frac{M^{\ddagger'}}{M^{\ddagger}}\right)^{3/2} \left(\frac{A_r B_r C_r}{A'_r B'_r C'_r} \times \frac{A^{\ddagger'} B^{\ddagger'} C^{\ddagger'}}{A^{\ddagger} B^{\ddagger} C^{\ddagger}}\right)^{1/2}$$

$$\times \prod_i^{3n-6} \frac{\sinh\left(\frac{U'_i}{2}\right)}{\sinh\left(\frac{U_i}{2}\right)} \prod_i^{3n-7} \frac{\sinh\left(\frac{U^{\ddagger}_i}{2}\right)}{\sinh\left(\frac{U^{\ddagger'}_i}{2}\right)}$$

(II-48)

The above expression can be simplified by the use of identies derived from the Redlich-Teller product rule[21].

These same identities can be obtained by equating classical partition functions with the high-temperature limit of quantum mechanical partition functions, as suggested by Bigeleisen and Meyer[5]. The expression derived for the reactants is

$$\left(\frac{m'}{m}\right)^{1/2} \left(\frac{M}{M'}\right)^{3/2} \left(\frac{A\,B\,C}{A'B'C'}\right)^{1/2} \prod_i^{3n-6} \frac{U_i'}{U_i} = 1 \qquad (II\text{-}49)$$

for the activated complex when motion in the reaction coordinate is considered as a vibration is

$$\left(\frac{m'}{m}\right)^{1/2} \left(\frac{M^{\ddagger}}{M^{\ddagger}{}'}\right)^{3/2} \left(\frac{A^{\ddagger}\,B^{\ddagger}\,C^{\ddagger}}{A^{\ddagger}{}'B^{\ddagger}{}'C^{\ddagger}{}'}\right)^{1/2} \prod_i^{3n-6} \frac{U_i^{\ddagger}{}'}{U_i^{\ddagger}} = 1; \qquad (II\text{-}50)$$

and that for the activated complex where motion in the reaction coordinate is considered as a translation is

$$\left(\frac{m'}{m}\right)^{1/2} \left(\frac{M^{\ddagger}}{M^{\ddagger}{}'}\right)^{3/2} \left(\frac{A^{\ddagger}\,B^{\ddagger}\,C^{\ddagger}}{A^{\ddagger}{}'B^{\ddagger}{}'C^{\ddagger}{}'}\right)^{1/2} \left(\frac{M_o}{M_o'}\right)^{1/2} \prod_i^{3n-7} \frac{U_i^{\ddagger}{}'}{U_i^{\ddagger}} = 1$$

$$(II\text{-}51)$$

If we combine Eq. II-49 and Eq. II-51 we get

$$\left(\frac{M^{\ddagger}{}'M_r}{M^{\ddagger}M_r'}\right)^{3/2} \left(\frac{A_r B_r C_r}{A_r'B_r'C_r'} \times \frac{A^{\ddagger}{}'B^{\ddagger}{}'C^{\ddagger}{}'}{A^{\ddagger}B^{\ddagger}C^{\ddagger}}\right)^{1/2} = \left(\frac{M_o}{M_o'}\right)^{1/2} \prod_i^{3n-7} \frac{U_i^{\ddagger}{}'}{U_i^{\ddagger}} \prod_i^{3n-6} \frac{U_i}{U_i'}$$

$$(II\text{-}52)$$

By combining Eq. II-48 and Eq. II-52 we have

$$\left(\frac{k'}{k}\right)\left(\frac{\sigma_r\sigma^{\ddagger}{}'}{\sigma_r'\sigma^{\ddagger}}\right) = \left(\frac{M_o}{M_o'}\right) \prod_i^{3n-6} \frac{U_i\sinh\left(\frac{U_i'}{2}\right)}{U_i'\sinh\left(\frac{U_i}{2}\right)} \prod_i^{3n-7} \frac{U_i^{\ddagger}{}'\sinh\left(\frac{U_i^{\ddagger}}{2}\right)}{U_i^{\ddagger}\sinh\left(\frac{U_i^{\ddagger}{}'}{2}\right)}$$

$$(II\text{-}53)$$

or

$$\left(\frac{k'}{k}\right)\left(\frac{\sigma_r \sigma\,'}{\sigma_r'\sigma}\right) = \left(\frac{\nu_x'}{\nu_x}\right) \prod_i^{3n-6} \frac{U_i \sinh(\frac{U_i}{2})}{U_i' \sinh(\frac{U_i'}{2})} \prod_i^{3n-7} \frac{U_i' \sinh(\frac{U_i'}{2})}{U_i \sinh(\frac{U_i}{2})}$$

<div align="right">(II-54)</div>

where ν_x is the average frequency of motion in the reaction coordinate.

In the case of intramolecular isotope effects, the reactants are identical for the pair of reactions, and $(Q_r/Q_r') = 1$. Then, Eq. II-53 or Eq. II-54 can be written as

$$\left(\frac{k'}{k}\right)\left(\frac{\sigma_r \sigma\,'}{\sigma_r'\sigma}\right) = \left(\frac{\nu_x'}{\nu_x}\right) \prod_i^{3n-7} \frac{U_i' \sinh(\frac{U_i'}{2})}{U_i \sinh(\frac{U_i}{2})}$$

$$= \left(\frac{M_o}{M_o'}\right) \prod_i^{3n-7} \frac{U_i' \sinh(\frac{U_i'}{2})}{U_i \sinh(\frac{U_i}{2})}$$

<div align="right">(II-55)</div>

In Eq. II-53 or II-54 it is obvious that the first term of the right-hand side is the "Temperature-Independent Factor" (TIF), and the second term of the right-hand side is the "Temperature-Dependent Factor" (TDF). Thus the theoretical expressions for rate constant ratios of isotopic reactions can be written in the general form

$$\frac{k'}{k} = (TIF)\ (TDF)$$

<div align="right">(II-56)</div>

The temperature-dependent factor is a function of the frequencies of motions orthogonal to the reaction coordinate. In the case of intermolecular reactions, it

depends also upon the fundamental frequencies of the reactants. The temperature-independent factor, (v_x'/v_x) has been generally considered as the equivalent of (m_0/m_0') , which in actual computation involves considerable uncertainty. This calculated uncertainty, however, would not influence the temperature-dependent factor. This problem has, in 1958, been reviewed by Bigeleisen and Wolfsberg,[22] and they have given a particular formula [23] for the temperature-independent function to be used in the case of three-centered reactions. [24]

In Eq. II-55 the term U_i, as defined, is equal to $\frac{hc\omega_i}{kT}$ where ω_i is a fundamental frequency of vibration. In order to calculate the ratio, two sets of fundamental frequencies must be known. Therefore, a detailed development and general method of calculating these sets of fundamental frequencies are desirable. The following chapter is devoted to this purpose.

Chapter III - Molecular Vibrations

Chapter III - Molecular Vibration

Throughout this investigation the atoms are treated as point masses connected by forces which keep the atoms near their equilibrium positions. The electronic effects are neglected.[16] The rigorous and logical way to begin the treatment of molecular vibrations, is to prove that when the proper coordinate system is used, the total energy of a molecule can be approximately separated into three components, translational energy, rotational energy, and vibrational energy.

I.   Separation of Energies

The coordinate system used here is constructed as
follows: The three Cartesian coordinates whose origin
is located at the center of mass of the molecule; the
three Eulerian angles of a rotating system of Cartesian
coordinates, the axes of which coincide with the prin-
cipal axes of inertia of the undistorted molecule; and
the Cartesian coordinates of the atoms with respect to
the rotating coordinate system.   The system whose ori-
gin is located at the center of mass of the molecule is
denoted by I, and the other one is denoted by S.   If we
have a particle P in the space of S, there results
three types of movements; relative motion, P|S, is the
motion of P with respect to S;   leading motion, S|I, is
the motion of S with respect to I; absolute motion,
P|I, is the motion of P with respect to I.   If the
three coordinates of I are x,y,z with unit vectors
$\hat{i}$, $\hat{j}$, $\hat{k}$, respectively, and the coordinates of S are
u, v, w with unit vectors $\hat{l}$, $\hat{m}$, $\hat{n}$, we have defined the
position of the point mass P.   And we can denote P as
a function of six coordinates: P (x, y, z, u, v, w).
The relative position is shown in Fig. III-I.

Fig. III-I   The relative position of S and I systems in
three dimensional space.

With reference to Fig. III-I it is clear that

$$\hat{OP} = \hat{OO'} + \hat{O'P} = \hat{OO'} + (u\hat{l} + v\hat{m} + w\hat{n}) \quad (III-I)$$

By differentiating Eq. III-I with respect to time, t, we
get the absolute velocity V_{ab} in terms of leading velo-
city V_{ℓ}, and relative velocity, V_r.

$$V_{ab} = \frac{d\hat{OP}}{dt} = \frac{d\hat{OO'}}{dt} + \frac{d\hat{O'P}}{dt}$$

$$= \frac{d\hat{OO'}}{dt} + \frac{d}{dt}[u\,\hat{l} + v\,\hat{m} + w\,\hat{n}]$$

$$= \frac{d\hat{OO'}}{dt} + (u\frac{d\hat{l}}{dt} + \hat{l}\frac{du}{dt}) + (v\frac{d\hat{m}}{dt} + \hat{m}\frac{dv}{dt}) + (w\frac{d\hat{n}}{dt} + \hat{n}\frac{dw}{dt})$$

$$= \hat{V}_\ell + \hat{V}_r \quad (III-2)$$

where $V_\ell = \frac{d\hat{OO'}}{dt} + (u \frac{d\hat{l}}{dt} + v \frac{d\hat{m}}{dt} + w \frac{d\hat{n}}{dt})$ (III-3)

$V_r = \frac{du}{dt} \hat{l} + \frac{dv}{dt} \hat{m} + \frac{dw}{dt} \hat{n}$ (III-4)

Now, let us take a look at system S. (Fig. III-2)

Fig. III-2. S - system

Since $\hat{l}$ and $\dot{\hat{l}}$ are orthogonal then

$$\dot{\hat{l}} = a\hat{m} + b\hat{n} \tag{III-5}$$

where a and b are constants.

Consider

$$\hat{m}\cdot\dot{\hat{l}} = a\hat{m}\cdot\hat{m} + b\hat{m}\cdot\hat{n} = a \tag{III-6}$$

$$\hat{n}\cdot\dot{\hat{l}} = a\hat{n}\cdot\hat{m} + b\hat{n}\cdot\hat{n} = b \tag{III-7}$$

By substituting Eq. III-6 and III-7 into Eq. III-5,

we get

$$\dot{\hat{l}} = (\hat{m}\cdot\dot{\hat{l}})\,\hat{m} + (\hat{n}\cdot\dot{\hat{l}})\,\hat{n}. \tag{III-8}$$

Since $\hat{l}\cdot\hat{n} = 0$, we know that

$$\hat{l}\cdot\dot{\hat{n}} + \hat{n}\cdot\dot{\hat{l}} = 0$$

$$\therefore \quad \hat{n}\cdot\dot{\hat{l}} = -\hat{l}\cdot\dot{\hat{n}} \tag{III-9}$$

By combining Eq. III-8 and Eq. III-9,

$$\dot{\hat{l}} = (\hat{m}\cdot\dot{\hat{l}})\,\hat{m} - (\hat{l}\cdot\dot{\hat{n}})\,\hat{n}$$

$$= (\dot{\hat{l}}\cdot\hat{m})(\hat{n}\times\hat{l}) + (\dot{\hat{n}}\cdot\hat{l})(\hat{m}\times\hat{l}) + (\dot{\hat{m}}\cdot\hat{n})(\hat{l}\times\hat{l})$$

$$= [(\dot{\hat{l}}\cdot\hat{m})\,\hat{n} + (\dot{\hat{n}}\cdot\hat{l})\,\hat{m} + (\dot{\hat{m}}\cdot\hat{n})\hat{l}] \times \hat{l}$$

$$= \hat{\omega} \times \hat{l}$$

where $\hat{\omega}$ is the angular velocity of the particle P.

Since $\hat{l}$, $\hat{m}$, and $\hat{n}$ are cyclic permutative, we can write

down

$$\dot{\hat{l}} = \hat{\omega} \times \hat{l} \tag{III-10}$$
$$\dot{\hat{m}} = \hat{\omega} \times \hat{m}$$
$$\dot{\hat{n}} = \hat{\omega} \times \hat{n}$$

If we combine Eqs. III-l0 and III-3, we get

$$\hat{V}_\ell = \dot{\hat{OO'}} + \hat{\omega} \times (u\hat{i} + v\hat{m} + w\hat{n})$$

$$= \dot{\hat{OO'}} + \hat{\omega} \times \hat{OP} \qquad\qquad (III-11)$$

So the absolute velocity (Eq. III-2) can be written

$$\hat{V}_{ab} = (\dot{\hat{OO'}}) + (\hat{\omega} \times \hat{OP}) + \hat{V}_r = \dot{\hat{R}} + \hat{\omega} \times \hat{r} + \hat{V}_r \quad (III-12)$$

The kinetic energy T of the whole molecule, therefore, can be written

$$2T = \dot{\hat{R}}^2 \sum_i m_i + \sum_i m_i (\hat{\omega}\times\hat{r}) \cdot (\hat{\omega}\times\hat{r}) + \sum_i m_i \hat{V}_i^2$$

$$+ 2\dot{\hat{R}}\cdot\hat{\omega} \times \sum_i m_i \hat{r}_i + 2\dot{\hat{R}}\cdot\sum_i m_i \hat{V}_i + 2\hat{\omega}\cdot\sum_i (m_i \hat{r}_i \times \hat{V}_i)$$

$$(III-13)$$

Since the origin, O, is the center of gravity of the whole molecule, at every instant it must be true that

$$\sum_i m_i \hat{r}_i = 0 \qquad\qquad (III-14)$$

and $\sum_i m_i \dot{\hat{r}}_i = \sum_i m_i [(\hat{\omega}\times\hat{r}_i) + \hat{V}_i] = 0$

$$\sum_i m_i \hat{V}_i = 0$$

Equation III-13 becomes

$$2T = \dot{\hat{R}}^2 \sum_i m_i + \sum_i m_i (\hat{\omega}\times\hat{r})\cdot(\hat{\omega}\times\hat{r}) + \sum_i m_i \hat{V}_i^2 + 2\hat{\omega}\cdot\sum_i m_i (\hat{r}_i \times \hat{V}_i)$$

$$(III-15)$$

= translational energy + rotational energy + vibrational energy + Coriolis energy[26]

Thus far we have proved that the total energy of a molecule can be approximately separated into translational, rotational, vibrational, and Coriolis energies. Hereafter, the discussion will be centered upon the vibrational energy and related functions.

