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# THEORY OF UNIMOLECULAR REACTIONS



# Theory of Unimolecular Reactions

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## Preface

IF WE regard chemical kinetics as a territory to be surveyed, and confine ourselves to the comparatively simple region of homogeneous dissociations of pure gases, we find that there are two well-established viewpoints. One is the activated-complex or Eyring viewpoint, situated on a saddle point. This commands a clear view of the problems of absolute calculations of reactions of fixed order. If, however, we are interested in dissociations of which the order is changing with concentration, we are usually driven back to a slightly older viewpoint, marked HKRR. These are the initials of Hinshelwood, Kassel, Rice, and Ramsperger, who developed "collisional" theories in which the change of a rate constant with concentration is seen as the result of competition between the processes of dissociation and collisional transfers of energy.

I have tried to establish an intermediate position, from which much of the territory commanded separately by the Eyring and HKRR viewpoints should be in range. For this purpose I have treated the molecule as a completely analyzed vibrating system, of which the time to dissociation is determined by the vibrational behavior, so that both the absolute rate constants and the relative effects of concentration become calculable. This is a purely mechanistic picture, with its own shortcomings but free at least of quasi-thermodynamics. It should be regarded not as supplanting but as supplementing and reconciling the older viewpoints. It involves incidentally an analysis of the behavior of sums of vibrations, which has bearings on problems outside the field of kinetics.

At a time when this theory was attracting some practical applications and a need was felt for a connected account, I was fortunate in being invited to spend a semester at Cornell University and to give there an extensive series of lectures, on which this monograph is based. I am deeply indebted to the Baker Laboratory of Chemistry at Cornell

University for support and hospitality, to the United States government for a Fulbright travel grant and also to the University of Leeds. In Ithaca I owe particular thanks to F. A. Long and Mildred Moakley for their hospitality, and to those who turned out on many snowy nights to listen and criticize. I am indebted also to Harvard University and to Professor G. B. Kistiakowsky there for hospitality, and to some fifteen other United States and Canadian institutions and many kind people in them.

My indebtedness to particular scientists will be apparent from the text, but I owe particular gratitude to F. S. Dainton, H. S. Johnston, K. J. Laidler, and A. F. Trotman-Dickenson for long-continued encouragement. Useful criticisms of parts of the text have been made by E. F. Caldin, K. J. Ivin, M. Kac, M. S. Longuet-Higgins, B. Widom, and M. Wolfsberg. For essential help with the typescript, diagrams, and proof reading, I am greatly obliged to Margaret Turner, N. F. M. Henry, and R. J. R. Hayward respectively.

Some corrections of textual details have been made as a result of conversations at a symposium held last month in the Naval Research Laboratory of the University of Wisconsin. I am grateful to the Laboratory, its director Dr. J. O. Hirschfelder, and the Office of Ordnance Research for enabling me to participate in this.

N. B. S.

*Leeds, England*  
*May 12, 1959*

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# THEORY OF UNIMOLECULAR REACTIONS



## CHAPTER 1

# Introduction

THIS book is based on a course of lectures which I was invited to give in the Baker Laboratory of Cornell University in the fall semester of 1955–1956. The theme suggested was the development of theories of the rates of unimolecular reactions in gases, with particular reference to my own researches. In the present text I have amplified my account of the background material, particularly concerning molecular vibrations and the basic concepts of early but still useful rate theories; and I have added some new developments.

In this introduction the basic ideas are sketched, and in Section 1.2\* the whole argument is summarized. Some bibliographical notes are added in 1.3 concerning the course of the development.

### 1.1 NATURE AND SCOPE OF THE ARGUMENT

The thermal decomposition of a uniform gas is termed “unimolecular” if at a fixed temperature and sufficiently high values of the concentration  $c$ , the proportion  $k = -c^{-1}dc/dt$  decomposing per second is independent of  $c$ . This proportion  $k$ , the first-order rate “constant,” generally tends in fact to decrease at sufficiently low concentrations, and the reaction is then sometimes given the name “quasi-unimolecular”; but I shall usually include this characteristic behavior under the general name “unimolecular.”†

Unimolecular first-order reactions are not typical of small molecules, of two, three, or four atoms; a greater complexity or “atomicity” is

\* **Note on numbering of sections and formulas.** I denote the second section of Chapter 1 by 1.2. *Displayed formulas* are numbered (1), (2), (3), . . . in each separate chapter. Equation (79) of Chapter 3 (occurring in 3.6) is referred to, throughout that chapter, as (79); a reference to it in Chapter 5 is given as 3.6(79).

*Tables and figures* are numbered by the sections in which they appear; thus Table 3.8 and Figure 3.8 are in 3.8.

† A wider but more precise definition (which would be out of place here) is given in 2.1. Illustrations of the behavior of  $k$  as a function of concentration will be found in Fig. 8.3 (p. 174).

generally required. Now the increasing complexity and energy capacity of larger molecules are associated mainly with their vibrations; so we may suspect some connection exists between vibrations and unimolecular behavior.

This suspicion is strengthened by the observation that the complex vibrations of a polyatomic molecule may well cause a *time lag* between the receipt by collision of the high energy needed for dissociation, and the occurrence of dissociation. Such a time lag will explain unimolecular behavior; for at high concentrations the relatively frequent collisions will shuttle the molecules rapidly in and out of energized states, maintaining in this case an effectively steady population of highly energetic molecules, of which only a small proportion ( $-c^{-1}dc/dt$ ) arrives at dissociation. At lower concentrations the chances of dissociation are improved by the greater rarity of collisions; and ultimately the dissociations  $-dc/dt$  will be proportional to the number of collisions and so to  $c^2$ . Thus we have a first-order rate constant deserving the name at high concentrations (it will in future be written  $k^\infty$  to distinguish it from the variable value  $k$  of lower concentrations), with a decline toward a second-order reaction at very low concentrations.

The central question is: How well can we explain or predict the limiting value  $k^\infty$  and the declining value  $k$  in terms of a time lag related to molecular vibrations? As a useful lead,  $k^\infty$  was estimated by Polanyi and Wigner for the elementary representation of a molecule as a linear array of elastically linked equal masses; they assumed that decomposition occurred when some vital link became excessively stretched. The links of such an array, or the bonds or interatomic distances in a molecule, vibrate not as individual harmonic oscillators, but in a highly complicated way which can be broken down (to a close approximation in the molecular case) into a sum of *normal modes* of vibration. It is the separate normal modes that are harmonic; each has a characteristic frequency which it imparts to all the bonds. Thus decomposition occurs when the normal modes (with adequate energy) come sufficiently *into phase* to give the vital link or bond its critical stretch; and the time lag to dissociation is the time for this situation to arise. Polanyi and Wigner estimated the rate constant  $k^\infty$  from a particular estimate of this time lag.

It was at the suggestion of R. H. Fowler that I took up this sketch and developed it into the present picture. The main difficulty lay in finding a general formula for the average time interval (or its reciprocal, the average frequency) of the attainment of a critical high value by a sum of harmonic vibrations. Otherwise it was merely a matter of replacing Polanyi and Wigner's linear chain by any general (or par-

ticular) molecule, and assuming that decomposition occurs when the sum of the normal mode vibrations gives a critical deformation of some realistically chosen bond or internal dimension of the molecule. Knowing the vibrational characteristics of a particular gas and assuming only the value of the critical deformation (or equivalently the activation energy), we can then predict  $k^\infty$ ; the further assumption of an effective "collision diameter" gives also the general rate constant  $k$  as a function of the concentration; there are no other adjustable parameters to help in a case of disagreement with experiment.

After a survey of early theories and background material, the main text is devoted to this classical model and to a detailed comparison with transition-state or activated-complex theory. In the final chapters new rate theories are developed on classical and quantum models. These again are too simple to be fully realistic; but they may provide useful bases for further development.

## 1.2 SUMMARY

In this brief summary each subsequent chapter of the book is represented by a correspondingly numbered paragraph. The arrangement is much as in my Cornell lectures. Results or methods described here as "new" are nearly all unpublished and date from after those lectures.

2 *General concepts and earlier theories:* These two themes are closely interwoven. After an account of Lindemann's time-lag hypothesis (which was sketched in 1.1 above), there are formulations of a general rate constant  $k$ , on the basis of a set of energized molecular states 1, 2, 3, . . . with specific dissociation rates  $k_1, k_2, k_3, \dots$  (corresponding roughly to reciprocals of time lags). This is illustrated first by Hinshelwood's theory, with a single specific rate  $k_1$ , and later by Kassel's, in which the  $k_s$ s increase with the total energy of the molecule. Kassel's model, unlike Hinshelwood's, gives an "Arrhenius" form,  $k^\infty = A \exp(-B/T)$  with  $A$  and  $B$  constant; and I place between the accounts of the two models some new results concerning the restrictions imposed on a theory by requiring  $k^\infty$  to be of this form; these restrictions have implications also concerning the quasi-unimolecular behavior. In the final section Tolman's theorem on activation energy is discussed, and it is shown (newly but not unexpectedly) that, if the specific rate  $k_s$  increases with the energy of the activated molecule, the activation energy increases with concentration. We are concerned in the historical parts mainly with the relative rate  $k/k^\infty$ ; but there is a note near the end on Polanyi and Wigner's "vibrational" estimate of the absolute value of  $k^\infty$ , and this approach should be kept in mind through the next preparatory chapters.

3 *Molecular vibrations and normal modes:* This chapter is an essential preliminary to a vibrational model of dissociation, and the concepts and notations will be important later. The use of interatomic distances as internal coordinates is discussed, and illustrated by a new calculation of nitril chloride vibrations. Some of the analysis concerns a mean  $\nu$  of the vibration frequencies weighted with respect to the "amplitude factors" of a specified internal coordinate, and this brings up some new points on dynamically constrained motions and their frequencies.

4 *The average behavior of a sum of vibrations:* The problem here is the average frequency with which a given sum of vibrations rises to a specified value. This is closely related to problems in communication engineering and other fields, and so is given a separate account. The main formulas are an integral representation due to Kac (which is used in Chapter 5) and a new Fourier series form which is useful for numerical cases.

5 *Unimolecular first-order reactions on the classical harmonic model:* Treating a molecular internal coordinate as a sum of harmonic mode vibrations which disrupts when it reaches a critical value, we calculate the first-order constant  $k^\infty$  as the average frequency of this event for a Boltzmann distribution of the normal-mode energies (as affecting the amplitudes of the vibrations). The value found is  $\nu \exp(-E_0/\kappa T)$ , where  $\nu$  is the mean vibration frequency mentioned in 3, and  $E_0$  is the minimum energy for dissociation. A new calculation of the average specific reaction rate for molecules of given total energy is appended.

6 *Unimolecular first-order reactions and transition-state theory:* The formulation of  $k^\infty$  in Chapter 5 is now transformed into a flow over a critical boundary (corresponding to the breaking deformation) in coordinate-momentum phase space. This is very close to the basic model of the transition state; I take the opportunity here of giving a precise classical account of this, and of discussing also the transcription into quantum partition functions. The simplicity (or crudity) of my type of dissociation configuration, compared with the saddle-point potential of transition-state theory, gives a simplified picture of characteristics such as the frequencies of the activated complex; there is also a discussion of the effects of isotopic substitution. I include some calculations which were designed to test the effects of anharmonicity in my model; they are treated here as also giving a closer approach to the transition-state model.

7 *Theory of general and second-order rate constants:* The harmonic model of  $k^\infty$ , based as in Chapter 5 on the mean frequency of the critical stretch, is extended by a general method of Chapter 2 to give  $k$  at any

concentration. I first discuss very low concentrations, beginning with a demonstration, new but simple, that models with continuous energies do in fact give rates tending to a second-order law. My second-order rate constant is found to be smaller than Kassel's because of my exclusion of energy transfers between normal modes; here it seems that one should allow some transfer when the rarity of collisions leaves almost unlimited time for dissociation. We return after this to general values of  $k$ . An approximate representation of the relative decline  $k/k^\infty$  is found as a particular function (not to be interpreted as a Bessel function)  $I_{\frac{1}{2}(n-1)}(\theta)$ , where  $n$  is the number of vibration frequencies and the parameter  $\theta$  varies as the concentration  $c$ . Kassel's form of  $k/k^\infty$  for a molecule of  $n$  oscillators is rather roughly represented by  $I_{n-1}(\theta)$ , which makes an interesting contrast. Some new formulas are appended, on the approach of a rate constant to its limiting forms and the decline of activation energy with concentration.

8 *Numerical results and comparisons:* For the theory of the preceding chapter I give tables of  $I_n(\theta)$ , of the ratio  $\theta/c$ , and of the decline of activation energy. The general inferences are that the curve of  $\log k/k^\infty$  against  $\log c$  changes quite gradually toward a greater spread on the  $\log c$  axis as  $n$  increases; and that, the smaller  $n$  (or the simpler the molecule), the larger is the concentration at which the reaction approaches the first order; this concentration also depends, however, on vibrational characteristics and on the ratio  $E_0/\kappa T$  mentioned in 5 above. The theory is illustrated by a new calculation of the decomposition of nitril chloride, and there are discussions of the isomerization of cyclopropane and of more recent work.

9 *A new approach to rate theory:* In the previous chapters, as in other collisional theories, the incidence of dissociation of energized molecules has been assumed to be "random" (i.e., like the incidence of collisions), with a mean frequency corresponding to the reciprocal of the time lag. Here I discard this assumption and obtain incidentally what appears to be, formally at least, a valid extension of the transition-state formulation to quasi-unimolecular rates. For the harmonic or normal-mode model, the new theory demands a knowledge of the statistical distribution of time lags of a given (fixed amplitude) sum of vibrations. This is a mathematical problem sorely in need of a general solution. Enough progress is made to allow a fairly close estimate to be made of the new rate constant as a function of concentration and to indicate that the old assumption of "random" dissociation is not very bad.

10 *Quantum harmonic oscillator models:* The main model here is that of elements of a continuous probability distribution (in the coordi-

nate-momentum phase space representing the internal configuration of the molecule) flowing over a critical surface to dissociation. The distribution is based on the "statistical" distribution of the quantum normal-mode oscillators; that the flow can be treated classically is a consequence of the harmonic nature of the oscillators. This leads to an elegant formulation of general rate constants which, however, appears less satisfactory in its predictions than the previous classical and semiclassical models. A new feature here is the combination of this quantum model with the ideas of Chapter 9 to obtain a more general formulation. A deeper consideration of the role of total energy, and probably of anharmonic effects, is required to give this model a firmer basis.

### 1.3 HISTORY OF THE DEVELOPMENT

The first fifteen references at the end of this introduction are to my work on unimolecular theory and allied vibrational problems; corresponding or related chapters and sections of the present book are noted (in bold type) alongside the references. A few remarks on the development may be of interest.

The first version<sup>1</sup> of the high-concentration rate theory appeared in 1939. This contained the useful approximation given in **4.6** for the average frequency of peaks of a sum, but otherwise was cumbersome. I did not publish the extension to general-concentration rates<sup>2</sup> (although the results here were essentially correct) and was otherwise engaged from 1939 to 1945. When I saw about 1946 Kac's precise solution (**4.3**) of the vibrational sum problem, I hesitated in face of its apparent complexity; but when attacked it gave within the hour the precise formula of Chapter 5 for  $k^\infty$ , and this led me back to reaction kinetics.<sup>3</sup> Conversations with M. G. Evans and G. S. Rushbrooke and a correspondence with H. Pelzer<sup>4</sup> led me to produce a full account of the high-concentration theory, covering also a transition-state transcription and ideas of specific energy rates.<sup>5</sup> In between some work on sums of vibrations<sup>6,7</sup> and some preliminary trials on vibrations in terms of distance coordinates,<sup>8,9</sup> I gave an account of the theory of general rate constants (including low pressures and also degenerate vibrations)<sup>10</sup> and a detailed analysis of the isomerization of cyclopropane.<sup>11</sup>

At this stage the classical harmonic theory was fairly complete, and it was time to consider refinements of quantization and anharmonization, which are not so easy. I began with an overlong paper, which was broken up into the main quantum theory<sup>12</sup> of Chapter 10 and a review of specific energy rates and formulations,<sup>13</sup> the latter was accompanied

by a first attack on anharmonic classical theory.<sup>14</sup> The new formulation<sup>15</sup> in Chapter 9 was begun at Cornell. Relevant subsequent work has mostly been incorporated in this text. Two summaries of discussions<sup>16,17</sup> are listed, of which the former is of particular interest in connection with the theory.

**Other references.** There is a useful account of the present theory, and much other material, in Trotman-Dickenson's book,<sup>18</sup> and a review article by Johnston makes some good points concerning lines of development.<sup>19</sup> Texts I have found useful in general study are the books listed in the references following Chapter 2, together with Frost and Pearson.<sup>20</sup> For activated complex theory I have used Glasstone, Laidler, and Eyring,<sup>21</sup> but I have unduly neglected the relevant part of Eyring, Walter, and Kimball.<sup>22</sup>

**Neglected developments.** It is appropriate to end this introduction by mentioning some further sins of omission. (i) I have concentrated on theory, to the comparative neglect of experimental comparisons, although the comparisons made by H. S. Johnston and by F. K. Gill, K. J. Laidler, B. S. Rabinovitch, E. W. Schlag, and others have helped considerably toward filling this gap recently. There is still a large field here, for example, in the experimental work of Howlett, Maccoll, and others mentioned at the symposium,<sup>16</sup> that of Pritchard and others<sup>23</sup> on cyclobutane, and much other work on isotopic effects. These examples are cited because to a considerable extent they have been posed as a direct challenge to theory. (ii) I have not widened the model to include rotations and internal rotations, and with them a possible mechanical equivalent in this picture to "entropy of activation." (iii) There are many quantum theories which receive no attention in this book, such as that of Golden<sup>24,25</sup> and the stochastic theory of Montroll and Shuler,<sup>26</sup> which has interesting affinities with the present work. These last omissions are more pardonable, for it would be excessive to add any more theories into this present volume.

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References 1-15 are to the author; relevant sections of the present book are indicated on the right.

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## ERRATA

The dot in the expression  $\dot{Q}_1$  does not always appear when it should.

On pages 51 and 55 the first  $Q_1$  in equations (33), (34), and (62) should be  $\dot{Q}_1$ .

On pages 212 and 213 the second  $Q_1$  in equations (15), (18), and (19) should also be  $\dot{Q}_1$ .

[Slater, *Theory of Unimolecular Reactions*]



## CHAPTER 2

# General Concepts and Earlier Theories

THE years 1921 to 1928 saw the theory of unimolecular reactions advance from a rudimentary toward a plausible and realistic form. The main early theories are described here, with interpolated sections dealing with general aspects of the problem. The interpolations may be found to contain some unhistorically novel points of view; but the continuing use of the early theories and their mathematical simplicity make them a proper theme for thinking around the nature of the unimolecular rate problem.

In 2.1 unimolecular processes are defined in a way that includes "quasi-unimolecular" effects, or the change of order at lower concentrations. In 2.2 the history begins, with a note on Perrin's radiation hypothesis leading to an account of Lindemann's more fruitful hypothesis of a time lag between the collision-energization and the dissociation of the molecule. In 2.3 there are two formulations of general rates on this hypothesis; the conventional "steady state" method is supplemented by a simpler method based on the assumed random incidence of the time lag.

Hinshelwood's theory is described in 2.4 (together with some statistical-mechanical formulas which are also widely used in later parts). This theory indicated how the complexity of a polyatomic molecule provided a semiquantitative explanation of the maintenance of the first-order rate constant down to fairly low concentrations. The theory implied, however, too simple a relation of rate and concentration, and did not give a high-concentration rate constant  $k^\infty$  of the Arrhenius form,  $A \exp(-E_0/\kappa T)$ , favored by experimenters. In 2.5, being wise after the event, we find what restrictions the Arrhenius form places on theoretical models. These restrictions determine in particular the specific rate  $k_E$  of molecules of energy  $E$ , and so may sometimes determine also the manner of the decline of rate constant at low concentrations.

Kassel's theory is described (with Rice and Ramsperger's) in 2.6; there is here a molecule of  $n$  "oscillators," dissociating when internal interchanges carry a critical energy  $E_0$  into a particular oscillator. In the resulting Arrhenius rate constant the  $A$ -factor is interpretable as the mean frequency of these internal interchanges; the implications of this Arrhenius rate are discussed in some detail. Notes are added on the decline of the rate constant, and also on the quantum versions of the theory and their ultimate generalization.

In 2.7 attention is turned to Polanyi and Wigner's sketch of a theory of the magnitude of the Arrhenius  $A$ -factor, in terms of the phase interference of normal modes of vibration. As the following chapters develop this type of theory, there would be advantages in stopping the history at this point. But for completeness there is an account in 2.8 of Activation Energy; this includes Tolman's illuminating (but often misunderstood) theorem, and a general investigation of concentration effects.

## 2.1 DEFINITION OF A UNIMOLECULAR PROCESS

Attention is confined to gas reactions of an ideally pure and simple type. The reactions are to be "homogeneous," the containing walls providing merely the physical control of pressure and temperature, and no chemical effects. The gas is to begin as a single polyatomic species, raised to a suitable temperature at which the molecules proceed to break up or change form. We treat only of this initial dissociation (or isomerization or racemization); if further reaction processes follow speedily, this isolated calculation of the initial process (as a rate-determining step) can still be of value.

If  $c$  is the concentration of the original molecular species, the *first-order rate constant* of the dissociation is defined as the fraction dissociating per second, and will be called  $k_{\text{uni}}$  or simply  $k$ :

$$k \equiv k_{\text{uni}} \equiv -c^{-1}dc/dt. \quad (1)$$

Similarly the *second-order rate constant* will be called  $k_{\text{bim}}$  (I reserve the symbols  $k_1$  and  $k_2$  for a quite different meaning); this is defined as

$$k_{\text{bim}} \equiv -c^{-2}dc/dt. \quad (2)$$

If for fixed temperature and an appropriate range of concentration the first- or the second-order rate constant is truly constant, the reaction in this range is said to be of the first or the second order respectively; in other circumstances *both* the constants are variables.

\* This peculiar use of the word "constant" is so well established that I must adhere to it in the present work. Glasstone, Laidler, and Fyring use the better word "coefficient" for a variable  $k_{\text{uni}}$ . In many papers I have misleadingly

If throughout the available range of concentration the simple reaction described in the first paragraph were of the first or alternatively of the second order, we should not hesitate to follow an old usage and call it "unimolecular" or "bimolecular" respectively; and this is the basis of the subscripts in (1) and (2). There is, however, a logical distinction between the *molecularity* (describing the theoretical mechanism) and *order* (determined by the observations) of a reaction; this has been stressed, by Fowler and Guggenheim<sup>1</sup> for example, and is important in more complicated situations. A characteristic behavior of a simple dissociation is to be first order at high concentrations, with a decline of  $k_{\text{uni}}$  at lower concentrations. This type of *over-all* behavior will be regarded as the typical unimolecular process; it is sometimes called "quasi-unimolecular," although I shall use that term rather to describe the behavior in the region where  $k_{\text{uni}}$  is actually changing with concentration, and the reaction is of "intermediate order."

It may happen that  $k_{\text{uni}}$  increases with concentration and appears to be converging toward a limiting value at the highest available concentrations, although a limit is not reached; this also will be regarded as a unimolecular process. In such cases, at low concentrations the reaction may reach, or nearly reach, a second-order form, with  $k_{\text{bim}}$  tending to become constant. As, however, we shall be more concerned with the neighborhood of the first-order region, the "constant"  $k \equiv k_{\text{uni}}$  will be much more in evidence than  $k_{\text{bim}}$ .

## 2.2 EARLY THEORIES

Early experiments revealed the existence of first-order reactions, although the decline of rate constants with concentration was still to be found. The first-order rate constants were strongly dependent on the absolute temperature  $T$  and so were expressed in the Arrhenius form, which has continued to be adequate for most experimental work. This "Arrhenius" rate constant is

$$k = A \exp(-E_0/\kappa T) \equiv A \exp(-E'_0/RT) \text{ sec}^{-1}, \quad (3)$$

where  $A$  is a constant (often called the *frequency factor* or  $A$ -factor),  $\kappa$  and  $R$  denote Boltzmann's constant and the gas constant, and  $E_0$  (per molecule) or  $E'_0$  (per mole) is a large experimental energy-constant.

The temperature dependence of the rate constant clearly indicated that the dissociation of a molecule required it to have high energy. The independence of rate constant from concentration seemed to indi-

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called  $k_{\text{uni}}$  simply a "rate," whereas a rate almost universally means  $-dc/dt$  in kinetics. For example, on a loan of \$1,000 a kineticist would annually pay a rate of \$50, as long as the rate constant remained at 5 percent.

cate that this energy was not acquired by collision. This led F. Perrin to elaborate, between 1913 and 1919, the *radiation hypothesis*, according to which the dissociation follows the absorption by the individual molecule of radiation of frequency  $E_0/h$ , where  $h$  is Planck's constant. This process would make  $k$  independent of the concentration even at the lowest concentrations. The theory could, however, be discredited for other reasons, of which Daniels has given clear accounts.<sup>2,3</sup>

A main value of Perrin's idea was that it provoked a rival hypothesis from Lindemann.<sup>4</sup> This not merely dealt the radiation theory a mortal blow, but provided the basis of most subsequent theories; thus it deserves a full account.

If we abandon the agency of radiation, we are driven back on molecular collisions as the source of the high energy required for dissociation. As, however, the frequency of a molecule's collisions is proportional to the concentration  $c$ , then if dissociation immediately followed an energizing collision the reaction would be of the second order, contradicting (3). Lindemann here directed attention to the internal motions of the molecule; little was then known about them, save that they were likely to be complicated. These motions might at rare intervals carry a molecule into a configuration of precarious stability, and if it also happened to be rotating very fast it might burst centrifugally at one of these rare configurations. This idea of centrifugal bursting has been discarded, but the idea of rare unstable configurations retained. It carries the implication that not only must the molecule obtain high energy by collision, but also there ensues some *time lag* before the molecule reaches an internal configuration favorable to dissociation. The odds are that, in any reasonably dense concentration of gas, the molecule will suffer a further collision before it reaches this configuration; and the odds in that case are that this collision will remove its high energy and so its capacity for dissociating. In this way we have an almost steady state; molecules are shunted up and down the energy ladder much as in a nondissociating gas, with just a few happening to reach the dissociation configuration while energized. The number dissociating will then be proportional to the nearly steady number of energetic molecules present, and so to  $c$ ; and the reaction is of the first order.

At lower concentrations, however, the time between collisions will become longer compared with the time lag to dissociation, so that energized molecules will have more chance of dissociating. At low enough concentrations nearly all energized molecules will manage to dissociate, and the rate will tend toward the second order, like the collision frequency.

This low-concentration trend, predicted by Lindemann, was confirmed soon after, and has been assimilated into the definition of a unimolecular process in 2.1. Indeed, there seems to be no logical distinction between unimolecular and bimolecular dissociations of pure gases; the practical distinction is whether the time lag to dissociation is ever long compared with the collision interval at realizable concentrations of gas. If, as in the case of diatomic molecules, the time lag is relatively short even at the highest concentrations, we have "bimolecular" behavior. Unimolecular behavior is expected, therefore, to be a characteristic of more polyatomic gases.

### 2.3 GENERAL FORMALISM OF UNIMOLECULAR REACTIONS

Before theories based on Lindemann's idea are described, a general formalism will be enunciated which effectively underlies them all.

It is assumed from the start that molecules have to be put into some very special states (characterized by high energy) to be able to dissociate, and that the vast majority of molecules are at any time in a harmless condition quite incapable of dissociation. These special states are called, by some, "activated states." Others call them "energized," reserving the name "activated" for molecules which are not merely capable of dissociation but are on the verge of it. To avoid confusion I shall often call the special states *interesting states* (implying not that something is about to happen, but that it may happen sometime); the alternative name "energized states" will be used more when we are concerned with the collisional processes which make a molecule interesting. Let  $r=1, 2, 3, \dots$  be an enumeration of these states.\* The  $r$ th state may conventionally be characterized as having a mean lifetime  $\tau_r$  before dissociation. It will be shown later, however, that most theories do not in fact imply that an interesting molecule tends to exist for a certain time  $\tau_r$  and then dissociate. They imply rather that the lifetimes are *randomly distributed*, just as the times of free paths between collisions are distributed; so the relevant  $\tau_r$  is the mean of these random lifetimes, forming a fairly close analog to the mean time of a free path in collision theory. This being the case, we prefer to use the reciprocal of  $\tau_r$ , which is the *specific dissociation rate*  $k_r$ . We may define this directly by saying that for any short time  $\Delta t$ ,  $k_r \Delta t$  is the probability of dissociation, within  $\Delta t$ , of any  $r$ -state molecule; or  $k_r \Delta t$  is the fraction of existing  $r$ -state molecules dissociating within  $\Delta t$ .

**The high-concentration rate constant.** As in the sketch of Linde-

\* The states may not admit of a *discrete* enumeration and may in fact be specified by several parameters, continuous or discrete; but the corresponding generalizations of notation are unnecessary at the present stage.

mann's idea in 2.2, at sufficiently high concentrations the loss of molecules by dissociation is comparatively negligible, so that even "interesting" molecules will effectively be present in the same proportions as for a nondissociating gas at the same temperature. Let  $f_r$  denote the *statistical equilibrium probability* of the  $r$ th state in such a gas at this temperature; then of a total concentration  $c$  there are  $cf_r$  interesting molecules in this state; and, out of these,  $cf_r k_r \Delta t$  dissociate in a short time  $\Delta t$ . Thus the first-order rate constant has the constant value

$$k = k^\infty = \sum_r f_r k_r, \quad (4)$$

the sum being over all interesting states. The superscript  $\infty$  on  $k$  will denote the *limiting high-concentration rate constant* always.

**The general rate constant on the steady-state assumption.** I give first the customary method of extending the formulation from high- to general-concentration reactions.

If the concentration  $c$  is not very large, we may no longer assume that the equilibrium proportion  $f_r$  of  $r$ -molecules (i.e., molecules in the  $r$ -state) is present as for a nondissociating gas; for there may now be an appreciable depletion by dissociation. We assume, therefore, that the actual number of  $r$ -molecules is

$$cg_r \quad (5)$$

and proceed to determine  $g_r$  from the *steady-state assumption*, namely, that  $cg_r$  is effectively steady, with a balance between losses by dissociation and de-energizing collisions, and gains by collisional energizations. The loss of  $r$ -molecules by dissociation is, by (5) and the definition of  $k_r$ ,

$$cg_r k_r \text{ per second.} \quad (6)$$

The collisional effects require more discussion.

*The rate of de-energizations:* There are different kinds and definitions of "collision," depending on what type of molecular change or process is under consideration; for example, collisions affecting the molecule's momentum are relevant to viscosity but not to our present problem, where we require changes in the internal state of motion (vibration in particular) affecting the "interesting" condition for dissociation. For any specific type of collision, however, we may define a corresponding parameter  $\omega$ , called the *collision frequency per molecule*, such that the chance of a molecule making a collision of this sort in time  $\Delta t$  is

$$\omega \Delta t. \quad (7)$$

Moreover this collision frequency is for normal concentrations  $c$  proportional to  $c$ :

$$\omega = zc \quad (8)$$

where  $z$  is a temperature-dependent parameter.

At present we are interested in collisions that change the internal state relevant to dissociation; we may call these "vibrationally effective collisions." Now any such collision made by an "interesting" molecule is nearly always with one of the very numerous uninteresting molecules, and this will tend to make it less interesting. It is possible that a highly interesting molecule will require two or more such encounters before it completely loses interest; and theoretical developments of this type are under way.<sup>5</sup> We shall not introduce this complication, however, but merely define a single parameter  $\omega$ , as in (7) and (8), to represent the frequency of de-energizing collisions per molecule; thus the number of  $r$ -molecules de-energized per second is, by (5),

$$cf_r\omega. \quad (9)$$

It would be a complementary refinement to the one just mentioned to write here

$$\omega = \omega_r, \quad (10)$$

implying that the chance of de-energization varies with the degree of excitation. This refinement will not be pursued, and it is as well now to come down to earth by remarking that the  $\omega$  mostly used in reaction theory has been the plain kinetic theory frequency determined as for phenomena like viscosity. This is likely to be an overestimate, which may be gross for small molecules but not large for polyatomics.

*The rate of energizations:* In a nondissociating gas, or more realistically in the actual dissociating gas at very high concentration, the number of molecules in the  $r$ th state would be  $cf_r$ , the "equilibrium" number. Of these the number removed from this state per second by collision would be

$$cf_r\omega, \quad (11)$$

where (a vital point)  $\omega$  is the same parameter as occurred in (9). (If we introduced the refinement (10), then we should similarly have the same  $\omega_r$  here as there.)

By the principle of detailed balancing, this same number would be raised per second by collision from uninteresting states to the  $r$ -state.\* So far we have been talking about a fictitious nondissociating or high-concentration state of the gas; but the actual dissociating gas (at general concentration), although deficient in "interesting" molecules, may

\* With the model of multistage de-energization mentioned earlier, we should of course have to introduce corresponding complications in the argument here on energization.

be assumed to possess essentially its full complement of uninteresting molecules in their various uninteresting states. Collisions between these will have the same effect as in the equilibrium gas—for they do not know the “doom” that awaits them if collision renders them interesting.\* Thus the number of collision-energizations in the actual gas is as in the artificial or high-concentration gas; and this (as at the beginning of this paragraph) is given by (11).

The argument presented here is essentially that of Rice and Ramsperger and of Kassel, and there are some useful supporting calculations in Kassel's book.<sup>6</sup> It is important to realize, in contradiction to some more recent formulations, that we do not introduce two separate parameters for energization and de-energization rates; a single collision parameter  $\omega$  (or a single set  $\omega_r$ ) suffices.

*Completion of the steady-state formulation:* We can now determine  $g_r$  by equating the rate of gain of  $r$ -molecules, (11), to the sum of the losses, (9) and (6):

$$c\omega f_r = c(\omega + k_r)g_r. \quad (12)$$

Thus

$$g_r = \omega f_r / (\omega + k_r). \quad (13)$$

The total number of dissociations per second is  $c \sum g_r k_r$ , so that the *first-order rate constant* defined as in (1) is

$$k = \sum g_r k_r \quad (14)$$

$$= \sum \omega k_r f_r / (\omega + k_r). \quad (15)$$

At high concentrations,  $\omega \rightarrow \infty$ , and  $k$  approaches the limiting first-order form  $k^\infty$  of (4). At low concentrations  $\omega \rightarrow 0$ . The behavior of (15) in this case requires closer examination (see 7.2 below), but it is natural to assume that (15) tends to the form

$$k \approx \omega \sum f_r, \quad (16)$$

which represents a second-order rate. The second-order rate constant (2) is, with  $\omega = zc$  as in (8),

$$k_{\text{bin}} = z \sum f_r. \quad (17)$$

\* The allusion here is to Thomas Gray's lines:

“Alas! regardless of their doom  
The little victims play!  
No sense have they of ills to come  
Nor care beyond to-day.”

**A direct formulation of the general rate.** The following short method avoids the use of the  $g_r$  of (5) and will lead later to important developments.

An  $r$ -molecule is liable to two independent random fates, dissociation and de-energization, which have the respective probabilities  $k_r\Delta t$  and  $\omega\Delta t$  of occurring in time  $\Delta t$ . As will be shown below, it follows that the *absolute* probability (not "per unit time") that an  $r$ -molecule will dissociate, rather than be de-energized, is

$$k_r/(\omega + k_r). \quad (18)$$

Now the number of  $r$ -molecules formed per second is (11), so that the number dissociating per second is

$$c\omega k_r f_r / (\omega + k_r).$$

Summing over  $r$  and dividing by  $\rho$ , we find that the rate constant  $k$  is again given by (15).

*The proof of (18):* Let  $p(t)$  be the probability that an  $r$ -molecule suffers *no* collision in the time interval  $(0, t)$ . The probability of no collision in the interval  $(0, t + \Delta t)$  may then be expressed in two ways, namely,

$$\begin{aligned} p(t + \Delta t) &= p(t) + (dp/dt)\Delta t \\ &= p(t) \{1 - \omega\Delta t\}. \end{aligned}$$

In the last form  $\omega\Delta t$  represents the probability of a collision in time  $(t, t + \Delta t)$ , embodying here the hypothesis of random incidence; and  $1 - \omega\Delta t$  represents the probability of no collision in  $(t, t + \Delta t)$ . From this equation

$$dp/dt = -\omega p(t).$$

Hence, since  $p(0) = 1$ ,

$$p(t) = e^{-\omega t}. \quad (19)$$

If the incidence of dissociation is similarly assumed to be random, the chance that the  $r$ -molecule does *not* dissociate in the interval  $(0, t)$  is

$$\exp(-k_r t). \quad (20)$$

Thus the probability that the molecule does dissociate in the interval  $(t, t + \Delta t)$  is the chance of no previous collision or dissociation in  $(0, t)$ , multiplied by  $k_r\Delta t$ , namely,

$$\exp\{-(\omega + k_r)t\} k_r \Delta t. \quad (21)$$

Hence the absolute probability that the molecule does dissociate some-time between  $t=0$  and  $\infty$  is

$$\int_0^{\infty} \exp \{ -(\omega + k_r)t \} k_r dt, \quad (22)$$

which yields the result (18).

This elementary "free path" discussion emphasizes the point that the standard form (15) of general rate constant contains an implicit or explicit assumption that dissociation has random incidence. The validity of this assumption will be discussed further at a later stage.

#### 2.4 HINSHELWOOD'S THEORY AND SOME RELATED STATISTICS

Hinshelwood's theory<sup>7</sup> may be regarded as the first major development of Lindemann's idea, stressing the role of the complexity of the molecule (that is, of its many degrees of freedom) as affecting the concentration at which the unimolecular rate constant declines. Since its inception in 1926 the theory has continued in use for the estimation of the effective complexity from the decline of rate constant.

The basic assumption of the theory is that a molecule must possess a certain total internal energy  $E_1$  to be able to dissociate; and if it has this energy or more, it has a specific dissociation rate  $k_1$  independent of the amount of excess energy. In the language of 2.3, molecules have just one "interesting" state  $r=1$ , with a fixed but unknown  $k_1$ . Thus if  $f_1$  denotes the equilibrium (or high-concentration) proportion of molecules with energy at least  $E_1$ , the high-concentration and general rate constants (4) and (15) are

$$k^{\infty} = k_1 f_1, \quad k = \omega k_1 f_1 / (\omega + k_1). \quad (23)$$

Eliminating  $f_1$  gives

$$k^{\infty}/k = 1 + (k_1/\omega). \quad (24)$$

Since for fixed temperature the collision frequency  $\omega$  is proportional to the concentration  $c$  or pressure  $p$ , this implies that the plot of  $1/k$  against  $1/c$  is a straight line. This result can obviously be generalized to the form:

*Any theory dividing molecules into just two classes, those incapable of dissociation, and those capable and having a fixed specific rate, gives a linear relation between  $1/k$  and  $1/c$ .* (25)

Such a linear relation is not generally obeyed by more recent and accurate experimental measurements; so the division of molecules into just two classes has not proved adequate. But to see the usefulness

of Hinshelwood's theory in estimating orders of magnitude, we must examine the parameter  $f_1$  in (23). As a preparatory step some statistical mechanical results will be given which will be widely used later.

**Statistical results.** Some general statistical results are stated first, and then some simpler forms directly relevant to the present work.

For an assembly, at temperature  $T$ , of  $N$  nearly independent classical systems (or molecules), each with Hamiltonian energy  $H(q_1, \dots, p_n)$ , the proportion having values  $q_1$  to  $q_1+dq_1, \dots, p_n$  to  $p_n+dp_n$  of the general coordinates and momenta is

$$dN/N = \exp \left\{ -H(q_1, \dots, p_n)/\kappa T \right\} dq_1 \dots dp_n / \Phi, \quad (26)$$

where the *phase integral*  $\Phi$  is

$$\Phi \equiv \Phi(T) = \int \dots \int \exp(-H/\kappa T) dq_1 \dots dp_n, \quad (27)$$

integrated over the full allowed range of the variables. If we seek the proportion having  $p_1$ , say, in an assigned range irrespective of the other variables, we integrate (26) over those variables. If, for example,  $q_1$  is absent from  $H$ , and  $p_1$  occurs only in a term  $\epsilon_1 = \beta p_1^2$  of  $H$  (corresponding to a free rotational coordinate), then the proportion having  $\epsilon_1$  in the range  $\epsilon_1$  to  $\epsilon_1+d\epsilon_1$  is found to be

$$(\pi \kappa T \epsilon_1)^{-\frac{1}{2}} e^{-\epsilon_1/\kappa T} d\epsilon_1. \quad (28)$$

More generally, if a group of coordinates  $q_1, q_2, \dots$  and their momenta  $p_1, p_2, \dots$  appear in  $H$  only as a set of squared terms  $E = \beta_1 q_1^2 + \dots + \beta_1' p_1^2 + \dots$ , where  $E$  is not necessarily the whole of  $H$ , and if there are in all  $m$  squared terms in this set, then the proportion of systems having energy  $E$  to  $E+dE$  in this set is

$$f(E)dE = (E/\kappa T)^{\frac{1}{2}m-1} e^{-E/\kappa T} dE / \left\{ \kappa T \Gamma\left(\frac{1}{2}m\right) \right\}, \quad (29)$$

where the last factor is the Gamma function. The result (28) is the case  $m=1$  of (29).

We now build up some simpler forms. For an assembly of *simple harmonic oscillators* (corresponding to  $m=2$  in (29)), the proportion having energy  $\epsilon$  to  $\epsilon+d\epsilon$  is

$$e^{-\epsilon/\kappa T} d\epsilon / \kappa T. \quad (30)$$

If the molecules are each equivalent to a set of  $n$  simple oscillators with energies  $\epsilon_1, \epsilon_2, \dots, \epsilon_n$ , the proportion having simultaneously energies  $\epsilon_1$  to  $\epsilon_1+d\epsilon_1, \dots, \epsilon_n$  to  $\epsilon_n+d\epsilon_n$  in their respective oscillators is a product of expressions of the form (30), and so is

$$e^{-E/\kappa T} d\epsilon_1 \dots d\epsilon_n / (\kappa T)^n, \quad (31)$$

where

$$E = \epsilon_1 + \cdots + \epsilon_n \quad (32)$$

is the total energy (only vibrational energy being counted here) of the molecule.

We observe next that (with all the  $\epsilon_i$  always positive)

$$\begin{aligned} \int_{\sum \epsilon_i \leq E} \cdots \int d\epsilon_1 \cdots d\epsilon_n &= \int_0^E d\epsilon_1 \int_0^{E-\epsilon_1} d\epsilon_2 \cdots \int_0^{E-\epsilon_1 \cdots -\epsilon_{n-1}} d\epsilon_n \\ &= E^n/n! \end{aligned} \quad (33)$$

so that for the range

$$E < \sum \epsilon_i < E + dE \quad (34)$$

we have

$$\int \cdots \int d\epsilon_1 \cdots d\epsilon_n = E^{n-1}dE/(n-1)! \quad (35)$$

The equilibrium proportion of molecules with total energies  $E$  to  $E+dE$  is the integral of (31) over the range (34) and is therefore, by (35),

$$f(E)dE = (E/\kappa T)^{n-1} e^{-E/\kappa T} (dE/\kappa T)/(n-1)! \quad (36)$$

This is also the proportion of systems having this energy in any  $2n$  square terms, as is seen from (29); but the present method of reaching the result is useful and simple.

**Continuation of the discussion of Hinshelwood's theory.** In Hinshelwood's theory the molecular energy relevant to dissociation is comprised in a number of square terms which for convenience we take to be even; if the number is  $2n$ , this is as if the molecule comprised  $n$  vibrational freedoms. The quantity  $f_1$  in the rate constants (23) is the equilibrium proportion with energies  $E$  exceeding  $E_1$ ; so this is the integral of (36) from  $E_1$  to infinity. Thus

$$f_1 = e^{-b_1} \{ b_1^{n-1}/(n-1)! + b_1^{n-2}/(n-2)! + \cdots + 1 \}, \quad (37)$$

where

$$b_1 \equiv E_1/\kappa T. \quad (38)$$

Usually  $b_1$  is around 50 and  $n$  around 10, so that the first term of (37) gives the order of magnitude of  $f_1$ .

By (23), Hinshelwood's high-concentration rate constant  $k^\infty$  is  $k_1 f_1$ , which differs from the Arrhenius form (3) because of the bracketed factor in (37). In practice the empirical constant  $E_0$  in (3) is deter-

mined from measurements of  $k^\infty$  at different temperatures by means of the formula (compare 2.8 below)

$$E_0 = \kappa T^2 d \ln k^\infty / dT, \quad (39)$$

which is true if (3) is accurately true. The corresponding gradient for the rate constant  $k^\infty = k_1 f_1$  is  $\kappa T^2 d \ln f_1 / dT$ . If we equate this to (39) we obtain the relation

$$E_0 = E_1 / \{1 + (n-1)/b_1 + \dots + (n-1)!/b_1^{n-1}\}. \quad (40)$$

Using this relation to define  $E_1$  in terms of  $E_0$  ensures that  $k^\infty = k_1 f_1$  will have the correct temperature gradient, so that it may be identified with (3) over at least a small range of temperature. It will be observed that, if  $E_0/(n-1)\kappa T$  is reasonably large, the *approximate* solution of (40) is

$$E_1 = E_0 + (n-1)\kappa T. \quad (41)$$

We may now see how Hinshelwood's theory can be used to estimate  $n$ , representing the "effective complexity" of the molecule. For a given temperature  $T$ , let  $c_{50}$  be the concentration at which the rate constant  $k$  has fallen to 50 percent of the high-pressure value  $k^\infty$ , and let

$$\omega_{50} = Zc_{50} \quad (42)$$

(compare (8)) be the corresponding collision frequency. Then by (24)

$$2 = k^\infty/k = 1 + k_1/\omega_{50},$$

so that

$$k_1 = \omega_{50} = Zc_{50}. \quad (43)$$

Thus the previously unknown  $k_1$  (introduced in the second paragraph of this section) is now determined as the collision frequency at which the rate constant is halved. Equating the experimental high-concentration rate constant (3) to the theoretical rate constant  $k_1 f_1$  gives now, by (37),

$$k^\infty = A e^{-E_0/\kappa T} = \omega_{50} e^{-b_1} \{b_1^{n-1}/(n-1)! + \dots + 1\}, \quad (44)$$

where  $b_1 \equiv E_1/\kappa T$  is to be determined from (40).

With  $A$ ,  $E_0$ , and  $c_{50}$  known from experiments on a particular gas, and  $\omega_{50}$  estimated from  $c_{50}$  by a kinetic collision formula, we may now regard (44) as an equation for  $n$ . If, for example,  $A = 10^{14} \text{ sec.}^{-1}$ ,  $E_0/\kappa T = 40$ ,  $\omega_{50} = 10^8 \text{ sec.}^{-1}$ , we find that (44) is best fitted by choosing  $n = 11$ . It is clear that when, as in this realistic example,  $\omega_{50}/A$  is

small, then  $n$  must be quite large in order to enhance the bracketed factor in (44) to compensate for the smallness of  $\omega_{50}$ .

This calculation indicates the use of Hinshelwood's theory. It shows also that the bracketed factor in (44), which at first sight makes the rate constant so different in form from the usual (3), plays an essential role in the experimental comparisons. This factor symbolizes the effect of the "complexity" of the molecule in enhancing the energization rate. Although there is indeed a similar enhancement in the later and more refined theories, we shall tend to lose sight of it there in the mathematical manipulations.

**The bimolecular rate constant.** As  $\omega$ , or the concentration  $c$ , tends toward zero in the second equation of (23), we approach the rate

$$k \approx k^0, \quad k^0 = \omega f_1 = z c f_1 \quad (45)$$

(compare (8)). The corresponding limiting or *bimolecular* rate constant defined as in (2) is  $k_{\text{bim}}^0 = k^0/c$ ; so by (45)

$$k_{\text{bim}}^0 = z f_1, \quad (46)$$

which is naturally independent of  $c$ . The ratio of the high-concentration first-order constant,  $k_{\text{uni}}^\infty = k^\infty = k_1 f_1$  of (23), to  $k_{\text{bim}}^0$  is thus

$$k_{\text{uni}}^\infty / k_{\text{bim}}^0 = k_1 / z. \quad (47)$$

This ratio of a specific molecular rate  $k_1$  to a collision parameter  $z$  shows in fact the nature of the relation of a  $k_{\text{uni}}$  and  $k_{\text{bim}}$ . We may also write it, by (43), as

$$k_{\text{uni}}^\infty / k_{\text{bim}}^0 = c_{50}, \quad (48)$$

namely, as the concentration at which the (first-order) rate has fallen to half its high-concentration value. This result could have been deduced directly from (25); and, as can be seen from the earlier discussion, the result (48) holds for *any theory dividing molecules into just two classes*, as in (25).

## 2.5 ARRHENIUS CONSTANTS AND SPECIFIC ENERGY RATES

Having seen that Hinshelwood's theory does not give a high-concentration rate constant of the Arrhenius form (3), namely,

$$k^\infty = A \exp(-E_0/\kappa T), \quad (49)$$

we pause to investigate what restrictions such a form places on the molecular model, and also on the specific rates of molecules of given

energy.<sup>8,9</sup> We confine attention at first to high gas concentrations at which the equilibrium distribution is present and the reaction is of the first order.

**Classical energies.** With the omission of terms in coordinates and momenta (such as translational components) irrelevant to the dissociation process, let the rest of the molecular Hamiltonian be  $H(q_1, \dots, p_n)$ . If the corresponding classical phase integral (27) is expressed in the form

$$\Phi = \int_0^{\infty} p(E) e^{-E/\kappa T} dE, \quad (50)$$

then  $p(E)$  may be called the *weight factor* of states of energy  $H = E$  to  $E + dE$ ; and reference to (26) and (27) shows that the proportion of molecules with energies  $E$  to  $E + dE$  is

$$f(E) dE \equiv p(E) e^{-E/\kappa T} dE / \Phi, \quad (51)$$

a formula equivalent to (29), for example, if  $H$  is a sum of  $m$  square terms.

If the "interesting states" introduced early in 2.3 are characterized solely by their total energy  $E$ , then the classification number  $r$  is replaced by the continuous variable  $E$ , and the corresponding  $k_r$  by  $k_E$ , the *specific rate for E-molecules* (molecules of energy  $E$ ). It is possible, however, that the dissociation probability may depend on a whole set of parameters (such as the individual oscillator energies which appeared in (31)). In this case we may average the dissociation probability, with an appropriate weighting, over all values of the parameters corresponding to a total energy  $E$ ; and the result is an average specific rate for  $E$ -molecules, which again we call  $k_E$ . In either case we have now for the total high-concentration rate constant, corresponding to (4),

$$k^{\infty} = \int_0^{\infty} k_E f(E) dE, \quad (52)$$

displaying  $k^{\infty}$  as a sum of contributions from elementary energy-ranges. It is convenient to take zero as the lower limit of integration in (52), although we are confident that  $k_E$  will be zero for low energies.

Let us assume now that the rate constant is strictly of the Arrhenius form (49). Then by (51) and (52)

$$k^{\infty} = \int_0^{\infty} k_E p(E) e^{-E/\kappa T} dE / \Phi = A e^{-E_0/\kappa T}. \quad (53)$$

Using the form (50) of  $\Phi$  and writing  $z = 1/\kappa T$ , this gives

$$\int_0^{\infty} k_E p(E) e^{-Ez} dE = A e^{-E_0 z} \int_0^{\infty} p(E) e^{-Ez} dE. \quad (54)$$

Since  $E \geq 0$ , we may formally define  $p(E)$  to be zero for  $E < 0$ . Thus if on the right-hand side of (54) we write  $E_0 + E = E'$ , the equation becomes (dropping the prime)

$$\int_0^{\infty} k_E p(E) e^{-Ez} dE = A \int_0^{\infty} p(E - E_0) e^{-Ez} dE. \quad (55)$$

Since classically we assume  $k_E$  and  $p(E)$  are continuous, as well as nonnegative, this equation implies that

$$k_E = 0 \quad \text{if } E \leq E_0, \quad (56)$$

$$k_E = A p(E - E_0) / p(E) \quad \text{if } E \geq E_0. \quad (57)$$

These results have three interesting implications, if the rate constant is of the Arrhenius form and the classical picture is adequate. First, from (56),

*the minimum energy for dissociation is the Arrhenius parameter  $E_0$ .* (58)

Secondly, from (57), since  $p(E) \rightarrow \infty$  as  $E \rightarrow \infty$  on any classical model, and  $p(E - E_0) / p(E) \rightarrow 1$ ,

*the specific rate for molecules of very high energy (namely  $\lim k_E$  as  $E \rightarrow \infty$ ) is the Arrhenius frequency factor  $A$ .* (59)

(This is a more interesting interpretation of  $A$  than as the limiting over-all rate  $A e^{-E_0/\kappa T}$  as  $T \rightarrow \infty$ .) Thirdly,

*the (average) specific rate  $k_E$  must be the particular function (57) of the classical weight factors.* (60)

This last result may appear alarmingly restrictive. In fact several theories give over-all rates of the form (49) and are found to obey (57). Among these are the classical versions of the theories of Kassel, myself, and the activated complex. Actually the Hamiltonians used or implied in these theories are reducible to a sum of square terms. If there are  $m$  square terms, then comparison of (51) and (29) shows that

$$p(E) \sim E^{1/2m-1}, \quad (61)$$

so that (57) gives, for  $E \geq E_0$ ,

$$k_E = A \left\{ (E - E_0) / E \right\}^{1/2m-1}, \quad (62)$$

which is the form which has been found (or in one case assumed on plausible grounds) for  $k_E$  in the theories mentioned above. Often  $n$  has been an even number,  $2n$ , say, as for a set of  $n$  oscillators or normal modes. In this case the result (which follows also directly from (36), (51), and (57)) is

$$k_E = A \{ (E - E_0)/E \}^{n-1}, \quad (63)$$

where  $A$  is still the Arrhenius parameter.

**Quantized energies.** Assuming now that the total molecular energy relevant to dissociation is quantized, let the successive energy levels be  $\epsilon_0, \epsilon_1, \epsilon_2 \dots$ , where for convenience we take  $\epsilon_0 = 0$  and where  $0 < \epsilon_1 < \epsilon_2 < \dots$ . Let  $p_r$  be the total quantum weight of the  $r$ th level, so that in a high concentration or equilibrium distribution the proportion of molecules with energy  $\epsilon_r$  is

$$f_r = p_r x^{\epsilon_r} / \sum p_j x^{\epsilon_j}, \quad (64)$$

where

$$x \equiv e^{-1/\kappa T}. \quad (65)$$

Let  $k_r$  be the specific rate for energy  $\epsilon_r$ ,  $k_r$  being either basic or itself an average, like the earlier  $k_E$ . The over-all first-order rate constant is therefore

$$k^\infty = \sum k_r f_r. \quad (66)$$

Let us assume again that this is of the Arrhenius form (49), which is  $Ax^{E_0}$  by (65). We have now, by (64) and (66), the identity

$$\sum k_r p_r x^{\epsilon_r} = A \sum p_r x^{E_0 + \epsilon_r}. \quad (67)$$

This is to hold in the range  $0 < x < 1$ . There is no reason a priori to suppose the partition function  $\sum p_r x^{\epsilon_r}$  is a power series in the normal sense, but we can begin with  $x$  small and so in (69) equate the lowest terms in  $x$  and then the successive terms. With  $\epsilon_0 = 0$ , the lowest power on the right-hand side is  $E_0$ ; hence

$$k_r = 0 \quad \text{if } \epsilon_r < E_0, \quad (68)$$

which indicates (as in (58)) that the Arrhenius parameter  $E_0$  is the minimum energy for dissociation. If  $k_p$  is the first nonzero  $k_r$ , then the first surviving term on the left in (67) gives

$$\epsilon_p = E_0 \quad (69)$$

and

$$k_p = A p_0 / p_p. \quad (70)$$

Let us assume now that

$$k_r > 0 \quad \text{for all } r > \rho, \quad (71)$$

that is, that molecules with more than the critical energy have a non-zero chance of dissociation. This is a natural and common assumption but, as we shall see later, may not always be valid even in classical mechanics. We may, with the assumption (71), infer for the succeeding terms in (67) that

$$\epsilon_r = \epsilon_\rho + \epsilon_{r-\rho} \quad (r \geq \rho), \quad (72)$$

and, from the coefficients,

$$k_r = A p_{r-\rho} / p_r \quad (r \geq \rho), \quad (73)$$

which is the quantal equivalent of (57).

The general solution of (72) has  $\epsilon_1, \epsilon_2, \dots, \epsilon_{\rho-1}$  arbitrary, the pattern of spacing of the levels then repeating after  $\epsilon_\rho$  and after  $\epsilon_{2\rho}$ , and so on. This is an unrealistic pattern if  $\epsilon_\rho \equiv E_0$  is large, and the only "physical" solution of (72) is

$$\epsilon_{r+1} - \epsilon_r = \text{const.}, \quad \epsilon_r = r\epsilon_1 \quad (\epsilon_1 = E_0/\rho). \quad (74)$$

That this is the pattern of levels of a simple harmonic oscillator is of small interest, for a simple oscillator could represent generally only a diatomic molecule. But it is also the pattern of levels of a set of degenerate oscillators, where by "degenerate" we mean that either

(i) the frequencies of the oscillators are all  $\nu = \epsilon_1/h$ , or

(ii) they are  $\nu$  and whole multiples of  $\nu$ , not necessarily all distinct.

We conclude that, if the energies are quantized and (71) is assumed, then

*the only molecular model giving the Arrhenius rate is that of a set of degenerate oscillators.* (75)

If in case (i) there are  $n$  oscillators per molecule, the quantum weight of the  $r$ th level (of energy  $\epsilon_r = r h \nu$ ) is the number of ways of assigning  $r$  indistinguishable objects to  $n$  boxes, namely,

$$p_r = (r + n - 1)! / r!(n - 1)! \quad (76)$$

Hence by (73) the specific rate for this level is

$$k_r = A r!(r - \rho + n - 1)! / (r - \rho)!(r + n - 1)! \quad (77)$$

The classical formula (63) is the limiting form of this for large  $r$  and  $\rho$ , with  $E/E_0 = r/\rho$ .

**The extension of an Arrhenius rate to general concentrations.** If the only parameter determining reactivity is the total energy of the

molecule, so that  $k_E$  or  $k_r$  is a basic specific rate and not itself an average, then we can determine the general-concentration rate constant  $k$  from an assumed Arrhenius form of  $k^\infty$  together with the weight factors. In the classical case, for example, if in (52)  $k_E$  is a basic specific rate, then, as we saw, it corresponds to the specific rate  $k_r$  of (4) and  $f(E)dE$  corresponds to  $f_r$  in (4). Thus the general rate constant (15) has the form

$$k = \int_0^\infty \omega k_E (\omega + k_E)^{-1} f(E) dE, \quad (78)$$

with  $f(E)$  as in (51). The formula (78) is unjustifiable if  $k_E$  is itself an *average* over more detailed specific rates, for then the summation in (15) should be over the detailed specification.<sup>10,8</sup>

If now the first-order rate constant  $k^\infty$  has the Arrhenius form (49), then  $k_E$  must have the form (56), (57); and this determines (78) in terms of  $p(E)$  and the related  $f(E)$ . In particular, if the Hamiltonian is of  $2n$  square terms, then, by (63) and the corresponding form (36) of  $f(E)$ , (78) becomes

$$k = \frac{A}{(n-1)!(\kappa T)^n} \int_{E_0}^\infty \frac{(E - E_0)^{n-1} e^{-E/\kappa T} dE}{1 + A\omega^{-1}(1 - E_0 E^{-1})^{n-1}}, \quad (79)$$

where  $k^\infty = A \exp(-E_0/\kappa T)$ . Introducing a dimensionless parameter  $b$  and a variable  $x$  by

$$b = E_0/\kappa T, \quad (80)$$

$$x = (E - E_0)/\kappa T, \quad (81)$$

we obtain for the fractional decline of the rate constant at collision frequency  $\omega$

$$\frac{k}{k^\infty} = \frac{1}{(n-1)!} \int_0^\infty \frac{x^{n-1} e^{-x} dx}{1 + A\omega^{-1} \{x/(b+x)\}^{n-1}}. \quad (82)$$

This form shows that the decline of an "Arrhenius" rate constant (for a model of  $2n$  square terms with reactivity depending solely on total energy) is completely determined by

$n$ , representing the molecular complexity,

$b$ , or the ratio  $E_0/T$ , and

$A/\omega$ , the ratio of the Arrhenius frequency factor in  $k^\infty$  to the effective collision frequency.

The corresponding formula for quantized energies is easily deduced for the case of degenerate equal frequencies.

### 2.6 THE THEORIES OF RICE AND RAMSPERGER AND OF KASSEL

Hinshelwood's theory was soon followed by the more elaborate theories of Rice and Ramsperger<sup>11</sup> and Kassel<sup>12,13</sup> in 1927-1928. These included both classical and quantum forms. We will concentrate nominally on the first, or classical-mechanical, version of Kassel's theory (although he attached more importance to his quantum version), but some of the detail of the argument will be based on Rice and Ramsperger's paper.

The molecule is pictured as a system of  $n$  harmonic oscillators, which by means of small coupling forces can pass energy from one to another. Thus the gas is in a way a doubly statistical assembly; the molecules interchange energy at collisions, and also the oscillators in a molecule interchange energy between the times of collisions.

The molecule is assumed to dissociate if and when an energy exceeding an amount  $E_0$  is collected into one particular or "critical" oscillator. A molecule is "interesting" in the sense of 2.3 if collisions have given it an energy  $E$  exceeding  $E_0$ ; the Lindemann time lag to dissociation is then the time taken for the internal interchanges to give at least  $E_0$  of this energy to the critical oscillator.

We find the dependence of this time lag on  $E$  by applying ideas of "detailed balancing" to the internal statistics. (The argument given here is rather closer to Rice and Ramsperger's than to Kassel's.) Suppose first that the molecules are *not* dissociating. The chance that an  $E$ -molecule has energy exceeding  $E_0$  in a particular oscillator is the chance that it has less than  $E - E_0$  in the remaining  $n - 1$ . From the equilibrium distribution (31) this chance is

$$\int \cdots \int_{\sum_2^n \epsilon_s = E - E_0} d\epsilon_2 \cdots d\epsilon_n / \int \cdots \int_{\sum_2^n \epsilon_s \leq E} d\epsilon_2 \cdots d\epsilon_n. \quad (83)$$

Evaluation as in (33) gives for this

$$\{(E - E_0)/E\}^{n-1}. \quad (84)$$

A frequency factor  $A$  (called by Kassel a "proportionality constant")

\* I find that these oscillators are generally thought of as corresponding roughly to interatomic bonds, although Kassel associated them merely with "degrees of freedom." In the harmonic approximation the various normal modes of vibration (which truly constitute "oscillators") may all contribute to the motion in a bond. Nevertheless the characteristic frequencies associated with certain atomic groupings give an element of reality to the correspondence of bonds with oscillators, although this is not an exact picture.

is now introduced; I picture it as playing the same role in relation to the internal energy interchanges as the effective collision frequency  $\omega$  plays in the over-all energy changes. We could thus define  $A$  by saying that  $A\Delta t$  is the probability that in time  $\Delta t$  there is an internal energy change in the critical oscillator; this implies that these interchanges occur randomly like collisions. Just as external collisions usually de-energize "interesting" molecules, so will a high energy in the critical oscillator nearly always disappear in an internal interchange. Hence the proportion of  $E$ -molecules (with  $E > E_0$ ) which *cease*, in  $\Delta t$ , to have a concentration  $E_0$  (or more) in the critical oscillator is  $\{(E - E_0)/E\}^{n-1}A\Delta t$ , by (84).

Applying "detailed balancing" to the internal rearrangements, we deduce that this same proportion of  $E$ -molecules concentrate energy  $E_0$  into their critical oscillator in  $\Delta t$ . So far our gas has been in equilibrium and inhibited from dissociating. If now we introduce the hypothesis that the concentration of  $E_0$  causes immediate dissociation, we may assume that the rate at which  $E$ -molecules enter the concentrated state is thereby unaffected; the poetic footnote in 2.3 is again relevant. Hence the proportion of  $E$ -molecules dissociating per second, the *specific rate*, is

$$k_E = A \{(E - E_0)/E\}^{n-1} \quad (E \geq E_0). \quad (85)$$

Now the number of  $E$ -molecules in a high concentration  $c$  is  $cf(E)dE$ , where  $f(E)$  is given by (36) since we have here systems of  $n$  oscillators. Using this and (85), we find that the high-concentration rate constant is

$$k^\infty = \int_{E_0}^{\infty} k_E f(E) dE = \frac{A}{(n-1)!(\kappa T)^n} \int_{E_0}^{\infty} (E - E_0)^{n-1} e^{-E/\kappa T} dE, \quad (86)$$

whence

$$k^\infty = A e^{-E_0/\kappa T}, \quad (87)$$

which is of the Arrhenius form.

The scrutiny of this simple result yields considerable insight into reaction theory; so that a series of points will be made concerning the derivation of (87) and its extension to general concentrations.

**Points in Kassel's theory.** (i) Using the perhaps overprecise interpretation I gave to Kassel's parameter  $A$  after equation (84), we may infer *directly*<sup>8</sup> that  $k^\infty = A \exp(-E_0/\kappa T)$ . For in an equilibrium non-dissociating gas of  $c$  molecules, the number with energy above  $E_0$  in one particular oscillator (irrespective of the state of the other oscillators) is  $c \exp(-E_0/\kappa T)$ , as is seen from (37) with  $n=1$ . The number

leaving this  $E_0$ -concentrated state per second by internal interchanges is  $cA \exp(-E_0/\kappa T)$ , by the definition of  $A$  as the interchange rate; and the same number enter this state, by "detailed balancing." In the actual dissociating gas we assume that the same number gain the critical concentration  $E_0$ , but now dissociate; so that the first-order rate is  $A \exp(-E_0/\kappa T)$ . This "short cut" recalls activated-complex ideas.

(ii) In the earlier argument, when we reached the form (85) of  $k_E$ , we were bound to find an Arrhenius rate, since (85) agrees with (63), which was found in 2.5 as the required  $k_E$  (for an  $n$ -oscillator classical system) for the Arrhenius rate. The agreement of (85) with (63) may be traced back to an earlier stage; for the energy factor in (85) is the ratio of the integrals (83), which are ways of distributing energy  $E$  where in the numerator a part  $E_0$  has been previously assigned. Thus this ratio corresponds to  $p(E-E_0)/p(E)$  in (57), of which (63) is the appropriate form here.

(iii) The agreement of the "short-cut" method of (i) with the previous method involving  $k_E$  is strictly a high-concentration phenomenon; for at high concentrations all oscillators have essentially the equilibrium distribution, and we obtain the same rate of flow to the critical oscillator whether we consider it alone (as in (i)), or in conjunction with the energies of the other oscillators (as in the previous method, where we brought them in in (86) and then integrated them out!).

(iv) In extending the theory to *lower concentrations*, we must not use the "short cut." Collisions affect the total energy  $E$ , not merely the energy in one oscillator; and the failure of the rarer collisions (at lower concentrations) to maintain the distribution is spread fairly harmlessly over all the oscillators. If this failure were concentrated on the critical oscillator, there would be a sharp falling off of rate as if the molecule were merely diatomic. The function of the other oscillators is as a heat bath or reservoir of energy.<sup>14</sup>

(v) *General rates.* The extension of the  $n$ -oscillator Arrhenius rate to general concentrations is in fact as in (78)–(82), and formula (79) is originally due to Kassel. It is clear that  $k_E$ , as found in (85) here, is a basic specific rate, as was required in 2.5; it cannot be viewed in any natural way as an average over detailed specific rates connected with states of the  $n$  oscillators of the molecule.

(vi) The Arrhenius parameter  $A$  is often of the order of magnitude,  $10^{14}$  sec.<sup>-1</sup>, of molecular vibration frequencies. It plays the role (in the present exposition) of the rate of occurrence of internal energy interchanges of an oscillator. Thus the oscillators suffer discontinuities of energy about once per "vibration" and so are hardly recognizable as

performing oscillations. It is perhaps helpful to link this kind of "indeterminacy" of the oscillators with the imprecise view of their nature mentioned in the footnote on page 30.

The *practical value* of the theory has not been given due weight in this discussion. It has lain in the comparison of the theoretical decline of rate constant (with concentration) with experimental results. In the theoretical decline (82), the number  $n$  of oscillators is a main parameter; and a main object of experimental comparisons has been to see whether a value of  $n$ , reasonably consonant with knowledge of the molecule considered and its conjectured mechanism of rupture, gives an observed curve of decline. Some important problems of curve fitting have been discussed by Johnston,<sup>15</sup> Kassel,<sup>16</sup> and Powell.<sup>17</sup>

**The theory of Rice and Ramsperger.**<sup>11</sup> This theory\* differs from Kassel's in taking as the condition for dissociation the accumulation of energy  $\epsilon_0$  in one coordinate or "square term"† instead of in an oscillator or pair of square terms. Consequently the high-concentration rate constant  $k^\infty$  is (by the short-cut method (i) above) the product of an interchange frequency and of the integral of (28) from  $\epsilon_1 = \epsilon_0$  to infinity; thus  $k^\infty$  is not precisely of the Arrhenius form. The authors were not so much concerned with  $k^\infty$  as with the decline of  $k/k^\infty$  with pressure; they found for  $k/k^\infty$  a form similar to that, (82), given just afterward by Kassel.

**Kassel's quantum version.** Kassel followed up the classical theory,<sup>12</sup> discussed above, with two quantum models.<sup>13</sup> In the simpler of these, which is the one used in his book,<sup>6</sup> there are  $n$  quantal oscillators all of frequency  $\nu$ , and the molecule dissociates when energy  $E_0 = \rho h\nu$  is accumulated in one critical oscillator. (As in 2.5, we omit zero-point energy.) On statistical grounds he postulates the form (77) for the specific rate  $k_r$  ( $r \geq \rho$ ). Now the equilibrium probability of energy  $r h\nu$  is

$$f_r = (1 - \alpha)^n \alpha^r p_r, \quad \alpha = \exp(-h\nu/\kappa T), \quad (88)$$

where  $p_r = (r+n-1)!/r!(n-1)!$  as in (76). Thus the high-concentration rate constant  $\sum k_r f_r$  is found by (88) to be

$$k^\infty = A \alpha^\rho = A \exp(-E_0/\kappa T). \quad (89)$$

This is in accordance with the discussion in 2.5, and corresponds to case (i) in (75).

\* I mean here Theory II of Rice and Ramsperger; their Theory I is an explicit version of Hinshelwood's ideas.

† The single term is referred to in the original paper as a "degree of freedom," and a set of  $s$  square terms as implying  $s$  "degrees of freedom."

The *general-concentration rate constant* on this model is (15), with  $k_r$  and  $f$ , as given here; this is the form most used in Kassel's experimental comparisons.<sup>6</sup>

In Kassel's second quantum model,<sup>13</sup> there are  $s$  oscillators of frequency  $\nu$ , and  $r$  of frequency  $t\nu$ , with  $t$  an integer; dissociation requires energy  $\rho h\nu$  in one of the slow oscillators. The high-concentration rate constant found is again (89); this can be seen also from the "short-cut" method in Point (i) earlier in this section. This second model can be viewed as a particular case of an Arrhenius-type model (ii) of (75).

The theoretical advantage of these degenerate oscillators is that they are amenable to the energy interchanges which the dissociation model requires; the practical disadvantage is that, except in the case of complete degeneracy (all  $\nu$ s equal), the general concentration rate constant is cumbersome. The extreme (but most realistic) case is that of a set of  $n$  oscillators whose frequencies are rational (but not all integral) multiples of the slowest and critical oscillator. This may be shown to give an Arrhenius high-concentration rate constant, although it does not satisfy (71) of 2.5 and so is not included in the classification made in that section.

## 2.7 THE THEORY OF POLANYI AND WIGNER

The theories described in 2.2, 2.4 and 2.6 were concerned mainly with the relative decline,  $k/k^\infty$ , of the rate constant with concentration. We come now to attempts to estimate the magnitude of  $k^\infty$ , in particular the pre-exponential factor of an Arrhenius, or nearly Arrhenius, rate constant.

Rodebush<sup>18</sup> in 1923 suggested that dissociation might result from energy-transferring collisions between the atoms of the molecule. The collision frequency for this internal process would be roughly twice a vibration frequency. This was useful in suggesting an  $A$ -factor of the order of magnitude of vibration frequencies.

Polanyi and Wigner<sup>19</sup> in 1928 were the first to use normal modes of vibration with any precision in dissociation theory. They considered a very simple molecule, namely, a linear chain of equal masses, and estimated the distribution of its normal frequencies of vibration. They assumed the molecule dissociates if a link or "bond" in the chain is unduly stretched. There is no suggestion here that this link is to be regarded as a single oscillator gathering to itself a large amplitude. The link varies in length as a sum of the various normal-mode vibrations with their various frequencies; and the critical stretch happens when all the modes come "into phase," all pulling the link out together. By a mixture of plausible and rigorous statistics, the authors found a high-concentration rate constant

$$k^\infty = 1.15\nu \exp(-E_0/\kappa T), \quad (90)$$

where  $\nu$  is the fastest normal frequency. Their estimated generalization for three-dimensional distortions was

$$k^\infty \cong 2\nu(E_0/\kappa T) \exp(-E_0/\kappa T). \quad (91)$$

The theory described in the following chapters is essentially a precise and generalized treatment of Polanyi and Wigner's idea, beginning with their notion of *phase coincidence* of normal modes.