2. Coordinate Systems

A. Generalized Coordinate System

If a set of properly defined coordinates, as stated in the previous section, is chosen, the vibration of a molecule can be treated as a conservative small oscillation system. Let us consider a polyatomic molecule, as a conservative system, which can be described in terms of a set of generalized coordinates, q_k, and the time, t. If the molecule possesses n degrees of freedom, then $k = 1,2,....., n$. We specify that a configuration of stable equilibrium exists for the system, and that at equilibrium the generalized coordinates have values q_{k0}. In such a configuration Lagrange's equation

$$\frac{\partial L}{\partial q_k} - \frac{d}{dt} \frac{\partial L}{\partial \dot{q}_k} = 0 \quad k = 1,2,....., n \quad (III-16)$$

will be satisfied by

$$q_k = q_{k0}; \quad \dot{q}_k = 0; \quad \ddot{q}_k = 0; \quad k = 1,2,....., n$$

Now, at the least every nonzero term of the form $(\frac{d}{dt} \frac{\partial L}{\partial \dot{q}_k})$ must contain either $\dot{q}_k$ or $\ddot{q}_k$, so that all such terms vanish at equilibrium. Therefore, from Lagrang's equation, we have

$$\frac{\partial L}{\partial q_k}\bigg|_0 = \frac{\partial T}{\partial q_k}\bigg|_0 - \frac{\partial U}{\partial q_k}\bigg|_0 = 0 \quad (III-17)$$

where the subscripts, 0, designates that the quantity is evaluated at equilibrium.

It is assumed that the transformation equations defining the generalized coordinates of the system, $q_1, \ldots, q_n$, do not involve the time explicitly. Thus, time-dependent constraints are to be excluded. Then potential energy is a function of position only, and the kinetic energy is a function of velocity only.

Kinetic Energy in Generalized Coordinate System

In a rectangular coordinate system, the kinetic energy is given by

$$T = 1/2 \sum_{\alpha=1}^{n} \sum_{i=1}^{3} m_\alpha \dot{X}_{\alpha,i}^2 \qquad (III-18)$$

If we adopt a set of generalized coordinates explicitly including the time, then the set of transformations connecting the rectangular system and the generalized system can be written as

$$X_{\alpha,i} = X_{\alpha,i} (q_1, q_2, \ldots q_h, t)$$

where $\alpha = 1, 2, \ldots, n$; $i = 1, 2, 3$; then

$$X_{\alpha,i} = X_{\alpha,i} (q_j, t) \qquad (III-19)$$

where $j = 1, 2, \ldots, h$.

The generalized velocity is

$$\dot{X}_{\alpha,i} = \dot{X}_{\alpha,i} (q_j, \dot{q}_j, t), \qquad (III-20)$$

We may also write the inverse transformation as

$$q_j = q_j (X_{\alpha,i}, t) \qquad (III-21)$$

$$\dot{q}_j = \dot{q}_j (X_{\alpha,i}, \dot{X}_{\alpha,i}, t) \qquad (III-22)$$

Eq. III-20 can be written as

$$\dot{X}_{\alpha,i} = \sum_{j=1}^{h} \frac{\partial X_{\alpha,i}}{\partial q_j} \dot{q}_j + \frac{\partial X_{\alpha,i}}{\partial t} \qquad \text{(III-23)}$$

Then,

$$(\dot{X}_{\alpha,i})^2 = (\sum_{j=1}^{h} \sum_{k=1}^{h} \frac{\partial X_{\alpha,i}}{\partial q_j} \frac{\partial X_{\alpha,i}}{\partial q_k} \dot{q}_j \dot{q}_k)$$

$$+ 2(\sum_{j=1}^{h} \frac{\partial X_{\alpha,i}}{\partial q_j} \frac{\partial X_{\alpha,i}}{\partial t} \dot{q}_j) + (\frac{\partial X_{\alpha,i}}{\partial t})^2$$

$$\text{(III-24)}$$

And Eq. III-18 becomes

$$T = 1/2 \sum_{\alpha=1}^{n} \sum_{i=1}^{3} m_\alpha [(\sum_{j=1}^{h} \sum_{k=1}^{h} \frac{\partial X_{\alpha,i}}{\partial q_j} \frac{\partial X_{\alpha,i}}{\partial q_k} \dot{q}_j \dot{q}_k)$$

$$+ 2(\sum_{j=1}^{h} \frac{\partial X_{\alpha,i}}{\partial q_j} \frac{\partial X_{\alpha,i}}{\partial t} \dot{q}_j) + (\frac{\partial X_{\alpha,i}}{\partial t})^2 \quad] \quad \text{(III-25)}$$

If the system is scleronomic, so that time does not
appear explicitly in the equations of transformation,
then the partial time derivatives vanish, and therefore
the kinetic energy is a homogeneous quadratic function
of the generalized velocities:

$$T = \sum_{\alpha} \sum_{i\,jk} (1/2) m_\alpha \frac{\partial X_{\alpha,i}}{\partial q_j} \frac{\partial X_{\alpha,i}}{\partial q_k} \dot{q}_j \dot{q}_k \qquad \text{(III-26)}$$

Thus, we can write down the kinetic energy

$$T = 1/2 \sum_{j,k=1}^{n} m_{jk} \dot{q}_j \dot{q}_k \qquad \text{(III-27)}$$

And, in general

$$\frac{\partial T}{\partial q_k} = 0 \qquad k = 1,2,\ldots, n.$$ \hfill (III-28)

Potential Energy in Generalized Coordinate System

Therefore from Eq. III-17 and Eq. III-28 we have

$$\frac{\partial T}{\partial q_k}\Big|_0 = 0, \qquad k = 1,2,\ldots, n$$ \hfill (III-29)

Eq. III-29 means that the potential energy has an extremum at the equilibrium configuration of the system, q_{k0}, where $k = 1,2,\ldots, n$. If the configuration is initially at the zero equilibrium position, we choose $q_{k0} = 0$. If, originally, $q'_{k0} \neq 0$, we can always use a linear transformation to set $q_{k0} = 0$. Now, if we expand the potential energy in a Taylor series about the equilibrium configuration, we get

$$U(q_1,q_2,\ldots,q_n) = U_0 + \sum_{k=1}^{n} \frac{\partial U}{\partial q_k}\Big|_0 q_k$$
$$+ 1/2 \sum_{j,k=1}^{n} \frac{\partial^2 U}{\partial q_j \partial q_k}\Big|_0 q_j q_k + \ldots$$

\hfill (III-30)

In Eq. III-30, the terms linear in q_k vanish automatically in consequence of the equilibrium conditions (Eq. III-29). The first term in Eq. III-30 is the potential energy of the equilibrium position, and by shifting the arbitrary zero of potential to coincide

with the equilibrium potential, this term may also be
made to vanish. Then, if the motion of the generalized
coordinate system is restricted to be small, all the
terms in the expansion which contain products of the
q_k of degree higher than second may be neglected.
This is equivalent to restricting our interest to
simple harmonic oscillations, in which case only the
terms quadratic in the coordinates are left. Thus,

$$U = 1/2 \sum_{j=1}^{n} \sum_{k=1}^{n} f_{j,k} \ q_j \ q_k, \qquad (III-31)$$

where we define

$$f_{k,j} = f_{j,k} = \frac{\partial^2 U}{\partial q_j \partial q_k} \bigg|_0 \qquad (III-32)$$

The motion of the system is specified to take
place in the vicinity of the equilibrium configuration,
and the potential energy has an extremum when the
system is in this configuration. Since the potential
energy, U, is chosen to be zero at equilibrium, in
general U must be greater than or equal to zero. And
it is clear that both potential energy and kinetic
energy are positive definite quantities, unless the
coordinates, in the case of U, or the velocities, in
the case of T, are zero, in which case they vanish.

Coefficients of the Energy Equations in Generalized Coordinate System

We have concluded that the kinetic energy and the potential energy in the generalized coordinate system have the same form:

$$T = 1/2 \sum_{j=1}^{n} \sum_{k=1}^{n} m_{j,k} \dot{q}_j \dot{q}_k \qquad (III-33)$$

$$U = 1/2 \sum_{j=1}^{n} \sum_{k=1}^{n} f_{j,k} q_j q_k ,$$

By comparing Eqs. III-26 and III-27, it is clear that the $m_{j,k}$ are, in general, functions of coordinates q_k, and they may be expanded in a Taylor series about the equilibrium configuration,

$$m_{j,k} (q_1, \ldots q_n) = m_{jk} (q_{\ell 0}) + \sum_{\ell} \frac{M_{jk}}{q_\ell} \Big|_0 q_\ell + \ldots \ldots$$
$$(III-34)$$

The lowest nonvanishing approximation to T, since in Eq. III-33 T is already quadratic in q_ks, is obtained by dropping all but the first term in Eq. III-34. Thus the coefficients, m_{jk}, become constants and we rewrite equation III-27 in the form

$$T = 1/2 \sum_{j=1}^{n} \sum_{k=1}^{n} m_{jk} \dot{q}_j \dot{q}_k \qquad (III-35)$$

From Eq. III-32, the coefficients f_{jk} are only numbers. Thus, in Eq. III-33, the m_{jk} and the f_{jk} are n by n arrays of numbers which specify the way in which the motions of the various coordinates are coupled.

Equations of Motion in Generalized Coordinate System

From Eq. III-33, the Lagrangian is given by

$$L = 1/2 \sum_{j=1}^{n} \sum_{k=1}^{n} (m_{jk} \dot{q}_j \dot{q}_k - f_{jk} q_j q_k)$$

(III-36)

But, since T is a function only of the generalized velocities and U is a function only of the generalized coordinates Lagrange's equation for the kth coordinate becomes

$$\frac{\partial U}{\partial q_k} + \frac{d}{dt} \frac{\partial T}{\partial \dot{q}_k} = 0$$

(III-37)

The first-order partial differentiations with respect to the coordinate system of Eq. III-33 are

$$\frac{\partial U}{\partial q_k} = (1/2) \sum_{j=1}^{n} f_{jk} q_j$$

(III-38)

$$\frac{\partial T}{\partial \dot{q}_k} = (1/2) \sum_{j=1}^{n} m_{jk} \dot{q}_j$$

The equations of motion then become

$$\sum_{j=1}^{n} f_{jk} q_j + m_{jk} \ddot{q}_j = 0,$$

(III-39)

where explicit use has been made of the symmetry property
of the f_{jk} and m_{jk} coefficients. Each of the equations
III-39 will involve, in general, all of the coordinates
q_k, and it is this set of simultaneous differential equa-
tions which must be solved to obtain the motion near the
equilibrium.

The equations of motion, III-39, are a set of n
second-order linear homogeneous differential equations
with constant coefficients. Since we are dealing with an
oscillatory system, we expect a solution of the form

$$q_j (t) = a_j \exp i (\omega t - \delta) \qquad\qquad (III-40)$$

where a_j gives the complex amplitude of the oscillation
for each coordinate, and the phase, δ, has been included
to give the two arbitrary constants, a_j and δ, required
by the second-order nature of each of the differential
equations. It is understood, of course, that it is the
real part of Eq. III-40 which is to correspond to the
actual motion. Substitution of the solution, Eq. III-40,
into the equations of motion leads to the following
equations for the amplitude factors:

$$\sum_{j=1}^{n} (f_{jk} - \omega^2 m_{jk}) a_j = 0 \qquad\qquad (III-41)$$

This is a set of n linear homogeneous algebraic equations
that the a_j must satisfy. For a nontrivial solution to
exist, the determinant of the coefficients must vanish.

If ω^2 is denoted by λ, then

$$|f_{jk} - \lambda m_{jk}| = 0 \tag{III-42}$$

To be more explicit, this is a determinant of the order n x n:

$$\begin{vmatrix} f_{11} - \lambda m_{11} \cdots\cdots\cdots f_{1n} - \lambda m_{1n} \\ \vdots \qquad\qquad\qquad\qquad \vdots \\ f_{n1} - \lambda m_{n1} \cdots\cdots\cdots f_{nn} - \lambda m_{nn} \end{vmatrix} = 0 \tag{III-43}$$

The equation which is represented by this determinant is called the characteristic equation or secular equation of the system, and is an equation of degree n in ω^2. The roots of the determinant provide the frequencies for which Eq. III-40 represents a correct solution to the equations of the motion. For each of these values of ω^2, the Eqs. III-41 may be solved for n-l of the amplitudes in terms of remaining a_j. For the case of degeneracy, the problem can be solved by specific algebraic techniques which are omitted in this discussion.

Since the principle of superposition applies for the Eqs. III-41, the general solution for q_j must be written as the superposition of the solutions for each of the n values:

$$q_j(t) = \sum_{r=1}^{n} a_{jr} \exp i(\omega_r t - \delta_r) = \sum_r a_{jr} \cos(\omega_r t - \delta_r) \tag{III-44}$$

The motion of the coordinate q_j is therefore compounded of motions with each of the n values of the frequencies.

Hence, simplified coordinate systems are desirable.

B. Mass-Weighted Cartesian Coordinates (MWCC)
    and the Principal Axis Transformation

Mass-Weighted Cartesian Coordinates

Suppose the appropriate generalized coordinates were the Cartesian coordinates of the system particles. The kinetic energy then would contain only the squares of the velocity components. By introducing generalized coordinates, which are the Cartesian components multiplied by the square root of the particle mass, the kinetic energy can be put in the form

$$T = 1/2 \sum_{j=1}^{n} \sum_{k=1}^{n} \delta_{jk} \dot{q}_j \dot{q}_k \qquad \text{(III-45)}$$

The Kronecker delta, δ_{jk}, equals unity if $j = k$, and is zero otherwise. By comparing Eqs. III-27 and III-45, we see that in this coordinate system $m_{jk} = \delta_{jk}$. This coordinate system is called mass-weighted Cartesian coordinates. And the kinetic energy can be written

$$T = (1/2) (\sum_{j=1}^{n} \dot{q}_j^2) \qquad \text{(III-46)}$$

Hency, Eqs. III-39 become

$$\ddot{q}_j + \sum_{k=1}^{n} f_{jk} q_j = 0 \qquad \text{(III-47)}$$

and Eq. III-41 can be written

$$\sum_{j=1}^{n} (f_{jk} a_j - \delta_{jk} \omega^2 a_j) = 0 \qquad \text{(III-48)}$$

If we replace ω^2 by λ, Eq. III-48 is of the form

$$\sum_{j=1}^{n} (f_{jk} - \delta_{jk} \lambda) a_j = 0 \qquad \text{(III-49)}$$

According to the same argument as in the previous section, Eq. III-43 in this case is written

$$\begin{vmatrix} f_{11} - \lambda \cdots\cdots\cdots f_{1n} \\ f_{21} \quad f_{22} - \lambda \cdots\cdots \\ \vdots \\ f_{n1} \cdots\cdots f_{nn} - \lambda \end{vmatrix} = 0 \qquad \text{(III-50)}$$

The Principal Axis Transformation

For a given set of particles, in view of the identification between tensor quantities and the Hermitian matrices, one can find a set of Cartesian axes for which the tensor elements under investigation will be diagonal. This set of axes is called the "principal axes". If the initial set of coordinates is not principal axes, one can always transform this initial set to the principal axes by a particular orthogonal transformation, known as the "Principal Axis Transformation".