It may be asked why their promising start was not further developed at the time. For one thing, there was no adequate mathematical machinery for the discussion of the phase effects; and (for other reasons also) Wigner, Polanyi, Pelzer and others transferred attention to the calculation of rates as flows through a critical configuration in the abstract coordinate-momentum phase space of the molecule. From this was developed "activated complex" theory, which will be discussed in Chapter 6.

## 2.8 ACTIVATION ENERGY

Having glanced in 2.7 at theories of the  $A$ -factor of the high-concentration rate constant, we should for completeness deal with the theory of the exponential factor. This, however, lies outside our general scope, the critical energy being regarded mainly as an empirical quantity. The empirical exponential factor is closely connected with the concept of activation energy, so we shall discuss the definition of this energy, the theorem of Tolman, and the dependence of activation energy on concentration.

**High-concentration rates.** Observing that experimenters determine the parameter  $E_0$  of an assumed Arrhenius rate constant (3) as the slope of a plot of  $-\ln k^\infty$  against  $1/\kappa T$  (compare (39)), we *define* the activation energy  $E_a^\infty$  at high concentrations to be

$$E_a^\infty = \kappa T^2 d \ln k^\infty / dT = -\kappa d \ln k^\infty / d(1/T). \quad (92)$$

In the Arrhenius (and Kassel) case, this reduces to the constant  $E_0$ . The formula (92) is the natural generalization for non-Arrhenius rates, where  $E_a^\infty$  will depend on  $T$ ; we are assuming (rather optimistically) that there is a sufficiently smooth mean experimental plot of  $-\ln k^\infty$  against  $1/\kappa T$  for us to measure the slope (92) of a tangent at a given  $T$ . An older definition of activation energy was as the critical (minimum) energy for dissociation. This agrees with the present definition when the rate is strictly Arrhenius, since then by (58) and (68) the critical energy is the Arrhenius parameter  $E_0$ , and this is then also the  $E_a^\infty$  of (92).

*Tolman's theorem:* Although the present work applies also to con-

tinuous energies, we use for simplicity notations of 2.3 and (64), (65) of 2.5, as if the molecule had discrete energies  $\epsilon_1, \epsilon_2, \epsilon_3, \dots$ \* But (differing here from 2.3) we include now the uninteresting levels in the enumeration of the  $\epsilon$ 's, and use the *summation signs*:

$$\sum \equiv \text{sum over all } r, \quad \sum' \equiv \text{sum over interesting } r. \quad (93)$$

Thus in the high-concentration region the proportion of molecules in level  $\epsilon_r$  is (as (64), (65))

$$f_r = p_r x^{\epsilon_r} / \sum p_s x^{\epsilon_s}, \quad x \equiv \exp(-1/\kappa T), \quad (94)$$

and the rate constant (4) is

$$k^\infty = \sum' k_r f_r = \sum' k_r p_r x^{\epsilon_r} / \sum p_s x^{\epsilon_s}. \quad (95)$$

By (94) the operator  $\kappa T^2 d/dT$  in (92) equals  $x d/dx$ ; so by (92) and (95)

$$\begin{aligned} E_a^\infty &= (\sum' k_r p_r \epsilon_r x^{\epsilon_r}) / (\sum' k_r p_r x^{\epsilon_r}) - (\sum p_s \epsilon_s x^{\epsilon_s}) / (\sum p_s x^{\epsilon_s}) \\ &= (\sum' k_r f_r \epsilon_r) / (\sum' k_r f_r) - \sum f_s \epsilon_s \\ &= \bar{\epsilon}' - \bar{\epsilon}. \end{aligned} \quad (96)$$

$$= \bar{\epsilon}' - \bar{\epsilon}. \quad (97)$$

Here  $\bar{\epsilon}$  is the average energy of all molecules, generally indistinguishable from the average energy of the normal or "uninteresting" molecules;  $\epsilon$  is the average energy of the interesting molecules *which dissociate in unit time*. The omission of this last phrase has sometimes caused confusion; for the average energy of the existing interesting molecules is

$$\bar{\epsilon}' = \sum' f_r \epsilon_r / \sum' f_r, \quad (98)$$

and this is appreciably smaller than  $\bar{\epsilon}$  in cases where  $k_r$  rises sharply with energy, since the weighting factor  $k_r$  (represented in words by the italics below equation (97)) in  $\bar{\epsilon}'$  boosts the upper levels.

The result (97) is a case of Tolman's theorem.<sup>20</sup> As an example of its use, we deduce that for a classical  $n$ -oscillator molecule with an Arrhenius rate ( $E_a^\infty = E_0$ ),

$$= E_0 + n\kappa T, \quad (99)$$

since in this case  $\bar{\epsilon} = n\kappa T$ .

**General concentrations.** We bear in mind for general concentrations the "steady-state" formulation in 2.3, so that the general rate constant is

$$k = \sum' k_r g_r = \sum' \omega k_r f_r / (\omega + k_r), \quad (100)$$

\* There is here no suggestion that the rate constant should be restricted to the Arrhenius form, however.

where

$$g_r = \omega f_r / (\omega + k_r) \quad (101)$$

is the steady proportion in the  $r$ th state at collision frequency  $\omega$ . (Here and in some of the subsequent formulas where  $\omega$  is left inside the summation, we might introduce a variable value  $\omega = \omega_r$ , as in (10).)

The natural generalization of (92) when the rate constant  $k$  depends on concentration is

$$E_a = \kappa T^2 \partial \ln k / \partial T, \quad (102)$$

the *partial* differentiation implying that concentration, or pressure, is to be kept constant. These variables enter  $k$  through the collision frequency  $\omega$ . We therefore write

$$E_a = \bar{E}_a + E_{\text{coll}} \quad (103)$$

where  $\bar{E}_a$  is calculated from (102) with  $\omega$  fixed and so arises from the temperature dependence of  $f_r$  in (100); and  $E_{\text{coll}}$  is calculated with  $f_r$  fixed and  $\omega$  varying as a function of temperature.

The *collisional contribution*  $E_{\text{coll}}$  is relatively unimportant. If we use a gas-kinetic form of  $\omega$ , we write at concentration  $c$ , with  $m$  and  $\sigma$  the molecular mass and "diameter,"

$$\omega = zc, \quad z = 4\sigma^2 \sqrt{(\pi \kappa T / m)}. \quad (104)$$

Since the pressure  $p$  is proportional to  $cT$ ,  $\omega$  varies as  $T^{-1}$  at constant pressure. Hence

$$\kappa T^2 \partial \omega / \partial T = \pm \frac{1}{2} \kappa T \omega, \quad (105)$$

the *upper and lower signs* referring in this section to constant  $c$  and  $p$  respectively. It follows from (100) and (102) that

$$E_{\text{coll}} = \pm \frac{1}{2} \kappa T \sum' k_r^2 \omega f_r (\omega + k_r)^{-2} / k. \quad (106)$$

From this we infer that

$$E_{\text{coll}} \rightarrow 0 \quad \text{or} \quad \pm \frac{1}{2} \kappa T \quad \text{as } \omega \rightarrow \infty \quad \text{or} \quad 0, \quad (107)$$

since  $k \sim \sum' \omega f_r$  as  $\omega \rightarrow 0$ . More generally,  $E_{\text{coll}}$  increases numerically as the concentration falls, but nevertheless remains small.

Corresponding to the two signs of  $E_{\text{coll}}$ , there are two values of  $E_a$  in (102) and  $\bar{E}_a$  is the *mean* of these. We shall therefore concentrate on this mean energy.

*Generalization of Tolman's theorem:* If we use (94) in (100), the mean activation energy (102), (103) is

$$\bar{E}_a = x \partial / \partial x \ln \left\{ \sum' \omega k_r (\omega + k_r)^{-1} p_r x^{e_r} / \sum p_r x^{e_r} \right\}. \quad (108)$$

The operator  $x\partial/\partial x$  produces factors  $\epsilon_r, \epsilon_s$  in the sums, so that by (101)

$$\bar{E}_a = (\sum' k_r g_r \epsilon_r) / (\sum' k_s g_s) - \sum f_r \epsilon_r \quad (109)$$

$$= \bar{\epsilon}_\omega - \bar{\epsilon}, \quad (110)$$

which is the generalized theorem. Here  $\bar{\epsilon}_\omega$  is the mean energy of the molecules dissociating per unit time, when the collision frequency is  $\omega$ ; this follows from the interpretation of the  $g_r$  as the relative steady population of the  $r$ -level (compare 2.3), and the weighting  $k_r$  comes in as before. The term  $\bar{\epsilon}$  is not quite the "average energy of all molecules," since the sum  $\sum f_r \epsilon_r$  makes no allowance for the depletion of high levels at low concentrations; but the approximate interpretation of  $\bar{\epsilon}$  as the average energy of uninteresting molecules is at least as good as in the previous case under (97).

Tolman's own general-concentration version of his theorem has a rather more complicated formalism.

**The variation of activation energy with concentration.** Let  $\omega$  and  $\omega'$  be collision frequencies for two different concentrations at given  $T$ ,  $\bar{E}_a$  and  $\bar{E}'_a$  the corresponding mean activation energies,  $g_r$  as in (101), and  $g'_r = \omega' f_r / (\omega' + f_r)$ . Then by (109)

$$\begin{aligned} \bar{E}'_a - \bar{E}_a &= (\sum' k_r g'_r \epsilon_r) / (\sum' k_s g'_s) - (\sum' k_r g_r \epsilon_r) / (\sum' k_s g_s) \\ &= \frac{1}{2} \sum' \sum' k_r k_s (\epsilon_r - \epsilon_s) (g'_r g_s - g_r g'_s) / (\sum' k_r g_r \sum' k_s g'_s), \end{aligned}$$

the second form coming by interchanging suffixes  $r$  and  $s$ . Using the forms of  $g_r$  and  $g'_s$ , we find, with  $P_{rs}$  positive quantities that need not be specified,

$$\bar{E}'_a - \bar{E}_a = (\omega' - \omega) \sum' \sum' P_{rs} (\epsilon_r - \epsilon_s) (k_r - k_s). \quad (111)$$

This is positive for  $\omega' > \omega$ , provided the last two factors have the same sign. Hence if  $k_r > k_s$  when  $\epsilon_r > \epsilon_s$ ,  $\bar{E}'_a - \bar{E}_a$  has the same sign as  $\omega' - \omega$ . Thus

*If the dissociation probability increases with energy, the mean activation energy decreases toward lower concentrations.* (112)

This trend in  $\bar{E}_a$  generally swamps the trend in  $E_{\text{coll}}$  with lowering concentration or pressure.

At very low concentrations the assumed limiting form (16) is (with a superscript 0 for low concentration, and our present "primed" summation)

$$k^0 = \omega \sum' f_r = \omega \sum' p_r x^{\epsilon_r} / \sum p_s x^{\epsilon_s}. \quad (113)$$

The corresponding mean activation energy is

$$\bar{E}_a^0 = \sum' f_r \epsilon_r / (\sum' f_r) - \sum f_s \epsilon_s = \bar{\epsilon}' - \bar{\epsilon}, \quad (114)$$

where  $\bar{\epsilon}'$  is as in (98), although it should still officially be termed the mean energy of interesting molecules in a high concentration. (With a little care we may again express (114) as a Tolman theorem, but this is not very helpful here.) The total decline of  $\bar{E}_a$  over the whole range is, by (97),

$$E_a^\infty - \bar{E}_a^0 = \bar{\epsilon} - \bar{\epsilon}', \quad (115)$$

and this quantity, as was mentioned under (98), may be appreciable if  $k$ , increases with  $\epsilon_r$ .

**Examples.** (i) *Hinshelwood's theory.* In any theory having a fixed specific rate  $k_1$  for all interesting molecules, we see from (111), or less grandiosely from (23), that the mean activation energy is independent of concentration and pressure. In Hinshelwood's case, this energy is given by the right-hand side of (40) in terms of the critical energy, there called  $E_1$ ; so clearly  $\bar{E}_a$  is not equal to the critical energy in this theory.

(ii) *Kassel's theory.* With here an Arrhenius rate constant, the high-concentration  $E_a^\infty$  equals  $E_0$ , the Arrhenius parameter or critical energy. The manner of decline of  $\bar{E}_a$  with concentration will be discussed in a later chapter (see 7.9 below). At the limit of low concentration the (classical) rate constant  $k^0$  is (with  $b = E_0/\kappa T$ )

$$k^0 = \omega f_1 = \omega e^{-b} \int_0^\infty (b+x)^{n-1} e^{-x} dx / (n-1)! \quad (116)$$

where  $f_1$  is the equilibrium proportion of  $n$ -oscillator molecules with more than the critical energy (here  $E_0$ , not  $E_1$  as in (37)). We may also regard (116) as the limiting form of (82) as  $\omega \rightarrow 0$ . As in (37), we find

$$f_1 = e^{-b} \{ b^{n-1}/(n-1)! + \dots + 1 \}, \quad b \equiv E_0/\kappa T, \quad (117)$$

and the low-concentration mean activation energy is (compare (40))

$$\begin{aligned} \bar{E}_a^0 &= \kappa T^2 \partial \ln f_1 / \partial T \\ &= E_0 / \{ 1 + (n-1)/b + \dots + (n-1)!/b^{n-1} \}. \end{aligned} \quad (118)$$

If  $(n-1)/b \equiv (n-1)\kappa T/E_0$  is fairly small, we have approximately

$$\bar{E}_a^0 = E_0 - (n-1)\kappa T. \quad (119)$$

We may view this result in two equivalent ways, one practical, the other theoretical. First, the over-all decline in activation energy (cor-

responding to (115)) is roughly  $(n-1)\kappa T$ , which may be an appreciable fraction of  $E_0$ . Secondly, the important energy-values of interesting molecules at high and low concentrations may be typified by the respective averages  $\bar{\epsilon}$  and  $\bar{\epsilon}'$ , where by (99), (114) and (119)

$$\bar{\epsilon} = E_0 + n\kappa T, \quad \bar{\epsilon}' \cong E_0 + \kappa T. \quad (120)$$

The implication of this low  $\bar{\epsilon}'$  is, naturally, that at low concentrations there is so much more time for a molecule to dissociate that it does not need so much energy.

We shall return to this subject of the effects of low concentration only after a lengthy discussion of high-concentration rate constants.

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## Molecular Vibrations and Normal Modes

THIS chapter is concerned with the vibrations of a molecule treated as a stable nondissociating system. Not until Chapter 5 will it be allowed to burst, although parts of the present treatment of vibrations are slanted toward the dissociation theory. Much fuller and better accounts of vibrations have been given by Wilson, Decius and Cross<sup>1</sup> (whom we refer to as WDC) and Herzberg.<sup>2</sup> The present account may usefully drive the reader to their treatises, but there are here a few interesting novelties. Before summarizing the main heads of the chapter, I shall risk giving first an informal introduction to *normal modes*, which are still a source of some confusion.

If we attach two equal, small masses to the points of trisection of a taut mathematical (massless and frictionless) string, and then simultaneously give the masses small, equal parallel kicks perpendicular to the string, they will begin to execute a harmonic vibration, say  $a_1 \sin 2\pi\nu_1 t$ , keeping in step. If instead we give them equal but contrary kicks, they will again vibrate harmonically but keep exactly out of step, with the respective displacements  $\pm a_2 \sin 2\pi\nu_2 t$ , where  $\nu_2 = \nu_1\sqrt{3}$ . Finally, if we give them unequal kicks (still in the same direction as before), they will execute tangly aperiodic motions. The first two periodic motions are normal modes of the system; the third or general (linear) motion could be disentangled by a stroboscopic eye into a superposition of the two normal modes. If we set the masses going in the direction perpendicular to the previous motions and to the string, we shall find two more normal modes, again of the frequencies  $\nu_1$  and  $\nu_2 = \nu_1\sqrt{3}$ ; and the most general lateral plane motions of the masses can be broken up into superpositions of the two pairs,  $\nu_1, \nu_1$  and  $\nu_2, \nu_2$ , of "degenerate" normal modes.

With some refinements of technique we treat molecular vibrations in a corresponding way. The variables or "coordinates"  $q_r$  used to describe the internal configuration of the vibrating molecule are often the changes of interatomic distances or angles from their equilibrium

values. The molecule has normal modes of vibration in any one of which the atoms move linearly and *all* the coordinates  $q_r$  vibrate together; for example  $q_r = A_r \cos 2\pi(\nu_r t + \psi_r)$  in the  $i$ th mode. (Usually some of the  $A_r$  are negative, so that some coordinates are out of step with others; the pattern of in and out of step usually differs in all single modes.) Thus a normal mode is a characteristic motion of the whole molecule, not of a particular internal distance or angle. Conversely the behavior of an internal distance in a general motion of the molecule is not even approximately that of a harmonic oscillator; it is a sum of harmonic mode oscillations.

Three further points should be mentioned. (a) If the molecule has certain symmetries, there will be degenerate pairs of normal modes such that, if just one pair is excited, the atoms move in ellipses (like the bobs on the string for the perpendicular modes  $\nu_1, \nu_1$  with a phase difference). (b) The analysis into normal modes requires the displacements to be small. (c) The classical vibrations in the modes should strictly be represented by quantum oscillators, but the analysis into modes is not thereby affected.

**Outline of the chapter.** In 3.1 the molecular kinetic and potential energies are formulated in general internal coordinates  $q_r$ ; the standard forms are (6), (10), and (11), but the final remark on WDC's symbolism should be noted. Sections 3.2 and 3.3 form a digression of practical importance, on distance and angle coordinates and on symmetry coordinates. In the central section 3.4 the transformation to *normal coordinates* is fully explored; the peculiar normalization (34) and the transformation (35) should be noted particularly. This leads in 3.5 to a standard form (66) of the vibrational motion in terms of *amplitude factors*  $\alpha_{ri}$ . Three other methods of solution are sketched, including a "Lagrangian-momentum" method.

We then proceed to some specialized results and illustrations. In 3.6 we associate with  $q_1$ , one of the (nonnormal) coordinates, a mean frequency  $\nu$  as defined in (79). This frequency also has the forms (87) and (92) in terms of constrained motions (these forms are connected by a general theorem (93) on constrained frequencies) and an important special form (96) when  $q_1$  is an interatomic distance. The calculation of amplitude factors and of  $\nu$  is illustrated in 3.7 for a linear triatomic molecule. I have retained here a rather displaced discussion of "activated complex" frequencies which arose primarily out of an argument on isotope effects. Finally in 3.8 the vibrations of nitryl chloride are examined; this example provides an opportunity to discuss and illustrate the use of symmetry coordinates in calculating amplitude factors.

## 3.1 KINETIC AND POTENTIAL ENERGY

A gas molecule will be idealized into a system of  $N$  "point-atoms" of masses  $m_a$  ( $a=1, 2, \dots, N$ ). If  $x_a, y_a, z_a$  are their Cartesian coordinates in a fixed external frame, we take for the molecular kinetic energy the sum

$$T = \frac{1}{2} \sum_{a=1}^N m_a (\dot{x}_a^2 + \dot{y}_a^2 + \dot{z}_a^2) \quad (\dot{\ } \equiv d/dt). \quad (1)$$

(We shall call it  $T'$  later, when plain  $T$  is needed to denote temperature again.)

By considering the motion of, and relative to, the mass center, we may break  $T$  up into four parts for (i) internal vibrations (including internal rotations), (ii) over-all translation, (iii) over-all rotation, and (iv) Coriolis cross terms connecting vibration and over-all rotation. We shall be concerned almost wholly, however, with changes of shape of the molecule, as leading toward dissociation or isomerization. These changes of shape are predominantly vibrational effects. We therefore remove the terms (ii), (iii), and (iv), by treating the molecule as if its mass center were at rest and (a less justifiable procedure) as if there were no over-all rotational angular momentum. The conditions so imposed are, with a suitable choice of origin,

$$\sum m_a x_a = \sum m_a y_a = \sum m_a z_a = 0, \quad (2)$$

and for angular momentum (which when (2) holds is the same about any point)

$$\sum m_a (y_a \dot{z}_a - z_a \dot{y}_a) = 0. \quad (3)$$

There are generally three independent conditions (on permuting  $x, y$  and  $z$ ) of type (3), but only two are independent if the atoms are collinear. It is convenient for small vibrations to replace (3) by the equivalent form

$$\sum m_a (\bar{y}_a \Delta z_a - \bar{z}_a \Delta y_a) = 0, \quad (4)$$

where  $\bar{x}_a$  denotes the equilibrium value and  $\Delta x_a = x_a - \bar{x}_a$  is the displacement.

Instead of  $3N$  rectangular coordinates linked by these 6 or 5 conditions (2) and (3), we commonly use  $n$  *generalized coordinates*, such as interatomic distances or interbond angles, which describe the configuration without reference to the position or orientation of the molecule. If these are to be independent and a complete set,\* they must

\* It is sometimes convenient to use a larger set, including redundant coordinates, but we shall not deal with this case.

number

$$n = 3N - 6 \text{ (general),} \quad 3N - 5 \text{ (linear molecule),} \quad (5)$$

since they do not specify the position of the mass center or the orientation. In such coordinates  $q_1, \dots, q_n$ , the kinetic energy takes the form

$$T = \frac{1}{2} \sum_1^n \sum_1^n a_{rs} \dot{q}_r \dot{q}_s \quad (a_{rs} \equiv a_{sr}), \quad (6)$$

which is in full

$$T = \frac{1}{2} a_{11} \dot{q}_1^2 + a_{12} \dot{q}_1 \dot{q}_2 + \frac{1}{2} a_{22} \dot{q}_2^2 + \dots + \frac{1}{2} a_{nn} \dot{q}_n^2.$$

The  $a_{rs}$  are generally functions of the  $q_s$ , but for small vibrations they are treated as constants, with the values they assume at the equilibrium configuration.

The Lagrangian form (6) may be converted to Hamiltonian form by introducing the generalized momenta  $p_r$ :

$$p_r = \partial T / \partial \dot{q}_r = \sum_{s=1}^n a_{rs} \dot{q}_s \quad (r = 1, \dots, n). \quad (7)$$

The solution of (7) for the  $\dot{q}_r$  is

$$\dot{q}_r = \sum g_{rs} p_s \quad \text{where} \quad g_{rs} = A_{rs} / A, \quad (8)$$

and  $A$  denotes the *determinant*,  $\|a_{rs}\|$ , of the  $a_{rs}$ , and  $A_{rs}$  the cofactor of  $a_{rs}$  in  $A$ . With the notation  $\mathbf{a}$ ,  $\mathbf{g}$  for the *matrices*  $\{a_{rs}\}$ ,  $\{g_{rs}\}$ , the last relation is

$$\mathbf{g} = \mathbf{a}^{-1}. \quad (9)$$

Substituting (8) in (6) gives the *Hamiltonian form*

$$T = \frac{1}{2} \sum \sum g_{rs} p_r p_s. \quad (10)$$

(There is a comment on this notation at the end of this section.) It is to be observed that the  $g_{rs}$ , like the  $a_{rs}$  above, are treated as *constants* in small vibrations.

The *potential energy* relevant to vibration is fundamentally the quasi-static eigen-energy (in the Born-Oppenheimer approximation) of any instantaneous configuration  $q_1, \dots, q_n$ ; this may be considered to include the main electronic kinetic energy which was conspicuously omitted from  $T$ . We shall not pay much attention to this fundamental view, but generally treat the potential energy as determined as far as possible by the observed spectrum. This energy, then, is expressed as

$V(q_1, \dots, q_n)$ . At the equilibrium configuration its first derivatives vanish. We adjust the *origin* of the  $q$ s to this configuration, and also take  $V=0$  here. Thus as far as quadratic terms,

$$V(q_1, \dots, q_n) = \frac{1}{2} \sum \sum b_{rs} q_r q_s \quad (b_{rs} \equiv b_{sr}). \quad (11)$$

Since the equilibrium at  $q_1 = \dots = q_n = 0$  is stable, this  $V$  is (like  $T$ ) essentially positive.

It is to be remarked that the  $b_{rs}$  are always regarded as constants. When, much later, we desire a more general form of  $V$ , we keep the  $b_{rs}$  constant and add higher (e.g., cubic) terms to (11).

**Notations.** The symbols  $a_{rs}$  and  $b_{rs}$  for the coefficients in (6) and (11) are of long standing. The  $g_{rs}$  in (10) correspond to the  $G_{rs}$  of WDC (I reserve capitals for cofactors usually). The potential energy coefficients or "force constants"  $b_{rs}$  correspond to their  $F_{rs}$ .

### 3.2 TYPES OF INTERNAL COORDINATES

This section (like the next) may be regarded as a digression, but it gives solidity to the vibration problem by introducing techniques used to reduce the energy functions to manageable forms. In this section we introduce internal coordinates which are interatomic distances and angles, and explore the former type rather fully. The important results on the kinetic energy coefficients are proved vectorially in WDC; the present nonvectorial approach may provide a useful alternative.

**General kinetic energy forms.** The classic Lagrangian approach is to treat the  $3N$  variables ( $x_a, y_a, z_a$ ) of (1) as functions of the general coordinates  $q_1$  to  $q_n$ , so that comparison of (1) with (6) gives the kinetic energy matrix (in terms of the  $q_r$ ) as

$$a_{rs} = \sum_{a=1}^N m_a (\partial x_a / \partial q_r) (\partial x_a / \partial q_s) + \dots, \quad (12)$$

where in equations of this section  $\dots$  denotes *similar terms* in  $y$  and  $z$  to those stated in  $x$ . The momentum restrictions (2) and (3) are here taken care of by the specification of ( $x_a, \dots$ ) in terms of  $q_1$  to  $q_n$ .

Alternatively a specification of  $q_1$  to  $q_n$  in terms of the ( $x_a, \dots$ ) leads us to the Hamiltonian form. The Hamiltonian form of (1) is

$$T = \frac{1}{2} \sum_1^N m_a^{-1} \dot{X}_a^2 + \dots, \quad (13)$$

where

$$X_a = \partial T / \partial \dot{x}_a = m_a \dot{x}_a \quad (14)$$

is the  $x$ -momentum of atom  $a$ . If we change to general  $q_r$  with momentum  $p_r = \partial T / \partial \dot{q}_r$ , (14) becomes

$$X_a = \sum_r (\partial T / \partial \dot{q}_r) (\partial \dot{q}_r / \partial \dot{x}_a) = \sum_r p_r \partial q_r / \partial x_a \quad (15)$$

(legitimately canceling dots). The differentiation here is performed as if the  $(x_a, \dots)$  were  $3N$  independent variables unrestricted by (2) and (3); but these momentum conditions are automatically satisfied by the resulting  $X_a$  if the  $q_r$  are as in (5). Substituting (15) in (13) gives directly the Hamiltonian form (10), with

$$g_{rs} = \sum_{a=1}^N m_a^{-1} (\partial q_r / \partial x_a) (\partial q_s / \partial x_a) + \dots, \quad (16)$$

although this must be expressed in terms of the  $q_r$ . This is a most useful result. We could of course have got it from (12) by using (9), but we should have had to consider carefully how the momentum conditions (2) and (3) affected the inversion of  $\mathbf{a}$  into  $\mathbf{g}$ .

*Some consequences of (16) are worth noting, particularly in cases where we introduce fresh sets of general coordinates, keeping one or more unchanged (for example, keeping  $q_1$  and  $q_2$  as particular interatomic distances and changing  $q_3$  from a distance to an angle). It is seen from (16) that if we keep the same  $q_r$ , then  $g_{rr}$  is unchanged by any changes in definition of the other  $q_s$ ; the form of the function  $g_{rr}(q_1, q_2, \dots, q_n)$  may of course change, but certainly the equilibrium-configuration value (which alone is used in small vibrations) will remain the same. Similarly if we keep the same  $q_r$  and  $q_s$  and redefine the other  $q_t$ , then  $g_{rs}$  is unchanged. Finally we see from (16) that, if the  $q_s$  are defined in terms of Cartesian coordinates of the atoms, a cross term  $g_{rs}$  can appear only if both  $q_r$  and  $q_s$  involve a common coordinate  $(x_a, y_a, \text{ or } z_a)$  of a common atom. To sum up:*

$$g_{rr} \text{ is determined by } q_r, \quad g_{rs} \text{ by } q_r \text{ and } q_s; \quad (17)$$

$$g_{rs} = 0 \text{ if } q_r \text{ and } q_s \text{ involve no common atomic coordinate.} \quad (18)$$

**Distances as coordinates.**<sup>3</sup> Let coordinate  $q_1$  be the distance from atom  $a$  to atom  $b$ , namely,

$$q_1 = \{(x_a - x_b)^2 + \dots\}^{\frac{1}{2}}, \quad (19)$$

so that

$$\partial q_1 / \partial x_a = - \partial q_1 / \partial x_b = (x_a - x_b) / q_1, \quad \partial q_1 / \partial x_c = 0, \quad (20)$$

where  $c$  is any other atom. Thus for  $r=s=1$  in (16), we have only

terms in  $m_a$  and  $m_b$ ; and we find

$$q_{11} = m_a^{-1} + m_b^{-1} = M_{ab}^{-1}, \quad (21)$$

where  $M_{ab} = m_a m_b / (m_a + m_b)$  is the *reduced mass* of atoms  $a$  and  $b$ . This always appears as the effective inertia in the relative motion of  $a$  and  $b$ ; we shall also find the result (21) important in isotopic effects.

With the same  $q_1$ , let  $q_2$  be the distance between atoms  $a$  and  $c$ . With  $r=1, s=2$  in (16), the only surviving terms involve  $m_a$ , the mass at the common terminal of  $q_1$  and  $q_2$ . Using (20), we find

$$\begin{aligned} q_{12} &= (m_a q_1 q_2)^{-1} \{ (x_a - x_b)(x_a - x_c) + \dots \} \\ &= m_a^{-1} \cos(bac) \end{aligned} \quad (22)$$

where  $bac$  is the angle at  $a$  subtended by  $b$  and  $c$ . These results are independent of the nature of  $q_3, q_4, \dots$  although the form of the cosine depends on them in general motions. For small motions the results (21) and (22) are derived vectorially in Chapter 4 of WDC.

*Complete sets of distances:* For a molecule of  $N=3$  atoms, or of  $N=4$  atoms which are not coplanar (for example, phosphorus<sup>4</sup>), there are respectively  $n=3$  or 6 independent distances. If we take these as the  $q_s$ , then the whole kinetic energy (10) is made up of terms like (21) and (22), so that

$$T = \frac{1}{2} \sum_{\alpha}^n M_{\alpha}^{-1} p_{\alpha}^2 + \sum_{\alpha < \beta}^n m_{\alpha\beta}^{-1} p_{\alpha} p_{\beta} \cos(\alpha\beta), \quad (23)$$

where  $M_{\alpha}$  is the reduced mass of the terminal atoms of  $q_{\alpha}$ ,  $m_{\alpha\beta}$  the mass at the junction of  $q_{\alpha}$  and  $q_{\beta}$ , and  $(\alpha\beta)$  the angle at  $m_{\alpha\beta}$  between  $q_{\alpha}$  and  $q_{\beta}$  (drawn from  $m_{\alpha\beta}$ ). If  $q_{\alpha}$  and  $q_{\beta}$  have no common terminal (for example, the opposite edges of a tetrahedron), there is no term in  $p_{\alpha} p_{\beta}$ , in agreement with (18). In large motions\* we express the cosines in terms of the  $q_s$  in a simple way; for small motions they are effectively constant. In all cases the  $q_{\alpha}$  need not be the actual distances but may be the distances diminished by constants  $k_{\alpha}$ , such as the equilibrium separations.

For a nonplanar molecule of  $N \geq 5$  atoms, the method requires care, since the distances are no longer all independent.<sup>3</sup> We may in general select a set of  $n=3N-6$  independent distances as coordinates, and so again have the whole kinetic energy in the form (23).

For the *collinear* motion of  $N$  points there are  $n=N-1$  independent distance coordinates; for *coplanar* motion,  $n=2N-3$  (this includes the general

\* See for example Wintner's account<sup>5</sup> of the three-body astronomical problem, where rotational and Coriolis terms are also stated.

motion of  $N = 3$  points, where  $3N - 6 = 2N - 3 = 3$ ). In particular, for  $N = 4$  points there are  $n = 5$  coordinates in plane motion, a case of interest in some dissociation problems. For the present method to work for nonplanar motions (where  $n = 3N - 6$ ), it appears that we cannot allow any three particles to be collinear unless  $N \geq 6$ , nor four to be coplanar unless  $N \geq 7$ .

**Angular coordinates.** If a triatomic molecule  $abc$  (or a triatomic set  $abc$  in a larger molecule) has a valence angle at atom  $a$ , it is often convenient to take this angle  $\phi = bac$  as an internal coordinate; let us write  $g_3 = \phi$  or  $\phi - \phi_0$ , where  $\phi_0$  is the equilibrium value of  $\phi$ . Now

$$\cos \phi = \{(x_a - x_b)(x_a - x_c) + \dots\} / (ab)(ac) \quad (24)$$

where  $(ab)$  denotes the distance from atom  $a$  to  $b$ . We find from (16) by differentiation and the triangle cosine formula, that

$$g_{33} = (ab)^{-2}(ac)^{-2} \{ (bc)^2 m_a^{-1} + (ac)^2 m_b^{-1} + (ab)^2 m_c^{-1} \}, \quad (25)$$

and this result is of course independent of the other coordinates chosen. If coordinates  $q_1$  and  $q_2$  are the distances  $(ab)$  and  $(ac)$  as before (considered here as interatomic bonds), then we may express (25) as

$$g_{33} = 1/(M_{ab}q_1^2) + 1/(M_{ac}q_2^2) - 2 \cos \phi / (m_a q_1 q_2); \quad (26)$$

and we find also from (16) that

$$g_{13} = -\sin \phi / (m_a q_2), \quad g_{23} = -\sin \phi / (m_a q_1). \quad (27)$$

Thus for the triatomic molecule with coordinates the "bonds"  $q_1, q_2$ , and included angle  $q_3$ , the complete set of  $g_{rs}$  is (26) and (27) together with (21) and (22), namely,

$$g_{11} = M_{ab}^{-1}, \quad g_{22} = M_{ac}^{-1}, \quad g_{12} = \cos \phi / m_a. \quad (28)$$

This complete set is to be contrasted with (23), where  $q_3$  was the third side  $(bc)$  and not the angle. For the present coordinates the results (26)–(28) are of course still valid when the set  $abc$  is part of a larger molecule.

For more complicated internal coordinates, reference should be made to WDC.

### 3.3 SYMMETRY COORDINATES

Having expressed the molecular energies in terms of Cartesian coordinates  $x_a$  or internal coordinates  $q_r$ , we do not usually proceed directly to the determination of the vibration modes. We first examine what symmetry the molecule has, and then set up appropriate *symmetry coordinates*.<sup>1</sup> This often breaks down the vibration problem into several smaller problems, as we shall see. WDC have provided a full

and indispensable exposition of the effects of symmetry, but the following rather loose account may be of use and interest.

We are concerned here only with molecules containing sets of identical atoms, for example ammonia or ethane. The equilibrium configuration of such a molecule generally has such symmetry that there is a *group* of geometrical operations ("GeO's") of rotation and reflection which interchange or permute specific identical atoms (for example, the hydrogens in ammonia). The word "group" implies that two successive GeO's  $A$  and  $B$  have the same net result as some other GeO  $C$  (or, " $BA = C$ "); that there is a unit operation  $I$  which corresponds to doing nothing; and that for any  $A$  there is a reverse operation  $D$  restoring the original arrangement (so  $DA = I$ ).

If we apply these same GeO's to a distorted configuration of the molecule, we permute the displacements and velocities along with the corresponding atoms; so that, for example, near the position where we had atom  $a$  with velocity  $\dot{x}_a$  a GeO may give us an identical atom with velocity  $\pm \dot{x}_b$ . Here, if we are using Cartesians ( $x_a, y_a, z_a$ ), it is well to give them all local origins at the equilibrium atomic positions; and also, if (as is common) there is an axis of highest-order rotational symmetry, we should orient our  $z$ -coordinates along it and our  $x$ -axes to meet it perpendicularly. Alternatively, if we are using interatomic distances (and perhaps angles) as coordinates, we should choose such sets that the GeO's permute them along with their terminal atoms.

We may represent the GeO's of the group abstractly by numbers (or matrices) having the same multiplication table; for instance, if the GeO's  $A$  and  $B$  in the definition above were represented by  $+1$  and  $-1$ , then their "product"  $C$  would necessarily be represented by  $-1$ . The simplest or *one-dimensional irreducible representations* ( $1-IR$ 's) of the group are in fact of this nature, namely, a set of  $+1$ 's, or certain sets of  $+1$ 's and  $-1$ 's.