Let us now return to Eq. III-41 which, in matrix form, can be written

$$FA = \Lambda MA \qquad \text{(III-51)}$$

The effect of F on A is such as to produce a multiple of the result of M acting on A, not merely to produce $\Sigma\lambda a$. In consequence of the Hermitian property of F and M, it will be shown that the eigenvalues, λ, for which equation III-51 can be satisfied are all real and positive, and the eigenvectors, a, which are the column vectors of matrix A, are orthogonal. In addition, the matrix of the eigenvectors, A, diagonalizes both M and F, the former to the unit matrix, E, and the latter to a matrix whose diagonal elements are the eigenvalues, λ.

If we let a_{jk} represent the jth component of the kth eigenvector, Eq. III-41 can be written as

$$\sum_{j=1}^{n} F_{ij}\, a_{jk} = \lambda_k \sum_{j=1}^{n} M_{ij}\, a_{jk} \qquad\qquad \text{(III-52)}$$

The complex conjugate of the similar equation for λ_ℓ has the form

$$\sum_{i=1}^{n} F_{ij}\, a^*_{i\ell} = \lambda^*_\ell \sum_{i=1}^{n} M_{ij}\, a^*_{i\ell} \qquad\qquad \text{(III-53)}$$

We multiply Eq. III-53 by a_{jk}, sum over j, and subtract the resulting equation from the similar product of Eq. III-52 with $a^*_{i\ell}$ summed over i. The left-hand side of the difference equation vanishes, leaving only

$$0 = (\lambda_k - \lambda^*_k) \sum_{i=1}^{n} \sum_{j=1}^{n} M_{ij}\, a_{jk}\, a^*_{i\ell} \qquad\qquad \text{(III-54)}$$

Consider first the special case of Eq. III-54 when $\ell = k$:

$$(\lambda_k - \lambda_k^*) \sum_{i=1}^{n} \sum_{j=1}^{n} M_{ij} \, a_{jk} \, a_{ik}^* = 0 \qquad \text{(III-55)}$$

The sum over i and j will now be shown to be real and positive definite. To verify this statement, separate a_{jk} into its real and imaginary components:

$$a_{jk} = (\alpha_{jk}, \, \beta_{jk}) \qquad \text{(III-56)}$$

The summation can then be written:

$$\sum_{i=1}^{n} \sum_{j=1}^{n} M_{ij} \, a_{jk} \, a_{ik}^* = [\sum_{i=1}^{n} \sum_{j=1}^{n} M_{ij} \, \alpha_{jk} \, \alpha_{ik}$$

$$+ \sum_{i=1}^{n} \sum_{j=1}^{n} M_{ij} \, \beta_{jk} \, \beta_{ik},$$

$$\sum_{i=1}^{n} \sum_{j=1}^{n'} M_{ij} \, (\beta_{jk} \, \alpha_{ik} - \beta_{jk} \, \alpha_{jk})]$$

$$\text{(III-57)}$$

The imaginary term in Eq. III-57 vanishes in consequence of the symmetry of M_{ij}, for an interchange of the dummy indices, i and j, changes the sign of the summation. Hence the sum is real. Furthermore, it is seen from the definition of the coefficients M_{ij}, Eq. III-34, the summation in Eq. III-55 cannot be zero for real and positive, definite kinetic energy. It follows that

$$\lambda_k = \lambda_k^*, \qquad \text{(III-58)}$$

and eigenvalues λ_k must be real.

Since the eigenvalues are real, the ratio of the
eigenvector components a_{jk} determined by Eq. III-52 must
all be real. Multiply Eq. III-52 by a_{ik} and sum over i:

$$\sum_{i=1}^{n} \sum_{j=1}^{n} F_{ij} a_{ik} a_{jk} = \lambda_k \sum_{i=1}^{n} \sum_{j=1}^{n} M_{ij} a_{ik} a_{jk}$$

(III-59)

we get an equation which can be solved for λ_k:

$$\lambda_k = \frac{\Sigma\Sigma F_{ij} a_{ik} a_{jk}}{\Sigma\Sigma M_{ij} a_{ik} a_{jk}}$$

(III-60)

In Eq. III-60 neither numerator nor denominator can be
negative, and the denominator cannot be zero. Hence λ
is always finite and positive or zero. Therefore, as λ
stands for ω^2, positive λ corresponds to real frequencies
of oscillation.

In view of the reality of the eigenvalues and eigen-
vectors, Eq. III-54 can be written

$$(\lambda_k - \lambda_\ell) \sum_{i=1}^{n} \sum_{j=1}^{n} M_{ij} a_{i\ell} a_{jk} = 0$$

(III-61)

If all the roots of the secular equation are distinct,
then Eq. III-61 can hold only if the summation vanishes
for ℓ not equal to k:

$$\sum_{i=1}^{n} \sum_{j=1}^{n} M_{ij} a_{i\ell} a_{jk} = 0 \qquad \ell \neq k$$

(III-62)

If we require that

$$\sum_{i=1}^{n} \sum_{j=1}^{n} M_{ij} a_{i\ell} a_{jk} = 1 \quad \text{when } \ell = k \qquad \text{(III-63)}$$

Eqs. III-62 and III-63 can be combined as:

$$\sum_{i=1}^{n} \sum_{j=1}^{n} M_{ij} a_{i\ell} a_{jk} = \delta_{\ell k} \qquad \text{(III-64)}$$

In matrix notation, Eq. III-64 can be written as

$$\widetilde{A}MA = E \qquad \text{(III-65)}$$

Eq. III-65 is the orthogonality condition for the matrix A in the configuration space whose metric tensor is M.

In a Cartesian space the metric tensor is the unit tensor E and the condition III-65 is reduced to

$$\widetilde{A}A = E \qquad \text{(III-66)}$$

This is the ordinary orthogonality requirement.

In the Eq. III-52, if we define $\lambda_{\ell k} = \lambda_k \delta_{\ell k}$, the expression can be written

$$\sum_{j=1}^{n} F_{ij} a_{jk} = \sum_{j=1}^{n} M_{ij} a_{jk} \lambda_{\ell k}, \qquad \text{(III-67)}$$

which becomes in matrix notation:

$$FA = MA\Lambda. \qquad \text{(III-68)}$$

Multiplying $\widetilde{A}$ from the left, Eq. III-68 takes the form

$$\widetilde{A}FA = \widetilde{A}MA\Lambda, \qquad \text{(III-69)}$$

which, by Eq. III-65 reduces to

$$\widetilde{A}FA = \Lambda. \qquad \text{(III-70)}$$

Eq. III-69 states that a congruent transformation of F by
A changes it into a diagonal matrix whose elements are the
eigenvalues λ_k.

The matrix A thus simultaneously diagonalizes both F
and M. The diagonalization process is interpreted as
follows: A is the matrix of a linear transformation from
a system of inclined axes to Cartesian orthogonal axes.
At the same time, the new axes are the perpendicular
principal axes of F, so that the matrix F is diagonal in
the transformed coordinate system. Therefore, we can con-
clude that the entire process of obtaining the fundamental
frequencies of small oscillation is a particular type of
principal axis transformation.

C. Normal Coordinates and Normal Mode of Vibration

The coordinate system used in the previous sections
are not, in general, the separation coordinates of the
problem, because not every one of them is simply periodic
and each solution is not necessarily representing a funda-
mental frequency of the particle system under consideration.
However, we can obtain such a set of periodic coordinates
by a point transformation from the previous set of
coordinates q_j.

We can define a new set of coordinates ξ_j related to
the original coordinates by the equations

$$q_i = \sum_j a_{ij} \xi_j \qquad\qquad \text{(III-71)}$$

If q_j and ξ_j are represented as the elements of single-column matrices Q and Ξ respectively, the defining equation, Eq. III-71, appears as

$$Q = A\Xi \qquad \text{(III-72)}$$

The potential energy can be written as

$$U = (1/2)\ \widetilde{Q}FQ, \qquad \text{(III-73)}$$

and the kinetic energy can be expressed as

$$T = (1/2)\ \widetilde{Q}M\dot{Q} \qquad \text{(III-74)}$$

Now, since

$$Q = \widetilde{A}\Xi = \widetilde{\Xi}\widetilde{A} \qquad \text{(III-75)}$$

Eq. III-73 becomes $U = (1/2)\ \widetilde{\Xi}\widetilde{A}FA\Xi \qquad \text{(III-76)}$

According to Eq. III-70, the potential energy reduces simply to

$$U = (1/2)\ \widetilde{\Xi}\Lambda\Xi \qquad \text{(III-77)}$$

Written explicitly, Eq. III-77 appears as

$$U = (1/2)\ \sum_k\ \omega_k^2\ \xi_k^2 \qquad \text{(III-78)}$$

In the new coordinates, the kinetic energy can be written

$$T = (1/2)\ \widetilde{\dot{\Xi}}\widetilde{A}MA\dot{\Xi} \qquad \text{(III-79)}$$

and according to Eq. III-65

$$T = (1/2)\ \widetilde{\dot{\Xi}}\dot{\Xi} \qquad \text{(III-80)}$$

In terms of the new velocities, the kinetic energy is therefore

$$T = (1/2)\ \sum_k\ \dot{\xi}_k^2 \qquad \text{(III-81)}$$

Equations III-79 and III-81 state that in the new coordinates both the potential and kinetic energies are sums

of squares only, without any cross terms. The Lagrange
equations for ξ_k are

$$\ddot{\xi}_k + \omega_k^2 \, \xi_k = 0 \qquad\qquad (III-82)$$

These equations have solutions

$$\xi_k = C_k \, \exp(-i\omega_k t) \qquad\qquad (III-83)$$

It is easily seen that each of the new coordinates is a
simply periodic function involving only one of the reson-
ant frequencies. Customarily, ξ's are called normal
coordinates of the system.

Each normal coordinate corresponds to a vibration of
the system with only one frequency, and these component
oscillations are spoken of as the normal modes of vibra-
tion. All of the particles in each mode vibrate with the
same frequency and with the same phase, the relative
amplitudes being determined by the matrix elements a_{ik}.
The complete motion is built up out of the sum of the
normal modes weighted with appropriate amplitude and
phase factors contained in the C_k's.

D. Internal Coordinates

In order to set up and carry out the actual compu-
tation in this investigation, it is more convenient to
apply the six conditions of no rotation and no translation
before the solution of the secular equation. This kind of
reduction in the number of original coordinates may be
carried out in two ways. One method is to use the six

conditions to express six of the original coordinates in terms of the remaining 3N-6 coordinates. The other method is to introduce a new set of 3N-6 coordinates S_1, S_2,....., S_{3N-6} which are defined by means of the six conditions and 3N-6 relations connecting the S's with the original coordinates. These coordinate systems, which describe the internal configuration of the molecule without regard for its position as a whole in space, are known as internal coordinates.

The set of 3N-6 internal coordinates used in this paper is provided by changes in interatomic distances and changes in the angles between chemical bonds. This type of coordinate provides the most physically significant set of coordinates for use in describing the potential energy of the molecule. But the kinetic energy is more easily set up in terms of Cartesian displacement coordinates of the atoms. A relation between the two types is therefore demanded. Each of the 3N-6 internal coordinates can be considered as the linear combination of the 3N Cartesian displacement coordinates. If S_t represents one of the 3N-6 internal coordinates and ξ_i one of 3N Cartesian displacement coordinates, then

$$S_t = \sum_{i=1}^{3N} B_{ti} \, \xi_i \qquad t = 1,2,....., 3N-6 \qquad (III-84)$$

where the coefficients B_{ti} are constants determined by the geometry of the molecule. If we define a vector $\hat{\rho}_\alpha$

whose components along the three axis directions are the Cartesian displacement coordinates ξ_i, ξ_j, ξ_k for atom α, and a vector $\hat{S}_{t\alpha}$ whose components are $\hat{B}_{ti}$, $\hat{B}_{tj}$, $\hat{B}_{tk}$ associated with atom α, then Eqs. III-84 can be written as[27]

$$S_t = \sum_{\alpha=1}^{N} \hat{S}_{t\alpha} \cdot \rho_\alpha \qquad \text{(III-85)}$$

Physically, the direction of $\hat{S}_{t\alpha}$ is the direction in which a given displacement of atom α will produce the greatest increase of S_t. The modulus of $S_{t\alpha}$ is equal to the increase in S_t produced by unit displacement of the atom in this most effective direction.

G Matrix and the Secular Equations in Terms of Internal Coordinates

In terms of mass-weighted Cartesian coordinates the kinetic energy is given by Eq. III-45. In matrix notation it is

$$T = (1/2) \, \tilde{\dot{Q}}\dot{Q} \qquad \text{(III-86)}$$

In terms of momentum P,

$$\text{where } p_i = \frac{\partial T}{\partial \dot{q}_i} = \dot{q}_i \qquad \text{(III-87)}$$

Eq. III-86 is written

$$T = (1/2) \, \tilde{P}P \qquad \text{(III-88)}$$

We let the transformation from the mass-weighted Cartesian displacement coordinates to internal coordinates be

$$S = DQ \qquad \text{(III-89)}$$

where $D_{tj} = B_{tj} m_j$, m being the mass of the particle involved. If we consider T, the kinetic energy, as a function of velocities in the internal coordinates system, then

$$p_i = \frac{\partial T}{\partial \dot{q}_i} = \sum_t \frac{\partial T}{\partial \dot{S}_t} \frac{\partial \dot{S}_t}{\partial \dot{q}_i} \qquad \text{(III-90)}$$

But

$$\frac{\partial T}{\partial \dot{S}_t} = P_t \qquad \text{(III-91)}$$

and

$$\frac{\partial \dot{S}_t}{\partial \dot{q}_i} = \frac{\partial S_t}{\partial q_i} = D_{ti} \qquad \text{(III-92)}$$

so Eq. III-90 can be written as

$$p_i = \sum_t P_t D_{ti}, \qquad \text{(III-93)}$$

and in matrix notation

$$\tilde{p} = \tilde{P}D \qquad \text{(III-94)}$$

According to Eq. III-88, we get

$$T = (1/2) \tilde{P}D\tilde{D}P \qquad \text{(III-95)}$$

where

$$(D\tilde{D})_{tt'} = \sum_i D_{ti} \tilde{D}_{it'}$$

$$= \sum_i D_{ti} D^*_{t'i}$$

$$= \sum_i M_i^{-1} B_{ti} B^*_{t'i}$$

In Euclidean space, we can define[28]

$$G_{tt'} = \sum_{i=1}^{3N} \frac{1}{m_i} B_{ti} B_{t'i} \qquad \text{(III-96)}$$

where t, t' = 1,2,....., 3N-6.

In terms of vectors, $G_{tt'}$ is given by

$$G_{tt'} = \sum_{\alpha=1}^{N} \mu_\alpha \, \hat{S}_{t\alpha} \cdot \hat{S}_{t'\alpha} \qquad (III\text{-}97)$$

where $\mu_\alpha = \frac{1}{m_\alpha}$ is the reciprocal of the mass of atom α.

The kinetic energy now can be written as

$$T = (1/2) \, \tilde{P}GP. \qquad (III\text{-}98)$$

If the determinant of G does not vanish and the inverse of G exists, then

$$\dot{S}_t = \frac{\partial T}{\partial P_t} \qquad (III\text{-}99)$$

and $\quad \dot{S} = GP.$ $\qquad (III\text{-}100)$

Equation III-88 can be written as[29]

$$T = (1/2) \, \tilde{\dot{S}} \, G^{-1} \, \dot{S}. \qquad (III\text{-}101)$$

Similarly, we can express the potential energy in terms of the same internal coordinates

$$V = (1/2) \, \tilde{S}FS \qquad (III\text{-}102)$$

Then the problem of small vibration leads to the secular equation

$$|F - G^{-1} \lambda| = 0 \qquad (III\text{-}103)$$

By applying matrix algebra to the above equation, Eq. III-103 becomes

$$|GF - E\lambda| = 0 \qquad (III\text{-}104)$$

where F is the matrix of force constants whose elements can be estimated directly in terms of bond distances and angles between involved atoms.

Since both F and G matrices are symmetrical, rows
and columns in Eq. III-104 can be interchanged to yield
the following form

$$|FG - E\lambda| = 0 \qquad\qquad (III-105)$$

where $\lambda = 4\pi^2 c^2 \omega_i^2$.

Eq. III-105 is the secular equation used in this
investigation to calculate the vibrational frequencies.

Chapter IV - Formulations and Calculations

I. Molecular Fragmentation Method

A. General Description

According to Eq. II-55 we see that the transition state formulation for the ratio of rate constants for uni-molecular reactions differing in isotopic constitution is

$$\frac{k'}{k} = \frac{\nu'_x}{\nu_x} \prod_i^{3N-6} \frac{U_i \sinh(\frac{U'_i}{2})}{U'_i \sinh(\frac{U_i}{2})} \prod_i^{3N-7} \frac{U_i^{\ddagger'} \sinh(\frac{U_i^{\ddagger}}{2})}{U_i^{\ddagger} \sinh(\frac{U_i^{\ddagger'}}{2})} \qquad (IV-1)$$

where primed and unprimed quantities refer to the two iso-topic species and $\ddagger$ refers to the transition-state struc-ture, ν_x is the frequency (or average frequency) of motion in the reaction coordinate, and $U_i = hc\omega_i/KT$ where ω_i is a vibrational frequency (or a fundamental frequency of vibration).

The vibrational frequencies of the activated complex are often calculated by Wilson's F,G, matrix methods [29]. The G matrix is specified by assuming a physically reasonable structure for the activated complex. The dia-gonal elements of the F matrix can be estimated from the assumed structure by analogy to stable molecules; the off-diagonal elements might be set equal to zero or adjusted to conform to assumption about the nature of the reaction coordinate [30, 31]. The vibrational frequencies are obtained from the roots of Eq. III-105. The reactant frequencies may be obtained by a similar calculation or from spectroscopic data. However, the continued product

involving reactant frequencies in Eq. IV-I reduces to
unity for an intramolecular isotope effect, where both
reactant species are identical. In this investigation a
specific example chosen is the decarboxylation of
end-labelled malonic acid

$$
\begin{array}{c}
C^{13}OOH \\
\quad\quad \xrightarrow{k_3}\; C^{12}H_3C^{12}OOH \;+\; C^{13}O_2 \\
C^{12}H_2 \\
\quad\quad \xrightarrow{k_4}\; C^{12}H_3C^{13}OOH \;+\; C^{12}O_2 \qquad\qquad (IV\text{-}2)\\
C^{12}OOH
\end{array}
$$

where k_4/k_3 is a measure of a carbon-12/carbon-13 intra-
molecular isotope effect. Since the rate-constant ratio
depends only on the vibrational frequencies of the acti-
vated complexes for this type of isotope effect, approxi-
mations and assumptions about the transition state that
simplify the secular equations are particularly useful in
these cases.

B. Molecular Fragmentation Method

If the assumption is made that the activated complex
can be treated as vibrationally decoupled fragments, its
secular equation is considerably simplified. Uncoupled,
freely rotating models for the activated complex have
been used in a number of absolute-rate theory calcula-
tions of rate constants[32]. These applications have been

quite properly limited to dissociations with abnormally
large pre-exponential factors (and the reverse recombina-
tions), since the change of several internal modes of
vibration in the reactant to free rotations in the acti-
vated complex must be associated with abnormally large
entropies of activation. However, in calculations of
ratios of rate constants for isotopic molecules, the
decoupled fragment approximation has a broader range of
validity. If the activated complex has a "loose" struc-
ture, with weakly coupled fragments, motions between
fragments involve vibrations of much lower frequency
than motions within fragments. The approximate separa-
tion of high and low frequencies [29] can then be applied
to factor the secular equation into intra- and inter-
fragment parts. The low-frequency, inter-fragment
vibrations, although very important in calculations of
an individual rate constant, have little effect on the
continued product in Eq. IV-I, since $[(U/2)^{-1} \sinh (U/2)]$
approaches unity for small U. The rows and columns of
the secular equation that correspond to inter-fragment
motions can therefore be deleted, and the approximate
frequencies of internal vibrations of the fragments,
obtained from the reduced secular equation are used in
Eq. IV-I.

For a reaction involving rupture (or formation) of
one bond, AB = A+B, the activated complex is treated as
two fragments, and motion in the reaction coordinate is

change in the distance between the centers of mass of the two fragments. The theoretical expression for an intra-molecular isotope effect for this case becomes:

$$k'k = [\frac{M'_{AB}}{M_{AB}}]^{3/2} \; [\frac{I'_{AB}}{I_{AB}}]^{1/2} \; [\frac{A'B'C'}{A \; B \; C}]_A^{1/2} \; [\frac{A'B'C'}{A \; B \; C}]_B^{1/2}$$

$$\prod_i^{3n-6_A} \frac{\sinh(U^{\ddagger}_{Ai}/2)}{\sinh(U^{\ddagger'}_{Ai}/2)} \quad \prod_i^{3n-6_B} \frac{\sinh(U^{\ddagger}_{Bi}/2)}{\sinh(U^{\ddagger'}_{Bi}/2)} \qquad (IV\text{-}3)$$

Eq. IV-3 is the ratio of the total partition function of the activated complexes with 3n-6 degrees of vibrational freedom for each fragment, three rotational degrees of freedom for each fragment, and three translational degrees of freedom for each fragment subject to the constraint that the distance between the centers of gravity of the two fragments is constant.

Applying the product rule [5] to the complete system yields

$$[\frac{\mu_{AB}}{\mu'_{AB}}]^{1/2} \; [\frac{M_{AB}}{M'_{AB}}]^{3/2} \; [\frac{I_{AB}}{I'_{AB}}][\frac{A \; B \; C}{A'B'C'}]_A^{1/2} \; [\frac{A \; B \; C}{A'B'C'}]_B^{1/2}$$

$$\prod_i^{3n-6_A} \frac{U^{\ddagger'}_{Ai}}{U^{\ddagger}_{Ai}} \quad \prod_i^{3n-6_B} \frac{U^{\ddagger'}_{Bi}}{U^{\ddagger}_{Bi}} \; = 1 \qquad\qquad (IV\text{-}4)$$

where $\mu_{AB} = \frac{M_A \times M_B}{M_A + M_B}$, the reduced mass of two fragments.

Alternatively, one can apply the product rule to each fragment independently:

$$\overset{3n_A}{\underset{i}{\prod}} [\frac{M'_i}{M_i}]^{1/2} [\frac{M_A}{M'_A}]^{3/2} [\frac{A\,B\,C}{A'B'C'}]^{1/2}_A \overset{3n-6}{\underset{i}{\prod}} \frac{U^{\ddagger}_{Ai}}{U'^{\ddagger}_{Ai}} = 1 \qquad (IV\text{-}5)$$

and

$$\overset{3n_B}{\underset{i}{\prod}} [\frac{M'_i}{M_i}]^{1/2} [\frac{M_B}{M'_B}]^{3/2} [\frac{A\,B\,C}{A'B'C'}]^{1/2}_B \overset{3n-6}{\underset{i}{\prod}} \frac{U^{\ddagger}_{Bi}}{U'^{\ddagger}_{Bi}} = 1 \qquad (IV\text{-}6)$$

Consequently, Eq. IV-4 becomes:

$$k'/k = (\mu_{AB}/\mu'_{AB})^{1/2} \overset{3n-6}{\underset{i}{\prod}} \frac{U^{\ddagger}_{Ai}\sinh(U^{\ddagger}_{Ai}/2)}{U'^{\ddagger}_{Ai}\sinh(U'^{\ddagger}_{Ai}/2)} \overset{3n-6}{\underset{i}{\prod}} \frac{U^{\ddagger}_{Bi}\sinh(U^{\ddagger}_{Bi}/2)}{U'^{\ddagger}_{Bi}\sinh(U'^{\ddagger}_{Bi}/2)}$$

$$(IV\text{-}7)$$

The reaction coordinate in this case is the distance between the centers of gravity of the two fragments, A and B. Since the average relative velocity[33] of two independent systems is inversly proportional to the square root of their mechanical reduced mass,

$$TIF = \nu'_x/\nu_x = (\mu_{AB}/\mu'_{AB})^{1/2} \qquad (IV\text{-}8)$$

The extension to intermolecular isotope effects can be made by including a factor for the ratio of total partition functions for reactants:

$$k'/k = (\mu_{AB}/\mu'_{AB}) \prod_{i}^{3n-6} \frac{U_{Ri} \sinh(U'_{Ri}/2)}{U'_{Ri} \sinh(U_{Ri}/2)} \prod_{i}^{3n-6} \frac{U^{\ddagger}_{Ai} \sinh(U^{\ddagger}{}'_{Ai}/2)}{U^{\ddagger}{}'_{Ai} \sinh(U^{\ddagger}_{Ai}/2)}$$

$$\times \prod_{i}^{3n-6} \frac{U^{\ddagger}_{Bi} \sinh(U^{\ddagger}{}'_{Bi}/2)}{U^{\ddagger}{}'_{Bi} \sinh(U^{\ddagger}_{Bi}/2)} \qquad (IV-9)$$

However, the fragmentation method is not a good approximation for the reactant molecule, and the reactant frequencies in Eq. IV-9 are the conventional ones calculated for the reactant molecule as a whole.

The simplification provided by this method can be easily seen from the comparison of Eqs. IV-3 and IV-7. The calculation of vibrational frequencies for the activated complex is split into a vibrational analysis of each of the fragments. The resulting reduction in the order of the secular equation permits one to treat much more complicated systems than is possible with more rigorous methods.

Reactions involving simultaneous rupture or formation of two or more bonds can also be treated by this type of model in terms of three or more uncoupled fragments. General formulations of ν'_x/ν_x for three-centered models which have appeared in the literature [23, 24] are applicable in these cases. However, the reaction coordinate can be treated only in terms of inter-fragment motions; the reaction coordinate as a linear combination of internal displacements, within as well as between fragments,

cannot be incorporated in this approach.

The molecular fragmentation method, which assumes a "loose" activated complex, cannot be applied to reactions that do not involve bond rupture or formation in the rate determining step. In addition, of course, assumption of the validity of quasi-equilibrium theory is implicit in the general expression of Eq. IV-I.

Despite the limitations mentioned above, the molecular-fragment models have a wide range of application. This approach should be particularly useful and valuable in dealing with large, complicated structures, because it provides simple, pictorial representations for various reaction mechanisms and greatly simplifies the calculation of activated-complex vibrational frequencies. Thus the method could be used, as the next approximation beyond noting the presence or absence of kinetic isotope effects, in distinguishing between alternate mechanisms, such as concerted or step-wise rupture of two bonds. It could also be used to estimate substituent effects in a series of analogous isotopic reactions.

C. Application of Molecular Fragmentation Method to the
   Decarboxylation of Malonic Acid

The decarboxylation of dibasic carboxylic acids is perhaps the type of reaction whose carbon isotope effect has been most thoroughly studied by different research workers. The compound $CH_2(COOH)_2$ has two different

isotopic isomers containing one heavy carbon atom. The one which contains the heavy atom in the methylene group could expel carbon dioxide in two identical ways, the molecule being isotopically symmetric. The unsymmetric isomer could react in two different ways, the heavy carbon being contained either in the carbon dioxide or in the acetic acid.

The reaction scheme of a sample containing both isomers of mono-heavy malonic acid together with the ordinary compound is illustrated below for the case of C^{13} (the mass number of carbon is assumed to be 12 if not indicated):

$$\begin{array}{c} COOH \\ | \\ CH_2 \\ | \\ COOH \end{array} \xrightarrow{k_1} CH_3COOH + CO_2 \qquad (IV-10)$$

$$\begin{array}{c} COOH \\ | \\ C^{13}H_2 \\ | \\ COOH \end{array} \xrightarrow{k_2} C^{13}H_3COOH + CO_2 \qquad (IV-11)$$

$$\begin{array}{c} C^{13}OOH \\ | \\ CH_2 \\ | \\ COOH \end{array} \begin{array}{l} \xrightarrow{k_3} CH_3COOH + C^{13}O_2 \\ \\ \xrightarrow{k_4} CH_3C^{13}OOH + CO_2 \end{array} \qquad (IV-12)$$

Eq. IV-12 presents the problem of interest in this work. The malonic acid, with eleven atoms, has twenty-six normal modes of vibration. Theoretically, even if the complete vibrational analysis could be carried out, so many parameters would be involved that a meaningful

interpretation would be virtually impossible. Therefore, for the purpose of actual computation and analysis, a simplified model for the transition-state is desirable.