For a given  $1-IR$ , we may write down a maximum set of independent linear combinations  $s_1, s_2, \dots$  of atomic or internal coordinates (such as  $s_1 = (x_a + x_b + x_c)$  in local Cartesians or  $(q_\alpha + q_\beta + q_\gamma)$  in distance coordinates) which are all *unchanged* when we apply to the coordinates any GeO which is represented by  $+1$  in our  $IR$ , and which all *reverse* ( $s_r$  becoming  $-s_r$ ) when we apply any GeO with representative  $-1$ . These linear combinations\*  $s_1, s_2, \dots$  are called the *sym-*

\* A simple (but not the most economical) rule for their construction is: pick a particular coordinate, say  $q_\alpha$ ; operate on it with all the GeO's in turn (giving  $q_\alpha$  for  $I$ ,  $q_\beta$  say for operation  $A$ , etc.); multiply the results  $q_\alpha, q_\beta$  by the respective  $IR$  number,  $+1$  or  $-1$ , of the GeO concerned; then the sum of these products is either a symmetry coordinate or is zero. The procedure is repeated until the maximum set is obtained.

metry coordinates associated with the given IR; there is one independent set for each 1-IR.

We may also have two-dimensional IR's, in which the GeO's  $A$ ,  $B$ ,  $\dots$  are represented abstractly by two-by-two orthogonal matrices  $A_{uv}$ ,  $B_{uv}$ ,  $\dots$  with the same multiplication table. For a given 2-IR, we may construct two maximum sets, say  $s_3, s_4, \dots$  and  $s'_3, s'_4, \dots$ , of independent linear combinations of the  $x_a$  or  $q_a$ , which have the following property: if any GeO,  $A$  say, is applied to the  $x_a$  or  $q_a$ , then

$$s_r \rightarrow s_r \cos \theta_A - s'_r \sin \theta_A, \quad s'_r \rightarrow \pm (s_r \sin \theta_A + s'_r \cos \theta_A), \quad (29)$$

where  $\theta_A$  (and the  $\pm$  sign) is the same for *all* pairs  $r=3, r=4, \dots$ , one from each set.\* These combinations  $s_3, s_4, \dots, s'_3, s'_4, \dots$  are said to form two degenerate sets of symmetry coordinates for the 2-IR considered. Similarly three-dimensional IR's (occurring with cubic groups) give rise to triply degenerate sets.

It can be shown that, from the  $n$  internal coordinates  $q_1, \dots, q_n$  (or Cartesians with linear and angular momenta eliminated) we arrive by these constructions at exactly  $n$  symmetry coordinates  $s_1, s_2, s_3, s_4, s'_3, s'_4, \dots$  as independent linear combinations; and we may solve these relations to obtain the  $q$ s in terms of the  $s$ s. Using these results, we express the kinetic energy (6) in terms of  $\dot{s}_1, \dot{s}_2, \dots$ ; and we find that there are no cross terms connecting different sets of symmetry coordinates. For ammonia, for example (compare WDC, Sec. 6-2), when the over-all momenta have been removed, there remain two symmetry coordinates  $s_1, s_2$  belonging to one 1-IR, and one 2-IR with sets  $s_3, s_4$  and  $s'_3, s'_4$ . Thus the kinetic energy  $T(\dot{q}_1, \dots, \dot{q}_6)$  transforms into

$$T = T_1(\dot{s}_1, \dot{s}_2) + T_2(\dot{s}_3, \dot{s}_4) + T_2(\dot{s}'_3, \dot{s}'_4) \quad (30)$$

$$= a\dot{s}_1^2 + b\dot{s}_1\dot{s}_2 + c\dot{s}_2^2 + d\dot{s}_3^2 + e\dot{s}_3\dot{s}_4 + f\dot{s}_4^2 \\ + d\dot{s}'_3^2 + e\dot{s}'_3\dot{s}'_4 + f\dot{s}'_4^2, \quad (31)$$

the coefficients in the  $T_2$ s being the same. Clearly the value of  $T$  (in any form) is unaffected by the GeO's. To check this for symmetry coordinates, we recall that for the 1-IR coordinates, neither or both of  $s_1$  and  $s_2$  reverse under a GeO; so  $T_1$  is invariant. For the 2-IR coordinates we see from (29) that  $\dot{s}_3^2 + \dot{s}'_3^2$  and so forth are invariant under the GeO's; so in (30)  $T_2 + T_2$  is invariant. Cross terms between different sets (for example,  $\dot{s}_2\dot{s}_3$  or  $\dot{s}_3\dot{s}'_4$ ) could not be invariant (individually or in sum) for all GeO's, and are absent.

\* One rule of construction for a set is: operate on a  $q_a$  with the GeO  $A$  and multiply by  $A_{uv}$ ; then sum these results over all operators, keeping  $u$  and  $v$  fixed; repeat for distinct coordinates  $q_b, \dots$  and both values of  $v$  or  $u$

A quadratic potential  $V$ , with the necessary symmetry to be unchanged under the GeO's, breaks down in the same way into (in this example)  $V_1(s_1, s_2) + V_2(s_3, s_4) + V_2(s_3', s_4')$ . Thus the whole dynamical problem of vibrations separates into smaller problems, one for each 1-IR and two identical problems for the two sets of symmetry coordinates of each 2-IR (which give rise therefore to degenerate vibrations). The vibrations of the symmetry coordinates of one IR are said to constitute one *symmetry species*.

### 3.4 NORMAL COORDINATES

Having discussed internal and symmetry coordinates, we now introduce normal coordinates. The determination of these is equivalent to the solution of the vibration problem (which follows in 3.5), but they deserve a separate account because some of the formulas are important in the later theory.

We begin with the energies in the form (6) and (11), which we write

$$\left. \begin{aligned} T &= T(\dot{q}_1, \dots, \dot{q}_n) = \frac{1}{2} \sum_1^n \sum a_{rs} \dot{q}_r \dot{q}_s \\ V &= V(q_1, \dots, q_n) = \frac{1}{2} \sum_1^n \sum b_{rs} q_r q_s \end{aligned} \right\} \quad (32)$$

The present theory applies equally to  $T$  and  $V$  in terms of symmetry coordinates, and most usefully to the partial energies  $T_r$  and  $V_r$  containing a single set of symmetry coordinates of one IR (for example,  $T_2(s_3, s_4)$  and  $V_2(s_3, s_4)$  at the end of 3.3). To fix ideas, however, let us consider at present that we are dealing with a whole unsymmetrical molecule with internal coordinates  $q_1, \dots, q_n$ .

*Normal coordinates* are linear combinations  $Q_i$  of  $q_1, \dots, q_n$  in terms of which  $T$  and  $V$  reduce to sums of squares:

$$T = \sum_1^n a_i \dot{Q}_i^2, \quad V = \sum_1^n b_i Q_i^2. \quad (33)$$

The  $a_i$  or  $b_i$  are arbitrary, the ratios  $a_i/b_i$  determinate. It will be convenient to scale the normal coordinates  $Q_i$  by demanding that the forms be

$$T = \sum_1^n \dot{Q}_i^2 / \lambda_i, \quad V = \sum_1^n Q_i^2 \quad (34)$$

(although these forms may be regarded by some as an abnormal re-normalization). Since for a vibrating system  $V$  as well as  $T$  is positive,

so also are the constants  $\lambda_i$ ; they will in fact be found to be  $(2\pi\nu_i)^2$ , where the  $\nu_i$  are the possible vibration frequencies.

Let the transformation turning (32) into (34) be

$$q_r = \sum_{i=1}^n \alpha_{ri} Q_i, \quad (r = 1, \dots, n); \quad (35)$$

we associate suffixes  $r, s, u$  with internal coordinates  $q$ , and  $i$  and  $j$  with normal coordinates  $Q$  and normal modes. As we require this to be a nonsingular transformation, we must have a nonzero determinant:

$$\|\alpha_{ri}\| \neq 0. \quad (36)$$

Substituting (35) in (32) and identifying coefficients with (34), we find

$$\sum_r \sum_s a_{rs} \alpha_{ri} \alpha_{sj} = 0, \quad \sum_r \sum_s b_{rs} \alpha_{ri} \alpha_{sj} = 0 \quad (i \neq j) \quad (37)$$

and also

$$\frac{1}{2} \sum_r \sum_s a_{rs} \alpha_{ri} \alpha_{sj} = 1/\lambda_j, \quad \frac{1}{2} \sum_r \sum_s b_{rs} \alpha_{ri} \alpha_{sj} = 1, \quad (38)$$

which may be written formally, by (32), as •

$$T(\alpha_{1j}, \dots, \alpha_{nj}) = 1/\lambda_j, \quad V(\alpha_{1j}, \dots, \alpha_{nj}) = 1. \quad (39)$$

Multiplying the first equation in either (37) or (38) by  $\lambda_j$  and subtracting the corresponding second equation gives, for all  $j$ ,

$$\sum_r \alpha_{ri} f_r = 0 \quad (i = 1, \dots, n), \quad (40)$$

where

$$f_r \equiv \sum_s (a_{rs} \lambda_j - b_{rs}) \alpha_{sj}. \quad (41)$$

Since by (36)  $\|\alpha_{ri}\| \neq 0$ , the unique solution of (40) is  $f_r = 0$ ; that is, by (41),

$$\sum_s (a_{rs} \lambda_j - b_{rs}) \alpha_{sj} = 0 \quad (r = 1, \dots, n). \quad (42)$$

By (36),  $\alpha_{1j}, \dots, \alpha_{nj}$  cannot all vanish; so the equations (42) for fixed  $j$  imply that

$$\|a_{rs} \lambda_j - b_{rs}\| = 0. \quad (43)$$

Hence  $\lambda_1, \dots, \lambda_n$  in (34) are the roots (assumed here for simplicity to be distinct) of the *secular equation* in  $\lambda$ :

$$\|a_{rs} \lambda - b_{rs}\| = 0 \quad (r, s = 1, \dots, n). \quad (44)$$

One root  $\lambda_j$  of this determines one column  $(\alpha_{1j}, \dots, \alpha_{nj})$  of the matrix  $\{\alpha_{rj}\}$ . For, considering (42) as a set of equations for  $\alpha_{1j}, \dots, \alpha_{nj}$ , we see from (43) that they are satisfied by

$$\alpha_{1j}/H_1 = \alpha_{2j}/H_2 = \dots = \alpha_{nj}/H_n = k_j, \quad (45)$$

where  $k_j$  is arbitrary and  $H_1, \dots, H_n$  are the cofactors of the elements in any one row of the determinant  $\|a_{rs}\lambda_j - b_{rs}\|$ .<sup>\*</sup> The  $\alpha_{sj}$  of (45) give "unnormalized" normal coordinates as in (33). To obtain the "normalized" form (34) we substitute (45) in either of equations (38) (or of (39)); this gives, for example,

$$k_j^{-2} = \frac{1}{2} \sum \sum b_{rs} H_r H_s \equiv V(H_1, \dots, H_n). \quad (47)$$

Thus, finally, we can calculate the  $\alpha_{rj}$  from either of the forms

$$\alpha_{rj} = H_r \{V(H_1, \dots, H_n)\}^{-\frac{1}{2}} = H_r \{\lambda_j T(H_1, \dots, H_n)\}^{-\frac{1}{2}}, \quad (48)$$

where  $H_1, \dots, H_n$  are the cofactors of a row in  $\|a_{rs}\lambda_j - b_{rs}\|$ .

**Matrix notation.** It is worth while to repeat and extend some of the results in matrix notation. We denote the matrix  $\{\alpha_{ri}\}$  by  $\alpha$ , its *transpose* by  $\alpha'$  (so  $\alpha_{ir}' = \alpha_{ri}$ ), and the unit (diagonal) matrix by  $\mathbf{1}$ ; we also construct a diagonal matrix  $\lambda$  as

$$\lambda = \begin{pmatrix} \lambda_1 & \cdot & \cdot & \cdot \\ \cdot & \lambda_2 & \cdot & \cdot \\ \cdot & \cdot & \cdot & \lambda_n \end{pmatrix}. \quad (49)$$

The conditions (37) and (38), involving the  $\lambda_j$ , may now be written jointly as

$$\frac{1}{2} \alpha' \alpha \lambda = \lambda^{-1}, \quad \frac{1}{2} \alpha' \mathbf{b} \alpha = \mathbf{1}. \quad (50)$$

Thus if  $x$  is a variable number,

$$\frac{1}{2} \alpha' (ax - \mathbf{b}) \alpha = \lambda^{-1} x - \mathbf{1}. \quad (51)$$

This implies, using (36), that the determinant  $\|ax - \mathbf{b}\|$ , as a polynomial in  $x$ , is a multiple of  $\|\lambda^{-1}x - \mathbf{1}\|$  or equivalently of  $\|x\mathbf{1} - \lambda\|$ . It therefore has the same factors. Now by (49)  $\|x\mathbf{1} - \lambda\|$  has factors  $x - \lambda_j$ ; hence the  $\lambda_j$  are the roots of  $\|ax - \mathbf{b}\| = 0$ , or (writing plain  $\lambda$  for  $x$ ) of

$$\|a\lambda - \mathbf{b}\| = 0, \quad (52)$$

<sup>\*</sup> If we regard the equations (suggested by (42))

$$\sum_r (a_{rs}\lambda - b_{rs})x_s = 0 \quad (r = 1, \dots, n) \quad (46)$$

as determining a "vector"  $(x_1, x_2, \dots, x_n)$ , then the roots of (44) may be called the "eigenvalues" of  $\lambda$ , for which (46) has a nontrivial solution; and for  $\lambda = \lambda_j$  the solution  $(x_1, \dots, x_n)$ , corresponding to (45), is the corresponding "eigenvector."

which is again the result (43).

Another form of the secular equation is obtained if we introduce a matrix  $\mathbf{c}$ , an epitome of the dynamical behavior, as

$$\mathbf{c} = \mathbf{a}^{-1}\mathbf{b} \equiv \mathbf{g}\mathbf{b} \quad (53)$$

(compare (9)). For if we premultiply (52) by  $\|\mathbf{a}^{-1}\|$ , we have the new form

$$\|\lambda\mathbf{1} - \mathbf{c}\| = 0, \quad (54)$$

where now  $\lambda$  occurs only on the principal diagonal.

**Further matrix formulas.** By introducing pairs of reciprocal matrices we write (53) as

$$\mathbf{c} = \boldsymbol{\alpha}(\boldsymbol{\alpha}^{-1}\mathbf{a}^{-1}\boldsymbol{\alpha}'^{-1})(\boldsymbol{\alpha}'\mathbf{b}\boldsymbol{\alpha})\boldsymbol{\alpha}^{-1}. \quad (55)$$

The first bracket is the reciprocal of  $(\boldsymbol{\alpha}'\mathbf{a}\boldsymbol{\alpha})$ , which occurs in (50), as does the second bracket; hence by (50)

$$\mathbf{c} = \boldsymbol{\alpha}\boldsymbol{\lambda}\boldsymbol{\alpha}^{-1}. \quad (56)$$

Forming successive powers of (56), we obtain

$$\boldsymbol{\alpha}\boldsymbol{\lambda}^m\boldsymbol{\alpha}^{-1} = \mathbf{c}^m. \quad (57)$$

These results (56) and (57) also follow from the fact that the columns of  $\boldsymbol{\alpha}$  are the eigenvectors of the secular equation, and so the results hold also for the "unnormalized" eigenvectors corresponding to the forms (33). To obtain a useful form of (57) for our "normalization" (34), we postmultiply (57) by  $\boldsymbol{\alpha}\boldsymbol{\alpha}'$ , obtaining

$$\boldsymbol{\alpha}\boldsymbol{\lambda}^m\boldsymbol{\alpha}' = \mathbf{c}^m\boldsymbol{\alpha}\boldsymbol{\alpha}'. \quad (58)$$

Now, by (50),  $\mathbf{b} = 2\boldsymbol{\alpha}'^{-1}\boldsymbol{\alpha}^{-1} = 2(\boldsymbol{\alpha}\boldsymbol{\alpha}')^{-1}$ . Hence (58) is

$$\boldsymbol{\alpha}\boldsymbol{\lambda}^m\boldsymbol{\alpha}' = 2\mathbf{c}^m\mathbf{b}^{-1} = 2\mathbf{c}^m\mathbf{h}, \quad (59)$$

where  $\mathbf{h} = \mathbf{b}^{-1}$  is the reciprocal of the force-constant matrix. This result (59) will be used in the quantum theory. In classical theory we shall use only the cases  $m=0, 1$  (which are really inverted forms of (50)), namely,

$$\boldsymbol{\alpha}\boldsymbol{\alpha}' = 2\mathbf{b}^{-1} \equiv 2\mathbf{h}, \quad \boldsymbol{\alpha}\boldsymbol{\lambda}\boldsymbol{\alpha}' = 2\mathbf{a}^{-1} \equiv 2\mathbf{g}. \quad (60)$$

In particular, we shall need the (1, 1) element of these matrix equations, namely,

$$\sum_i \alpha_{1i}^2 = 2B_{11}/B \equiv 2h_{11}, \quad \sum_i \alpha_{1i}^2\lambda_i = 2A_{11}/A \equiv 2g_{11}. \quad (61)$$

## 3.5 SOLUTION OF THE MOTION

Four methods of solution are given, of which (i) and (ii) are the most important. Method (i) completes the argument of 3.4, using the normal coordinates; the notations given here are largely used in later work. The Lagrangian method (ii) is simple and direct, starting from the original energy forms. The Hamiltonian method (iii) is mainly a bridge to a new "Lagrangian-momentum" method (iv), which has a bearing later on the dissociation problem. Attention is confined here to classical mechanics.

(i) **Normal coordinates.** With the form (34) of the energies, the classical (and similarly the quantum) problem separates into  $n$  problems, one for each normal coordinate. In the  $i$ th coordinate we have energies

$$T_i = \dot{Q}_i^2/\lambda_i, \quad V_i = Q_i^2. \quad (62)$$

This is seen to represent a linear harmonic oscillator of frequency  $\nu_i$ , where

$$\lambda_i = 4\pi^2\nu_i^2, \quad (63)$$

and the solution of the motion is

$$Q_i = A_i \cos 2\pi(\nu_i t + \psi_i) \quad (0 \leq \psi_i < 1), \quad (64)$$

with amplitude  $A_i$  and phase constant  $\psi_i$ . We have therefore  $n$  normal modes, one for each coordinate  $Q_i$ .

If the energy in the  $i$ th mode is  $T_i + V_i = \epsilon_i$ , then substituting (64) in (62) gives  $A_i^2 = \epsilon_i$ ; the unconventional normalization in (34) was chosen for the sake of this simple relation. Thus in terms of the energy in the mode,

$$Q_i = \sqrt{\epsilon_i} \cos 2\pi(\nu_i t + \psi_i). \quad (65)$$

Finally, the motion in the original coordinates  $q_r$  is, by (35),

$$q_r = \sum_{i=1}^n \alpha_{ri} Q_i = \sum_{i=1}^n \alpha_{ri} \sqrt{\epsilon_i} \cos 2\pi(\nu_i t + \psi_i). \quad (66)$$

This can be regarded as the superposition of  $n$  oscillations; in any one normal mode the coordinates  $q_1, \dots, q_n$  have the same frequency  $\nu_i$  and the same  $\psi_i$ , and the amplitudes are proportional to  $|\alpha_{1i}|, \dots, |\alpha_{ni}|$ . We cannot say strictly that the phases in  $q_1, \dots, q_n$  are all the same, since  $\alpha_{1i}, \alpha_{2i}, \dots, \alpha_{ni}$  are generally some positive and some negative; the phases are thus equal or "opposite." Because of their role in (66), the  $\alpha_{ri}$  will be called *amplitude factors*.

The total energy of the system is, by (34) and (65),

$$E = \sum_1^n \epsilon_i, \quad (67)$$

namely, the sum of the energies in the modes. This can be verified rather painfully by adding the original energies (6) and (11), substituting (66) for  $q_r$ , and using (37) and (38).

(ii) **Lagrangian method.** The Lagrangian equations

$$\frac{d}{dt} \left( \frac{\partial L}{\partial \dot{q}_r} \right) = \frac{\partial L}{\partial q_r} \quad (68)$$

with the Lagrangian function  $L = T - V$  and the *original* forms (6) and (11) of  $T$  and  $V$ , are

$$\sum_s a_{rs} \ddot{q}_s = - \sum_s b_{rs} q_s \quad (r = 1, \dots, n), \quad (69)$$

when the  $a_{rs}$  are treated as constants. Assuming a solution with the  $q_s$  proportional to  $\cos(t\sqrt{\lambda} + \phi)$  gives

$$\sum_s (a_{rs}\lambda - b_{rs}) q_s = 0. \quad (70)$$

The condition on  $\lambda$  for a nonzero solution  $q_1, \dots, q_n$  is (44), the secular equation as before; the roots in  $\lambda$  give the normal-mode solutions, with the (signed) amplitudes of  $q_1, \dots, q_n$  in a mode forming an eigenvector as before.

(iii) **A Hamiltonian method.** The Hamiltonian  $H = \sum_r p_r \dot{q}_r - L$ , expressed by means of (8) in terms of  $p_s$  and  $q_s$ , takes the form  $T + V$  given by (10) and (11). The Hamiltonian equations,

$$\dot{q}_r = \partial H / \partial p_r, \quad \dot{p}_s = - \partial H / \partial q_s \quad (71)$$

are therefore

$$\dot{q}_r = \sum_s g_{rs} p_s, \quad \dot{p}_s = - \sum_u b_{su} q_u. \quad (72)$$

Differentiating the former and substituting for  $\dot{p}_s$  from the latter relation gives

$$\ddot{q}_r = - \sum_u c_{ru} q_u, \quad (73)$$

where  $c_{ru} = \sum_s g_{rs} b_{su}$  as in (53). Assuming again a periodic solution, we obtain this time the secular equation in the form (54).

Another Hamiltonian treatment is given in WDC, page 65.

(iv) **A Lagrangian-momentum method.** From a Hamiltonian function  $H(q, p)$  based on a quadratic potential, we may form a "Lagrangian-momentum" function  $M$  defined as

$$M = H + \sum \dot{p}_r q_r, \quad (74)$$

where  $\dot{p}_r$  is defined by the second group in (71); these same equations are used to eliminate the  $q$ s and so to express  $M$  as a function of the  $\dot{p}$ s and  $p$ s. It is easily verified (in much the same way as we could recover the Lagrange equations (68) from (71)) that the equations of motion in terms of  $M$  are

$$\frac{d}{dt} \left( \frac{\partial M}{\partial \dot{p}_r} \right) = \frac{\partial M}{\partial p_r}. \quad (75)$$

For the present type of problem it is seen that  $M = T - V$ , where  $T$  is in the form (10), and  $V$  is (11) converted into a function of the  $\dot{p}$ s by means of the second set of (72); so

$$V = \frac{1}{2} \sum \sum h_{rs} \dot{p}_r \dot{p}_s, \quad (76)$$

where  $\mathbf{h} = \mathbf{b}^{-1}$  as in (59). The equations (75) are therefore

$$-\sum_s h_{rs} \ddot{p}_s = \sum_s g_{rs} p_s. \quad (77)$$

Assuming again a periodic solution we find a *secular equation*:

$$\|h_{rs}\lambda - g_r\| = 0. \quad (78)$$

This is seen to be equivalent to the earlier forms, since  $\mathbf{h} = \mathbf{b}^{-1}$  and  $\mathbf{g} = \mathbf{a}^{-1}$ .

### 3.6 MEAN AND CONSTRAINED FREQUENCIES

We shall discuss a parameter  $\nu$ , which is of the nature of a frequency but is associated with a particular internal (nonnormal) coordinate. It will be prominent in the later dissociation theory, which also centers on the behavior of such a coordinate; and (to reveal the plot prematurely)  $\nu$  will in fact turn out to be the Arrhenius  $A$ -factor of a classical rate constant. The parameter is first defined baldly as a certain weighted average vibration frequency, but it will also be connected with frequencies in constrained molecular configurations, foreshadowing the "activated complex." I interpolate in this work a general theorem which it suggested concerning products of constrained frequencies, and I add some important special forms of  $\nu$  for distance coordinates.

**Definition of  $\nu$ .** We fix attention on one of the internal coordinates  $q_1, \dots, q_n$ ; let us choose  $q_1$ . We define  $\nu$  as the root mean square of the normal frequencies  $\nu_1, \dots, \nu_n$  weighted with the amplitude factors (compare 3.5(i))  $\alpha_{11}, \dots, \alpha_{1n}$  of the respective normal modes as they affect  $q_1$ . Thus

$$\nu = \left\{ \sum_1^n \alpha_{1i}^2 \nu_i^2 / \sum_1^n \alpha_{1i}^2 \right\}^{\frac{1}{2}}. \quad (79)$$

For the corresponding parameter  $\bar{\lambda}$ , defined by analogy with (63) as

$$\bar{\lambda} = 4\pi^2\nu^2, \quad (80)$$

we have, by (79) and (63),

$$\bar{\lambda} = \sum \alpha_{1i}^2 \lambda_i / \sum \alpha_{1i}^2. \quad (81)$$

From its definition as a mean, we see that

$$\nu \text{ lies between the greatest and least of the normal frequencies.} \quad (82)$$

**Constrained systems and the activated complex.** By comparing (81) with (61), it is seen that

$$4\pi^2\nu^2 \equiv \bar{\lambda} = (B/A)(A_{11}/B_{11}), \quad (83)$$

where  $A$  and  $B$  are the kinetic and potential determinants and  $A_{11}$  and  $B_{11}$  the cofactors of  $a_{11}$  and  $b_{11}$ . Now  $\lambda_1, \dots, \lambda_n$  are the roots of (44) in 3.4; so their product is the constant term in that equation divided by the coefficient of  $\lambda^n$ , or

$$\lambda_1\lambda_2 \dots \lambda_n = B/A. \quad (84)$$

Consider our dynamical system, with energies (32), but with  $q_1$  constrained to be zero, so that also  $\dot{q}_1=0$ . The constrained system lacks all terms with a suffix 1 in (32), and its secular equation is therefore (44) with the first row and column omitted. Thus if the new roots are  $\lambda'_2, \dots, \lambda'_n$ ,

$$\lambda'_2\lambda'_3 \dots \lambda'_n = B_{11}/A_{11}, \quad (85)$$

since, for example,  $A_{11} = \|a_{rs}\|$  with  $r, s=2, \dots, n$ . Hence, by (83)–(85),

$$\bar{\lambda} = \lambda_1\lambda_2 \dots \lambda_n / (\lambda'_2\lambda'_3 \dots \lambda'_n). \quad (86)$$

The corresponding result for frequencies is

$$\nu = \nu_1\nu_2 \dots \nu_n / (\nu'_2\nu'_3 \dots \nu'_n), \quad (87)$$

where  $\nu'_2, \dots, \nu'_n$  are the frequencies with  $q_1$  constrained to be zero. They are equally the frequencies with  $q_1$  fixed at any value  $q$ ; for although this constraint leaves terms  $q \sum_{s=2}^n b_{1s} q_s$  in  $V$  (compare (32)), these can be removed by a change of origin of  $q_2, \dots, q_n$  without affecting the frequencies. Thus

*$\nu$  is the product of the molecular frequencies divided by the frequencies for fixed  $q_1$ .* (88)

When later we associate a value  $q$  of  $q_1$  with an "activated complex," the frequencies  $\nu'_2, \dots, \nu'_n$  in (87) will be associated with the complex.

**Momentum constraints.** Again comparing (81) with (61), we see that

$$\bar{\lambda} = g_{11}/h_{11} \quad (89)$$

in terms of the inverse kinetic and potential matrices. This recalls the Lagrangian-momentum method of 3.5(iv). If the momenta  $p_2, \dots, p_n$  are constrained to be zero (and so also  $\dot{p}_2, \dots, \dot{p}_n$ ), the function  $M$  becomes

$$M = \frac{1}{2} g_{11} p_1^2 - \frac{1}{2} h_{11} \dot{p}_1^2. \quad (90)$$

This system has a single frequency,  $\nu_1''$  say, where

$$\lambda_1'' = 4\pi^2 \nu_1''^2 = g_{11}/h_{11}, \quad (91)$$

which is the same as (89). Thus

*$\nu$  is the frequency  $\nu_1''$  of the system when all the momenta except  $p_1$  are constrained to be zero.* (92)

This seems the only way in which we can associate  $\nu$  directly with motion (rather than absence of motion) in the relevant coordinate.

The equality of  $\nu_1 \dots \nu_n / (\nu'_2 \dots \nu'_n)$  in (87) with  $\nu_1''$  in (92) is the case  $f=1$  of the following theorem:

Let the system be constrained either (i) by holding coordinates  $q_1, \dots, q_f$  zero, or (ii) by holding momenta  $p_{f+1}, \dots, p_n$  zero. Let the frequencies of the constrained system (i) be  $\nu'_{f+1}, \dots, \nu'_n$ , and of (ii) be  $\nu'_1, \dots, \nu'_f$ . Then the product of all these frequencies equals the product of the unconstrained frequencies:

$$\nu_1'' \dots \nu_f'' \cdot \nu'_{f+1} \dots \nu'_n = \nu_1 \nu_2 \dots \nu_n. \quad (93)$$

To prove this, we observe that the secular equations in cases (i) and (ii) are: (i), (44) with the first  $f$  rows and columns deleted, and (ii), (78) with the last

\* By an old theorem, one frequency of such a constrained system lies between each pair of the unconstrained frequencies, if these are arranged in order of size. This theorem, applied to (87) as in 6.7 (131)–(133) below, confirms the result (82).

$n-f$  rows and columns deleted. Thus for the parameters  $\lambda_s$ , corresponding to frequencies, we have (compare (84))

$$(i) \quad \lambda'_{f+1} \cdots \lambda'_n = \|b_{rs}\| / \|a_{rs}\| \quad (r, s = f+1, \cdots, n) \quad (94)$$

$$(ii) \quad \lambda_{1''} \cdots \lambda_{f''} = \|g_{rs}\| / \|h_{rs}\| \quad (r, s = 1, \cdots, f). \quad (95)$$

Remembering that  $g_{rs} = A_{rs}/A$ ,  $h_{rs} = B_{rs}/B$  and using a result on determinants of cofactors, we find that the product of the right-hand sides of (94) and (95) is  $B/A$ , or  $\lambda_1 \lambda_2 \cdots \lambda_n$  by (84). The result (93) now follows on replacing all  $\lambda_s$  by  $\nu_s$ . The theorem may be of some dynamical value.

**Special values of  $\nu$ .** If our coordinate  $q_1$  is the *stretch of the distance between atoms* of masses  $m_a$  and  $m_b$ , then  $g_{11}^{-1}$  is their reduced mass  $M_{ab} = m_a m_b / (m_a + m_b)$ , by (21). Hence in (89)

$$4\pi^2 \nu^2 \equiv \bar{\lambda} = 1 / (h_{11} M_{ab}). \quad (96)$$

Thus  $\nu$  is independent of the masses of the other atoms.<sup>6</sup>

In the *special case* where also  $q_1$  is a nearly "isolated" bond, the off-diagonal force constants  $b_{12}, b_{13}, \cdots, b_{1n}$ , connecting  $q_1$  with other coordinates in (32), are small compared with  $b_{11}$ . In this case

$$B = \sum_1^n b_{1s} B_{1s} \cong b_{11} B_{11};$$

so that

$$h_{11} = B_{11}/B \cong 1/b_{11}. \quad (97)$$

The result is now

$$\nu \cong (2\pi)^{-1} (b_{11}/M_{ab})^{1/2}; \quad (98)$$

that is to say,  $\nu$  is very nearly the frequency of an imaginary diatomic molecule of atoms  $m_a$  and  $m_b$ , with the same force constant  $b_{11}$  as in the actual polyatomic molecule. This result is of much narrower application than (96), for (96) holds even if the direct bonding  $b_{11}$  between  $m_a$  and  $m_b$  is negligible.

By (17) in 3.2, the nature of  $g_{11}$  is determined by the type of the coordinate  $q_1$ ; so that, by (89), we can gain useful information about  $\nu$  (or  $\bar{\lambda}$ ) by looking at the type of  $q_1$ . For example, if  $q_1$  is an *angle* defined by an array of three atoms  $m_a, m_b, m_c$  within a molecule, then by (25)  $\nu$  depends on these masses and no others.

The main application of this type of result is to *isotopic substitutions*. If we assume that the force constants are unchanged, then the change in  $\nu$ , for an isotopic change of  $m_a$  or  $m_b$  at an end of a distance coordinate  $q_1$ , is as the change in  $M_{ab}^{-1/2}$ , by (96). Isotopic effects on angle-coordinate  $\nu$ s similarly depend on the adjacent atoms only, through

(25). An isotopic substitution not affecting the atoms defining  $q_1$  leaves  $\nu$  unaltered.

### 3.7 A SIMPLE EXAMPLE

Some of these methods and results of vibrational analysis will be illustrated here by the simple case of a linear triatomic molecule. We represent this schematically as

$$m_1 - (q_1) - m_0 - (q_2) - m_2, \quad (99)$$

$m_1, m_0, m_2$  being the atomic masses and  $q_1, q_2$  the stretches of the distances beyond equilibrium. Ignoring out-of-line distortions, we assume a potential energy

$$V = \frac{1}{2}b_1q_1^2 + \frac{1}{2}b_2q_2^2 \quad (100)$$

which is (11) with  $b_{12}=0$ . For the kinetic energy we have, from (21), (22), and (8),

$$2T = \mu_{01}p_1^2 - 2\mu_{01}p_1p_2 + \mu_{02}p_2^2 = \sigma^{-1} \{ \mu_{02}\dot{q}_1^2 + 2\mu_{01}\dot{q}_1\dot{q}_2 + \mu_{01}\dot{q}_2^2 \}, \quad (101)$$

where, with  $r, s=0, 1, 2$ ,

$$\mu_r \equiv m_r^{-1}, \quad \mu_{rs} \equiv \mu_r + \mu_s, \quad \sigma \equiv \sum_{r < s} \mu_r \mu_s. \quad (102)$$

Assuming vibrations of frequency  $\lambda^{1/2}/(2\pi)$ , the Lagrangian equations are, as in (70),

$$(\lambda\mu_{02} - \sigma b_1)q_1 + \lambda\mu_{02}q_2 = 0 = \lambda\mu_{01}q_1 + (\lambda\mu_{01} - \sigma b_2)q_2, \quad (103)$$

and the secular equation (44), obtained by eliminating  $q_1/q_2$  from (103), is

$$\lambda^2 - (b_1\mu_{01} + b_2\mu_{02})\lambda + b_1b_2\sigma = 0. \quad (104)$$

The roots, giving the *normal frequencies*  $\lambda_i^{1/2}/(2\pi)$ , are (with the *upper and lower signs* referring in (105) and (108) to modes 1 and 2 respectively)

$$\lambda_1, \lambda_2 = \frac{1}{2}(b_1\mu_{01} + b_2\mu_{02} \pm \beta) \quad (105)$$

where

$$\beta^2 \equiv \gamma^2 + 4b_1b_2\mu_0^2, \quad \gamma \equiv b_1\mu_{01} - b_2\mu_{02}. \quad (106)$$

*Amplitude factors*  $\alpha_{r_i}$  (compare (35) and (66)) of coordinate  $q_r$  in mode  $i$  are most easily found from (48) and the form (100) of  $V$ ; thus, for example, in the first mode

$$\alpha_{r_1} = II_r \left\{ \frac{1}{2}b_1H_1^2 + \frac{1}{2}b_2H_2^2 \right\}^{-1/2} \quad (r = 1, 2), \quad (107)$$

where  $H_1/H_2 = (\mu_{01} - \sigma b_2 \lambda_1^{-1}) / (-\mu_0)$ , namely, a  $q_1/q_2$  value of (103) with  $\lambda = \lambda_1$ . We find, using (105) and (106),

$$\begin{aligned} \text{for } q_1: \quad \alpha_{11}, \alpha_{12} &= \pm \left\{ (1 \pm \gamma/\beta)/b_1 \right\}^{\frac{1}{2}} \\ \text{for } q_2: \quad \alpha_{21}, \alpha_{22} &= - \left\{ (1 \mp \gamma/\beta)/b_2 \right\}^{\frac{1}{2}} \end{aligned} \quad (108)$$

The alternate sign outside the bracket illustrates the general rule that the sets of amplitude factors  $(\alpha_{11}, \alpha_{21}, \alpha_{31}, \dots)$ ,  $(\alpha_{12}, \alpha_{22}, \alpha_{32}, \dots)$ ,  $(\alpha_{13}, \alpha_{23}, \alpha_{33}, \dots)$  for different modes all have different combinations of relative signs, provided that either  $T$  or  $V$  in (32) is a sum of square terms.\* This proviso is met here by the form (100) of  $V$ .

The mean frequency  $\nu$  of 3.6 may now be illustrated; we suppose, as there, that  $q_1$  is the coordinate specially considered, corresponding to the "breaking coordinate" in the later reaction theory of Chapter 5. For the present case, (105) and (108) give in (81)

$$\alpha_{11}^2 + \alpha_{12}^2 = 2/b_1, \quad \alpha_{11}^2 \lambda_1 + \alpha_{12}^2 \lambda_2 = 2\mu_{01}, \quad (109)$$

and these results are seen to illustrate the matrix relations (61) for the energy forms (100) and (101). The mean frequency  $\nu = \bar{\lambda}^{1/2}/(2\pi)$  of (81) is thus given by

$$\bar{\lambda} = b_1 \mu_{01}, \quad (110)$$

so that  $\nu$  is the frequency of the diatomic  $m_0, m_1$  with force constant  $b_1$ , in the "absence" of  $m_2$ . This is a precise example of (96) or (98), since our special coordinate  $q_1$  is the  $m_0 - m_1$  stretch and there is no cross term  $q_1 q_2$  in  $V$ .

The constrained system of 3.6 (defined between (84) and (85)) is obtained by putting  $q_1 = 0 = \dot{q}_1$  in (100) and (101) (or alternatively fixing  $q_1$  at any value). It has the one frequency  $\lambda_2'^{1/2}/(2\pi)$ , where

$$\lambda_2' = b_2 \sigma \mu_{01}^{-1}, \quad (111)$$

which corresponds exactly to (85). Using (102) we may write (111) as

$$\lambda_2' = b_2 \left\{ \frac{1}{m_2} + \frac{1}{m_0 + m_1} \right\}, \quad (112)$$

which has the clear interpretation that when  $q_1$  is fixed,  $m_0$  and  $m_1$  move together, so that the frequency corresponds to the relative motion of masses  $m_0 + m_1$  and  $m_2$  under a force constant  $b_2$ .

\* This general rule, with this proviso, is an immediate consequence of (37), since the  $a_{rr}$  and  $b_{rr}$  are essentially positive. Thus if  $T$  or  $V$  in (32) is diagonal, the products  $\alpha_{11}\alpha_{1j}$ ,  $\alpha_{21}\alpha_{2j}$ ,  $\alpha_{31}\alpha_{3j}$ ,  $\dots$  cannot all have the same sign. When neither is diagonal the "rule" has no legal force, although in fact it is still commonly obeyed; compare Table 3.8 below.

The product of the  $\lambda$ , corresponding to the normal frequencies is given by (104) as  $\lambda_1\lambda_2 = b_1b_2\sigma$ . Hence by (110) and (111)

$$\bar{\lambda} = \lambda_1\lambda_2/\lambda_2', \quad (113)$$

which illustrates the general result (86) or (87) for  $\bar{\lambda}$  in terms of the normal  $\lambda$ , and the frequencies (here there is only one, namely,  $\lambda_2'^{1/2}/(2\pi)$ ) of the constrained system.

In the reaction theory of Chapters 5 and 6, the mean frequency  $\nu = \bar{\lambda}^{1/2}/(2\pi)$  associated with coordinate  $q_1$  will reappear as the  $A$ -factor of the rate constant  $k^\infty$ , if dissociation depends only on the critical stretching of coordinate  $q_1$ . The constrained frequency  $\lambda_2'^{1/2}/(2\pi)$ , of the system with  $q_1$  fixed, will then correspond to the "frequency of the activated complex." The relation (87) for the  $A$ -factor (here represented in our special case by (113)) is also a general formula of classical activated-complex theory (see 6.5(94) below).

It has been suggested to me recently that the  $A$ -factor should not depend solely on the masses  $m_0$  and  $m_1$  connected by the breaking coordinate (compare (110)), but also on the other masses, represented in the present example by  $m_2$ , which move away with  $m_0$  when  $q_1$  is broken. The natural  $A$ -factor suggested by this idea is  $\bar{\lambda}^{1/2}/(2\pi)$ , where

$$\bar{\lambda} = b_1 \left\{ \frac{1}{m_1} + \frac{1}{m_0 + m_2} \right\}, \quad (114)$$

which is (110) modified by adding  $m_2$  to  $m_0$ . If we adopted this, we should be bound to take as the new "frequency of the complex" the quantity  $\lambda_2''^{1/2}/(2\pi)$ , where (taking (87) as a general result of activated-complex theory now that in (114) we have abandoned my model)

$$\bar{\lambda} = \lambda_1\lambda_2/\lambda_2''. \quad (115)$$

From (114) and the value  $\lambda_1\lambda_2 = b_1b_2\sigma$  as before, we find

$$\lambda_2'' = b_2\mu_{02} = b_2 \left\{ \frac{1}{m_0} + \frac{1}{m_2} \right\}. \quad (116)$$

Thus\* the new frequency  $\lambda_2''^{1/2}/(2\pi)$  of the complex is (unlike (112)) independent of the mass  $m_1$  of an essential constituent of the complex; this seems to me an unlikely and undesirable result.

Presumably one could extend this type of argument to breaking

\* It is seen by comparison of (110) and (116) that  $\lambda''^{1/2}/(2\pi)$  is in fact my  $A$ -factor for  $q_2$  as critical coordinate; and  $\bar{\lambda}^{1/2}/(2\pi)$  is the corresponding constrained frequency for fixed  $q_2$ . This re-enforces the point that (114) is an unsuitable basis for an  $A$ -factor.

coordinates in larger molecules; but the present simple case serves as a warning against the dangers that lurk in modifications of the  $A$ -factor to "allow" for the effects of other masses.

### 3.8 NITRYL CHLORIDE AND THE DETERMINATION OF AMPLITUDE FACTORS

We pass now to a slightly more complicated type of molecule, namely, the planar  $XYZ_2$  type as exemplified by nitryl chloride,  $\text{NO}_2\text{Cl}$ . As well as being of interest in reaction kinetics, this molecule provides a simple illustration of the use of symmetry coordinates in

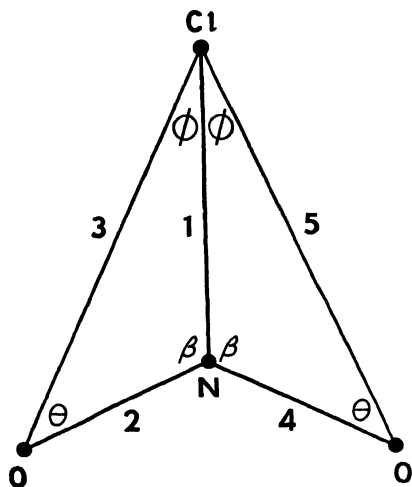


FIG. 3.8 -Nitryl chloride.

calculating vibrational amplitudes. After setting up the energy matrices for nitryl chloride, we discuss in more general terms the problem of determining force constants and vibration amplitudes. The results for nitryl chloride are then given in Table 3.8.

**Nitryl chloride.** The planar configuration of  $\text{NO}_2\text{Cl}$  (which was established by Millen and Sinnott<sup>7</sup>) is shown in Fig. 3.8, with symbols for the various angles and distances. Dr. D. R. Herschbach has very kindly given me his full vibrational analysis, which is based on the

$\text{NO}$  and  $\text{NCl}$  distances and  $\text{ONCl}$  angles (and the out-of-plane bending). While using his primary data, I prefer here to reanalyze the plane vibrations in terms of distances only, for this method has attractive features. Confining attention throughout to plane motions, we see that five of the six internuclear distances may be varied independently, so that we take the stretches (beyond equilibrium) of the distances 1, . . . , 5 of the figure as coordinates  $q_1, \dots, q_5$ . We write  $\mu_{\text{C}}, \mu_{\text{N}}, \mu_{\text{O}}$  for the reciprocals of the Cl, N, and O masses,  $\mu_{\text{CN}}$  for  $\mu_{\text{C}} + \mu_{\text{N}}$ , and, for example,  $c2\phi$  for  $\cos(2\phi)$ . In terms of the momenta  $p_r$  conjugate to the  $q_r$ , the kinetic energy (compare (23)) is

$$T = \frac{1}{2} \{ \mu_{\text{CN}} p_1^2 + \mu_{\text{NO}} (p_2^2 + p_4^2) + \mu_{\text{CO}} (p_3^2 + p_5^2) \} + \mu_{\text{O}} (p_2 p_3 + p_4 p_5) c\theta + \mu_{\text{C}} \{ p_1 (p_3 + p_5) c\phi + p_3 p_5 c2\phi \} + \mu_{\text{N}} \{ p_1 (p_2 + p_4) c\beta + p_2 p_4 c2\beta \}, \quad (117)$$

where the angles have their equilibrium values. For the potential energy, we take

$$V = \frac{1}{2} \{ k_1 q_1^2 + k_2 (q_2^2 + q_4^2) + k_3 (q_3^2 + q_5^2) \} \\ + k_{12} q_1 (q_2 + q_4) + k_{24} q_2 q_4 + k_{35} q_3 q_5; \quad (118)$$

thus we treat the two oxygens equally (by having equal coefficients for the pairs  $q_2, q_4$  and  $q_3, q_5$ ) and omit some possible cross terms which we like to think unimportant and which would be indeterminate in the present analysis.

Although the molecule has the symmetry  $C_{2v}$  in space, in the plane motion we need only the 2-element group  $C_2$  with operation  $I$ , the identity, and  $\sigma$ , the reflection in (or a half-turn around) the ClN line; the latter operation interchanges the oxygens, and so  $q_2$  with  $q_4$  and  $q_3$  with  $q_5$ . The irreducible representations of these operations are ( $A$ ) (symmetrical) 1, 1 and ( $B$ ) (antisymmetrical) 1,  $-1$ . Thus the rule of the first footnote in 3.3 gives the two sets of symmetry coordinates as ( $A$ )  $s_1, s_2, s_3$  and ( $B$ )  $s_4, s_5$ , where

$$s_1 = q_1, \quad s_2 = (q_2 \pm q_4)/\sqrt{2}, \quad s_3 = (q_3 \pm q_5)/\sqrt{2}, \quad (119)$$

the factors  $1/\sqrt{2}$  making the transformation matrix orthogonal. The reverse transformation is the same, namely,

$$q_1 = s_1, \quad q_2 = (s_2 \pm s_4)/\sqrt{2}, \quad q_3 = (s_3 \pm s_5)/\sqrt{2}, \quad (120)$$

and it is easily seen (compare (15)) that the *same* transformation connects the momenta  $p_r$  and  $P_r$ , conjugate respectively to the  $q_r$  and  $s_r$ .

This transformation breaks the energies (117) and (118) into forms  $T_A + T_B$  and  $V_A + V_B$  of the type

$$T_A, T_B = \frac{1}{2} \sum \sum g_{ru} P_r P_u, \quad V_A, V_B = \frac{1}{2} \sum \sum b_{ru} s_r s_u, \quad (121)$$

where  $r, u = 1, 2, 3$  in  $T_A, V_A$  and  $4, 5$  in  $T_B, V_B$ . From (117) and (118) the nonzero  $g_{ru}$  and  $b_{ru}$  are

$$\left. \begin{aligned} g_{11} &= \mu_{CN}, & g_{22} &= \mu_{ON} + \mu_N c2\beta, & g_{33} &= \mu_{OC} + \mu_C c2\phi, \\ & & g_{44} &= \mu_{ON} - \mu_N c2\beta, & g_{55} &= \mu_{OC} - \mu_C c2\phi, \\ g_{12} &= \mu_N \sqrt{2} c\beta, & g_{13} &= \mu_C \sqrt{2} c\phi, & g_{23} &= g_{45} = \mu_O c\theta, \\ b_{11} &= k_1, & b_{22} &= k_2 + k_{24}, & b_{33} &= k_3 + k_{35}, & b_{12} &= k_{12} \sqrt{2}, \\ & & b_{44} &= k_2 - k_{24}, & b_{55} &= k_3 - k_{35}. \end{aligned} \right\} \quad (122)$$

Thus, as was indicated in 3.3, we have separate vibrational problems for the symmetry species  $A$  and  $B$ . Before giving solutions of these, we discuss force constants and amplitude factors in a general way.

**Force constants.** Until the quantum chemists have put in some more hard work, we are unlikely to know the force constants  $k_r$  or  $b_{rn}$  of many particular molecules. We are more likely to have experimental frequencies  $\nu_i$ , reasonably assigned to symmetry species  $A, B, \dots$ . In this case, we expand the secular equation ((52), for example) of one species in powers of  $\lambda$  and equate the corresponding coefficients, involving the  $b_{rs}$ , to the symmetric sums  $4\pi^2 \sum \nu_i^2$ ,  $(4\pi^2)^2 \sum \nu_i^2 \nu_j^2$ ,  $\dots$ , of the experimental frequencies. These nonlinear equations in the  $b_r$ , we attempt to solve. Unless we are helped by isotopic frequencies, we have too many  $b_r$  to determine, so that we are driven to abolish some (as in (118), or in more drastic valence force assumptions) or to appeal to results for similar bonds in other molecules. The nonlinearity of the equations in the  $b_r$ , may still deny us a unique solution, so that the results are at best plausible rather than firm; and this insecurity carries over into the calculation of the amplitude factors, which we now consider.

**Amplitude factors.** From the force constants and kinetic energy coefficients, we may proceed to calculate the amplitude factors  $\alpha_{ri}$ , which were defined in (35), namely,

$$q_r = \sum_i \alpha_{ri} Q_i, \quad (123)$$

and evaluated in (48); we recall from (66) that, in a given mode with normal coordinate  $Q_i = \sqrt{\epsilon_i} \cos 2\pi(\nu_i t + \psi_i)$ , the "amplitudes"  $\alpha_{1i}, \dots, \alpha_{ni}$  show the relative behavior of  $q_1, \dots, q_n$ . Usually, however, we first calculate the amplitude factors,  $\beta_{ri}$ , say, of the *symmetry coordinates*  $s_r$ ; with the  $Q_i$  as before, we define the  $\beta_{ri}$  by the transformation

$$s_r = \sum_i \beta_{ri} Q_i. \quad (124)$$

This is a simpler calculation; for if we take the partial energies  $T_A, V_A$  of one symmetry species containing (in  $\text{NO}_2\text{Cl}$ , for example) just the coordinates  $s_1, s_2, s_3$ , then these energies transform into sums of just three square terms of the sets (34). Thus by labeling the normal coordinates similarly ( $Q_1, Q_2, Q_3$  in this example), we have in (124)

$$\beta_{ri} = 0 \text{ if } r, i \text{ belong to different species.} \quad (125)$$

So we calculate first the small block of  $\beta_{ri}$  for the energies  $T_A, V_A$  (these  $\beta_{ri}$  are in fact given by the appropriate cases of (48)), and then proceed to the other symmetry species  $T_B, V_B, \dots$ .

If the transformation from the original coordinates  $q_r$  to the  $s_r$  is ((120) being an example)

$$q_r = \sum \gamma_{ru} s_u, \quad (126)$$

then from (123) to (126) we finally obtain the amplitude factors of the  $q_r$  as

$$\alpha_{ri} = \sum_u \gamma_{ru} \beta_{ui}; \quad (127)$$

The values of  $u$ , for given  $i$ , run through the species containing the  $i$ th mode.

It is clear that the whole theory of 3.4 and 3.5 applies not only (i) to  $T$  and  $V$  in terms of the  $q_r$ , but equally (ii) to  $T$  and  $V$  in terms of the  $s_r$  and (iii) to  $T_A$  and  $V_A$  in terms of the  $s_r$  of one species  $A$ . In cases (ii) and (iii), we replace the  $\alpha_{ri}$  (for example, in equations (35)–(42), (48), (55) (61)) by  $\beta_{ri}$ , and use the appropriate energy matrices. Thus for example, (61) becomes for species  $A$  of  $\text{NO}_2\text{Cl}$ , with coordinates  $s_1, s_2, s_3$ ,

$$\sum_1^3 \beta_{1i}^2 = 2B_{11}/B, \quad \sum_1^3 \beta_{1i}^2 \lambda_i = 2g_{11}, \quad (128)$$

where  $B = \det \|b_{11}, \dots, b_{33}\|$  in (121),  $g_{11} = \mu c_N$ , and the  $\lambda_i^{1/2}/(2\pi)$  are the species  $A$  frequencies. Relations like (128) are, incidentally, useful checks on calculated  $\beta_{ri}$ s. A more academic exercise is to use the relation  $\alpha = \gamma\beta$  of (127) to deduce the results (60) for  $q_r$  coordinates, from the symmetry coordinate form of (60) for the  $\beta$  matrix.

**The calculations for nitryl chloride.** Returning now to the matrix elements (121), we see that all we need for the  $g_{rs}$  are two independent (equilibrium) angles of Fig. 3.8. These may be determined from the equilibrium configuration, in which (from the work of Millen and Sinnott<sup>8</sup>) the  $\text{NCl}$  and  $\text{NO}$  distances are 1.840 and 1.202 ångströms and the angle  $\text{ONO}$  is  $130^\circ 35' \pm 15'$ . For the force constants I take in (118) the values, in units  $10^4$  dyne/cm.,

$$\left. \begin{aligned} k_1 &= 54.93, & k_2 &= 93.48, & k_3 &= 27.09, \\ k_{12} &= 30.84, & k_{24} &= 1.62, & k_{35} &= 13.71. \end{aligned} \right\} \quad (129)$$

I gave myself a starting point by borrowing  $k_1 = b_{11}$  from Herschbach's analysis, although this appropriation is not strictly justifiable as he used two angular coordinates in place of  $q_3$  and  $q_5$  (with a diagonal matrix in symmetry coordinates). The remaining force constants (129) were calculated afresh from the experimental frequencies (due to

Ryason and Wilson<sup>9</sup> but with an interchange of  $\nu_3$  and  $\nu_6$  as suggested by Herschbach).

From the energy matrices I calculated the  $\beta_{ri}$ , the coefficients of the symmetry coordinates  $s_r$  in terms of the normal coordinates  $Q_i$ , and hence the amplitudes  $\alpha_{ri}$  of the  $q_r$  in the  $Q_i$ . The results are in Table

TABLE 3.8  
AMPLITUDES AND FREQUENCIES OF NITRYL CHLORIDE

	$Q_1$	$Q_2$	$Q_3$	$Q_4$	$Q_5$
$s_1$	0.37	2.18	0.90	0.0	0.0
$s_2$	0.95	-1.51	0.35	0.0	0.0
$s_3$	1.36	0.47	-1.68	0.0	0.0
$s_4$	0.0	0.0	0.0	1.47	-0.16
$s_5$	0.0	0.0	0.0	0.41	3.84
$q_1$	0.37	2.18	0.90	0.0	0.0
$\left. \begin{matrix} q_2 \\ q_4 \end{matrix} \right\}$	0.67	-1.07	0.25	$\pm 1.04$	$\mp 0.11$
$\left. \begin{matrix} q_3 \\ q_5 \end{matrix} \right\}$	0.96	0.33	-1.19	$\pm 0.29$	$\pm 2.72$
$\nu_1$	3.88	2.38	1.23	5.05	1.10

The amplitude factor  $\beta_{ri}$  ( $s_r = \sum \beta_{ri} Q_i$ ) is at the intersection of the  $s_r$  row and the  $Q_i$  column; the amplitude factor  $\alpha_{ri}$  ( $q_r = \sum \alpha_{ri} Q_i$ ) at the intersection of the  $q_r$  row and the  $Q_i$  column.

The amplitudes  $\beta_{ri}$  and  $\alpha_{ri}$  have as unit  $10^{-3}$  cm. erg<sup>-1/2</sup>, and the frequencies  $\nu_i$  have  $10^{13}$  sec.<sup>-1</sup>

3.8, with the "experimental" frequencies  $\nu_i$  (all values here rounded to two decimals). Formally, the  $\alpha_{ri}$  are given by (127) with the  $\gamma_{ru}$  the coefficients in (120). But a simpler way of putting this is to observe that the expressions (120) for the  $q_r$  in terms of the  $s_u$  hold equally when the system is vibrating in just, say, the  $i$ th mode; so that, for example, the  $q_2$  amplitude  $\alpha_{2i}$  is formed from the  $\beta_{ui}$  just as  $q_2$  is formed from  $s_u$ . Thus we can read off directly from (120) that

$$\alpha_{2i} = (\beta_{2i} + \beta_{4i})/\sqrt{2}.$$

*Remarks on the results:* The main point of interest is the pattern of behavior of the five stretches  $q_1, \dots, q_5$  in the various modes; if we study these in conjunction with Fig. 3.8, we can see what is happening to the whole configuration. The symmetric distortions in the *A* modes 1, 2, 3 and the antisymmetric distortions in the *B* modes 4, 5 are the most obvious features.

In mode 1, with its high frequency, we see (from the positive  $\alpha_{ri}$ ) the NCl and NO links stretching together. In the slower mode 2, the main motion is of the nitrogen away from the chlorine (and toward the oxygens, the OCl distance changing little); and in mode 3, still slower, the distortion is mainly of the ONO angle. Of the fast and slow antisymmetrical modes 4 and 5, the former affects the ON distances most, and the latter the ONCl angles. These behaviors are much as we would expect in view of the relative frequencies  $\nu_i$ , except perhaps in modes 2 and 3.

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# The Average Behavior of a Sum of Vibrations

**I**N the last chapter we analyzed molecular motion into normal vibrations. The present chapter is about the behavior of one molecular coordinate represented as a sum of  $n$  harmonic vibrations. The main problem is that of the average frequency (number of times per second) with which the sum rises to a given value  $q$ , which is usually in later applications a large value near the sum of the amplitudes  $a_i$  of the vibrations. This average frequency corresponds in the chemical problem to the probability of attaining a "dissociation configuration." The mathematical problem, however, is also related to random walks, electrical communication theory, and other fields.

In 4.1 the two types of average passage-frequency, namely,  $L$ , the average over the vibration phases, and  $L'$ , the long-time average, are shown to be equal when the harmonic vibration frequencies  $\nu_i$  are "linearly independent." Two approaches to  $L$  or  $L'$  are then described. First, a formula of Kac for the number of zeros of a general function is sketched in 4.2 and applied in 4.3 to establish his double integral, equation (16), for  $L$ . Secondly, formulas are found in 4.4 for the distribution of values of a sum of vibrations (or of a "random walk") and of the "velocity" of the sum; this leads to a reformulation of  $L'$  akin to transition-state theory.

The rest is of more numerical interest. In 4.5 we find bounds to  $L'$  and a Gaussian approximation for a large number of vibrations, and also a computable general form of  $L'$  as a Fourier series. In 4.6 an approximation is found for the frequency of high peaks of a sum of vibrations; this approximation is still of importance in the reaction theory.

**Historical note.** Many of the formulas have been collected in a survey.<sup>1</sup> The first formula for  $L'$  was given in 1935 by Stein<sup>2</sup> for the case of  $n=2$  vibrations; Kac and others<sup>3</sup> published a different approach

to this in 1939. At that time I gave the approximate  $L'$  for high peaks and general  $n$ , in the first account of the reaction theory,<sup>4</sup> and Stein proceeded to generalize his 1935 formula (see 4.3). Kac beat out the vital formula<sup>5,6</sup> (16) in 1943, but it was some years before I saw it and discussed it in a physical setting.<sup>7</sup> The Fourier series in 4.5 arose in drafting this chapter.

#### 4.1 TIME AVERAGES AND PHASE AVERAGES

We represent a sum of harmonic vibrations of the type 3.5 (66) by the function  $f(t)$  or  $F(\nu_1 t + \psi_1, \dots, \nu_n t + \psi_n)$ :

$$f(t) = F(\nu_1 t + \psi_1, \dots) = \sum_{i=1}^n a_i \cos 2\pi(\nu_i t + \psi_i), \quad (1)$$

where the *frequencies*  $\nu_i$  are positive, the  $a_i$  for convenience are positive and so may be called "amplitudes," and the *initial phases*  $\psi_i$  range from 0 to 1. The *dots*  $\dots$  in (1) and later expressions denote the rest of a set of  $n$  such quantities; thus  $d\psi_1 \dots$  will mean the product  $d\psi_1 d\psi_2 \dots d\psi_n$ .

Let

$$G(T; \psi_1, \dots) \quad (2)$$

be the number of times  $f(t)$  takes a given value  $q$  for  $0 \leq t < T$  (we occasionally write  $G_q$  to be more explicit). Our interest is in the *frequency of upzeros* of  $f(t) - q$ , or the number of times per second  $f$  rises to the value  $q$ . This is effectively  $\frac{1}{2}G(T; \psi_1, \dots)/T$ ; but to obtain a calculable form, we have to perform some averaging process, which also removes the dependence on  $T$  or  $\psi_1, \dots$ .

*The phase-averaged frequency:* Averaging (2) (for given  $T$  and  $q$ ) over random values of all the initial phases gives the function

$$\begin{aligned} \bar{G}(T) &= \int_0^1 \dots \int_0^1 G(T; \psi_1, \dots) d\psi_1 \dots \\ &= \int_0^1 \dots \int_0^1 G(T; \psi_1, \dots, \psi_n) d\psi_1 \dots d\psi_n. \end{aligned} \quad (3)$$

This exists as a Riemann integral.<sup>5</sup> Its value is proportional to  $T$ . For, counting zeros in two successive time intervals  $T$ ,

$$G(2T; \psi_1, \dots) = G(T; \psi_1, \dots) + G(T; \psi_1 + \nu_1 T, \dots),$$

and integrating this over appropriate unit ranges of the  $\psi_i$  gives  $\bar{G}(2T) = 2\bar{G}(T)$ , and so the result. It follows that the *phase-averaged frequency of upzeros*  $L$  (or  $L_q$ ), namely,

$$L = \frac{1}{2}\bar{G}(T)/T, \quad (4)$$

is independent of the time interval  $T$  for which it is calculated.

The asymptotic frequency of upzeros of  $f(t) - q$  is the long-time average:

$$L'(\psi_1, \dots) = \frac{1}{2} \lim_{T \rightarrow \infty} \{G(T; \psi_1, \dots)/T\} \quad (5)$$

The phase average of this, namely,

$$\bar{L}' = \int_0^1 \dots \int_0^1 L'(\psi_1, \dots) d\psi_1 \dots, \quad (6)$$

is equal to (4):

$$\bar{L}' = L. \quad (7)$$

Thus the phase-average frequency  $L$  is also the phase average of the asymptotic frequency  $L'$ .

To prove this perhaps exasperating statement, we observe that (4), being independent of  $T$ , may be written

$$L = \frac{1}{2} \lim_{T \rightarrow \infty} \{\bar{G}(T)/T\} = \frac{1}{2} \lim_{T \rightarrow \infty} \left\{ T^{-1} \int_0^1 \dots \int_0^1 G(T; \psi_1, \dots) d\psi_1 \dots \right\}.$$

Now  $G(T; \psi_1, \dots)/T$  is uniformly bounded for  $0 \leq \psi_i < 1$ ; so we may reverse the order of the limit and integral, obtaining

$$\begin{aligned} L &= \frac{1}{2} \int_0^1 \dots \int_0^1 \left\{ \lim_{T \rightarrow \infty} [G(T; \psi_1, \dots)/T] \right\} d\psi_1 \dots \\ &= \int_0^1 \dots \int_0^1 L'(\psi_1, \dots) d\psi_1 \dots = \bar{L}' \end{aligned}$$

by (5) and (6). This proves the result (7).

**Linearly independent frequencies.** The numbers  $\nu_1, \nu_2, \dots, \nu_n$  are said to be *linearly independent* in the field of rationals, or *l.i.* for short, if for all sets  $N_1, N_2, \dots, N_n$  of integers (of either sign but not all zero),

$$\sum_1^n N_i \nu_i \neq 0. \quad (8)$$

*L.i.* frequencies are important in both classical and quantum theory, and we shall consider them as typical rather than exceptional. When the  $\nu_i$  are *l.i.*, (1) is an "almost periodic function," in mathematical language; in homespun, over sufficiently long time-intervals it comes as near as we please to repeating itself. Over short intervals ( $t_0, t_0 + \Delta t$ ) its behavior depends on the initial phases  $\nu_i t_0 + \psi_i = \psi'_i$ , say; but all distributions of initial phase are equally represented in long stretches.

Thus the long-time behavior of (1) is the same as that of

$$F(\nu_1 t, \dots) = \sum_1^n a_i \cos 2\pi\nu_i t, \quad (9)$$

the effect of the phases  $\psi_i$  in (1) eventually disappearing.

It follows that for *l.i.* frequencies  $\nu_i$ , the asymptotic frequency (5) is independent of the  $\psi_i$  and may be written as

$$L' = \frac{1}{2} \lim_{T \rightarrow \infty} \{G(T; 0, \dots)/T\}. \quad (10)$$

Also in (6)  $\bar{L}'$  is now the same as  $L'$ , and (7) becomes

$$L' = L, \quad (11)$$

or the asymptotic frequency of upzeros (for any  $\psi_i$ ) is the same as the phase average (over any interval  $T$ ). This exemplifies a more general result, that long-time average properties of  $f(t)$  (for *l.i.*  $\nu_i$ ) agree with phase averages of the properties.

When the  $\nu_i$  are not *l.i.*, we prefer to use  $L$ , the phase average, rather than  $L'(\psi_1, \dots)$ .

#### 4.2 THE NUMBER OF ZEROS OF A FUNCTION

To calculate  $L$ , we require a formula of Кас<sup>5,6</sup> for the number of zeros of a function. Let  $\phi(t)$  be a function (such as (1)), whose derivative  $\phi'(t)$  is continuous with a finite number of zeros in  $0 \leq t \leq T$ . Then the number,  $G(T)$ , of zeros of  $\phi(t)$  itself in  $0 \leq t \leq T$  is

$$G(T) = \pi^{-1} \int_0^{\infty} dx \int_0^T \cos \{x\phi(t)\} |\phi'(t)| dt. \quad (12)$$

The proof of this formula is based on the standard integral

$$\frac{2}{\pi} \int_0^{\infty} \frac{dx}{x} \sin xu = \text{sign } u [= \pm 1 \text{ as } u \gtrless 0]. \quad (13)$$

Let  $t_1, t_2, \dots$  be the successive zeros of  $\phi'(t)$  and  $\phi_1, \phi_2, \dots$  the values of  $\phi$  at these points. Using (13) in the second step, we have for an integral resembling (12),

$$\begin{aligned} \pi^{-1} \int_0^{\infty} dx \int_{t_1}^{t_2} \cos \{x\phi(t)\} \phi'(t) dt &= \pi^{-1} \int_0^{\infty} dx (\sin x\phi_2 - \sin x\phi_1)/x \\ &= \frac{1}{2} (\text{sign } \phi_2 - \text{sign } \phi_1) = \left\{ \begin{array}{ll} 1 & \text{(i) } \phi_2 > 0 > \phi_1 \\ 0 & \text{if (ii) } \phi_2\phi_1 > 0 \\ -1 & \text{(iii) } \phi_1 > 0 > \phi_2 \end{array} \right\} \end{aligned} \quad (14)$$

In  $(t_1, t_2)$ ,  $\phi'(t)$  has constant sign and equals  $|\phi'|$  in case (i) and  $-|\phi'|$  in case (iii); in these cases, but not in case (ii),  $\phi(t)$  has a zero in  $(t_1, t_2)$ , from the signs of  $\phi_1$  and  $\phi_2$  shown in (14). Thus the contribution of the range  $(t_1, t_2)$  to the right-hand side of (12) is 1 or 0 according as  $\phi$  has or has not a zero in the range. Adding for the ranges  $(0, t_1)$ ,  $(t_1, t_2)$ ,  $\dots$ , we obtain the result (12). A zero at  $t_1$  or  $t_2, \dots$  is correctly counted (giving two  $\frac{1}{2}$ 's for adjacent ranges); but a zero at  $t=0$  or  $T$  is miscounted as  $\frac{1}{2}$  for the total  $G(T)$ .

Professor Kac has pointed out to me a useful *extension* of (12); if  $\psi(t)$  is another function, differentiable in  $(0, T)$ , then the sum of its values at the zeros  $t_a, t_b, \dots$  of  $\phi(t)$  in  $(0, T)$  is

$$\sum \psi(t_a) = \pi^{-1} \int_0^\infty dx \int_0^T \psi(t) \cos \{x\phi(t)\} |\phi'(t)| dt. \quad (15)$$

Formula (12) is the case  $\psi(t) \equiv 1$ .

#### 4.3 KAC'S AND STEIN'S FORMULAS FOR THE FREQUENCY OF ZEROS

Kac's formula<sup>5</sup> is

$$L = \pi^{-2} \int_0^\infty \int_0^\infty y^{-2} \cos(xq) \left[ \prod_{i=1}^n J_0(a_i x) - \prod_1^n J_0\{a_i \sqrt{x^2 + \lambda_i y^2}\} \right] dx dy, \quad (16)$$

where  $\lambda_i = 4\pi^2 \nu_i^2$  as in 3.5(63). He designed this\* as the asymptotic frequency  $L'$  of upzeros of  $f(t) - q$  (as defined in (1) and (5)) for *l.i.* frequencies  $\nu_i$ ; but we shall view (and prove) it as the *phase-average* frequency  $L$  of (4) for general  $\nu_i$ .

The equations (3) and (4) give the phase-average frequency of upzeros of  $f(t) - q$  as

$$L = (2T)^{-1} \int_0^1 \dots G(T; \psi_1, \dots) d\psi_1 \dots, \quad (17)$$

where  $G(T; \psi_1, \dots)$  is the number of zeros in  $(0, T)$ . Writing  $\phi(t) = f(t) - q$  in (12) and inserting that formula for  $G$ , we have

\* I take slight liberties with what he wrote, first by talking only of "upzeros" and secondly by halving the integration ranges in (16). I omit in this emasculated proof his points of rigor, especially the existence of the Riemann integral (3) and the justification of changes of order of integration. Professor Kac was not able to raise objections to this handling at my Cornell seminar.

$$L = (2\pi T)^{-1} \int_0^1 \cdots d\psi_1 \cdots \int_0^\infty dx \int_0^T \cos \{x[f(t) - q]\} |f'(t)| dt. \quad (18)$$

If the  $t$  integration is postponed, the quantities  $\nu, t + \psi_i$ , in  $f$  and  $f'$  (compare (1)) can be replaced by  $\psi_i$ , owing to their unit range; so  $f(t)$  becomes  $f(0)$  and the  $t$ -integration is merely  $\int_0^T dt = T$ . Hence we obtain a central formula:

$$L = (2\pi)^{-1} \int_0^1 \cdots d\psi_1 \cdots \int_0^\infty \cos \{x[f(0) - q]\} |f'(0)| dx, \quad (19)$$

where

$$f(0) = \sum_1^n a_i \cos 2\pi\psi_i, \quad f'(0) = -2\pi \sum_1^n a_i \nu_i \sin 2\pi\psi_i. \quad (20)$$

In (19) we replace  $|f'(0)|$  by the integral (akin to (13))

$$|f'(0)| = (2/\pi) \int_0^\infty \{1 - \cos [yf'(0)]\} y^{-2} dy. \quad (21)$$

Now (19) has become an  $(n+2)$ -fold integral, involving the cosines of the sums in (20). Expanding these cosines, and dropping the terms which yield zero on integration, leaves

$$L = \pi^{-2} \int_0^\infty \int_0^\infty \cos(xq) y^{-2} dx dy \int_0^1 d\psi_1 \cdots \prod_1^n \{ \cos(xa_i \cos 2\pi\psi_i) \} \\ \times \left[ 1 - \prod_1^n \cos(2\pi y \nu_i a_i \sin 2\pi\psi_i) \right]. \quad (22)$$

The Bessel function of order zero is

$$J_0(\xi) = \int_0^1 \cos(\xi \cos 2\pi\psi) d\psi, \quad (23)$$

and it can be deduced that

$$J_0[\sqrt{(\xi^2 + \eta^2)}] = \int_0^1 \cos(\xi \cos 2\pi\psi) \cos(\eta \sin 2\pi\psi) d\psi. \quad (24)$$

Using these in (22) for the  $\psi_i$  integrations gives the desired result (16).

*Note on signs:* Although we defined the  $a_i$  in (1) to be positive (so

that we could call them "amplitudes"), it is seen from the present work that any of them may be negative without affecting Kac's formula (16).

Stein's formula is

$$L = \sum_{i=1}^n \nu_i \int \cdots \int d\psi_1 \cdots d\psi_{i-1} d\psi_{i+1} \cdots d\psi_n, \quad (25)$$

where the integral is over values of  $\psi_j$  ( $j \neq i$ ) such that  $0 \leq \psi_j < 1$  and

$$\nu_i^2 \left( \sum_{j \neq i} a_j \cos 2\pi\psi_j - q \right)^2 + \left( \sum_{j \neq i} \nu_j a_j \sin 2\pi\psi_j \right)^2 \leq \nu_i^2 a_i^2. \quad (26)$$

This was the first general formula found, although it was not published until fairly recently.<sup>1</sup> It can be derived from (19), or by an extension of the method of Kac and others.<sup>3</sup> It will be found useful as a check on a later approximation.