If one assumes that during the course of reaction one carbon-carbon bond was very weak in the transition state, then this structure could be treated as two independent fragments.

A further simplification is the omission of the hydrogen atoms from the transition-state models. This is an application of the "cut-off" approximation of Stern and Wolfsberg.[34] Since no hydrogen is bonded directly to the carbon atoms which are isotopically substituted in the intramolecular pair of reactions, the characteristic group frequencies for hydrogen stretching and bending should be nearly identical for k_3 and k_4. However, the proton masses are included in calculating the fragment reduced-mass ratio for ν_x'/ν_x.

With these "fragmentation" and "cut-off" approximations, the eleven-center activated complex for malonic acid decarboxylation is treated as one four-center fragment and one three-center fragment (as shown in Fig. IV-I), and the 26th order secular equation is reduced to one 6th-order and one 3rd-order equation. The detailed step-wise mathematical derivation of the G matrices is given in the following section.

Fig. IV-1

2. The G Matrix

According to the discussion in Chapter III, the set of
internal coordinates chosen in this case are bond stretch-
ings and valence angle bendings. In the case of 3-center
model, the three internal coordinates (3x3-6) are two
valence bond stretchings and one valence angle bending.
In the 4-center case, the six internal coordinates (3x4-6)
are three valence bond stretchings and three valence angle
bendings.

The notations used here are the same as in Chapter
III and are shown in the corresponding figures.

A. The Three-Center Fragment

A non-linear triatomic fragment should possess
3x3-6 = 3 degrees of freedom. Therefore three coordi-
nates, two bond stretchings and one valence angle bending,
are chosen according to the internal coordinate system.

Valence Bond Stretching Coordinates

Fig. IV-2 The valence bond stretching coordinates.

A. The valence bond stretching between atom 3 and
atom 1.

B. The valence bond stretching between atom 3 and
atom 2.

The bond stretching coordinates in the three-center fragment S_1 and S_2 are chosen such that S_1 describes the stretching between atom 3 and atom 1 and S_2 describes the stretching between atom 3 and atom 2. In figure IV-2 $\hat{r}$'s are the direction bond distance and $\hat{e}$'s are the unit vectors defined as the maximum bond stretchings along the bond distances accordingly. Then the vectors $\hat{S}_{t\alpha}$ can be easily formulated as

$$\hat{S}_{t\alpha}: \quad t = 1; \quad \alpha = 1,2,3 \tag{IV-13}$$

$$\hat{S}_{11} = \hat{e}_{31}$$

$$\hat{S}_{12} = 0$$

$$\hat{S}_{13} = -e_{31}$$

$$t = 2; \quad \alpha = 1,2,3 \tag{IV-14}$$

$$\hat{S}_{21} = 0$$

$$\hat{S}_{22} = e_{32}$$

$$\hat{S}_{23} = -e_{32}$$

Valence Angle Bending Coordinate

The valence angle bending coordinate S_3 is defined according to Eq. III-85:

$$S_3 = \Delta\varphi = \sum_{\alpha=1}^{3} \hat{S}_{t\alpha} \cdot \hat{\rho}_\alpha \tag{IV-15}$$

The maximum displacement of φ is shown in figure IV-3.

Fig. IV-3   The maximum displacement of φ.

      A.   The diagram of the whole system.

      B.   The relation between atom 3 and atom 1.

From figure IV-3 we can write down the following relations immediately.

$$\hat{r}'_{3\alpha} = \hat{r}_{3\alpha} + \hat{\rho}_\alpha - \hat{\rho}_3 \quad \text{where } \alpha = 1,2$$

then

$$\hat{r}'_{3\alpha} - \hat{r}_{3\alpha} = \hat{\rho}_\alpha - \hat{\rho}_3 = \Delta\hat{r}_{3\alpha} \tag{IV-16}$$

If we take the inner product of $\hat{r}'_{3\alpha}$, we get

$$\hat{r}'_{3\alpha} \cdot \hat{r}'_{3\alpha} = (\hat{r}_{3\alpha} + \hat{\rho}_\alpha - \hat{\rho}_3) \cdot (\hat{r}_{3\alpha} + \hat{\rho}_\alpha - \hat{\rho}_3)$$

and

$$(\hat{r}'_{3\alpha})^2 = (\hat{r}_{3\alpha})^2 + 2\hat{r}_{3\alpha}(\hat{\rho}_\alpha - \hat{\rho}_3) + (\hat{\rho}_\alpha - \hat{\rho}_3)^2 \tag{IV-17}$$

The third term in the right-hand side of Eq. IV-17 is the square of the difference between two displacement vectors which is comparatively small and can be neglected. Then Eq. IV-17, according to the basic definition of unit vector, can be expressed as

$$\hat{e}_{3\alpha} \cdot (\hat{\rho}_\alpha - \hat{\rho}_3) = \Delta(r_{3\alpha})^2/2r_{3\alpha} \tag{IV-18}$$

But from Eq. IV-16, we know that

$$\Delta \hat{r}_{3\alpha} = \hat{\rho}_\alpha - \hat{\rho}_3$$

and

$$\hat{e}_{3\alpha} \cdot \Delta \hat{r}_{3\alpha} = \Delta r_{3\alpha}$$

$$\therefore \quad \Delta r_{3\alpha} = \hat{e}_{3\alpha} \cdot (\hat{\rho}_\alpha - \hat{\rho}_3) = \Delta(r_{3\alpha})^2/2/r_{3\alpha} \qquad \text{(IV-19)}$$

Now, look at figure IV-3A we can say that

$$\cos \varphi = \hat{e}_{31} \cdot \hat{e}_{32} \qquad \text{(IV-20)}$$

By differentiating Eq. IV-20, we get

$$d(\cos \varphi) = -\sin \varphi \, d\varphi = \hat{e}_{31} \cdot d\hat{e}_{32} + \hat{e}_{32} \cdot d\hat{e}_{31} \quad \text{(IV-21)}$$

According to the definition of unit vector, the first

differentiation of $\hat{e}_{3\alpha} = \hat{r}_{3\alpha}/r_{3\alpha}$ is

$$d\hat{e}_{3\alpha} = (r_{3\alpha} \, d\hat{r}_{3\alpha} - \hat{r}_{3\alpha} \, dr_{3\alpha})/(r_{3\alpha})^2 \qquad \text{(IV-22)}$$

Then

$$\hat{e}_{31} \cdot d\hat{e}_{32} = (r_{32})^{-1} (\hat{\rho}_2 - \hat{\rho}_3) \cdot \hat{e}_{31}$$

$$- (r_{32})^{-1} (\cos \varphi) \, \hat{e}_{32} \cdot (\hat{\rho}_2 - \hat{\rho}_3) \qquad \text{(IV-23)}$$

$$\hat{e}_{32} \cdot d\hat{e}_{31} = (r_{31})^{-1} (\hat{\rho}_1 - \hat{\rho}_3) \cdot \hat{e}_{32}$$

$$- (r_{31})^{-1} (\cos \varphi) \, \hat{e}_{31} \cdot (\hat{\rho}_1 - \hat{\rho}_3) \qquad \text{(IV-24)}$$

Substitute Eqs. IV-23 and IV-24 into Eq. IV-21, we have

$$-\sin\varphi d\varphi = (r_{31})^{-1} (\hat{e}_{32} - \cos \varphi \, \hat{e}_{31}) \cdot \hat{\rho}_1$$

$$+ (r_{32})^{-1} (\hat{e}_{31} - \cos \varphi \, \hat{e}_{32}) \cdot \hat{\rho}_2$$

$$+ [(\cos \varphi \, \hat{e}_{32} - \hat{e}_{31})(r_{32})^{-1}$$

$$+ (\cos \varphi \, \hat{e}_{31} - \hat{e}_{32}) (r_{31})^{-1}] \cdot \hat{\rho}_3$$

then

$$d\varphi = [(\cos \varphi \; \hat{e}_{31} - \hat{e}_{32}) \; (r_{31} \; \sin \varphi)^{-1}] \cdot \hat{\rho}_1$$

$$+ [(\cos \varphi \; \hat{e}_{32} - \hat{e}_{31}) \; (r_{32} \; \sin \varphi)^{-1}] \cdot \hat{\rho}_2$$

$$+ \{[(r_{31} - r_{32} \cos \varphi)\hat{e}_{31} + (r_{32} - r_{31} \cos \varphi) \; \hat{e}_{32}]$$

$$(r_{31} r_{32} \; \sin \varphi)^{-1}\} \cdot \hat{\rho}_3 \qquad\qquad (IV\text{-}25)$$

By comparing Eqs. IV-25 and IV-15, we conclude that

$$\hat{S}_{t\alpha}: \quad t = 3, \quad \alpha = 1,2,3. \qquad\qquad (IV\text{-}26)$$

$$\hat{S}_{31} = (r_{31} \; \sin \varphi)^{-1} \; (\cos \varphi \; \hat{e}_{31} - \hat{e}_{32})$$

$$\hat{S}_{32} = (r_{32} \; \sin \varphi)^{-1} \; (\cos \varphi \; \hat{e}_{32} - \hat{e}_{31})$$

$$\hat{S}_{33} = (r_{31} r_{32} \; \sin \varphi)^{-1}$$

$$\times [(r_{31} - r_{32} \cos \varphi)\hat{e}_{31} + (r_{32} - r_{31} \cos \varphi) \; \hat{e}_{32}]$$

The Elements of "G" Matrix for Three-Center Fragment

The "G" matrix elements now can be formulated according to Eq. III-97

$$g_{tt'} = \sum_{\alpha=1}^{3} \mu_\alpha \; \hat{S}_{t\alpha} \cdot \hat{S}_{t'\alpha}. \qquad\qquad (IV\text{-}27)$$

where

$$\mu_\alpha = (m_\alpha)^{-1}; \; t,t' = 1,2,3.$$

Eq. IV-27, in matrix notation, can be written as

$$G = \begin{pmatrix} g_{11} & g_{12} & g_{13} \\ g_{21} & g_{22} & g_{23} \\ g_{31} & g_{32} & g_{33} \end{pmatrix} = \begin{pmatrix} \mu_1 \\ \mu_2 \\ \mu_3 \end{pmatrix} \cdot \begin{pmatrix} \hat{S}_{11} & \hat{S}_{12} & \hat{S}_{13} \\ \hat{S}_{21} & \hat{S}_{22} & \hat{S}_{23} \\ \hat{S}_{31} & \hat{S}_{32} & \hat{S}_{33} \end{pmatrix} \cdot \begin{pmatrix} \hat{S}_{11} & \hat{S}_{21} & \hat{S}_{31} \\ \hat{S}_{12} & \hat{S}_{22} & \hat{S}_{32} \\ \hat{S}_{13} & \hat{S}_{23} & \hat{S}_{33} \end{pmatrix}$$

$$(IV\text{-}28)$$

By substituting Eqs. IV-13, IV-14, and IV-26 into Eq.
IV-28, the "G" matrix elements for the three-center
fragment are:

$$g_{11} = \mu_1 + \mu_3 \qquad\qquad\qquad\qquad \text{(IV-29)}$$

$$g_{12} = g_{21} = \mu_3 \cos \varphi$$

$$g_{13} = g_{31} = -(r_{32})^{-1} (\mu_3 \sin \varphi)$$

$$g_{22} = \mu_2 + \mu_3$$

$$g_{23} = g_{32} = - (r_{31})^{-1} (\mu_3 \sin \varphi)$$

$$g_{33} = (r_{31})^{-2}(\mu_1) + (r_{32})^{-2} (\mu_2)$$
$$+ [(r_{31})^{-2} + (r_{32})^{-2} - (2 \cos \varphi)(r_{31} r_{32})^{-2}] \mu_3$$

B. The Four-Center Fragment

This fragment is composed by four atoms, three valence
bonds, and three valence angles. Hence, we would have
3x4-6 = 6 degrees of freedom. The six internal coordinates
are three valence bond stretchings and three valence angle
bendings (Fig. IV-4)

Fig. IV-4 The four-center fragment

Valence Bond Stretching Coordinates

Based on the same assumptions made in the previous section, the three valence bond stretching coordinate S_1, S_2, and S_3 are shown in Fig. IV-5.

Fig. IV-5   The valence bond stretching coordinates

    A. The valence bond stretching between atom 4 and atom 1.

    B. The valence bond stretching between atom 4 and atom 2.

    C. The valence bond stretching between atom 4 and atom 3.

Then, the vectors $\hat{S}_{t\alpha}$ can be formulated as follows:

$$\hat{S}_{t\alpha}: \quad t = 1; \quad \alpha = 1,2,3,4. \tag{IV-30}$$

$$\hat{S}_{11} = \hat{e}_{41}$$
$$\hat{S}_{12} = 0$$
$$\hat{S}_{13} = 0$$
$$\hat{S}_{14} = -\hat{e}_{41}$$

$$t = 2; \quad \alpha = 1,2,3,4. \tag{IV-31}$$

$$\hat{S}_{21} = 0$$
$$\hat{S}_{22} = \hat{e}_{42}$$
$$\hat{S}_{23} = 0$$
$$\hat{S}_{24} = -\hat{e}_{42}$$

$$t = 3; \quad \alpha = 1,2,3,4. \qquad\qquad (IV\text{-}32)$$

$$\hat{S}_{31} = 0$$

$$\hat{S}_{32} = 0$$

$$\hat{S}_{33} = \hat{e}_{43}$$

$$\hat{S}_{34} = -\hat{e}_{43}$$

Valence Angle Bending Coordinates

The valence angle bending coordinates of the four center fragment are defined according to Eq. III-85.

$$S_t = \sum_{\alpha=1}^{4} \hat{S}_{t\alpha} \cdot \hat{\rho}_{\alpha} \qquad t = 4,5,6. \qquad\qquad (IV\text{-}33)$$

The maximum displacements of three φ's are shown in Fig. IV-6.

Fig. IV-6. The maximum displacements of φ's.