#### 4.4 DISTRIBUTION FUNCTIONS AND RANDOM WALKS

We sketch now a more physical approach<sup>7</sup> to  $L$ , with links to random walk and transition-state theory. Attention is confined formally to *l.i.*  $\nu_i$ 's, the better to connect phase and asymptotic averages.

We may reduce the steady motion of a point, with coordinate  $x$ , along an infinite line, to the repeated traverse of a unit length by replacing  $x$  by  $\theta \equiv \{x\}$  (meaning  $x$  minus its whole number part); to avoid discontinuity in the  $\theta$ -point we would bend this unit length into a circle of unit circumference. Similarly we may reduce an  $n$ -dimensional space, with typical vector  $\mathbf{x} = (x_1, \dots)$ , into a "torus"\* ( $\ominus$ ) with vector  $\boldsymbol{\theta} = (\theta_1, \dots)$  by putting

$$\theta_i = \{x_i\}. \quad (27)$$

If, as is suggested by (1), the vector  $\mathbf{x}$  varies with time as

$$\mathbf{x} = \mathbf{v}t + \boldsymbol{\psi} \quad (x_i = \nu_i t + \psi_i), \quad (28)$$

then the torus vector  $\boldsymbol{\theta}$  represents the instantaneous phase of the sum (1), which may be written

$$f(t) \equiv F(\theta_1, \dots) \equiv \sum_1^n a_i \cos 2\pi\theta_i. \quad (29)$$

If the  $\nu_i$  are *l.i.*, the terminal point  $P_t$ , say, of the torus vector  $\boldsymbol{\theta}$  defined by (27) and (28) traverses the "cube" on a fresh track for every cross-

\* I used to refer to  $\Theta$  as a "unit cube," since  $0 \leq \theta_i < 1$ , but this name lacks the sense of continuity which is provided by the circle picture for  $n=1$ .

ing; and over a long time,  $P_t$  spends (asymptotically) equal times in equal elements  $\delta\theta_1 \cdots \delta\theta_n$  of the torus or phase space; this result will be called *Weyl's theorem*.

If a random walker takes prescribed steps  $a_1, a_2, \cdots, a_n$  in arbitrary directions, at angles  $2\pi\theta_i$  to a fixed direction, then the sum (29) represents his total progress in that direction. This random walk corresponds to our vibrational sum, since we infer from Weyl's theorem that our  $\theta_i$ s in (29) are uniformly distributed (over a long time) from 0 to 1, like the walker's whims. This correspondence of problems is useful, but we shall proceed, for the sake of later developments, without appealing to known results for random walks.

**Distribution functions.** Let

$$m(q)\delta q = \lim_{T \rightarrow \infty} \{T^{-1} \text{meas}_T(q \leq f(t) < q + \delta q)\}, \quad (30)$$

where " $\text{meas}_T(\cdots)$ " is the measure of the set of values of  $t$ , in  $0 \leq t < T$ , for which  $(\cdots)$  holds. We call  $m(q)$  (defined first as here as an asymptotic fraction of time) the *distribution function* of the sum  $f(t)$  of (1).<sup>\*</sup> It is clear that

$$m(-q) = m(q), \quad m(q) = 0 \quad \text{when } q > a, \quad (31)$$

where

$$a \equiv \sum_1^n a_i \quad (32)$$

is the sum of the amplitudes in (1).

By Weyl's theorem  $m(q)\delta q$  equals the extension  $\int \cdots d\theta_1 \cdots$  of  $\Theta$ -space for which  $F(\theta_1, \cdots)$  of (29) lies between  $q$  and  $q + \delta q$ . Thus the Fourier cosine transform of  $m(q)$  is

$$\mu(x) = 2 \int_0^\infty m(q) \cos(qx) dq \quad (33)$$

$$= \int_0^1 \cdots \int_0^1 \cos[xF(\theta_1, \cdots)] d\theta_1 \cdots, \quad (34)$$

where in (33) we wrote  $2 \int_0^\infty$  (we could have written  $2 \int_0^a$ ) for  $\int_{-\infty}^\infty$  because of (31), and in (34) we used the Weyl result to replace  $m(q) dq$  by  $d\theta_1 \cdots$ . Replacing  $F(\theta_1, \cdots)$  by  $\sum a_i \cos 2\pi\theta_i$  and using (23), we obtain

$$\mu(x) = \prod_{i=1}^n J_0(a_i x). \quad (35)$$

<sup>\*</sup> We eschew the usual name "frequency function" to avoid confusion with other uses of "frequency." The term "distribution function" is more usually applied to  $\int^a m(q) dq$ .

The reciprocal Fourier transform gives us  $m(q)$ , namely,

$$m(q) = \pi^{-1} \int_0^{\infty} \mu(x) \cos qx dx = \pi^{-1} \int_0^{\infty} \cos qx \prod_1^n J_0(a_i x) dx, \quad (36)$$

which is also known as the distribution of a component of a plane random walk; it has been usefully graphed by Margaret Slack.<sup>8</sup>

The derivative or "velocity" of  $f(t)$  is  $f'(t)$ , where

$$f'(t) = -2\pi \sum a_i \nu_i \sin 2\pi(\nu_i t + \psi_i), \quad (37)$$

which we write, by (27) and (28),

$$F'(\theta_1, \dots) = -2\pi \sum a_i \nu_i \sin 2\pi\theta_i. \quad (38)$$

The simultaneous distribution of  $f(t)$  and  $f'(t)$  is defined by

$$m(q, \dot{q}) \delta q \delta \dot{q} = \lim_{T \rightarrow \infty} \{ T^{-1} \text{meas}_T \{ q < f < q + \delta q, \dot{q} < f' < \dot{q} + \delta \dot{q} \} \}. \quad (39)$$

This  $m(q, \dot{q})$  is an even function of  $q$  and  $\dot{q}$ , and certainly

$$m(q, \dot{q}) = 0 \quad \text{when} \quad q > a \quad \text{or} \quad \dot{q} > b \equiv 2\pi \sum a_i \nu_i. \quad (40)$$

Its double Fourier (cosine) transform is

$$\mu(x, y) = 4 \int_0^{\infty} \int_0^{\infty} m(q, \dot{q}) \cos(qx) \cos(\dot{q}y) dq d\dot{q} \quad (41)$$

$$= \int_0^1 \dots \cos \{ x F'(\theta_1, \dots) \} \cos \{ y F'(\theta_1, \dots) \} d\theta_1 \dots, \quad (42)$$

where we have applied Weyl's theorem to the measure in (39). Finally, using (24),

$$\mu(x, y) = \prod_1^n J_0[a_i(x^2 + \lambda_i y_i^2)^{\frac{1}{2}}], \quad (43)$$

where  $\lambda_i = 4\pi^2 \nu_i^2$ . Inverting the transform, we have for the double distribution

$$m(q, \dot{q}) = \pi^{-2} \int_0^{\infty} \int_0^{\infty} \mu(x, y) \cos qx \cos \dot{q}y dx dy. \quad (44)$$

**Transition-state ideas.** We now compute  $L'_q$ , the asymptotic frequency of upzeros of  $f(t) - q$ , by a method analogous to the "transition state." Out of a long time  $T$ , the time that  $f$  and  $f'$  lie simultaneously

in  $(q, q+dq)$  and  $(\dot{q}, \dot{q}+d\dot{q})$  is by (39) nearly

$$Tm(q, \dot{q})dq d\dot{q}. \quad (45)$$

The time taken by  $f$  to pass through  $dq$  with "velocity"  $f' = \dot{q}$  is

$$dq / |\dot{q}|. \quad (46)$$

The ratio (45)/(46) is the number of "passages," or the number of zeros of  $f - q$ , with a given value  $\dot{q}$  of  $f'$ . The total number of zeros in  $(0, T)$  is therefore

$$G(T) \sim T \int_{-\infty}^{\infty} m(q, \dot{q}) |\dot{q}| d\dot{q}, \quad (47)$$

and the asymptotic frequency,  $L'_q$  of (5), is

$$L'_q = \int_0^{\infty} m(q, \dot{q}) \dot{q} d\dot{q}. \quad (48)$$

To see this more explicitly as a "transition-state" formula, we introduce  $v_q$ , the mean speed in  $f$  for a given value  $q$ :

$$v_q = \int_{-\infty}^{\infty} m(q, \dot{q}) |\dot{q}| d\dot{q} / \int_{-\infty}^{\infty} m(q, \dot{q}) d\dot{q}. \quad (49)$$

The numerator here is twice  $L'_q$ ; the denominator is  $m(q)$  by the definition of  $m(q, \dot{q})$ . Hence

$$L'_q = \frac{1}{2} m(q) v_q, \quad (50)$$

namely,  $L'_q$  is one half the probability density of the configuration  $f = q$ , multiplied by the mean speed of passage; the factor  $\frac{1}{2}$  selects the "upward passages."

To evaluate  $L'_q$ , we insert in (48) the expression (44), with the primitive form (42) of  $\mu(x, y)$ , and integrate first for  $\dot{q}$  and  $y$ . This yields essentially the "central formula" (19), from which we proceed as before to Kac's formula. There are thus two routes to the central formula, corresponding to counting the passages: one is the formula of 4.2, applied in a phase average; the other is the present transition-state method, appearing first as a long-time average. The formula (48) was in fact developed and used by S. O. Rice for electrical "random noise" theory.<sup>9</sup>

#### 4.5 ORDERS OF MAGNITUDE AND FOURIER SERIES

The elegant formulas of 4.3 do not indicate (except to a superbrain) how big  $L$  is; so we give here estimates and approximations, and a Fourier series for exact computation.

**The order of magnitude for small  $q$ .** Suppose in (1) that  $\nu_1$  is the smallest and  $\nu_n$  the largest frequency. Over a long range of  $t$ ,  $f(t) - q$  has fewer zeros than its derivative  $f'(t)$ , and a fortiori fewer than its  $(4r)$ th derivative  $f^{(4r)}(t)$ . For sufficiently large  $r$ ,  $f^{(4r)}(t)$  is very nearly  $a_n(2\pi\nu_n)^{4r} \cos 2\pi(\nu_n t + \psi_n)$ , which has  $2\nu_n$  zeros per unit time. This is therefore an upper bound to  $2L'_q$ ; thus for all  $q$ ,

$$L'_q \text{ is less than the greatest vibration frequency.} \quad (51)$$

Similarly the  $(4r)$ th integral (with no added constants) of (1) is close to  $a_1(2\pi\nu_1)^{-4r} \cos 2\pi(\nu_1 t + \psi_1)$ , and this has fewer zeros than  $f(t)$ . Hence

$$L'_0 \text{ exceeds the smallest vibration frequency.} \quad (52)$$

This is true also of  $L'_q$  with  $q$  sufficiently small.

**The order of magnitude for large  $n$ .** Let us suppose that the amplitudes  $a_i$  are roughly all of the same order of magnitude, and likewise the frequencies  $\nu_i$ , or the  $\lambda_i \equiv 4\pi^2\nu_i^2$ , and let

$$a_0^2 = \sum_1^n a_i^2/n, \quad \nu_0^2 = \sum a_i^2\nu_i^2 / \sum a_i^2, \quad \lambda_0 = \sum a_i^2\lambda_i / \sum a_i^2. \quad (53)$$

Thus  $a_0$  is the root mean square amplitude,  $\nu_0$  a weighted mean frequency rather like 3.6 (79), and  $\lambda_0 = 4\pi^2\nu_0^2$ .

If we take for  $J_0(x)$  the approximation

$$J_0(x) \cong \exp(-\frac{1}{4}x^2) \{1 - x^4/64\}, \quad (54)$$

then Kac's formula (16) gives (if we trust the leading terms) for the case  $q=0$

$$L_0 = \nu_0 \left\{ 1 + (16n^3 a_0^4 \lambda_0^2)^{-1} \sum_1^n a_i^4 (\lambda_i - \lambda_0) (\lambda_i + 3\lambda_0) \right\}. \quad (55)$$

The sum here is at most of the order  $4na_0^4\lambda_0^2$ , and is likely to be smaller because of the varying signs of the  $\lambda_i - \lambda_0$ . Thus (55) is of the form  $\nu_0\{1 + c/n\}$ , approaching  $\nu_0$  for large  $n$ . (For equal frequencies  $\nu_i = \nu_1 = \nu_0$ , (55) becomes  $L_0 = \nu_1$ , which is exactly true.)

For small  $q$  we shall proceed by dropping from (54) the term  $x^4/64$  (which gave the  $c/n$  term in the previous case). Kac's formula (16), with  $\exp(-\frac{1}{4}x^2)$  for  $J_0(x)$ , is

$$L_q \cong \pi^{-2}XY, \quad (56)$$

where

$$X \equiv \int_0^{\infty} \cos(xq) \exp(-\frac{1}{4}na_0^2x^2)dx = (\pi/na_0^2)^{\frac{1}{2}} \exp(-q^2/na_0^2), \quad (57)$$

$$Y \equiv \int_0^{\infty} \{1 - \exp(-\frac{1}{4}na_0^2\lambda_0y^2)\}y^{-2}dy = \frac{1}{2}(\pi na_0^2\lambda_0)^{\frac{1}{2}}. \quad (58)$$

(These are standard integrals we shall need again.) Hence by (53)

$$L_q = \nu_0 \exp(-q^2/na_0^2). \quad (59)$$

This approximation represents  $L_q$  as having a Gaussian distribution; it is good for  $n$  large and  $q$  of the order  $a_0\sqrt{n}$ . It must not be pushed to have  $q$  near  $a \equiv \sum a_i$  (which is of the order  $a_0n$ ); a valid approximation for this region is given in 4.6.

Kac has given<sup>5,6</sup> a more rigorous account of (59) (as an asymptotic form with  $n$  tending to infinity) for the case of equal amplitudes. The use of (54) to get (55) here was suggested by Hauptman and Karle's treatment of a similar integral in a crystal problem.<sup>10</sup>

**Fourier series.** The distribution function  $m(q)$  of (30)–(36) is even and vanishes for  $q > a \equiv \sum a_i$ . By treating it as "periodic" for the range  $(-a, a)$ , we find the Fourier series, valid for  $|q| < a$ ,

$$m(q) = (2a)^{-1} + a^{-1} \sum_{k=1}^{\infty} \cos(\pi kqa^{-1}) \prod_{i=1}^n J_0(\pi k a_i a^{-1}), \quad (60)$$

a formula due to Bennett<sup>11</sup> (see also Miller<sup>12</sup>).

This suggests a similar treatment of the  $m(q, \dot{q})$  of (39)–(44). Let  $A, B$  satisfy

$$A > a \equiv \sum a_i, \quad B > b \equiv 2\pi \sum a_i \nu_i. \quad (61)$$

Then certainly  $m(q, \dot{q}) = 0$  when  $q \geq A$  or  $\dot{q} \geq B$  (compare (40)). Let us assume the double series for  $|q| \leq A$  and  $|\dot{q}| \leq B$ ,

$$m(q, \dot{q}) = \sum_{k,l=0}^{\infty} \sum_{\epsilon_k \epsilon_l} \epsilon_k \epsilon_l c_{kl} \cos(\pi kq/A) \cos(\pi l\dot{q}/B), \quad (62)$$

where

$$\epsilon_0 \equiv \frac{1}{2}, \quad \epsilon_1 = \epsilon_2 = \dots \equiv 1. \quad (63)$$

The coefficients in (62) are, assuming the usual rule,

$$ABc_{kl} = 4 \int_0^A \int_0^B m(q, \dot{q}) \cos(\pi kq/A) \cos(\pi l\dot{q}/B) dq d\dot{q}. \quad (64)$$

Now in (41) we could use  $A$  and  $B$  as upper limits instead of infinity. Hence (64) is

$$ABc_{kl} = \mu(\pi k/A, \pi l/B) = \prod_1^n J_0 \{ a_i \pi (k^2 A^{-2} + \lambda_i l^2 B^{-2})^{\frac{1}{2}} \}, \quad (65)$$

by (43). This determines the series (62).

To find  $L_q$ , we substitute (62) in (48), taking (legitimately) the upper limit as  $B$  instead of infinity. Integration of the factors  $\dot{q} \cos(\pi k \dot{q}/B)$  then gives the *Fourier series* for  $L_q$ :

$$L_q = \frac{1}{2} \beta_0 + \sum_{k=1}^{\infty} \beta_k \cos(\pi k q/A), \quad (66)$$

where

$$\beta_k = B/(4A) \left\{ \mu(\pi k/A, 0) - 8\pi^{-2} \sum_l' l^{-2} \mu(\pi k/A, \pi l/B) \right\} \quad (67)$$

$$= \frac{B}{4A} \left\{ \prod_1^n J_0 \left( \frac{\pi a_i k}{A} \right) - \frac{8}{\pi^2} \sum_l' \frac{1}{l^2} \prod_1^n J_0 \left[ \pi a_i \left( \frac{k^2}{A^2} + \frac{\lambda_i l^2}{B^2} \right)^{\frac{1}{2}} \right] \right\} \quad (68)$$

where the summation is for  $l=1, 3, 5, 7, \dots$ . The convergence of the series in (68) is quite rapid, so that with a good table<sup>13</sup> of  $J_0(x)$  the calculation of  $\beta_k$  for moderate values of  $n$  is not very tedious. It may be observed that by inserting a factor (before the first product in (68))  $(8/\pi^2) \sum_{\text{odd } l} l^{-2} \equiv 1$ , we may put the series (66) into a form exactly parallel to the integral (16).

#### 4.6 HIGH PEAKS OF A SUM

An approximation, namely equation (79) below, is found here for  $L_q'$  when  $q$  is near  $a \equiv \sum a_i$ . The result could be deduced from Stein's formula (25); but it is worth giving the original method<sup>4</sup> (which was based on a suggestion of A. S. Eddington), since this method may be useful for the deeper problem of the distribution of the gaps between the zeros of  $f(t) - q$  (compare Chapter 9). The method is, briefly, to examine which maxima of  $f(t)$  exceed  $q$ .

The calculation is viewed as that of the asymptotic frequency (5) for *l.i.*  $\nu_i$  (although the result equally represents the phase average (4) for general  $\nu_i$ ); so we may drop the initial phases  $\psi_i$  as in (9). Let  $\nu_n$  be the *largest* frequency, and by a change of time scale take  $\nu_n = 1$ .

Thus (1) becomes

$$f(t) = \sum_1^n a_i \cos 2\pi\nu_i t, \quad \nu_n = 1, \quad (69)$$

with  $\nu_1, \nu_2, \dots, \nu_{n-1}$  *i. i.* irrationals less than 1. Let the value  $q$  to be attained be near  $a$ , so that

$$a - q \equiv \sum_1^n a_i - q = 2\pi^2 h^2 \quad (70)$$

where  $h^2$  is small.

For any  $x$ , let  $\{x\}$  in this section denote  $x$  minus the *nearest* integer, so that  $-\frac{1}{2} < \{x\} \leq \frac{1}{2}$ ; thus in (69) we may replace  $\nu_i t$  by  $\{\nu_i t\}$ . In particular we write

$$\{t\} = \alpha, \quad t = r + \alpha \quad \left(-\frac{1}{2} \leq \alpha < \frac{1}{2}\right), \quad (71)$$

so  $r$  is the nearest integer to  $t$ . From (69)-(71),

$$\begin{aligned} f(t) - q &= \sum_1^{n-1} a_i [\cos 2\pi(\{\nu_i r\} + \nu_i \alpha) - 1] \\ &\quad + a_n (\cos 2\pi\alpha - 1) + 2\pi^2 h^2. \end{aligned} \quad (72)$$

This is generally negative but may rise above zero at times when  $|\alpha|$  is small and also (since  $\nu_i \leq 1$ ) the  $|\{\nu_i r\}|$  are small. Thus in the regions of interest we may replace  $1 - \cos x$  by  $\frac{1}{2}x^2$ , so that (72) becomes

$$f(t) - q = -2\pi^2 [\phi_r(\alpha) - h^2], \quad (73)$$

where

$$\phi_r(\alpha) = \sum_1^{n-1} a_i (\{\nu_i r\} + \nu_i \alpha)^2 + a_n \alpha^2. \quad (74)$$

There will be an "up" and a "down" zero of  $f(t) - q$  near those times  $t=r$  for which the minimum of  $\phi_r(\alpha)$  (for varying  $\alpha$ ) is less than  $h^2$ , by (73). The minimum occurs where  $d\phi_r/d\alpha=0$ ; if here  $\alpha=\alpha_r$ , we find

$$\alpha_r = -A_r^{-1} \sum_1^{n-1} a_i \nu_i \{\nu_i r\}, \quad A_r \equiv \sum_1^n a_i \nu_i^2, \quad (75)$$

and

$$\min \phi_r(\alpha) = \phi_r(\alpha_r) = \sum_1^{n-1} a_i \{\nu_i r\}^2 - A_r^{-1} \left( \sum_1^{n-1} a_i \nu_i \{\nu_i r\} \right)^2. \quad (76)$$

Let  $(\theta_1, \dots, \theta_{n-1})$  be Cartesian coordinates of a point  $P$  in a region

$|\theta_i| \leq \frac{1}{2}$  (similar to the "torus" of 4.4). Consider the hyperellipsoid (which is well within that region for  $h^2$  small) with the equation

$$\sum_1^{n-1} a_i \theta_i^2 - A_r^{-1} (\sum a_i \nu_i \theta_i)^2 = h^2. \quad (77)$$

Consider also the set of points  $P_r$  with coordinates  $\theta_i = \{\nu_i r\}$  ( $r=0, 1, 2, 3, \dots$ ). There is an upzero of  $f(t) - q$  (we discard the downzero) near  $t=r$  when  $\phi_r(\alpha_r) < h^2$ , and so by (76) and (77) when  $P_r$  lies inside the hyperellipsoid. Thus  $L'_q$ , the asymptotic frequency of upzeros, is the asymptotic proportion of points  $P_r$  ( $r=0, 1, 2, \dots, \infty$ ) which lie in (77). By Weyl's theorem (in its original form<sup>14</sup> rather than that used in 4.4) the points  $P_r$  are uniformly dense in the torus, because of the linear independence of the  $\nu_i$ . Hence  $L'_q$ , the proportion in (77), equals the extension or "volume" of the hyperellipsoid. This is easily calculated from (77) and is

$$L'_q = \frac{\pi^{1(n-1)} h^{n-1}}{\Gamma(\frac{1}{2}n + \frac{1}{2})} \left( \frac{A_r}{a_1 a_2 \dots a_n} \right)^{\frac{1}{2}}, \quad A_r = \sum_1^n a_i \nu_i^2, \quad (78)$$

or in terms of  $q$ , by (70),

$$L'_q = \frac{1}{\Gamma(\frac{1}{2}n + \frac{1}{2})} \left[ \frac{\sum_1^n a_i \nu_i^2}{a_1 a_2 \dots a_n} \right]^{\frac{1}{2}} \left( \frac{a - q}{2\pi} \right)^{\frac{1}{2}(n-1)}. \quad (79)$$

So far we have used an artificial time scale, with  $\nu_n t$  for  $t$  and  $\nu_n = 1$ ; but it is easily shown that (78) and (79) still hold as written, when  $\nu_1, \dots, \nu_n$  are any *l.i.* numbers.

This result shows clearly the behavior of  $L'_q$  near  $q=a$ ; it will be used in later chapters. The verification of (79) from Stein's formula (25) shows that the next term in the approximation is a multiple of  $(a-q)^{\frac{1}{2}(n+1)}$ .

*Distribution functions.* A similar technique (or an easier method based on 4.4) shows that the fraction of time for which  $f(t)$  exceeds  $q$  is (to a similar approximation)

$$\int_q^a m(q) dq = [(a - q)/2\pi]^{\frac{1}{2}n} / [\Gamma(1 + \frac{1}{2}n)(a_1 a_2 \dots a_n)^{\frac{1}{2}}]. \quad (80)$$

Thus for  $n > 2$  the approximate distribution function  $m(q)$  of 4.4 near  $q=a$  is

$$m(q) = (a - q)^{\frac{1}{2}n-1} / [\Gamma(n/2)(2\pi)^{\frac{1}{2}n}(a_1 a_2 \dots a_n)^{\frac{1}{2}}]. \quad (81)$$

A series beginning with this term is given by Rice<sup>15</sup> in the case of equal amplitudes.

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## CHAPTER 5

# Unimolecular First-Order Reactions on the Classical Harmonic Model

**A**FTER a chapter of dynamics and another of mathematics, a short chapter on kinetics is in place, and this is in fact the first focus of the argument. In Chapter 3 the emphasis was on the composite behavior of molecular coordinates as sums of normal-mode vibrations, and in Chapter 4 we examined in detail a single sum of vibrations. We now proceed to calculate the high-concentration rate constant in terms of the frequency with which the normal vibrations come sufficiently into phase to give a critical or breaking distortion of a molecular coordinate or configuration; this frequency or specific rate depends on the energies in the individual normal modes (supposed fixed between collisions), and has to be averaged over their equilibrium distribution to give the over-all rate constant  $k^\infty$ . The result is an Arrhenius form, with  $A$ -factor the mean vibration frequency  $\nu$  which was introduced in 3.6. As many, but not all, experimental  $A$ -factors are of the order of magnitude of vibration frequencies, it may be inferred that the present model may be on the right lines but lacks refinement.

The calculation of  $k^\infty$  in 5.4 is not long, but it is prefaced in 5.1 to 5.3 by a discussion of the model, of the energies, and of the use of the time and phase averages of 4.1 in formulating the rate constant. There is a postscript 5.5 on the specific rate  $k_E$  for molecules of total energy  $E$ . This may be found from the results of 2.5 for Arrhenius rate constants, but it is also calculated directly to show its true nature as an average of the specific rates, corresponding to different distributions of the normal-mode energies with a given sum  $E$ .

### 5.1 THE MODEL OF DISSOCIATION

The molecule is represented by the dynamical system of Chapter 3, having  $n$  independent internal coordinates  $q_1, \dots, q_n$  such as the stretches (beyond their equilibrium values) of interatomic distances

and angles. These coordinates are expressible as linear combinations of normal coordinates  $Q_1, \dots, Q_n$  which vibrate harmonically with the respective frequencies  $\nu_1, \dots, \nu_n$ . The amplitudes and phases of the normal coordinates (in this classical picture) are supposed to have been determined by the last collision of the molecule and to remain unchanged until the next collision, unless dissociation occurs before this.

The molecule is assumed to dissociate if and when it reaches one of a set of critical internal configurations. These configurations may be, for example, those in which a particular interatomic distance is critically large (or small) and the other distances are unspecified; or they may be those in which two or three interatomic distances have a critically large sum, the remaining part of the configuration being unspecified. In this general theory we assume that we can so choose the internal coordinates  $q_1, \dots, q_n$  that the set of critical configurations is fully specified by  $q_1$  attaining a particular large value  $q$ , irrespective of the values of  $q_2, \dots, q_n$ .\*

At high concentrations, we assume that the equilibrium distribution of energies obtains in all the normal modes of the molecules; and we calculate the first-order rate constant  $k^\infty$  by finding the probability (per second) of coordinate  $q_1$ , as a sum of normal vibrations of known energies or amplitudes, reaching the critical value  $q$ ; we then average this probability over the energy distribution.

In this calculation we take the typical molecule as having normal frequencies  $\nu$ , linearly independent in the sense of 4.1. This makes the behavior of coordinate  $q_1$ , averaged over uniformly random initial phases, the same as its long-time average behavior for any initial phase; moreover it would ensure, even in a quantum model, the fixity of the normal-mode energies between collisions (compare the end of 2.6). Thus the dissociation probability is correctly represented by the long-time average frequency with which  $q_1$  (with given mode energies and phases) rises to  $q$ . If the frequencies are *not l.i.*, the initial phases affect the average behavior, and we have to reformulate the rate as an average, over random phases, of the dissociations in a short time interval. There is no distinction, classically speaking, between the two cases in the first-order reaction region, where the random distribution of initial phase is part of the assumed equilibrium distribution. In 5.2 we assume linear independence, using notations which will be carried over to the quasi-unimolecular case in Chapter 7.

\* This may not give a convenient set of  $q$ 's, but practical ways of handling this difficulty will be illustrated later. We are also assuming in effect that atomic displacements are fairly small, so that we can handle all geometrical distortions as linear combinations of basic coordinates.

## 5.2 SPECIFICATION OF INTERESTING MOLECULES

The kinetic and potential energies of the vibrating molecule are taken to be 3.1(6) and (11). Between collisions the coordinates are the functions 3.4(66) of the time. In particular, for the reaction coordinate  $q_1$ ,

$$q_1 = \sum_{i=1}^n \alpha_{1i} \sqrt{\epsilon_i} \cos 2\pi(\nu_i t + \psi_i), \quad (1)$$

where the energy  $\epsilon_i$ , and initial phase  $\psi_i$ , in the  $i$ th mode are to be considered as fixed by the previous collision.

The constants  $\alpha_{1i}$ , were determined in terms of the kinetic and potential coefficients in 3.4. If any  $\alpha_{1i}$  is zero, we omit the corresponding mode  $j$  and also the energy  $\epsilon_j$  from all our discussions. Thus  $n$ , which was defined as the number of independent internal coordinates, is to be interpreted as the number of normal modes affecting the reaction coordinate  $q_1$ .

A molecule is *interesting* (compare 2.3), or capable of dissociation, if  $q_1$  can reach the critical value  $q$ . Now for *l.i.* frequencies  $\nu_i$ , the sum (1) takes all values up to the sum  $\sum |\alpha_{1i}| \sqrt{\epsilon_i}$  of the amplitudes. Thus "interesting" molecules are those having sets  $\epsilon_1, \dots, \epsilon_n$  of normal-mode energies such that

$$\sum_1^n |\alpha_{1i}| \sqrt{\epsilon_i} \geq q. \quad (2)$$

It is seen that this is a more complex specification than the mere requirement of a certain minimum *total* energy. It is useful, however, to find the minimum of the total energy,

$$E = \sum_1^n \epsilon_i, \quad (3)$$

for which (2) is satisfied. Let  $\epsilon_{10}, \dots, \epsilon_{n0}$  be the values of the  $\epsilon_i$  for which (3) is a minimum subject to the equality  $\sum |\alpha_{1i}| \sqrt{\epsilon_i} = q$ . It is easily found that

$$\epsilon_{i0} = q^2 \alpha_{1i}^2 / \alpha^4, \quad (4)$$

where

$$\alpha^2 = \sum_1^n \alpha_{1i}^2 \quad (\alpha > 0). \quad (5)$$

The minimum total energy,  $\sum \epsilon_{i0}$ , for dissociation is therefore

$$E_0 = q^2 / \alpha^2, \quad (6)$$

although a molecule with this energy is not interesting unless the energies are distributed according to (4). Similarly a molecule with energy exceeding  $E_0$  is not interesting unless (2) is satisfied.

The following *nondimensional parameters*  $\mu_i$  will be prominent later (compare (5)):

$$\mu_i = |\alpha_i| / \alpha = |\alpha_i| / (\sum \alpha_i^2)^{1/2}. \quad (7)$$

Thus

$$\sum_1^n \mu_i^2 = 1, \quad (8)$$

and the critical energy distribution (4) may be written, by (6),

$$\epsilon_{i,0} = \mu_i^2 E_0. \quad (9)$$

### 5.3 FORMULATION OF THE RATE CONSTANT

At high concentrations we assume, as in Chapter 2, that the equilibrium distribution, appropriate to the temperature  $T$  of the gas, is effectively maintained; thus the proportion of molecules with energy  $\epsilon_i$  to  $\epsilon_i + d\epsilon_i$  in the  $i$ th mode ( $i = 1, \dots, n$ ) is 2.4(31), namely,

$$e^{-E/\kappa T} d\epsilon_1 \dots d\epsilon_n / (\kappa T)^n \quad \left( E = \sum_1^n \epsilon_i \right). \quad (10)$$

The specific dissociation rate,  $k(\epsilon_1, \epsilon_2, \dots, \epsilon_n)$ , of a molecule with these internal mode energies is the chance per second that  $q_1$ , as the function (1), attains the critical value  $q$ . If the frequencies are *l.i.*, the behavior of this function over a long time is independent of the initial phases  $\psi_i$  in (1). It seems natural, therefore, to define  $k(\epsilon_1, \dots, \epsilon_n)$  as

$$k(\epsilon_1, \dots, \epsilon_n) = L'_q = \frac{1}{2} \lim_{\tau \rightarrow \infty} [G_q(\tau) / \tau], \quad (11)$$

where as in 4.1  $G_q$  is the number of zeros of  $q_1 - q$  in time  $(0, \tau)$ ; the factor  $\frac{1}{2}$  represents the choice of zeros with  $q_1$  increasing to the critical value. The over-all high-concentration rate constant is then the integral of (11) over the distribution (10), namely,

$$k^\infty = \int \dots \int_0^\infty L'_q e^{-E/\kappa T} d\epsilon_1 \dots d\epsilon_n / (\kappa T)^n. \quad (12)$$

The ranges of integration may be started at zero, since  $L'_q$  is identically zero where (2) is not satisfied.

**Alternative formulation.** In the above formulation we represented

the dissociation probability by a long-time average  $L'_q$ . We may alternatively use a phase average in the following way.

For a *short* time interval  $(0, \tau)$  the probability of dissociation of a molecule with given energies  $\epsilon_i$  and initial phases  $\psi_i$  is (compare 4.1(2))

$$G''_q(\tau; \psi_1, \dots, \psi_n), \quad (13)$$

where  $G''_q$  denotes the number of upzeros of  $q_1 - q$  in time  $(0, \tau)$ ; this is 1 if there is an upzero, and 0 if there is not (the chance of two upzeros in a short interval  $(0, \tau)$  being negligible). If we assume that (as befits an effectively equilibrium assembly) the distribution of phases  $\psi_i$  is uniform between  $\psi_i = 0$  and 1, then the proportion of molecules with energies and phases in specified ranges  $d\epsilon_1, \dots, d\psi_n$  is

$$e^{-E/\kappa T} d\epsilon_1 \dots d\epsilon_n d\psi_1 \dots d\psi_n / (\kappa T)^n. \quad (14)$$

Hence the proportion of molecules dissociating in time  $\tau$  is the product of (13) and (14), integrated over  $\epsilon_i$  and  $\psi_i$ ; and the first-order rate constant is this integral divided by  $\tau$ :

$$k^\infty = (\kappa T)^{-n} \int \dots \int_0^\infty e^{-E/\kappa T} d\epsilon_1 \dots \int \dots \int_0^1 G''_q(\tau; \psi_1 \dots) d\psi_1 \dots / \tau. \quad (15)$$

The second integral here is independent of  $\tau$  (compare 4.1) and in fact is the phase-averaged frequency  $L_q$  of 4.1(+). Thus

$$k^\infty = \int \dots \int_0^\infty L_q e^{-E/\kappa T} d\epsilon_1 \dots d\epsilon_n / (\kappa T)^n. \quad (16)$$

This result is independent of the nature of the  $\nu_i$ , and if they are *l.i.* is the same as (12), since then  $L_q = L'_q$ . If the  $\nu_i$  are not *l.i.*, we take (16) as the correct form of  $k^\infty$ , remembering that it implies the assumption of random phases.

#### 5.4 EVALUATION OF THE RATE CONSTANT<sup>1,2</sup>

The rate (12) or (16) is evaluated by using Kac's accurate formula 4.3(16) for  $L_q$ , the frequency of upzeros of  $q_1 - q = f(t) - q$ ; the parameters  $\alpha_1, \sqrt{\epsilon_i}$ , of  $q_1$  in (1) above are  $a_i$  of  $f(t)$  in 4.1(1), which appear in Kac's formula. We have then for (12), on inverting the order of integration,

$$k^\infty = \pi^{-2} \int \int_0^\infty y^{-2} \cos(qx) dx dy \left\{ \prod_i \int_0^\infty J_0(x\alpha_{1,\epsilon_i}) e^{-\epsilon_i/\kappa T} d\epsilon_i / (\kappa T) \right. \\ \left. - \prod_i \int_0^\infty J_0[\alpha_{1,\epsilon_i}^{\frac{1}{2}}(x^2 + \lambda y^2)^{\frac{1}{2}}] e^{-\epsilon_i/\kappa T} d\epsilon_i / (\kappa T) \right\}. \quad (17)$$

Using Weber's first exponential formula, namely,<sup>3</sup>

$$\int_0^{\infty} J_0(a\sqrt{t})e^{-t}dt = \exp(-\frac{1}{4}a^2), \quad (18)$$

we evaluate all the integrals in the braces  $\{ \}$  and separate (17) into

$$k^{\infty} = \pi^{-2} \int_0^{\infty} \cos(qx) \exp(-\frac{1}{4}\alpha^2 x^2 \kappa T) dx \cdot \int_0^{\infty} \{1 - \exp(-\frac{1}{4}\alpha^2 y^2 \bar{\lambda} \kappa T)\} y^{-2} dy, \quad (19)$$

where, as in (5) and 3.5(81),

$$\alpha^2 = \sum_1^n \alpha_{1i}^2, \quad \bar{\lambda} = \alpha^{-2} \sum \alpha_{1i}^2 \lambda_i. \quad (20)$$

The integrals in (19) occurred earlier as 4.5(57) and (58); from these results

$$k^{\infty} = \pi^{-2} \cdot \{ \pi / (\alpha^2 \kappa T) \}^{\frac{1}{2}} \exp \{ -q^2 / (\alpha^2 \kappa T) \} \cdot \frac{1}{2} (\pi \alpha^2 \bar{\lambda} \kappa T)^{\frac{1}{2}} \\ = \nu \exp \{ -q^2 / (\alpha^2 \kappa T) \}, \quad (21)$$

where  $4\pi^2\nu^2 = \bar{\lambda}$ , or as in 3.6(79)

$$\nu = (\sum \alpha_{1i}^2 \nu_i^2 / \sum \alpha_{1i}^2)^{\frac{1}{2}}. \quad (22)$$

In terms of the *minimum energy*  $E_0$  for dissociation, found in (6), the result is finally

$$k^{\infty} = \nu e^{-E_0/\kappa T}. \quad (23)$$

This rate constant is of the Arrhenius type 2.2(3), with  $E_0$  the minimum energy for dissociation. The pre-exponential or  $A$ -factor is the mean frequency  $\nu$  discussed in 3.6, lying between the least and greatest of the normal-mode frequencies. As these frequencies are of the order  $10^{13}$  to  $10^{14}$  sec.<sup>-1</sup>, our  $A$ -factor is limited to this range;\* this corresponds to the  $A$ -factor of a large number of experimental cases.