A. $S_4 = \Delta\varphi_3$

B. $S_5 = \Delta\varphi_1$

C. $S_6 = \Delta\varphi_2$

From Fig. IV-5, the unit vectors are defined as

$$\hat{e}_{4\alpha} = \hat{r}_{4\alpha}/r_{4\alpha} \qquad \alpha = 1,2,3 \qquad (IV-34)$$

The first differentiations of Eqs. IV-34 are

$$d\hat{e}_{4\alpha} = (r_{4\alpha})^{-2} (r_{4\alpha}d\hat{r}_{4\alpha} - \hat{r}_{4\alpha}dr_{4\alpha}) \qquad (IV-35)$$

Since

$$\hat{e}_{41} \cdot \hat{e}_{42} = \cos \varphi_3 \qquad (IV-36)$$

then

$$d \cos \varphi_3 = -\sin \varphi_3 d\varphi_3 = \hat{e}_{41} \cdot d\hat{e}_{42} + \hat{e}_{42} \cdot d\hat{e}_{41} \qquad (IV-37)$$

By going through the same derivations as Eqs. IV-21 to IV-25, we get

$$d\varphi_3 = (r_{41} \sin \varphi_3)^{-1} (\cos \varphi_3 \hat{e}_{41} - \hat{e}_{42}) \cdot \hat{\rho}_1$$

$$+ (r_{42} \sin \varphi_3)^{-1} (\cos \varphi_3 \hat{e}_{42} - \hat{e}_{41}) \cdot \hat{\rho}_2$$

$$+ (r_{41}r_{42} \sin \varphi_3)^{-1} (\hat{r}_{41} - r_{41}\hat{e}_{42}\cos\varphi_3$$

$$- r_{42}\hat{e}_{41}\cos\varphi_3 + r_{42}\hat{e}_{42}) \cdot \hat{\rho}_4 \qquad (IV-38)$$

According to Eqs. IV-33 and IV-38 we get

$$\hat{S}_{t\alpha}: \quad t = 4; \quad \alpha = 1,2,3,4 \qquad (IV-39)$$

$$\hat{S}_{41} = (r_{41} \sin \varphi_3)^{-1} (\cos \varphi_3 \hat{e}_{41} - \hat{e}_{42})$$

$$\hat{S}_{42} = (r_{42} \sin \varphi_3)^{-1} (\cos \varphi_3 \hat{e}_{42} - \hat{e}_{41})$$

$$\hat{S}_{43} = 0$$

$$\hat{S}_{44} = (r_{41}r_{42} \sin \varphi_3)^{-1} [(r_{41} - r_{42}\cos \varphi_3) \hat{e}_{41}$$

$$+ (r_{42} - r_{41}\cos \varphi_3) \hat{e}_{42}]$$

In formulating t=5 and t=6 the processes are exactly the same as t=4. Since the indexes are permutative, we can write down

$$\hat{S}_{t\alpha}: \quad t=5; \quad \alpha = 1,2,3,4. \tag{IV-40}$$

$$\hat{S}_{51} = 0$$

$$\hat{S}_{52} = (r_{42}\sin \varphi_1)^{-1}(\cos \varphi_1 \hat{e}_{42} - \hat{e}_{43})$$

$$\hat{S}_{53} = (r_{43}\sin \varphi_1)^{-1}(\cos \varphi_1 \hat{e}_{43} - \hat{e}_{42})$$

$$\hat{S}_{54} = (r_{42}r_{43}\sin \varphi_1)^{-1}[(r_{42} - r_{43}\cos \varphi_1)\hat{e}_{42}$$

$$(r_{43} - r_{42}\cos \varphi_1)\hat{e}_{43}]$$

$$\hat{S}_{t\alpha}: \quad t = 6; \quad \alpha = 1,2,3,4. \tag{IV-41}$$

$$\hat{S}_{61} = (r_{41}\sin \varphi_2)^{-1}(\cos \varphi_2 \hat{e}_{41} - \hat{e}_{43})$$

$$\hat{S}_{62} = 0$$

$$\hat{S}_{63} = (r_{43}\sin \varphi_2)^{-1}(\cos \varphi_2 \hat{e}_{43} - \hat{e}_{42})$$

$$\hat{S}_{64} = (r_{41}r_{43}\sin \varphi_2)^{-1}[(r_{41} - r_{43}\cos \varphi_2)\hat{e}_{41}$$

$$(r_{43} - r_{41}\cos \varphi_2)\hat{e}_{43}]$$

The Elements of "G" Matrix for Four-Center Fragment

According to Eqs. III-97, the "G" matrix elements in this case are

$$g_{tt'} = \sum_{\alpha=1}^{4} \mu_\alpha \hat{S}_{t\alpha} \hat{S}_{t'\alpha} \tag{IV-42}$$

where $\mu_\alpha = (m_\alpha)^{-1}$; t, t' = 1,.....,6.

$$G = \begin{pmatrix} g_{11} & \cdots & g_{16} \\ \vdots & & \vdots \\ g_{61} & \cdots & g_{66} \end{pmatrix} = \begin{pmatrix} \mu_1 \\ \mu_2 \\ \mu_3 \\ \mu_4 \end{pmatrix} \cdot \begin{pmatrix} \hat{S}_{11} & \cdots & \hat{S}_{14} \\ \vdots & & \vdots \\ \hat{S}_{61} & \cdots & \hat{S}_{64} \end{pmatrix} \cdot \begin{pmatrix} \hat{S}_{11} & \cdots & \hat{S}_{61} \\ \vdots & & \vdots \\ \hat{S}_{14} & \cdots & \hat{S}_{64} \end{pmatrix} \tag{IV-43}$$

By substituting Eqs. IV-30, IV-31, IV-32, IV-39, IV-40 and IV-41 into Eq. IV-43, we get the elements of the "G" matrix for the four-center fragment as follows: (IV-44)

$$g_{11} = \mu_1 + \mu_4$$

$$g_{12} = g_{21} = \mu_4 \cos \varphi_3$$

$$g_{13} = g_{31} = \mu_4 \cos \varphi_2$$

$$g_{14} = g_{41} = \mu_4 (r_{41} r_{42} \sin \varphi_3)^{-1} [(r_{42} \cos \varphi_3 - r_{41}) + (r_{41} \cos \varphi_3 - r_{42}) \cos \varphi_3]$$

$$g_{15} = g_{51} = \mu_4 (r_{42} r_{43} \sin \varphi_1)^{-1} [(r_{43} \cos \varphi_1 - r_{42}) \cos \varphi_3 + (r_{42} \cos \varphi_1 - r_{43}) \cos \varphi_2]$$

$$g_{16} = g_{61} = \mu_4 (r_{41} r_{43} \sin \varphi_2)^{-1} [(r_{43} \cos \varphi_2 - r_{41}) + (r_{41} \cos \varphi_2 - r_{43}) \cos \varphi_2]$$

$$g_{22} = \mu_2 + \mu_4$$

$$g_{23} = g_{32} = \mu_4 \cos \varphi_1$$

$$g_{24} = g_{42} = \mu_4 (r_{41} r_{42} \sin \varphi_3)^{-1} [(r_{42} \cos \varphi_3 - r_{41}) \cos \varphi_3 + (r_{41} \cos \varphi_3 - r_{42})]$$

$$g_{25} = g_{52} = \mu_4 (r_{42} r_{43} \sin \varphi_1)^{-1} [(r_{43} \cos \varphi_1 - r_{42}) + (r_{42} \cos \varphi_1 - r_{43}) \cos \varphi_1]$$

$$g_{26} = g_{62} = \mu_4 (r_{41} r_{43} \sin \varphi_2)^{-1} [(r_{43} \cos \varphi_2 - r_{41}) \cos \varphi_3 + (r_{41} \cos \varphi_2 - r_{43}) \cos \varphi_1]$$

$$g_{33} = \mu_3 + \mu_4$$

$$g_{34} = g_{43} = \mu_4 (r_{41} r_{42} \sin \varphi_3)^{-1} [(r_{42} \cos \varphi_3 - r_{41}) \cos \varphi_2 + (r_{41} \cos \varphi_3 - r_{42}) \cos \varphi_1]$$

$$g_{35} = g_{53} = \mu_4 (r_{42} r_{43} \sin \varphi_1)^{-1} [(r_{43} \cos \varphi_1 - r_{42}) \cos \varphi_1 + (r_{42} \cos \varphi_1 - r_{43})]$$

$$g_{36} = g_{63} = \mu_4 (r_{41} r_{43} \sin \varphi_2)^{-1} [(r_{43} \cos \varphi_2 - r_{41}) \cos \varphi_2 + (r_{41} \cos \varphi_2 - r_{43})]$$

$$g_{44} = \mu_1(r_{41})^{-2} + \mu_2(r_{42})^{-2} + \mu_4(r_{41}r_{42}\sin\varphi_3)^{-2}[(r_{41} -$$
$$r_{42}\cos\varphi_3)^2 - 2(r_{41} - r_{42}\cos\varphi_3)$$
$$\times(r_{42} - r_{41}\cos\varphi_3)\cos_3 + (r_{42} - r_{41}\cos\varphi_3)^2]$$

$$g_{45} = g_{54} = \mu_2(r_{42}^2\sin\varphi_1\sin\varphi_3)^{-1}(\cos\varphi_2 - \cos\varphi_1\cos\varphi_3)$$
$$+ \mu_4(r_{41}r_{42}^2r_{43}\sin\varphi_1\sin\varphi_3)^{-1}\{(r_{41} - r_{42}\cos\varphi_3)$$
$$\times[(r_{42} - r_{43}\cos\varphi_1)\cos\varphi_3$$
$$+(r_{43} - r_{42}\cos\varphi_1)\cos\varphi_2]$$
$$+(r_{42} - r_{41}\cos\varphi_3)[(r_{42} - r_{43}\cos\varphi_1)$$
$$+(r_{43} - r_{42}\cos\varphi_1)\cos\varphi_1]\}$$

$$g_{46} = g_{64} = \mu_1(r_{41}^2\sin\varphi_2\sin\varphi_3)^{-1}(\cos\varphi_1 - \cos\varphi_2 * \cos\varphi_3)$$
$$+ \mu_4(r_{41}^2r_{42}r_{43}\sin\varphi_2\sin\varphi_3)^{-1}\{(r_{41} - r_{42}\cos\varphi_3)$$
$$[(r_{41} - r_{43}\cos\varphi_2) + (r_{43} - r_{41}\cos\varphi_2)\cos\varphi_2]$$
$$+(r_{42} - r_{41}\cos\varphi_3)[(r_{41} - r_{43}\cos\varphi_2)\cos\varphi_3$$
$$+(r_{43} - r_{41}\cos\varphi_2)\cos\varphi_1]$$

$$g_{55} = \mu_2(r_{42})^{-2} + \mu_3(r_{43})^{-2} + \mu_4(r_{42}r_{43}\sin\varphi_1)^{-2}[(r_{42} -$$
$$r_{43}\cos\varphi_1)^2 + 2(r_{42} - r_{43}\cos\varphi_1)$$
$$\times(r_{43} - r_{42}\cos\varphi_1)\cos\varphi_1 + (r_{43} - r_{42}\cos\varphi_1)^2]$$

$$g_{56} = g_{65} = \mu_3(r_{43}^2\sin\varphi_1\sin\varphi_2)^{-1}(\cos\varphi_3 - \cos\varphi_1\cos\varphi_2)$$
$$+ \mu_4(r_{41}r_{42}r_{43}^2\sin\varphi_1\sin\varphi_2)^{-1}$$
$$\times\{(r_{42} - r_{43}\cos\varphi_1)[r_{41} - r_{43}\cos\varphi_2)\cos\varphi_3$$
$$+(r_{43} - r_{41}\cos\varphi_2)\cos\varphi_1] + (r_{43} - r_{42}\cos\varphi_1)$$
$$\times[(r_{41} - r_{43}\cos\varphi_2)\cos\varphi_2)\cos\varphi_2$$
$$+(r_{43} - r_{41}\cos\varphi_2)]\}$$

$$g_{66} = \mu_1(r_{41})^{-2} + \mu_3(r_{43})^{-2} + \mu_4(r_{41}r_{43}\sin\varphi_2)^{-2}[(r_{41} -$$
$$r_{43}\cos\varphi_2)^2 + 2(r_{41} - r_{43}\cos\varphi_2)(r_{43} - r_{41}\cos_2)\cos\varphi_2$$
$$+(r_{43} - r_{41}\cos\varphi_2)^2]$$

The above derivations are the general formulations of non-linear three-center (Eqs. IV-29), planar four-center (Eqs. IV-44) cases. There are infinite many models one can set up. But they are not of interest in this investigation. The numerical assignments of Eqs. IV-29 and IV-44 are given in the following sections.

3. Calculations and Results

Input parameters for several specific models were selected by arbitrarily assigning a bond order to each bond and then empirically relating bond orders to bond lengths, bond angles, and force constants.

Assigned bond orders were: for the four-center fragment, 1 for bond 2-4, 2-X for bond 1-4, and 1+X for bond 3-4; for the three-center fragment, 1+X for bond 2-3 and 2 for bond 1-3. All bonds are specified in terms of the notation of Fig. IV-1.C. A value of the parameter X from 0 to 1 was specified for each set of calculations; X=0 corresponds to the reactant structure and X=1 to the product structure, assuming enol formation in the rate-determining step.

The bond angle in the three-center fragment, φ, was assumed to be 120° for X=0, 180° for X=1, and a linear function of X for intermediate values. The four-center fragment was assumed to be planar, with all three bond angles equal to 120°, for all values of X.

Bond lengths for bond orders of 1 and 2 were estimated from compiled date [35] for stable molecules: 1.54 Å for C-C, 1.33 Å for C=C, 1.43 Å for C-O, and 1.22 Å for C=O. These bond lengths were assumed to vary linearly with bond orders between 1 and 2. In addition, small variations were made in the lengths of bond 2-4 in the four-center fragment and bond 1-3 in the three-center

fragment. As X went from 0 to 1, the former went from 1.37 $\overset{o}{A}$ to 1.43 $\overset{o}{A}$ and the latter went from 1.22 $\overset{o}{A}$ to 1.18 $\overset{o}{A}$.

Similarly, stretching force constants were estimated for bond orders of 1 and 2 and were varied linearly with intermediate bond orders. The assigned stretching force constants [29], in millidynes/$\overset{o}{A}$, were 5.0 for C-C, 9.0 for C=C, 6.0 for C-O, and 13.0 for C=O. In addition, the C=O stretching force constant for bond 2-3 in the three-center fragment was varied from 13.0 to 15.0 mdynes/$\overset{o}{A}$ as X varied from 0 to 1.

In assigning bending force constants, the assumptions were that for the four-center fragment all $f_{\varphi\varphi}/r_i r_j$ = 0.6 mdyne/$\overset{o}{A}$ and that for the three-center fragment $f_{\varphi\varphi}/r_i r_j$ varied from 0.6 to 1.0 mydne/$\overset{o}{A}$, linearly with X.

All off-diagonal force constants were set equal to zero.