Other forms of  $\nu$  are given in 3.6; these will appear more naturally in later developments.

The analysis in Chapters 4 and 5 leading to (23) may appear unduly

\* A symmetry factor may arise, increasing the theoretical rate when there is a set of equivalent critical coordinates; this factor is twelve in the model of cyclopropane isomerization described in 8.6 below.

heavy in view of the simplicity of the result, and short cuts will be given in Chapter 6. The foregoing method shows, however, that the rate constant can be calculated directly by averaging, over an equilibrium distribution, the actual frequency with which the dissociation configuration is attained. This approach also has the advantage that it can be extended to give rates at lower concentrations (see Chapter 7).

In my first attack<sup>4</sup> on the first-order rate constant, I had only the approximate formula 4.6(79) for the frequency  $L_q$ . This yielded an  $A$ -factor of the order of magnitude of  $\nu$ ; even in this approximation it was clear that  $\nu$ , defined as in (22), was a primary parameter of the rate constant. For the rate at lower concentrations, it appears still necessary to use the approximate form of  $L_q$ .

### 5.5 SPECIFIC RATES

If to get a clear picture of the dissociation process we want to find numerically the specific rate of dissociation of molecules of given internal mode energies  $\epsilon_1, \epsilon_2, \dots, \epsilon_n$ , we may use the Fourier series 4.5(66) for  $L$ , giving the "amplitudes"  $a_i$  the values  $\alpha_{1i}\sqrt{\epsilon_i}$ . If  $\sum |\alpha_{1i}| \sqrt{\epsilon_i} - q$  is small compared with  $q$ , we use the approximation 4.6(79).

More interest is usually attached to the average specific rate  $k_E$  of molecules of total energy  $E$ . We shall first calculate this directly as equation (37) below, and then get it indirectly from a result in 2.5 (a related method was given at the end of the original paper<sup>2</sup>). The reasons for the direct calculation are, first, that it shows the nature of  $k_E$  as an average over detailed states and, secondly, that this type of integration occurs also in some more difficult problems.

**Direct calculation of  $k_E$ .** The average specific rate for molecules of energy  $E$  is an average over all distributions of the internal energy with total  $E$ . Allowing a small variation in  $E$ , we obtain

$$k_E = \int \dots \int L d\epsilon_1 \dots d\epsilon_n / \int \dots \int d\epsilon_1 \dots d\epsilon_n \quad (24)$$

where both integrals are over positive values of the  $\epsilon_i$ ; restricted by

$$E \leq \sum_i^n \epsilon_i \leq E + dE. \quad (25)$$

The form (24) gives the correct equal weighting of equal elements  $d\epsilon_1 \dots d\epsilon_n$  in the averaging; it is only at this point that ideas of an "equilibrium distribution" enter the calculation.

We calculate first the integral (over positive  $\epsilon_i$ )

$$M(E) = \int_{\sum \epsilon_i \leq E} \cdots \int L d\epsilon_1 \cdots d\epsilon_n. \quad (26)$$

Inserting Kac's formula 4.3(16) with  $a_i = \alpha_{1i} \sqrt{\epsilon_i}$ , and integrating first for  $\epsilon_1, \cdots, \epsilon_n$ , we have for (26)

$$M(E) = \pi^{-2} \int \int_0^\infty dx dy \cos(qx) y^{-2} \{I(x, 0) - I(x, y)\}, \quad (27)$$

where

$$I(x, y) \equiv \int \cdots \int \prod_1^n J_0\{\alpha_{1i} \epsilon_i^{\frac{1}{2}}(x^2 + \lambda_i y^2)^{\frac{1}{2}}\} d\epsilon_1 \cdots d\epsilon_n, \quad (28)$$

the integration being for  $\sum \epsilon_i \leq E$ . The ranges are thus

$$\begin{aligned} \epsilon_1 &= \left(0, E - \sum_2^n \epsilon_i\right); & \epsilon_2 &= \left(0, E - \sum_3^n \epsilon_i\right); \cdots; \\ & & \epsilon_n &= (0, E). \end{aligned} \quad (29)$$

The procedure may be illustrated by the following simple case:

$$\begin{aligned} \int_0^E J_0(\epsilon_2^{\frac{1}{2}}) d\epsilon_2 \int_0^{E-\epsilon_2} J_0(\epsilon_1^{\frac{1}{2}}) d\epsilon_1 \\ = \int_0^E J_0(\epsilon_2^{\frac{1}{2}}) d\epsilon_2 \int_0^{E-\epsilon_2} J_1\{(E-\epsilon_2)^{\frac{1}{2}}\} \\ = 2E J_2\{(2E)^{\frac{1}{2}}\}. \end{aligned} \quad (30)$$

Here the first step was a simple Bessel function integral, and the second was the case  $\mu=0, \nu=1$  of "Sonine's second finite integral."<sup>6</sup>

For the general integral (28) with ranges (29), each successive integration raises the order of the old Bessel function by unity, using in the  $(r+1)$ th integration Sonine's formula for  $\mu=0, \nu=r$ . This gives for (28)

$$I(x, y) = \{4E/\alpha^2(x^2 + \bar{\lambda}y^2)\}^{\frac{1}{2}n} J_n\{\alpha E^{\frac{1}{2}}(x^2 + \bar{\lambda}y^2)^{\frac{1}{2}}\}, \quad (31)$$

with  $\alpha$  and  $\bar{\lambda}$  as in (20). The Bessel function is now represented by the contour integral (looping the origin counterclockwise, with ends at  $-\infty$ , in the  $u$ -plane)

$$J_n(z) = \frac{1}{2\pi i} \left(\frac{z}{2}\right)^n \int^{0+} \exp(u - \frac{1}{4}z^2/u) u^{-n-1} du. \quad (32)$$

Deferring the  $u$ -integration, (26) becomes, by (27), (31), and (32),

$$M(E) = \frac{E^n}{2\pi i} \int^{\circ+} \frac{e^u du}{u^{n+1}} \cdot \frac{1}{\pi^2} \int_0^\infty \cos(qx) \exp(-\frac{1}{4}\alpha^2 E x^2/u) dx \cdot \int_0^\infty \{1 - \exp(-\frac{1}{4}\alpha^2 \bar{\lambda} E y^2/u)\} y^{-2} dy. \quad (33)$$

Hence, using the integrals 4.5(57) and (58),

$$M(E) = \nu E^n / (2\pi i) \int^{\circ+} \exp\{u(E - E_0)/E\} u^{-n-1} du, \quad (34)$$

where  $E_0 = q^2/\alpha^2$  as in (6) and  $\nu = \bar{\lambda}^{1/2}/(2\pi)$  as before. Distorting the contour to the Bromwich form  $u = c^2 - i\infty$  to  $c^2 + i\infty$ , we deduce that

$$\left. \begin{aligned} M(E) &= \nu(E - E_0)^n/n! & (E > E_0), \\ &= 0 & (E \leq E_0). \end{aligned} \right\} \quad (35)$$

This completes the hard work. For, comparing (24) and (26), we find the numerator of (24) is

$$dM(E) = \nu(E - E_0)^{n-1} dE / (n - 1)! \quad (E > E_0), \quad (36)$$

and the denominator is  $E^{n-1} dE / (n - 1)!$  by 2.4(35). Hence (24), the average specific rate for molecules of energy  $E$ , is

$$\left. \begin{aligned} k_E &= \nu \{(E - E_0)/E\}^{n-1} & (E \geq E_0), \\ &= 0 & (E < E_0). \end{aligned} \right\} \quad (37)$$

**Indirect calculation of  $k_E$ .** In the present model, the molecule is a harmonic system of  $n$  degrees of freedom, and the rate constant (23) is of the Arrhenius form  $Ae^{-E_0/kT}$  with parameter  $A = \nu$ . It follows therefore from 2.5(63) that the average specific rate for total energy  $E$  is precisely (37), our previous result.

The result 2.5(58), that the Arrhenius parameter  $E_0$  is the minimum energy for dissociation, is easily confirmed, since in (6) above we found  $E_0 = q^2/\alpha^2$  as the least energy for the critical coordinate  $q_1$  to reach  $q$ . A peculiarity of the present model, noted in 5.2, is that a molecule may have energy above  $E_0$  and yet be unable to dissociate. This stresses the fact, apparent also from the heavy calculation given above, that  $k_E$  is not a basic but an *averaged* rate; thus the averaging in (24) includes regions of  $\epsilon_1, \dots, \epsilon_n$  where  $L = 0$ . This aspect of  $k_E$  may also be observed in the result 2.5(59), which becomes here

$$\lim_{E \rightarrow \infty} k_E = \nu. \quad (38)$$

This again is true merely for the averaged rate; for if we put unlimited energy into the *first* normal mode, we should have very nearly  $q_1 = \alpha_{11} \sqrt{E} \cos 2\pi\nu_1 t$ , so that the specific dissociation rate would be  $\nu_1$ ; for high energy in the second mode it would be  $\nu_2$ , and so on. Nevertheless, the interpretation of  $\nu$  as the *average* specific rate of high-energy molecules is perhaps the most interesting and direct.

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3. G. N. Watson, *Theory of Bessel Functions* (Cambridge: Cambridge University Press, 1922 or 1944), p. 393.
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# Unimolecular First-Order Reactions and Transition-State Theory

TRANSITION-state or "activated complex" theory has largely dominated kinetics for the last twenty years and is still fruitful and capable of development. The account of the theory given here is restricted to first-order unimolecular gaseous reactions, which form a relatively small part of the field of application. The account may tax the reader's stamina, partly because of a perhaps overcareful examination of the basic concepts, and also because the harmonic model of the present theory is carried on in parallel with the transition-state theory.

We begin, in fact, with the harmonic model of Chapter 5. The first-order rate constant was formulated there as the average frequency with which a coordinate  $q_1$  accumulates a critical extension  $q$  by phase coincidence in the normal modes of vibration. In 6.1 this rate constant is transformed by old-fashioned dynamics into an integral over coordinate-momentum phase space. This integral can be interpreted as the flow of the phase-space distribution through the critical configuration  $q_1 = q$  to dissociation, and in 6.2 the rate is set up directly in this form from the same simple principles as lie at the root of transition-state theory. In 6.3 this rate (still for the harmonic model) is evaluated directly, and also by using the properties of Gaussian distributions.

In formally introducing transition-state theory in 6.4, we discard the purely harmonic (quadratic) potential in favor of the customary type of potential surface having a col or saddle point (which is the dissociation configuration of least energy) on the energy barrier between normal and dissociated molecular configurations. We set up the rate constant again as the flow over the barrier, or as the product  $\frac{1}{2}P_0v$ , where  $P_0$  is the equilibrium probability density at the barrier and  $v$  is the mean velocity in the reaction coordinate  $x_1$  normal to the barrier (or parallel to the valley of the col). Only when this rate has been set up may we legitimately introduce the concept of "activated complexes"

as the occupants of a small phase-space region (called the "transition state") at the boundary, and of arbitrary thickness  $\delta$  along the reaction coordinate. This enables us, writing the rate constant as  $\frac{1}{2}P_0\delta \cdot v/\delta$ , to call  $P_0\delta$  the relative number of complexes and to express it as the ratio of the phase integrals (or partition functions) of activated complexes and normal molecules. In the course of the manipulation, however, we proceed to remove the reaction coordinate and momentum from the activated partition function, leaving a "modified" function (physically unnatural but very useful) which survives in the final formula for the rate constant.

This theory is worked out for classical mechanics in 6.5 in a general but slightly unorthodox manner, allowing cross terms in the kinetic energy between the reaction-coordinate velocity  $\dot{x}_1$  and the other velocities, and also leaving the potential energy unrestricted until we come to consider the usual harmonic approximations for normal molecules and complexes. In 6.6 there is a more conventional treatment, disallowing the above cross terms so that we can more comfortably use quantum partition functions; this treatment also introduces the "effective mass in the reaction coordinate" in connection with the mean velocity  $v$ .

We turn back in 6.7 to the original harmonic model with dissociation at an arbitrary boundary  $q_1 = q$ , and compare some details of this with the activated complex model. In particular, the comparison of formulas for  $v$  suggests an important effect (which is discussed more generally in 6.9) of isotopic substitution; and the classical harmonic result, that the pre-exponential rate factor  $\nu$  lies in the range of normal-mode frequencies, suggests (in some circumstances) similar ranges for the transition-state constant, even with quantum partition functions.

In 6.8 we try anharmonic modifications of the earlier harmonic model, namely, the addition of cubic terms to the original quadratic potential. On the assumption that the dissociation energy is unchanged, the addition of a  $q_1^3$  term to the potential is found to have only a small effect on the rate constant, although it indicates a considerable increase in the molecular distortion before dissociation. A second and slightly more complicated modification of the potential is tried; this gives the model a saddle point exactly suitable for illustrating the transition-state method.

**Historical note.** The standard text on transition-state theory continues to be *The Theory of Rate Processes*, by Glasstone, Laidler, and Eyring (1941);<sup>1</sup> we shall refer to this book (or to its collective authors) as GLE. Because of its general use through the years, I have to refer to its treatment of reactions as the "conventional" treatment, which is

unfair to its pioneering spirit; also because of its general use, I have to criticize some points as if the authors were not to be credited with modifications of their ideas over this span of time; but these points are not many.

Historical details will be found in GLE, but a few names should be mentioned here. The concept of a rate as a flow over a critical surface was used in 1914 by Marcelin.<sup>2</sup> The development of transition-state theory took place around 1930 and was intimately bound up with the investigation of the nature of the energy surfaces of simple atom-exchange reactions; the main pioneers were, alphabetically, H. Eyring (who became the main protagonist), F. London, H. Pelzer, M. Polanyi, and E. Wigner. The lively discussion (memorable also for the imperturbable good humor of Eyring) at the 1937 Faraday Society meeting<sup>3</sup> provides a useful picture of the early development.

The phase-space treatment in 6.2 and 6.3 of my harmonic model arose in the course of a published correspondence with Pelzer<sup>4</sup> and is in effect a generalization of his earlier work.<sup>5</sup> M. G. Evans encouraged me to relate this treatment to transition-state theory, but I have drawn less on an early account<sup>6</sup> of this (which is still of interest) than on a lecture given more recently at Columbia University.

### 6.1 A CONTACT TRANSFORMATION

Some remarks made here about dynamical contact transformations will be relevant also at a later stage; here they lead to a particular transformation which puts the reaction rate of Chapter 5 into a new form.

The kinetic energy of a vibrating molecule in 3.1 had the Lagrangian and Hamiltonian forms

$$T' = \frac{1}{2} \sum_1^n \sum_1^n a_r \dot{q}_r \dot{q}_s \quad (1)$$

$$= \frac{1}{2} \sum_1^n \sum_1^n g_{rs} p_r p_s, \quad (2)$$

and the potential energy, for harmonic vibrations, had the form

$$V = V(q_1, \dots, q_n) = \frac{1}{2} \sum_1^n \sum_1^n b_{rs} q_r q_s. \quad (3)$$

The Hamiltonian function  $H(q_1, \dots, p_n)$  is the sum of (2) and (3).

The instantaneous classical state of a molecule may be represented by a point  $Q$  with rectangular coordinates  $q_1, \dots, p_n$  in a  $2n$ -dimensional *phase space*, and the velocity of  $Q$  (representing the rate of change of the state) is given by Hamilton's equations 3.5(71). A *con-*

*tact* or *canonical transformation*<sup>7</sup> of the dynamical system is one to new coordinates  $q'_i$  and momenta  $p'_i$  such that the form of the Hamiltonian equations is preserved, and also the extension or volume element  $dq'_1 \cdots dp'_n$  of phase space.

The contact transformation we use here is to the coordinates  $q'_i = \psi'_i$  and momenta  $p'_i = J_i$ , which are called *angle* and *action variables* respectively. These are such that the Hamiltonian  $T' + V$  of (2) and (3) takes the form (with the  $\nu_i$  constants)

$$E = \sum_1^n \nu_i J_i. \quad (4)$$

Hamilton's equations 3.6(71) in the new variables are

$$dJ_i/dt = -\partial E/\partial \psi'_i \equiv 0, \quad d\psi'_i/dt = \partial E/\partial J_i = \nu_i, \quad (5)$$

which have the integrals (with  $\psi_{i0}$  constant)

$$\psi'_i = \nu_i t + \psi_{i0}, \quad J_i = \text{constant}. \quad (6)$$

If the  $\alpha_{r_i}$  are the amplitude factors of 3.4(35), it is easily verified from 3.4(37) and (38), or (50), that the transformation turning (2) + (3) into (4) is given by

$$q_r = \sum_i \alpha_{r_i} (\nu_i J_i)^{\frac{1}{2}} \cos 2\pi \psi'_i, \quad (7)$$

$$\sum_i g_{r_i} p_r = -2\pi \sum_i \alpha_{r_i} \nu_i (\nu_i J_i)^{\frac{1}{2}} \sin 2\pi \psi'_i; \quad (8)$$

the combinations  $\sum g_{r_i} p_r$  in (8) represent the velocities  $\dot{q}_r$ , which for the moment we are not using. We can identify the constants  $J_i$  of (6) (compare also (4)) as

$$J_i = \epsilon_i / \nu_i \quad (9)$$

where  $\epsilon_i$  is the energy in the  $i$ th mode; thus by (6) and (7) the solution of the motion is

$$q_r = \sum \alpha_{r_i} \sqrt{\epsilon_i} \cos 2\pi(\nu_i t + \psi_{i0}). \quad (10)$$

This corresponds precisely to the solution 3.5(66) of the motion as found earlier, so that the angle and action variables have provided a new route to that solution.

As an immediately useful application of action and angle variables, we recall the *phase integral* defined in 2.4(27), namely,

$$\Phi = \int \cdots \int \exp \{ -(T' + V)/\kappa T \} dq_1 \cdots dp_n. \quad (11)$$

The limits for each variable in the present case are  $(-\infty, \infty)$ ; for neatness, in this chapter a bare integral sign  $\int$  will always denote  $\int_{-\infty}^{\infty}$ . If now

we convert (11) to action and angle variables, using (7) and (8), then (i)  $T' + V$  takes the form (4); (ii)  $dq_1 \cdots dp_n$  becomes  $dJ_1 \cdots d\psi'_n$  by the conservation of volume elements; and (iii) the limits become  $J_i = (0, \infty)$ ,  $\psi'_i = (0, 1)$ . Thus (11) becomes

$$\Phi = \prod_i \left\{ \int_0^\infty \exp(-\nu_i J_i / \kappa T) dJ_i \int_0^1 d\psi'_i \right\}, \quad (12)$$

or

$$\Phi = \prod_1^n (\kappa T / \nu_i), \quad (13)$$

the  $\nu_i$  being the normal frequencies. It will be recalled that  $\Phi/h^n$  is the classical limit of the partition function.

**Application to the first-order rate constant.** We now use this transformation on the first-order rate constant. In the rate constant 5.3(12) or (16), we represent the specific rate  $L$  by the "central formula" 4.3(19), which we write (since the cosine is an even function)

$$L = (4\pi)^{-1} \int_0^1 \cdots d\psi'_1 \cdots d\psi'_n \int_{-\infty}^{\infty} \cos \{x(f - q)\} |f'| dx, \quad (14)$$

where, by 4.3(20),

$$f = \sum \alpha_{1i} \sqrt{\epsilon_i} \cos 2\pi\psi'_i, \quad f' = -2\pi \sum \alpha_{1i} \nu_i \sqrt{\epsilon_i} \sin 2\pi\psi'_i. \quad (15)$$

Thus the rate constant 5.3(12) or (16) is

$$k^\infty = (4\pi\Phi)^{-1} \int_0^1 \cdots d\psi'_1 \cdots \int_0^\infty \cdots dJ_1 \cdots \int dx \cos \{x(f - q)\} |f'| e^{-E/\kappa T}, \quad (16)$$

where  $\Phi$  denotes the expression (13) and the  $J_i$  are as in (9).

We regard (16) as an integral over all phase space in terms of action and angle variables  $\psi'_i$  and  $J_i$ . We now make the contact transformation to variables  $q_1, \cdots, p_n$ ; this is in fact the reverse of the passage from (11) to (12). By (7) and (8),  $f$  and  $f'$  of (15) become  $q_1$  and  $\dot{q}_1 = \sum_1^n g_{1i} p_i$ ; also  $E$  becomes  $T' + V$  by (4). Thus (16) transforms into

$$k^\infty = (4\pi\Phi)^{-1} \int \cdots \int |\dot{q}_1| \cos \{x(q_1 - q)\} \cdot \exp \left\{ -(T' + V) / \kappa T \right\} dq_1 \cdots dp_n dx. \quad (17)$$

Integration over  $q_1$  and  $x$ , as in Fourier transform theory, removes a factor  $(2\pi)^{-1} \cos \{ \cdots \}$  and replaces  $q_1$  in  $V$  by  $q$ , the critical value: we write

$$V_q \equiv V(q, q_2, \cdots, q_n). \quad (18)$$

Thus

$$k^\infty = \frac{1}{2} \Phi^{-1} \int \cdots \int |\dot{q}_1| \exp \{-(T' + V_q)/\kappa T\} dq_2 \cdots dp_n. \quad (19)$$

Using the form (11) of  $\Phi$ , we have finally the *new form of the rate constant*:

$$k^\infty = \frac{\frac{1}{2} \int \cdots \int |\dot{q}_1| \exp \{-(T' + V_q)/\kappa T\} dq_2 \cdots dp_n}{\int \cdots \int \exp \{-(T' + V)/\kappa T\} dq_1 \cdots dp_n}. \quad (20)$$

Since in (2) the  $g_{rs}$  are treated as constant, we may replace  $dp_1 \cdots dp_n$  in both integrals in (20) by  $d\dot{q}_1 \cdots d\dot{q}_n$  and use the form (1) of  $T'$ . Formula (20) may then be called *Pelzer's formula*. He gave and used it<sup>5</sup> for the case of a "linear chain" molecule, with  $q_1, \cdots, q_n$  the extensions of the links, and with the hypothesis that dissociation follows the excessive stretch of link  $q_1$  (not necessarily an end link). We have here extended the formula to the general energy forms (1) and (3), and it will be realized later that it holds for still more general forms of  $T'$  and  $V$ .

The constancy of the  $a_{rs}$  or  $g_{rs}$  in the present model enables us to separate out the  $q$ -integrations in (20) and to write it in the *standard form*

$$k^\infty = \frac{1}{2} P_q v, \quad (21)$$

where

$$P_q = \int \cdots \int \exp(-V_q/\kappa T) dq_2 \cdots dq_n / \int \cdots \int \exp(-V/\kappa T) dq_1 \cdots dq_n, \quad (22)$$

and

$$\begin{aligned} v &= \frac{\int \cdots \int |\dot{q}_1| e^{-T'/\kappa T} d\dot{q}_1 \cdots d\dot{q}_n}{\int \cdots \int e^{-T'/\kappa T} d\dot{q}_1 \cdots d\dot{q}_n} \\ &= \frac{\int \cdots \int |\sum g_{1s} p_s| e^{-T'/\kappa T} dp_1 \cdots dp_n}{\int \cdots \int e^{-T'/\kappa T} dp_1 \cdots dp_n}, \end{aligned} \quad (23)$$

according as (1) or (2) is used for  $T'$ .

## 6.2 PELZER'S FORMULA

We now seek a direct interpretation of Pelzer's formula (20) or (21). As we are dealing with the pure first-order reaction, we assume always that undissociated molecules are present in equilibrium numbers. Thus if we are using variables  $q$  and  $p$ , or  $q$  and  $\dot{q}$  (instead of the energies and phases  $\epsilon_i$  and  $\psi_i$  of Chapter 5), the number of molecules per unit extension  $\delta q_1 \cdots \delta p_n$  or  $\delta q_1 \cdots \delta \dot{q}_n$  of "phase space" is proportional to  $\exp \{ -(T' + V)/\kappa T \}$ . The equivalence of  $(q, \dot{q})$  to  $(q, p)$  space follows from the assumed constancy of the  $a_{rs}$  in (1); and this also entails the *independence* of the distribution of  $qs$  from that of the  $\dot{q}s$  or  $ps$ ; these distributions are proportional respectively to  $\exp(-V/\kappa T)$  and  $\exp(-T'/\kappa T)$ . Thus the proportions of molecules having  $q_1$  in the range  $(q, q+dq_1)$ , irrespective of the values of  $q_2, \dots, q_n$ , and  $\dot{q}_1, \dots, \dot{q}_n$ , is

$$P_q dq_1, \quad (24)$$

where  $P_q$  is as in (22). Also, the proportion of molecules having  $\dot{q}_1$  in the range  $(\dot{q}_1, \dot{q}_1+d\dot{q}_1)$  is

$$P(\dot{q}_1) d\dot{q}_1, \quad (25)$$

where

$$P(\dot{q}_1) = \int \cdots \int e^{-T'/\kappa T} d\dot{q}_2 \cdots d\dot{q}_n / \int \cdots \int e^{-T'/\kappa T} d\dot{q}_1 \cdots d\dot{q}_n. \quad (26)$$

The *mean velocity*, irrespective of direction, in coordinate  $\dot{q}_1$  is

$$v = \langle |\dot{q}_1| \rangle = \int_{-\infty}^{\infty} |\dot{q}_1| P(\dot{q}_1) d\dot{q}_1, \quad (27)$$

which is seen to be identical with (23). Thus the "standard rate" (21) is *one half the probability density in  $q_1$  at  $q$ , multiplied by the mean speed in the breaking coordinate*.

We shall now derive this result in a direct manner. The rate  $k^\infty$  is the limit, as  $\Delta t$  tends to zero, of  $(\Delta t)^{-1}$  times the proportion of molecules which dissociate in the interval  $\Delta t$ . Molecules dissociate when  $q_1$  rises to the value  $q$ ; thus they must have  $\dot{q}_1$  positive, and to dissociate in  $\Delta t$  they must initially have  $q_1$  in the range  $(q - q_1 \Delta t, q)$ ; the length  $\dot{q}_1 \Delta t$  of this range depends on their speed.\* Of the molecules with speed  $\dot{q}_1$ , a proportion  $P_q \dot{q}_1 \Delta t$  lie in this range, by (24). As a proportion  $P(\dot{q}_1) d\dot{q}_1$

\* The point of this remark (compare 6.4 below) is that the molecules of all speeds which are to dissociate in a fixed  $\Delta t$  cannot be those occupying a *fixed* range  $\delta$  of  $q_1$ .

of all molecules have velocities in  $(\dot{q}_1, \dot{q}_1 + d\dot{q}_1)$ , the total proportion rising to  $q$  in time  $\Delta t$  is therefore  $P_q \int_0^\infty \dot{q}_1 P(\dot{q}_1) d\dot{q}_1 \Delta t$ . Hence the rate constant is

$$k^\infty = P_q \int_0^\infty \dot{q}_1 P(\dot{q}_1) d\dot{q}_1. \quad (28)$$

From the nature of the kinetic energy,  $P(-\dot{q}_1) = P(\dot{q}_1)$ ; so the rate constant is

$$k^\infty = \frac{1}{2} P_q \int_{-\infty}^\infty |\dot{q}_1| P(\dot{q}_1) d\dot{q}_1. \quad (29)$$

By (27) this is (21), so that we have now proved this directly.

*Comments on formula (21):* (i) We observe that in establishing (21) directly, we made no use of the quadratic nature of  $V(q_1, \dots, q_n)$ ; so we may use (21) later with more general potentials.

(ii) It may be asked (especially in view of the last remark), why the formula (21), directly approached as here, should not be made the whole basis, and the phase-coincidence method of Chapter 5 be discarded? The reasons are the usefully clear physical picture provided by that method and, more importantly, the relative ease with which the phase-coincidence method can be extended from high- to general-concentration rates, as in Chapter 7 below.

(iii) An awkward factor  $\frac{1}{2}$  appears in (21). It is best to associate this with  $P_q$ , as picking out that half of the distribution which is moving toward dissociation; this half-distribution is then credited with the mean speed  $v$ .

(iv) This last procedure is to be contrasted with the exposition on page 186 of GLE in formulating activated-complex theory. They define the "average velocity in one direction, e.g., in the forward direction" as  $v'$  where (in the present notation)

$$v' = \int_0^\infty \dot{q}_1 P(\dot{q}_1) d\dot{q}_1. \quad (30)$$

Comparing this with (27) gives

$$v' = \frac{1}{2} v, \quad (31)$$

and for the rate constant

$$k^\infty = P_q v'. \quad (32)$$

The relation (31), arising from this unusual definition of "average velocity in one direction," must be borne in mind later in comparing GLE's exposition with the present discussion.

## 6.3 CALCULATION OF THE RATE CONSTANT

The new form (21) of the rate constant will now be evaluated directly (without using normal modes), foreshadowing the subsequent treatment of the "transition state." A second method is added, which links the normal modes of Chapter 5 with the present work, and will reappear in quantum form in Chapter 10.

**The direct calculation.**<sup>6</sup> We consider the factors  $v$  and  $P_q$  of (21). We use the first of the forms (23) of the mean velocity  $v$ , with  $T'$  as in (1). We make the transformation from  $\dot{q}_r$  to  $v_s$ :

$$\dot{q}_1 = v_1, \quad \dot{q}_s = v_s + A_{1s}v_1/A_{11} \quad (s = 2, \dots, n), \quad (33)$$

where  $A_{rs}$  is the cofactor of  $a_{rs}$  in  $A = ||a_{rs}||$ . This gives for (1)

$$T' = \frac{1}{2}Av_1^2/A_{11} + T'', \quad T'' \equiv \frac{1}{2} \sum_2^n \sum_2^n a_{rs}v_rv_s. \quad (34)$$

Substituting (33) and (34) in (23), we cancel the integrals in  $v_2, \dots, v_n$ , leaving

$$\begin{aligned} v &= \int |v_1| e^{-\phi} dv_1 / \int e^{-\phi} dv_1 \quad (\phi \equiv \frac{1}{2}Av_1^2/A_{11}\kappa T) \\ &= (2\kappa T A_{11}/\pi A)^{1/2}. \end{aligned} \quad (35)$$

This *mean velocity in the reaction coordinate* is discussed in subsequent sections of this chapter.

To calculate  $P_q$ , which is (22) with  $V$  as in (3) for the present harmonic model, we introduce variables  $x, x_2, \dots, x_n$ , where

$$q_1 = x, \quad q_s = x_s + B_{1s}x/B_{11} \quad (s = 2, \dots, n). \quad (36)$$

This gives for (3)

$$V = \frac{1}{2}Bx^2/B_{11} + V'', \quad (37)$$

where

$$V'' \equiv \frac{1}{2} \sum_2^n \sum_2^n b_{rs}x_r x_s. \quad (38)$$

Since  $V''$  (like  $V$  itself) is essentially positive for all nonzero values of the variables, the form (37) shows that the *minimum energy*  $E_0$  for dissociation, namely, the least energy for  $q_1$  to reach  $q$ , is

$$E_0 = \frac{1}{2}Bq^2/B_{11}. \quad (39)$$

(This agrees with the minimum energy  $q^2/\alpha^2$  of 5.2(6), since, by

3.4(61),  $\frac{1}{2}B/B_{11}=1/\alpha^2$ .) Thus when  $q_1$  (or  $x$ ) =  $q$ , we write (37), in the notation (18), as

$$V_q = E_0 + V'' = E_0 + \frac{1}{2} \sum_2^n \sum_2^n b_{rs} x_r x_s. \quad (40)$$

If now we make the change of variables (36) in (22), the integrals in  $x_2, \dots, x_n$  cancel, leaving

$$\begin{aligned} P_q &= e^{-E_0/\kappa T} \int \exp(-\frac{1}{2}Bx^2/B_{11}\kappa T) dx \\ &= e^{-E_0/\kappa T} (B/2\pi B_{11}\kappa T)^{\frac{1}{2}}. \end{aligned} \quad (41)$$

The *first-order rate constant* (21) is therefore, by (35) and (41),

$$k^\infty = \frac{1}{2\pi} \left( \frac{A_{11}}{A} \cdot \frac{B}{B_{11}} \right)^{\frac{1}{2}} e^{-E_0/\kappa T}, \quad (42)$$

which is its direct expression in terms of the kinetic and potential coefficients  $a_{rs}$  and  $b_{rs}$ . This is equivalent to the form  $\nu e^{-E_0/\kappa T}$  found in 5.4(23), by virtue of the result 3.6(83). But the most direct interpretation of (42) is, in terms of 3.6(84)-(87), as

$$k^\infty = \frac{\nu_1 \nu_2 \cdots \nu_n}{\nu'_2 \cdots \nu'_n} e^{-E_0/\kappa T}, \quad (43)$$

where  $\nu_1, \dots, \nu_n$  are the normal frequencies and  $\nu'_2, \dots, \nu'_n$  are the frequencies of the system with  $q_1$  fixed.

**Calculation from Gaussian distributions.** The following method<sup>8</sup> of calculating (21) might be held in reserve until Chapter 10 is reached.

Referring back to the forms 3.5(62) of the energies in normal coordinates and velocities, we see that the equilibrium distribution of values of  $Q_i$  and  $\dot{Q}_i$  is proportional to  $\exp \{ -(Q_i^2 + \dot{Q}_i^2/\lambda_i)/\kappa T \} dQ_i d\dot{Q}_i$ , as this is a factor of  $\exp \{ -(T+V)/\kappa T \}$  times the phase-space element. Hence  $Q_i$  and  $\dot{Q}_i$  have *independent Gaussian distributions* with mean squares

$$\langle Q_i^2 \rangle = \frac{1}{2} \kappa T, \quad \langle \dot{Q}_i^2 \rangle = \frac{1}{2} \lambda_i \kappa T \quad (\lambda_i \equiv 4\pi^2 \nu_i^2). \quad (44)$$

Thus  $q_1$  and  $\dot{q}_1$ , being the linear combinations  $\sum \alpha_i Q_i$  and  $\sum \alpha_i \dot{Q}_i$  (compare 3.4(35)), also have independent Gaussian distributions with mean squares  $\sigma^2$ ,  $\dot{\sigma}^2$ , where

$$\sigma^2 \equiv \langle q_1^2 \rangle = \sum \alpha_i^2 \langle Q_i^2 \rangle = \frac{1}{2} \alpha^2 \kappa T, \quad (45)$$

$$\dot{\sigma}^2 \equiv \langle \dot{q}_1^2 \rangle = \sum \alpha_i^2 \langle \dot{Q}_i^2 \rangle = \frac{1}{2} \alpha^2 \cdot 4\pi^2 \nu^2 \kappa T, \quad (46)$$

where as before

$$\alpha^2 = \sum \alpha_{1i}^2, \quad \nu^2 = \sum \alpha_{1i}^2 \nu_i^2 / \alpha^2. \quad (47)$$

Hence, quoting the standard form of a Gaussian distribution, we have for (24)

$$P_q = (2\pi\sigma^2)^{-1} \exp(-q^2/2\sigma^2); \quad (48)$$

and also by the relation of the arithmetic mean and mean square,

$$\nu \equiv \langle | \dot{q}_1 | \rangle = (2/\pi)^{1/2} \dot{\sigma}. \quad (49)$$

Thus the rate constant (21) is

$$k^\infty = \dot{\sigma} / (2\pi\sigma) \exp(-q^2/2\sigma^2), \quad (50)$$

a form which will reappear in the quantum theory, where, however, the mean squares are not given by (44). For the classical case (44)–(47), we have for (50)

$$k^\infty = \nu \exp(-q^2/\alpha^2\kappa T) = \nu e^{-E_0/\kappa T}, \quad (51)$$

where  $E_0$  is the minimum energy as before.