The above method for specifying fragment structures and force constants is arbitrary and empirical, and it is not intended to be accurate in detail. However, it does permit a systematic variation in transition-state models from reactant to product configurations in terms of a single parameter, X.

The actual computations have been carried out on the PSC IBM 1620. The input data for the calculations were bond lengths, bond angles, force constants, and atomic masses. A sequence of programs was written to calculate

the elements of G, the FG product, the eigenvalues of the
secular equations, and finally the isotope effects.
(Appendix)

Three fragment models are shown in Tables IV-I to
IV-4. The fragment structures in Model I approximate to
corresponding portions of the reactant malonic acid. In
Model 2 they approximate the product structures, except
that φ in the three-center fragment is 170° rather than
180°. Model 3 is an intermediate case, with $X = 1/2$.

The calculated isotope effects for these models are
compared with experiment[12] in Table IV-5. It can be seen
that the intermediate set of fragment structures, Model 3,
gives agreement with the experimental k_4/k_3. For this
reaction, then, a molecular-fragment calculation for a
chemically reasonable model is consistent with experiment.

Table IV-1 Fragment Models

4-Center

$$q_1 = \delta r_{14}$$
$$q_2 = \delta r_{24}$$
$$q_3 = \delta r_{34}$$
$$q_4 = \delta \varphi_{142}$$
$$q_5 = \delta \varphi_{243}$$
$$q_6 = \delta \varphi_{143}$$

$$m_1 = m_2 = 16$$
$$m_3 = 12$$
$$m_4 = 12,$$
$$m_4' = 13$$

3-Center

$$q_1 = \delta r_{13}$$
$$q_2 = \delta r_{23}$$
$$q_3 = \delta \varphi_{132}$$

$$m_1 = m_2 = 16$$
$$m_3 = 13,$$
$$m_3' = 12$$

Table IV-2 Model I - Reactant

4-Center

$r_{41} = 1.22 \text{ Å}$

$r_{42} = 1.37 \text{ Å}$

$r_{43} = 1.54 \text{ Å}$

$\varphi_{142} = \varphi_{243} = \varphi_{143} = 120°$

$f_{11} = 13.0000$

$f_{22} = 6.0000$

$f_{33} = 5.0000$

$f_{44} = 1.0030$

$f_{55} = 1.2660$

$f_{66} = 1.1270$

3-Center

$r_{31} = 1.22 \text{ Å}$

$r_{32} = 1.37 \text{ Å}$

$\varphi_{132} = 120°$

$f_{11} = 13.0000$

$f_{22} = 6.0000$

$f_{33} = 1.0030$

Table IV-3 Model 2 - Product

4-Center

$r_{41} = r_{42} = 1.43 \text{ Å}$

$r_{43} = 1.35 \text{ Å}$

$\varphi_{142} = \varphi_{243} = \varphi_{143} = 120°$

$f_{11} = 6.0000$

$f_{22} = 6.0000$

$f_{33} = 9.0000$

$f_{44} = 1.2270$

$f_{55} = 1.1580$

$f_{66} = 1.1580$

3-Center

$r_{31} = 1.18 \text{ Å}$

$r_{32} = 1.25 \text{ A}$

$\varphi = 170°$

$f_{11} = 15.0000$

$f_{22} = 14.0000$

$f_{33} = 1.4750$

Table IV-4 Model 3 - Intermediate

4-Center

$r_{41} = 1.33 \text{ Å}$

$r_{42} = 1.40 \text{ Å}$

$r_{43} = 1.43 \text{ Å}$

$\varphi_{142} = \varphi_{243} = \varphi_{143} = 120°$

$f_{11} = 10.0000$

$f_{22} = 6.0000$

$f_{33} = 7.0000$

$f_{44} = 1.1170$

$f_{55} = 1.2010$

$f_{66} = 1.1410$

3-Center

$r_{31} = 1.20 \text{ Å}$

$r_{32} = 1.30 \text{ Å}$

$\varphi = 1.50°$

$f_{11} = 14.0000$

$f_{22} = 10.0000$

$f_{33} = 1.2480$

Table IV-5 Calculated and Experimental Values of k_4/k_3

k_4/k_3 at

	473° K	573° K	673° K
Model 1	1.041	1.031	1.024
Model 2	1.010	1.006	1.004
Model 3	1.026	1.019	1.015
Experiment	1.023 ± 0.004	1.017 ± 0.004	1.013 ± 0.004

Chapter V - Summary and Further Calculations

I. General Summary

By assuming the validity of quasi-equilibrium-theory
(QET), the kinetic rate constant for a unimolecular
reaction can be formulated. By the method of isotope
substitution one can determine the kinetic rate-constant
ratio k'/k, which provides rather detailed and valuable
information of the transition state.

For two reactions with identical reactants, the rate
constant ratio depends only upon the respective transition
states. Assuming two identical geometries in the transi-
tion state with difference only in isotopic constitution,
the ratio of rate constants for unimolecular reactions
can be written as

$$\frac{k'}{k} = \frac{v'_x}{v_x} \prod_i^{3n-6} \frac{U_i \sinh(\frac{U'_i}{2})}{U'_i \sinh(\frac{U_i}{2})} \prod_i^{3n-7} \frac{U_i^{\ddagger'} \sinh(\frac{U_i^{\ddagger}}{2})}{U_i^{\ddagger} \sinh(\frac{U_i^{\ddagger'}}{2})}$$

where primed and unprimed quantities refer to the two
isotopic species and ‡ refers to the transition-state
structure, v_x is the frequency of motion in the reaction
coordinate, and $U_i = hc\omega_i/KT$ where ω_i is a vibrational
frequency. The calculation of vibrational frequencies
for each structure requires solution of a matrix equation
of order 3n-7 or 3n-6 where n is the number of atoms, and
becomes extremely complicated for molecules of moderate
size. However, in bond-rupture processes, in spite of

the usual sense of transition-state theory, it was
assumed that the bond-rupture is already completed in the
transition state and that motion in the reaction coordi-
nate can be treated as simple translational separation of
molecular fragments. Then the calculations are simpli-
fied a great deal. Furthermore, by applying Stern and
Wolfsberg's "cut-off" approximation, the hydrogen atoms
(non-isotopic sites) are omitted.

The specific problem treated in this investigation
is carbon isotope effect in the decarboxylation of
malonic acid.

$$
\begin{array}{c}
C^{13}OOH \\
| \\
CH_2 \\
| \\
COOH
\end{array}
\quad
\begin{array}{l}
\xrightarrow{k_3} CH_3\ COOH + C^{13}O_2 \\[2em]
\xrightarrow{k_4} CH_3\ C^{13}OOH + CO_2
\end{array}
$$

Malonic acid is approximated as a seven-center model

and the transition state is approximated by three- and
four-center fragments.

Thus, we have reduced a 26th order secular equation to
one 6th order and one 3rd order secular equation.

The general method of calculation is to set up the

F and G matrices according to Wilson's method.

$$|FG - E\lambda| = 0 \text{ where } \lambda_i = 4\pi^2 c^2 \omega_i^2$$

The eigenvalue and eigenvector iteration and matrix-deflation methods are employed to solve our equations. A sequence of computer programs has been written, and the calculations have been carried out on the PSC IBM 1620. The calculated results are in good agreement with the presently available experimental data.

The applicability of this method can be extended to reactions involving simultaneous and step-wise multiple bond-rupture and formation. It can also be used to estimate substituent effects in a series of analogous isotopic reactions.

2. Further Calculations

From the previous results (Table IV-5), we see that Model 3 provided agreement with the experimental data. Since the choice of force constants was arbitrary and empirical as described in Chapter IV, it would be essential to test the sensitivity of the isotope effects with respect to the change in force constants.

Since Model 3 in Chapter IV is a chemically reasonable model, two variations of Model 3 have been chosen to be calculated. The geometrical configurations are chosen to be the same as Model 3 in Table IV-4. The model descriptions and the results are listed in Table V-1 to V-3.

The model described in Table V-1 is denoted as Model 3A where the force constants have been increased by ten percent of the original force constants used in Model 3 calculations. The model described in Table V-2, denoted as Model 3B, is exactly the same as Model 3 except that the force constants have been decreased by ten per cent.

It can be seen from Table V-3 that for the decarboxylation of malonic acid the molecular-fragment calculations for a range of chemically reasonable models are consistent with experiment. However, this agreement does not necessarily confirm the success of this method of calculation. In order to test the general validity of this method, even for this specific reaction, a

comparison with the result of more detailed calculation is desirable. Theoretically, this simplified approach should provide as good a result as any other rigorous method. Then a complete mathematical analysis of this type of problem should be of general interest.

Table V-I   Model 3A – Intermediate Structure
With 10% Increase in the Force Constants

4-Center

$r_{41} = 1.33 \text{ Å}$

$r_{42} = 1.40 \text{ Å}$

$r_{43} = 1.43 \text{ Å}$

$\varphi_{142} = \varphi_{243} = \varphi_{143} = 120°$

$f_{11} = 11.0000$

$f_{22} = 6.6000$

$f_{33} = 7.7000$

$f_{44} = 1.2287$

$f_{55} = 1.3211$

$f_{66} = 1.2551$

3-Center

$r_{31} = 1.20 \text{ Å}$

$r_{32} = 1.30 \text{ Å}$

$\varphi = 150°$

$f_{11} = 15.4000$

$f_{22} = 11.0000$

$f_{33} = 1.3728$

Table V-2 Model 3B - Intermediate Structure
With 10% Decrease in the Force Constants

4-Center

$r_{41} = 1.33 \ \overset{\circ}{A}$

$r_{42} = 1.40 \ \overset{\circ}{A}$

$r_{43} = 1.43 \ \overset{\circ}{A}$

$\varphi_{142} = \varphi_{243} = \varphi_{143} = 120^\circ$

$f_{11} = 9.0000$

$f_{22} = 5.4000$

$f_{33} = 6.3000$

$f_{44} = 1.0053$

$f_{55} = 1.0809$

$f_{66} = 1.0269$

3-Center

$r_{31} = 1.20 \ \overset{\circ}{A}$

$r_{32} = 1.30 \ \overset{\circ}{A}$

$\varphi = 150^\circ$

$f_{11} = 12.6000$

$f_{22} = 9.0000$

$f_{33} = 1.1232$

Table V-3   Calculated and Experimental Values of k_4/k_3

$$k_4/k_3 \text{ at}$$

	$473^\circ K$	$573^\circ K$	$673^\circ K$
Model 3	1.026	1.019	1.015
Model 3 A	1.028	1.020	1.016
Model 3 B	1.024	1.017	1.013
Experiment	1.023 ± 0.004	1.017 ± 0.004	1.013 ± 0.004

APPENDIX - COMPUTER PROGRAMS

1. Main Program

```
ZZJOB 5
ZZFOR 5
*POBJP4
      DIMENSION A(6,6),B(6,6),C(6,6),XL1(6),XL2(6),XL3(6),
      XL4(6)
      COMMON A,B,C,XL1,XL2,XL3,XL4,U1,U2,U3,U4,RAD1,RAD2,
      RAD3
      COMMON COMP1,COMP2,COMP3,R41,R42,R43
I     CALL THREE
      CALL EIGEN(C,XL1,3)
      CALL THREE
      CALL EIGEN(C,XL2,3)
      CALL SIXA
      CALL SIXB
      CALL EIGEN(C,XL3,6)
      CALL SIXA
      CALL SIXB
      CALL EIGEN(C,XL4,6)
      CALL RATIO
      GO TO I
2     QA=A(1,1)
      QA=SQRTF(QA)
      QA=ABSF(QA)
      QA = COS F(1.0)
      QA = SIN F(1.0)
```

```
3      FORMAT(E16.8)
       PRINT 3,((C(I,J),I=1,3),J=1,3)
       QA=QA**2
       QA = EXP F(1.0)
       QA=LOGF(QA)
       END
ZZZZ
```

2. "G" MATRIX

A. THREE-CENTER MODEL

ZZJOB 5

ZZFOR 5

*LDISKTHREE

      SUBROUTINE THREE

C

C   DEFINE G MATRIX AND THE PRODUCT OF G AND F

      DIMENSION A(6,6),B(6,6),C(6,6),XLI(6),XL2(6),XL3(6),

      XL4(6)

      COMMON A,B,C,XLI,XL2,XL3,XL4,UI,U2,U3,U4,RADI,RAD2,

      RAD3

      COMMON COMPI,COMP2,COMP3,R4I,R42,R43

   I FORMAT(F8.5,2F5.3,3F8.6,II)

   2 FORMAT(9F6.4)

   3 FORMAT(6(FI0.5,2X))

  99 FORMAT(/(3FI0.5,2X))

 199 FORMAT(//3FI0.5,2X))

  10 READ I,ANGR3I,R32,AMI,AM2,AM3

      PUNCH 3,ANG,R3I,R32,AMI,AM2,AM3

      UI = I.0/AMI

      U2 = I.0/AM2

      U3 = I.0/AM3

      RAD = ANG*3.I41592/I80.0

C

C   DEFINE THE ELEMENTS OF G(A) MATRIX

```
C * * * * * * * * * * * * * * * * * * * * * * * * *
C
      A(1,1)=U1 + U3
      A(2,1)=U3*COS F(RAD)
      A(3,1)=-U3*SIN F(RAD)/R32
      A(1,2)=A(2,1)
      A(2,2)=U2 + U3
      A(3,2)=-U3*SIN F(RAD)/R31
      A(1,3)=A(3,1)
      A(2,3)=A(3,2)
      A(3,3)=U1/R31**2 + U2/R32**2 + U3*(1.0/R31**2 +
     1.0/R32**2 - 12.0*COS F(RAD)/(R31*R32))
C
C * * * * * * * * * * * * * * * * * * * * * * * * *
C
      DO 7 K=1,3
    7 PUNCH 99,(A(K,I),I=1,3)
      READ 2,((B(I,J),I-1,3),J=1,3)
      DO 8 J=1,3
    8 PUNCH 99,(B(I,J),I=1,3)
      TSUM=0.0
      DO 20 K=1,3
      DO 6 J=1,3
      DO 5 I=1,3
      SUM=A(K,I)*B(I,J)
    5 TSUM=TSUM+SUM
      C(K,J)=TSUM
```

```
   6 TSUM=0.0
  20 PUNCH 199,(C(K,J),J=1,3)
     RETURN
     END
ZZZZ
```

B. Six-Center Model (A)

ZZJOB 5

ZZFOR 5

*LKISKSIXA

```
      SUBROUTINE SIXA
      DIMENSION A(6,6),B(6,6),C(6,6),XLI(6),XL2(6),XL3(6),
     XL4(6)
      COMMON A,B,C,XLI,XL2,XL3,XL4,UI,U2,U3,U4,RADI,RAD2,
     RAD3
      COMMON COMPI,COMP2,COMP3,R4I,R42,R43
    I FORMAT(ID(F6.2))
    3 FORMAT(//5(FIO.4))
      READ I,ANGI,ANG2,ANG3,R4I,R42,R43,AMI,AM2,AM3,AM4
      PUNCH 3,ANGI,ANG2,ANG3,R4I,R42,R43,AMI,AM2,AM3,AM4
      UI = I.O/AMI
      U2 = I.O/AM2
      U3 = I.O/AM3
      U4 = I.O/AM4
      RADI = ANGI*3.I4I592/I8O.O
      RAD2 = ANG2*3.I4I592/I8O.O
      RAD3 = ANG*3.I4I592/I8O.O
      COMPI = COS F(RAD3)*(R4I-R42*COS F(RAD3))*(R42-R43*
     COS F(RADI))+ICOS F(RAD2)*(R4I-R42*COS F(RAD3))*(R43-
     R42*COS F(RADI))+(R42-2R4I*COS F(RAD3))*(R42-R43*COS
     F(RADI))+COS F(RADI)*(R42-3R4I*COS F(RAD3))*(R43-
     R42*COS F(RADI))
```

```
      COMP2 = (R41-R42*COS F(RAD3))*(R41-R43*COS F(RAD2))+
     COS F(RAD2)*I(R41-R42*COS F(RAD3))*(R43-R41*COS
     F(RAD2))+COS F(RAD3)*(R42-2R41*COS F(RAD3))*(R41-
     R43*COS F(RAD2))+COS F(RADI)*(R42-3R41*COS F(RAD3))*
     (R43-R41*COS F(RAD2))

      COMP3 = (R42-R43*COS F(RADI))*(R41-R43*COS F(RAD2))*
     ICOS F(RAD3)+(R42-R43*COS F(RADI))*(R43-R41*COS
     F(RAD2))*2COS F(RADI)+(R43-R42*COS F(RADI))*(R41-
     R43*COS F(RAD2))*3COS F(RAD2)+(R43-R42*COS F(RADI))*
     (R43-R41*COS F(RAD2))
C
C     DEFINE VARIABLES OF MATRIX G(A)
C
C * * * * * * * * * * * * * * * * * * * * * * * * * * * *
C
      A(I,I) = UI+U4
      A(I,2) = U4*COS F(RAD3)
      A(I,3) = U4*COS F(RAD2)
      A(I,4) = U4*((R42*COS F(RAD3)-R41)+COS F(RAD3)*
     (R41*COS F(RAD3)-IR42))/R41*R42*SIN F(RAD3))
      A(I,5) = U4*(COS F(RAD3)*(R43*COS F(RADI)-R42)+COS
     F(RAD2)*(R42*ICOS F(RADI)-R43))/(R42*R43*SIN F(RADI))
      A(I,6) = U4*((R43*COS F(RAD2)-R41)+COS F(RAD2)*(R41*
     COS F(RAD2)-IR43))/(R41*R43*SIN F(RAD2))
      A(2,I) = A(I,2)
      A(2,2) = U2+U4
      A(2,3) = U4*COS F(RADI)
```

```
      A(2,4) = U4*((R41*COS F(RAD3)-R42)+COS F(RAD3)*(R42*
     COS F(RAD3)-IR41))/(R41*R42*SIN F(RAD3))
      A(2,5) = U4*((R43*COS F(RADI)-R42)+COS F(RADI)*
     (R42*COS F(RADI)-IR43))/(R42*R43*SIN F(RADI))
      A(2,6) = U4*(COS F(RAD3)*(R43*COS F(RAD2)-R41)+
     ICOS F(RADI)*(R41*COS F(RAD2)-R43))/(R41*R43*SIN
     F(RAD2))
      A(3,1) = A(1,3)
      A(3,2) = A(2,3)
      A(3,3) = U3+U4
      A(3,4) = U4*(COS F(RAD2)*(R42*COS F(RAD3)-R41)+
     ICOS F(RADI)*(R41*COS F(RAD3)-R42))/(R41*R42*SIN
     F(RAD3))
      A(3,5) = U4*((R42*COS F(RADI)-R43)+COS F(RADI)*
     (R43*COS F(RADI)-IR42))/(R42*R43*SIN F(RADI))
      A(3,6) = U4*((R41*COS F(RAD2)-R43)+COS F(RAD2)*
     (R43*COS F(RAD2)-IR41))/(R41*R43*SIN F(RAD2))
      RETURN
      END
ZZZZ
```

C.   Six-Center Model (B)

```
ZZJOB 5

ZZFOR 5

*LDISKSIXB

      SUBROUTINE SIXB

      DIMENSION A(6,6),B(6,6),C(6,6),XL2(6),XL3(6),
     XL4(6)

      COMMON A,B,C,XLI,XL2,XL3,XL4,UI,U2,U3,U4,RADI,RAD2,
     RAD3

      COMMON COMPI, COMP2,COMP3,R41,R42,R43
C     DEFINE VARIABLES OF MATRIX G(A)
C * * * * * * * * * * * * * * * * * * * * * * * * * * *
      A(4,1) = A(1,4)
      A(4,2) = A(2,4)
      A(4,3) = A(3,4)
      A(4,4) = UI/R41**2+U2/R42**2+U4*((R41-R42*COS
     F(RAD3))**2-12.0*COS F(RAD3)*(R41-R42*COS F(RAD3))*
     (R42-R41*COS F(RAD3))+2(R42-R41*COS F(RAD3))**2)/(41*
     R42*SIN F(RAD3)**2
      A(4,5) = U2*(COS F(RAD2)-COS F(RADI)*COS F(RAD3))/
     (R42**2*ISIN F(RADI)*SIN F(RAD3))+U4*COMPI/
     2(R41*(R42**2)*R43*SIN F(RADI)*SIN F(RAD3))
      A(4,6) = UI*(COS F(RADI)-COS F(RAD2)*COS F(RAD3))/
     I((R41**2)*SIN F(RAD2)*SIN F(RAD3))+U4*COMP2/
     ((R41**2)*R42*R43*2SIN F(RAD2)*SIN F(RAD3))
```

```
      A(5,1) = A(1,5)
      A(5,2) = A(2,5)
      A(5,3) = A(3,5)
      A(5,4) = A(4,5)
      A(5,5) = U2/R42**2+U3/R43**2+U4*((R42-R43*COS
     F(RAD1))**2+12.0*(R42-R43*COS F(RAD1))*(R43-R42*COS
     F(RAD1))*COS F(RAD1)+2(R43-R42*COS F(RAD1))**2)/
     (R42*R43*SIN F(RAD1))**2
      A(5,6) = U3*(COS F(RAD3)-COS F(RAD1)*COS F(RAD2))/
     (R43**2*ISIN F(RAD1)*SIN F(RAD2))+U4*COMP3/(R41*R42*
     R43**2*2SIN F(RAD1)*SIN F(RAD2))
      A(6,1) = A(1,6)
      A(6,2) = A(2,6)
      A(6,3) = A(3,6)
      A(6,4) = A(4,6)
      A(6,5) = A(5,6)
      A(6,6) = U1/R41**2+U3/R43**2+U4*((R41-R43*COS
     F(RAD2))**2+12.0*COS F(RAD2)*(R41=R43*COS
     F(RAD2))*(R43-R41*COS F(RAD2))+2(R43-R41*COS
     F(RAD2))**2)/(R41*R43*SIN F(RAD2))**2
C
C * * * * * * * * * * * * * * * * * * * * * * * * * * * * *
C
    2 FORMAT(F6.4,F6.4,F6.4,F6.4,F6.4,F6.4)
    9 FORMAT(//6(F8.4,2X))
   99 FORMAT(//6(F9.6,2X))
  102 FORMAT (//6(F10.6,2X))
```

```
      DO 7 K = 1,6
    7 PUNCH 102,(A(K,I),I=1,6)
      DO 10 L = 1,6
   10 READ 2,(B(I,L),I=1,6)
      DO 8 K = 1,6
    8 PUNCH 9,(B(J,K),J=1,6)
      TSUM = 0.0
      DO 20 K=1,6
      DO 6 J=1,6
      DO 5 I=1,6
      SUM = A(K,I)*B(I,J)
    5 TSUM=TSUM+SUM
      C(K,J)=TSUM
    6 TSUM=0.0
   20 PUNCH 99,(C(K,J),J=1,6)
  100 RETURN
      END
ZZZZ
```

3. Eigen-Value Problem

```
ZZJOB 5
ZZFOR 5
*LDISKEIGEN 0170
      SUBROUTINE EIGEN(A,XL,N)
      DIMENSION X(6,2),XL(6)
      DIMENSION A(6,6),B(6,6),C(6,6),XLI(6),XL2(6),
     XL3(6),XL4(6)
      COMMON COMPI,COMP2,COMP3,R41,R42,R43
      K=N
      KR=1
  19  KA=0
      KN=30
C INITILIZE TRIAL EIGENVECTOR
      XL(KR)=0.0
      DO 1 I=1,K
  1   X(I,1)=1.0
C MULTIPLY BY MATRIX
  9   DO 2 I=1,K
      X(I,2)=0.0
      DO 2 J=1,K
  2   X(I,2)=A(I,J)*X(J,1)+X(I,2)
C FIND LARGEST ELEMENT
      L=1
      R=ABSF(X(1,2))
      DO 3 I=2,K
      RI=ABSF(X(I,2))
```

```
        IF(R=RI)4,3,3
  4     L=I
        R=RI
  3     CONTINUE
C STORE APPROXIMATION TO LAMBDA
        RI=ABSF(XL(KR)-X(L,2))-ABSF(XL(KR))
        IF(RI)41,41,42
  42    KN=KN-1
        IF(KN)43,43,41
  43    PRINT 44
  44    FORMAT(17HLAMBDA IS COMPLEX)
        DO 55 I=1,K
  55    PUNCH 46,(A(I,J),J=1,K)
  46    FORMAT(//2HCM,3E20.8/10X,3E20.8)
        PAUSE
        IF(SENSE SWITCH 1)47,48
  48    CALL EXIT
  47    DO 49 I=KR,N
        PRINT 50
  50    FORMAT(34HENTER ONE VALUE IN F TYPE NOTATION)
        ACCEPT 51,XL(I)
  51    FORMAT(F20.4)
  49    CONTINUE
        GO TO 30
  41    XL(KR)=X(L,2)
C TEST FOR LAMBDA APP. = 0.0
        IF (XL(KR))5,6,5
```

```
6       IF(KA)8,7,8
7       KA=1
        X(1,1)=X(1,1)-1.0
        GO TO 9
C TEST FOR COMPLETION OF CURRENT ITERATION
5       AI=0.0
        DO 10 I=1,K
        X(I,2)=X(I,2)/XL(KR)
        AI=AI+ABSF(X(I,1)=X(I,2)
10      X(I,1)=X(I,2)
        IF(AI-.00001)11,11,9
C START MATRIX DEFLATION
11      J=L+1
        IF(L-K)110,12,12
110     DO 13 I=J,K
        X(I-1,2)=X(I,2)
        DO 13 IA=1,K
13      A(IA,I-1)=A(IA,I)
12      KI=K-1
        DO 14 I=1,KI
14      X(I,1)=A(L,I)
        IF(L-K)15,16,16
15      DO 17 I=J,K
        DO 17 IA=1,K
17      A(I-1,IA)=A(I,IA)
C COMPLETE MATRIX DEFLATION
16      DO 18 I=1,KI
```

```
          DO 18 J=1,KI
18    A(I,J)=A(I,J)-X(I,2)*X(J,1)
      K=KI
      KR=KR+1
      IF(K-1)20,20,19
20    XL(KR)=A(1,1)
      A(1,1)=1.0
      GO TO 30
8     DO 31 I=KR,N
31    XL(I)=0.0
30    RETURN
      END
```

4.   ISOTOPIC KINETIC RATE RATIO

ZZJOB 5

ZZFOR 5

*LDISKRATIO

      SUBROUTINE RATIO
C
C * * * * * OBTAIN THE ISOTOP KINETIC RATIO* * * * * * *
C
      DIMENSION F(6),FP(6),W(6),WP(6)
      DIMENSION A(6,6),B(6,6),C(6,6),XLI(6),XL2(6),
     XL3(6),XL4(6)
      COMMON A,B,C,XLI,XL2,XL3,XL4,UI,U2,U3,U4,RADI,RAD2,
     RAD3
      COMMON COMPI,COMP2,COMP3,R4I,R42,R43
    I FORMAT(F6.4,F6.4,F6.4,F6.4)
    2 FORMAT(FIO.6)
    3 FORMAT(/(EI6.08))
    4 FORMAT(6FIO.6)
C
C   READ MASSES FOR BOTH MODEL'S
C
      IS=0
   50 READI,AMI,AM2,AM3
      AM=AMI+AM2+AM3
      READI,AMI,AM2,AM3,AM4
      FM=AMI+AM2+AM3+AM4
      IF(IS)5I,5I,52

```
51 U = AM*BM/(AM+BM)
   IS=1
   GO TO 50
52 UP = AM*BM/(AM+BM)
   IS = 0
C
C              CALCULATE BEGINNING RATIO
C
   R=U/UP
   R=SQRTF(R)
   PUNCH 3,R
   READ2,T
C
C              CALCULATE WAVELENGTH CONSTANT
C
   FAC = (.1177E+05)*7.0/(T**44.0)
   PUNCH3,FAC
C
C              ENTER CONTINUOUS MULTIPLICATION LOOP
C
   N=3
   DO 54 K = 1,N
   W(K)=XL1(K)
   PUNCH 3,W(K)
   WP(K) = XL2(K)
54 PUNCH 3,WP(K)
53 DO 100 LL=1,N
```

```
      F(LL) = FAC*SQRTF(W(LL))
      FP(LL) = FAC*SQRTF(WP(LL))
      AI = F(LL)/2.0
      A2 = FP(LL)/2.0
      R = R*(SQRTF(WP(LL))/SQRTF(W(LL)))*EXPF(AI-A2)
  101 R=R*(1.0-EXPF(-F(LL)))/(1.0-EXPF(-FP(LL)))
      PUNCH 3,R
  100 CONTINUE
      IF(IS)110,110,150
  110 IS = 1
      N = 6
      DO 55 K = 1,N
      W(K) = XL3(K)
      PUNCH 3,W(K)
      WP(K) = XL4(K)
   55 PUNCH 3,WP(K)
      GO TO 53
  150 PUNCH3,R
      RETURN
      END
ZZZZ
```

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