It is observed that in this method the factor  $\nu$  appears naturally as a root mean square frequency, as in Chapter 5, without any forcing of the mathematical form; and indeed the present method is intermediate between the method of Chapter 5 and the phase-space or transition-state method, to which we now proceed.

#### 6.4 THE BASIS OF TRANSITION-STATE THEORY

The following account of transition-state theory of first-order reactions is shaped to clarify the underlying hypotheses. The account is not adapted to the simple quadratic potential we have been using but centers on the more usual and realistic saddle-point potential. Methods of constructing potential functions (or surfaces) for actual molecules will, however, not be discussed in this book.

**The potential surface and coordinate systems.** If the molecule has internal coordinates  $q_1, \dots, q_n$ , we imagine a potential (hyper)surface

$$V = V(q_1, \dots, q_n) \quad (52)$$

constructed, with  $V$  as an "ordinate" in an  $(n+1)$ th dimension. The surface is to have a stable region, with minimum  $V=0$  at  $O$ , the point  $q_1 = \dots = q_n = 0$ . This region is separated by a barrier from the dissociated states of the molecule. The barrier has as lowest point a col or saddle point at  $Q_0(q_{10}, \dots, q_{n0})$ , where  $V=E_0$ . This point is the dissociation configuration of least energy; it is assumed that nearly all dissociations occur by paths in  $q$ -space which cross the barrier outward fairly near the saddle.

Clearly, with a minimum at  $O$  and a point of unstable equilibrium  $Q_0$ , the potential cannot be a mere quadratic in the  $q_r$ . Near  $O$ ,  $V$  will be of the form (3) as far as quadratic terms in the  $q_r$ . Similarly, near the unstable point  $Q_0$ ,  $V$  will be of the form (as far as quadratic terms in  $q_r - q_{r0}$ )

$$V = E_0 + \frac{1}{2} \sum_1^n \sum_1^n b_{rs}(q_r - q_{r0})(q_s - q_{s0}). \quad (53)$$

It is the essential feature of a saddle point that we can make an orthogonal transformation near  $Q_0$ , namely,

$$q_r - q_{r0} = \sum_{s=1}^n f_{rs}x_s, \quad (54)$$

such that in the new coordinates the approximation (53) becomes

$$V = E_0 - \frac{1}{2}b_1x_1^2 + V'', \quad (55)$$

$$V'' = \frac{1}{2} \sum_2^n \sum_2^n b''_{rs}x_r x_s, \quad (56)$$

where  $b_1$  is positive and  $V''$  is positive for all nonzero  $x_r$ . We then call  $x_1$  the *reaction coordinate*: it is not generally one of the original  $q$ -coordinates (unlike the earlier model).

Although the transformation (54) is set up primarily for small values of  $q_r - q_{r0}$  or of  $x_s$ , it is helpful to consider a complete (nonlinear) transformation from  $q_r$  to  $x_s$ , valid throughout the configuration space and reducing to (54) for small  $x_s$ . If, for example, the equation of the complete potential barrier (as a hypersurface in  $q$ -space) were  $\phi(q_1, \dots, q_n) = 0$ , we might choose  $x_1 = k\phi(q_1, \dots, q_n)$  so that we could say that the molecule would dissociate anywhere where  $x_1$  changed from negative to positive. With this type of extension of the  $x_r$  system, the potential  $V$  would be expressible everywhere as a function of the  $x_r$ , reducing approximately to (55) near the saddle point.

The kinetic energy  $T'$  is a quadratic form in the velocities or momenta; usually the coefficients of the form are treated as independent of the  $q_r$  (or  $x_s$ ), although this is hazardous for large deformations. It is also common (especially in discussing potential surfaces, as in GLF, Chapter III) to assume a form  $\frac{1}{2}m \sum \dot{q}_r^2$ . This lets us visualize the behavior of the molecule as the sliding of a particle (in  $n$  dimensions) on the potential surface; moreover an orthogonal transformation (54) at the saddle point will then give the similar form  $\frac{1}{2}m \sum \dot{x}_s^2$ . I rather dislike the form  $\sum \dot{q}_r^2$  in that it usually arises from a nonorthogonal transformation (a "skewing" of axes, involving the atomic masses in the transformation) of a more natural set of internal coordinates; but this is

perhaps a matter of taste unless isotopes are likely to be brought in. We shall find in 6.5 that we can (classically at least) handle cross terms  $\dot{q}_i \dot{q}_s$  (or  $\dot{x}_i \dot{x}_s$ ) in  $T'$ .

**Formulation of the reaction rate.** A correct formulation must be analogous to that of (28) above; here the corresponding procedure is to count the molecules which pass out over the "ridge,"  $x_1=0$ , of the dissociation barrier in a small given time  $\Delta t$ . Molecules with a positive velocity  $\dot{x}_1$  will dissociate in that time if initially they have values of  $x_1$  between  $-\dot{x}_1 \Delta t$  and 0.

In the assumed equilibrium distribution of undissociated molecules, the distributions of configuration and velocity are independent if we assume the kinetic energy has constant coefficients. Let

$$P_0 dx_1 \quad \text{and} \quad P(\dot{x}_1) d\dot{x}_1 \quad (57)$$

be the proportions of molecules with  $x_1$  in  $(0, dx_1)$  and  $\dot{x}_1$  in  $(\dot{x}_1, \dot{x}_1 + d\dot{x}_1)$  respectively. Of the proportion  $P(\dot{x}_1) d\dot{x}_1$  around a positive velocity  $\dot{x}_1$ , a fraction  $P_0 \dot{x}_1 \Delta t$  dissociate in time  $\Delta t$ , by the previous paragraph. Thus the total proportion dissociating is the sum of contributions  $P(\dot{x}_1) d\dot{x}_1 \cdot P_0 \dot{x}_1 \Delta t$  over ranges  $d\dot{x}_1$ , and the first-order rate constant is

$$k^\infty = P_0 \int_0^\infty \dot{x}_1 P(\dot{x}_1) d\dot{x}_1. \quad (58)$$

The velocity distribution is symmetrical about  $\dot{x}_1=0$ . Thus the rate constant may be written in the *standard form*

$$k^\infty = \frac{1}{2} P_0 v, \quad (59)$$

where  $v$  is the mean absolute speed in coordinate  $x_1$ , namely,

$$v \equiv \langle |\dot{x}_1| \rangle = \int_{-\infty}^{\infty} |\dot{x}_1| P(\dot{x}_1) d\dot{x}_1, \quad (60)$$

and  $P_0$  is the probability density in the  $x_1$  coordinate (after summing over  $x_2, \dots, x_n$ ) at  $x_1=0$ . The result (59) is the analog of (21); the removal of the factor  $\frac{1}{2}$  from (59) by using a "mean forward velocity"  $v' = \frac{1}{2}v$  could be engineered in the way discussed around equations (30)–(32) above.

It is easily seen that if the distributions in position and velocity were not independent, the combined probability in  $x_1$  and  $\dot{x}_1$  being  $P(x_1, \dot{x}_1) dx_1 d\dot{x}_1$ , then the rate constant (58) would be replaced by

$$k^\infty = \int_0^\infty \dot{x}_1 P(0, \dot{x}_1) d\dot{x}_1, \quad (61)$$

which is analogous to Rice's formula 4.4(48). While mentioning generalizations, one should refer to the geometrical formulation of the flow through the barrier by Horiuti<sup>9</sup> (with a sequel by Hirota and Horiuti<sup>10</sup>).

**An incorrect formulation.** It is customary to mark off an arbitrary small region,  $x_1 = -\delta$  to 0, along the reaction coordinate and to call this region the *transition state* and its occupants *activated complexes*. This concept is useful *after* (59) has been established, but should not be used to formulate (59); let us see what happens if we attempt this.

If an activated complex (defined as above in terms of a given length  $\delta$  along  $x_1$ ) has velocity  $\dot{x}_1$ , the time it takes to pass through the transition state—its life as an activated complex—is  $\delta/|\dot{x}_1|$ ; this lifetime depends on  $\dot{x}_1$ . The *mean life* of all activated complexes is the average

$$\tau = \delta \langle |\dot{x}_1|^{-1} \rangle = \delta \int_{-\infty}^{\infty} |\dot{x}_1|^{-1} P(\dot{x}_1) d\dot{x}_1. \quad (62)$$

The proportion of molecules which are in the transition state and moving toward dissociation is  $\frac{1}{2}P_0 \delta$ , by (57). If we follow page 187 of GLE in saying that "the fraction of the activated complexes crossing the barrier in unit time is  $1/\tau$ ," then the rate constant is

$$k^\infty = \frac{1}{2}P_0 \delta / \tau, \quad (63)$$

and this, by (62), is

$$k^\infty = \frac{1}{2}P_0 \langle |\dot{x}_1|^{-1} \rangle^{-1}. \quad (64)$$

This reduces to the required formula (59) if we put the average velocity in place of the reciprocal of the average of the reciprocal of the velocity. This is hazardous, since the integral (62) does not converge. In fact, GLE avoid this trap by saying that the mean life of the activated complexes is not (62) but

$$\tau = \delta \langle |\dot{x}_1| \rangle^{-1}, \quad (65)$$

and this used in (63) gives the rate (59). As, however, (65) is not the mean of  $\delta/|\dot{x}_1|$ , this leaves an uncomfortable feeling.

There is rather more in this criticism than a mere quibble over the meaning of "average lifetime"; it is common enough to speak of average life when the more relevant concept is average frequency. Activated complexes are distributed over a fixed *length*  $\delta$  and so do not flow over the barrier together in time, owing to their spread velocities; and a reaction rate, as flow per unit time, cannot be calculated firmly from the behavior of the occupants of a fixed length. Thus the concept of the activated complex should not be used in formulating the rate. But after the rate (59) has been set up, we may thereafter make use of

a fixed length  $\delta$ , and of the "activated complex," in manipulating the rate formula. This we proceed to do.

### 6.5 CLASSICAL PARTITION FUNCTIONS IN TRANSITION-STATE THEORY

Returning now to the point at which we had first established the rate constant (59), we write it as

$$k^\infty = \frac{1}{2}P_0\delta \cdot (v/\delta), \quad (66)$$

where  $\delta$  is some small number. We think of  $\delta$  as a length along the reaction coordinate  $x_1$  at  $x_1=0$ , and so delimit a thin  $n$ -dimensional region,  $-\delta < x_1 < 0$ , of the configuration space of the  $q$ , or  $x$ . This region is the "transition state." Molecules in it are "activated complexes," or "complexes" for short.\* Referring to (57), we see that the factor  $P_0\delta$  in (66) is the proportion of molecules which are complexes. (If we restricted the name "complex" to molecules moving *toward* dissociation, then the proportion of complexes would be the factor  $\frac{1}{2}P_0\delta$  in (66).)

As we assume that the equilibrium distribution holds right up to the dissociation configuration, the probability  $P_0\delta$  of being "complex" is  $\Phi'_\ddagger/\Phi$ , where  $\Phi$  is the classical phase integral (11) or 2.4(27), and  $\Phi'_\ddagger$  is the same integral except that the region of integration is the transition state  $-\delta < x_1 < 0$ . Thus with  $H = T' + V$  for the molecular Hamiltonian,

$$\Phi = \int \cdots \int e^{-H/kT} dq_1 \cdots dp_n \quad (\text{integral over all states}), \quad (67)$$

$$\Phi'_\ddagger = \int \cdots \int e^{-H/kT} dq_1 \cdots dp_n \quad (\text{over } -\delta < x_1 < 0). \quad (68)$$

The rate constant (66) is now

$$k^\infty = \frac{1}{2}(\Phi'_\ddagger/\Phi)(v/\delta). \quad (69)$$

The purpose of this section is to express this rate in terms of a *modified phase integral* (or partition function) of the complex in which the reaction coordinate is eliminated as a variable of integration; the results are in (88) and (91) below, but the manipulation is somewhat tedious.

\* The name "complex" stems from the earlier consideration of bimolecular reactions, where two molecules are momentarily associated into a joint configuration or complex. In the unimolecular case a single but distorted molecule provides the whole "complex."

The complete phase integral (67) was evaluated in (11)–(13) for purely harmonic vibrations; here we have a more general potential, although we are still ignoring over-all rotation. We need not discuss (67) here, although we may remark that the harmonic approximation is usually considered adequate for it.

To simplify (68), the phase integral of the complex, we must use the col coordinates  $x_r$  of (54). We assume that the potential  $V$  is like (55), although there is no need in this formal theory to restrict  $V''$  to a quadratic form. Thus the integral over potential energy (i.e., over the  $q_r$  transformed into  $x_s$ ) in (68) is, by (55),

$$\begin{aligned} \int \cdots \int e^{-V/\kappa T} dq_1 \cdots dq_n \\ &= e^{-E_0/\kappa T} \int_{-\delta}^0 e^{b_1 x_1^2/2\kappa T} dx_1 \int \cdots \int e^{-V''/\kappa T} dx_2 \cdots dx_n \\ &\cong \delta e^{-E_0/\kappa T} \int \cdots \int e^{-V''/\kappa T} dx_2 \cdots dx_n, \end{aligned} \quad (70)$$

to a sufficient approximation. The result implies that the effect of curvature (the  $\frac{1}{2}b_1 x_1^2$  term) along the reaction coordinate is of no importance.

The kinetic energy in col coordinates for the integral (68) is taken to be of the general quadratic form

$$T' = \frac{1}{2} \sum_1^n \sum a'_{rs} \dot{x}_r \dot{x}_s = \frac{1}{2} \sum_1^n \sum g'_{rs} p'_r p'_s \quad \left( p'_r = \sum_1^n a'_{rs} \dot{x}_s \right); \quad (71)$$

the momenta  $p'_r = \partial T' / \partial \dot{x}_r$  are conjugate to the  $x_r$ , not to the  $q_r$  coordinates. Referring to the discussion in 6.4, we deliberately include cross terms  $\dot{x}_r \dot{x}_s$  in (71) to show that they can be handled, although they will cause some complication.

The integral over kinetic energy in (68) is

$$\int \cdots \int e^{-T'/\kappa T} dp_1 \cdots dp_n = \int \cdots \int e^{-T'/\kappa T} dp'_1 \cdots dp'_n. \quad (72)$$

Now the mean velocity  $v$  in coordinate  $x_1$  is

$$v = \int \cdot \int |\dot{x}_1| e^{-T'/\kappa T} dp'_1 \cdots dp'_n / \int \cdot \int e^{-T'/\kappa T} dp_1 \cdots dp_n. \quad (73)$$

Hence, using this and collecting the factors (70) and (72) of  $\Phi'_1$ , we have for the rate constant (69)

$$\begin{aligned}\Phi k^\infty &= \frac{1}{2} \Phi'_1 v / \delta \\ &= \frac{1}{2} e^{-E_0/\kappa T} \int \cdots \int e^{-V''/\kappa T} dx_2 \cdots dx_n \\ &\quad \cdot \int \cdots \int |\dot{x}_1| e^{-T''/\kappa T} dp'_1 \cdots dp'_n.\end{aligned}\quad (74)$$

In this halfway stage, we have eliminated the auxiliary length  $\delta$  introduced in (66).

*Completion of the reduction:* The last integral in (74) will now be reduced to the form (85) below. First we transform the integral from momenta  $p'_r$  to velocities  $\dot{x}_r$ . By (71), the Jacobian is

$$\partial(p')/\partial(\dot{x}) = A' \equiv \|a'_{rs}\| \quad (r, s = 1, \cdots, n), \quad (75)$$

so that the last integral in (74) is

$$A' \int \cdots \int |\dot{x}_1| e^{-T''/\kappa T} d\dot{x}_1 \cdots d\dot{x}_n. \quad (76)$$

In this we make the transformation (with unit Jacobian)

$$\dot{x}_1 = v_1, \quad \dot{x}_s = v_s + A'_{1s}v_1/A'_{11} \quad (s = 2, \cdots, n), \quad (77)$$

where  $A'_{rs}$  is the cofactor of  $a'_{rs}$  in  $A'$ . This gives for (71)

$$T' = \frac{1}{2} A'_{11} v_1^2 / A'_{11} + T'', \quad (78)$$

where

$$T'' = \frac{1}{2} \sum_2^n \sum_2^n a'_{rs} v_r v_s. \quad (79)$$

Applying these results gives for (76)

$$\begin{aligned}A' \int |v_1| \exp(-\frac{1}{2} A'_{11} v_1^2 / A'_{11} \kappa T) dv_1 \int \cdots \int e^{-T''/\kappa T} dv_2 \cdots dv_n \\ = 2A'_{11} \kappa T \int \cdots \int e^{-T''/\kappa T} dv_2 \cdots dv_n.\end{aligned}\quad (80)$$

Finally we convert this integral back into "quasi-momenta"  $p_r''$  defined as

$$p_r'' = \sum_2^n a'_{rs} v_s \quad (r = 2, \dots, n). \quad (81)$$

The Jacobian of the transformation is

$$\partial(v_2, \dots, v_n) / \partial(p_2'', \dots, p_n'') = 1/A'_{11}, \quad (82)$$

and the energy  $T''$  of (79) is seen to become

$$T'' = \frac{1}{2} \sum_2^n \sum_2^n g''_{rs} p_r'' p_s'', \quad (83)$$

where

$$g''_{rs} = (\text{cofactor of } a'_{rs} \text{ in } A'_{11}) / A'_{11}. \quad (84)$$

The simplest view of  $T''$  is that in terms of *velocities* it is the  $T'$  of (71) with  $\dot{x}_1 = 0$ ; in terms of momenta it is the Hamiltonian form of this modified  $T'$ .

By (82), the integral (80) is

$$2\kappa T \int \dots \int e^{-T''/kT} dp_2'' \dots dp_n''. \quad (85)$$

Thus the expression (74), with (85) for the last integral, is

$$\Phi k^\infty = \frac{1}{2} \Phi_\ddagger v / \delta = \kappa T e^{-E_0/kT} \Phi_\ddagger, \quad (86)$$

where

$$\Phi_\ddagger = \int \dots \int e^{-V''/kT} dx_2 \dots dx_n \int \dots \int e^{-T''/kT} dp_2'' \dots dp_n''. \quad (87)$$

The rate constant (69) is therefore finally

$$k^\infty = \kappa T (\Phi_\ddagger / \Phi) e^{-E_0/kT}. \quad (88)$$

**Discussion of the result.** The energies in (87) are of the form

$$\left. \begin{aligned} V'' &= V''(x_2, \dots, x_n), \\ T'' &= \frac{1}{2} \sum_2^n \sum_2^n a'_{rs, \dot{x}_r, \dot{x}_s} \text{ with } p_r'' = \sum_2^n a'_{rs, \dot{x}_s}. \end{aligned} \right\} \quad (89)$$

Thus  $\Phi_{\ddagger}$  is the complete phase integral of the fictitious system obtained by omitting the minimum col energy  $E_0$  and the term in the reaction coordinate  $x_1$  from the potential (55), and also omitting all terms in  $\dot{x}_1$  from the (Lagrangian) kinetic energy (71); further, the calculation of  $\Phi_{\ddagger}$  is in coordinates centered at the saddle point. We may call  $\Phi_{\ddagger}$  *the modified phase integral of the complex*; the modification consists in dropping all terms involving the reaction coordinate and velocity. The modification does not leave us a physically real system, but one which may be mathematically tractable and may also be usefully analogous to a real system.

The formula (88) may be regarded as the general high-concentration rate constant given by classical mechanics in the spirit of transition-state theory. As a classical formula, it does not contain Planck's constant  $h$ .

The *classical partition function*, regarded as a limit of a quantum sum-over-states, is the phase integral divided by  $h^f$ , where  $f$  is the number of degrees of freedom. Now the normal molecule and the activated complex each have  $n$  degrees of internal freedom, and the "modified complex" has one less. Thus if  $F$ ,  $F'_{\ddagger}$ , and  $F_{\ddagger}$  are the normal, activated, and modified-activated partition functions,

$$F/\Phi = F'_{\ddagger}/\Phi_{\ddagger} = h^{-n}, \quad F_{\ddagger}/\Phi_{\ddagger} = h^{-n+1}. \quad (90)$$

The rate constant (88) may thus be written in terms of these partition functions as

$$k^{\infty} = (\kappa T/h) (F_{\ddagger}/F) e^{-E_0/\kappa T}, \quad (91)$$

which is the basic formula on page 15 or page 189 of G.I.F. (The form of (91) is unchanged if we include the rotational factors of  $F$  and  $F_{\ddagger}$ ; this is discussed below.) The present classical derivation did not entail the explicit calculation of the mean velocity  $v$  and so did not bring in the "effective mass in the reaction coordinate," which will appear later. The present derivation allows cross terms in the kinetic energy (in col coordinates), and also does not restrict the potential in  $F$  or  $F_{\ddagger}$  formally to quadratic terms.

**The harmonic approximation.** If we assume that normal molecules are characterized predominantly by harmonic vibrations, as for small values of the  $q_r$ , with frequencies  $\nu_1, \dots, \nu_n$ , then by (13) and (90) we have

$$\Phi = \prod_1^n (\kappa T/\nu_i), \quad F = \prod_1^n (\kappa T/h\nu_i), \quad (92)$$

an approximation which ignores the limited range of undissociated configurations (compare 6.7(i) and the end of 6.8 below).

If we assume also that the potential energy of dissociating molecules is adequately represented by (55) and (56), then for the modified phase integral (87) of the complex and the corresponding partition function (90) we have

$$\Phi_{\ddagger} = \prod_2^n (\kappa T / \nu'_i), \quad F_{\ddagger} = \prod_2^n (\kappa T / h\nu'_i), \quad (93)$$

where  $\nu'_1, \dots, \nu'_n$  are the normal frequencies of the imaginary dynamical system with energies  $V''$  as in (56) and  $T''$  as in (89). These are often called the *frequencies of the activated complex*; strictly, they belong to the "modified complex," omitting  $x_1$ , and so lack a direct physical significance.\*

The *harmonic approximation* to the transition-state rate constant is obtained by putting (92) and (93) in (91). The result (given by GLF as the limiting classical case of a quantum formula) is

$$k^{\infty} = \{(\nu_1\nu_2 \dots \nu_n) / (\nu'_1 \dots \nu'_n)\} e^{-E_0/\kappa T}. \quad (94)$$

It is to be observed that this is of the Arrhenius form  $Ae^{-E_0/\kappa T}$ . This allows us, for example, to infer from the results of 2.5 that the mean specific rate for molecules of total energy  $E$  is 2.5(63) with  $A$  as in (94) here (a result which has been calculated directly by Rosenstock, Wallenstein, Wahrhaftig, and Eyring<sup>11</sup>); but the result must of course be regarded as being as inexact as the present use of harmonic partition functions.

**Rotational effects.** If  $A$ ,  $B$ , and  $C$  are the principal moments of inertia of the molecule, there is an additional factor  $\Phi_{\text{rot}}$  in the phase integral for over-all rotation, which is  $\sqrt{\pi(8\pi^2\kappa T)^{3/2}(ABC)^{\frac{1}{2}}}$ ; the corresponding partition function (ignoring symmetry factors) is  $F_{\text{rot}} = \Phi_{\text{rot}}/h^3$ . Thus if we include over-all rotation, we should include this factor in  $F$  in (91) and a corresponding factor in  $F'_{\ddagger}$  or  $F_{\ddagger}$ . This affects the rate only if the moments  $A_{\ddagger}$ ,  $B_{\ddagger}$ ,  $C_{\ddagger}$  of the activated complex are appreciably different from those of the normal molecule, for the extra factor in the rate (for example in (94)) in this case is the ratio  $F_{\ddagger \text{ rot}}/F_{\text{rot}}$ , namely,

$$(A_{\ddagger}B_{\ddagger}C_{\ddagger}/ABC)^{\frac{1}{2}}. \quad (95)$$

\* To use the language of the "pathetic fallacy," we may say that while a molecule may in the moment of disruption feel it has a fresh set of normal modes, it has not time to execute them.

### 6.6 QUANTUM PARTITION FUNCTIONS IN TRANSITION-STATE THEORY

We give here a simpler and more conventional account of the manipulation of the rate constant (59). Conventionally, the reaction coordinate  $x_1$  and velocity are treated classically, while the remaining degrees of freedom of the complex, and all those of the normal molecule, receive quantum partition functions. To avoid an unpalatable mixture of classical and quantum mechanics, we follow the usual assumption\* that there are no cross terms in the kinetic energy of the type  $\dot{x}_i \dot{x}_s$  (or  $p'_i p'_s$ ). Thus the kinetic energy (71) in col coordinates becomes

$$T' = \frac{1}{2} m \dot{x}_1^2 + \frac{1}{2} \sum_2^n \sum a'_{rs} \dot{x}_r \dot{x}_s = \frac{1}{2} m^{-1} p_1'^2 + \frac{1}{2} \sum_2^n \sum g'_{rs} p'_r p'_s \quad (96)$$

The coefficient  $a'_{11} \equiv m$  of  $\frac{1}{2} \dot{x}_1^2$  is called *the effective mass in the reaction coordinate*. To see its significance, we calculate  $v$ , the mean absolute value of  $\dot{x}_1$ . As this is a classical calculation and there are no cross terms in  $\dot{x}_1$  in (96),

$$\begin{aligned} v &= \int |\dot{x}_1| \exp(-\frac{1}{2} m \dot{x}_1^2 / \kappa T) d\dot{x}_1 / \int \exp(\dots) d\dot{x}_1 \\ &= (2\kappa T / \pi m)^{\frac{1}{2}} \end{aligned} \quad (97)$$

This is the mean velocity (in one dimension) of a particle of mass  $m$  in an assembly at temperature  $T$ .

In the formula (66) for the rate constant, we take for  $P_0 \delta$ , the proportion of complexes,

$$P_0 \delta = F_1' / F, \quad (98)$$

namely, the ratio of the partition functions of complexes and normal molecules. We assume the form (96) for  $T'$  and (55) for  $V$  in the tran-

\* I have been told that the absence of cross terms is *not* an assumption, and that (in contrast with the transformation (54)) one should choose col coordinates  $x_r$ , which represent both kinetic and potential energy near the saddle point as sets of square terms. But the nonorthogonal transformation diagonalizing  $T'$  as well as  $V - E_0$  (unlike the orthogonal transformation (54) which was based on  $V$  only) would involve the atomic masses, and so would not continue to diagonalize  $T'$  if an isotopic substitution were made. One would therefore need to make a fresh choice of reaction coordinates for each isotopic substitution. To call the absence of cross terms an "assumption" (for the purposes of the present section) avoids this difficulty rather too simply; it would be better to keep the cross terms and investigate their treatment in the quantum model.

sition state, so that  $x_1$  and  $\dot{x}_1$  (or  $p_1'$ ) are separable from the other degrees of freedom, and we may write

$$F_{\ddagger}' = F_1 F_{\ddagger}' e^{-E_0/\kappa T}. \quad (99)$$

Here  $F_1$  is the "partition function" in coordinate  $x_1$  with  $-\delta < x_1 < 0$ ;  $F_{\ddagger}'$  is the partition function for the remaining degrees of freedom, and  $e^{-E_0/\kappa T}$  compensates for the difference of energy zero in  $F$  and  $F_{\ddagger}'$ .

Classically,  $F_1$  is the phase integral divided by  $h$ ; so by (55) and (96)

$$\begin{aligned} F_1 &= h^{-1} \int_{-\delta}^0 \exp(\frac{1}{2} b_1 x_1^2 / \kappa T) dx_1 \int \exp(-\frac{1}{2} p_1'^2 / m \kappa T) dp_1' \\ &\cong (2\pi m \kappa T)^{1/2} \delta / h. \end{aligned} \quad (100)$$

This is given by GLE as the partition function for a particle of mass  $m$  in a box of length  $\delta$ ; it arises there as a quantum partition function in which the states merge by close packing into a continuum; this is equivalent to our classical result.

We now insert the results (97) to (100) carefully in the rate constant (66) and see what happens. The insertion of (98) in (66) gives

$$k^\infty = \frac{1}{2} \frac{F_{\ddagger}'}{F} \cdot \frac{v}{\delta}, \quad (101)$$

which shows the rate constant as the proportion of well-directed complexes, multiplied by a "mean frequency  $v/\delta$  of passage" through the transition state. Next, the insertion of (99) gives

$$k^\infty = \left( \frac{1}{2} F_1 \frac{v}{\delta} \right) \cdot \frac{F_{\ddagger}'}{F} e^{-E_0/\kappa T}. \quad (102)$$

This looks unpromising until we observe from (97) and (101) that

$$\frac{1}{2} F_1 v / \delta = \kappa T / h. \quad (103)$$

This quantity  $\kappa T/h$  is called on page 189 of GLE a "universal constant . . . for each temperature; it represents the frequency with which any activated complex crosses the barrier . . ."; this should not be taken literally. The rate constant (102) is now

$$k^\infty = \frac{\kappa T}{h} \cdot \frac{F_{\ddagger}'}{F} e^{-E_0/\kappa T}. \quad (104)$$

So we arrive again at the standard formula, this time by following in the main the pioneer route described in GLE. It is to be observed

that in (104)  $F_{\ddagger}$  is not the partition function of the activated complex, but the function modified in the same way as in 6.5, by "omitting" the reaction coordinate; thus it is a mathematical rather than a physical construct.

We have now to choose appropriate partition functions  $F'$  and  $F_{\ddagger}$ . It is usual to employ quantum partition functions for vibration, although the classical forms at the end of 6.5 suffice for the rotational factors if these are required. The quantum partition function,  $\text{pf}^0(\nu_i)$ , of a simple harmonic oscillator of frequency  $\nu_i$ , referred to zero energy as origin, is

$$\text{pf}^0(\nu_i) = \sum_{s=0}^{\infty} \exp \left\{ -\left(s + \frac{1}{2}\right) h\nu_i / \kappa T \right\} = \frac{1}{2} \text{cosech} (h\nu_i / 2\kappa T). \quad (105)$$

If, however, we reckon from the *zero-point* or lowest energy level  $\frac{1}{2}h\nu_i$  as origin, we have the more usual form  $\text{pf}(\nu_i)$ , namely,

$$\text{pf}(\nu_i) = \sum_0^{\infty} \exp (-sh\nu_i / \kappa T) = \{1 - \exp (-h\nu_i / \kappa T)\}^{-1}; \quad (106)$$

the relation of the two forms is simply

$$\text{pf}^0(\nu_i) = \exp (-h\nu_i / 2\kappa T) \text{pf}(\nu_i). \quad (107)$$

As in the classical harmonic approximation of 6.5, we represent the normal molecule as a harmonic system with frequencies  $\nu_1, \dots, \nu_n$ , and the quasi-complex (the activated complex with  $p'_1$  and  $x_1$  omitted from the kinetic and potential energies, and also with energy-zero  $E_0$ ) as a mathematical system with frequencies  $\nu'_2, \dots, \nu'_n$ . Since the energy  $E_0$  in the rate (104) refers to a potential energy difference of zero levels of the two systems, it is clear that, if we are to use quantum partition functions, the form (105) and not (106) is appropriate. Thus in (104)

$$F' = \prod_1^n \text{pf}^0(\nu_i) = 2^{-n} \prod_1^n \text{cosech} (h\nu_i / 2\kappa T), \quad (108)$$

$$F_{\ddagger} = \prod_2^n \text{pf}^0(\nu'_i) = 2^{1-n} \prod_2^n \text{cosech} (h\nu'_i / 2\kappa T), \quad (109)$$

and the rate constant (104) is

$$k^{\infty} = (\kappa T / h) \left\{ 2 \prod_1^n \sinh (h\nu_i / 2\kappa T) / \prod_2^n \sinh (h\nu'_i / 2\kappa T) \right\} e^{-E_0 / \kappa T}, \quad (110)$$

with also a factor (95) if over-all rotation is included. By a simple transference of exponential factors, however, we may write (110) in the more *standard form*

$$k^\infty = (\kappa T/h) \left\{ \prod_1^n [1 - \exp(-h\nu_i/\kappa T)] \right. \\ \left. / \prod_2^n [1 - \exp(-h\nu'_i/\kappa T)] \right\} e^{-E'_0/\kappa T}, \quad (111)$$

where

$$E'_0 = E_0 + \frac{1}{2}h \sum_2^n \nu'_i - \frac{1}{2}h \sum_1^n \nu_i. \quad (112)$$

This is of the form (104), with the partition functions of the type (106) measured from the zero-point energy and with  $E'_0$  in place of  $E_0$ . This  $E'_0$  is the height of the lowest quantum energy level of the quasi-complex above the lowest quantum level,  $\frac{1}{2}h \sum_1^n \nu_i$ , of the normal molecule; it may be called the minimum quantum energy for dissociation. (The quantities here written  $E_0$  and  $E'_0$  correspond to  $E_c$  and  $E_0$  respectively on page 98 of GLE.) The rates (110) and (111) approach the limiting form (94) at high temperature, with exponential factor  $e^{-E_0/\kappa T}$ .

*Transmission coefficients:* The general rate (104) is conventionally given an extra factor, less than unity, called a transmission coefficient, which represents the fraction of complexes which *effectively* dissociate, that is, which do not re-form as molecules after passing through the transition state. Hulburt and Hirschfelder have discussed this concept vividly and fairly deeply,<sup>12</sup> and Wall, Hiller, and Mazur<sup>13</sup> have recently performed some calculations which are of great interest for simple bimolecular exchange. Nevertheless we may fairly safely take the transmission coefficient to be unity in the typically complicated cases of unimolecular decomposition (compare also Wigner's article<sup>3</sup>).

## 6.7 RELATIONS OF THE HARMONIC MODEL AND THE TRANSITION STATE

The purely harmonic model of Chapter 5 and 6.1–6.3, with its assumption of dissociation at  $q_1 = q$ , was treated in 6.2 in a way close to transition-state theory; and the calculation of the harmonic rate in 6.3 used devices which reappeared in the transition-state calculations of the last two sections. We go somewhat deeper here into the relation of the harmonic and transition-state models, in order to throw light on both. The most obvious difference, namely the lack of a

saddle point in the harmonic model, will be made up by introducing anharmonic terms in 6.8.

(i) **The limitation of configuration space.** As we were concerned only with normal and with just-dissociating molecules, we paid no attention in the harmonic model to the form of the potential  $V$  for  $q_1 > q$ , beyond the dissociation limit. This was reasonable, insofar as we treat only the early stages of a reaction, when the products of dissociation have negligible effects. To give slightly more realism to the harmonic model, however, we might assume that the potential  $V$  decreases rapidly for  $q_1 > q$ , so that we have a ridge at  $q_1 = q$ , corresponding roughly to the "barrier" in transition-state theory.

This, however, raises doubts as to the correct phase-integral  $\Phi$  of normal molecules;<sup>14</sup> for the configurational factor of  $\Phi$  has been taken (for example, in (22)) as

$$\Psi(\infty) = \int \cdots \int_{-\infty}^{\infty} e^{-V/\kappa T} dq_1 \cdots dq_n, \quad (113)$$

whereas if we limited this to undissociated configurations, we should replace (113) by  $\Psi(q)$ , namely, the same integral with limits  $(-\infty, q)$  for  $q_1$ . It is easily found, however, that

$$\Psi(\infty) = (2\pi\kappa T)^{1/2} B^{-1/2}, \quad (114)$$

where  $B$  is the determinant of the coefficients  $b_{rs}$  of  $V$  in (3); and by the change of variable (36) in 6.3 we find that

$$\Psi(q) = (2\pi\kappa T)^{1/2} B^{-1/2} \left\{ 1 - \frac{1}{2} e^{-b} (\pi b)^{-1/2} + \cdots \right\}, \quad (115)$$

where (compare (39))  $b = Bq^2/2B_{11}\kappa T = E_0/\kappa T$ . As  $b$  is usually of the order of 40, the ratio of (115) to (114) is very nearly unity. Thus the extension of the phase integral, as if the harmonic potential reached to infinity, causes no detectable error.

If we look at the phase integral or partition functions, (92) or (108), used in transition-state theory for normal molecules, we see that they also are calculated as if the harmonic potential, valid near equilibrium, stretched to infinity. This may cause some error (see the end of 6.8 below) but is unlikely to affect the order of magnitude.

(ii) **The critical configurations.** The set of dissociation configurations on the harmonic model is the hyperplane  $q_1 = q$ ; this corresponds to the complete barrier in transition-state theory. There is no saddle point, of course, on the harmonic potential surface defined by (3); but at least there is on the critical hyperplane a transition point  $Q_0$  corresponding to the least energy for dissociation, and this plays much the

same role as a saddle point. We find  $Q_0$  by applying in (3) the conditions

$$q_1 = q, \quad \partial V / \partial q_r = 0, \quad r = 2, 3, \dots, n. \quad (116)$$

This gives the position ( $q_{s0}$ ) of  $Q_0$  as

$$q_{s0} = B_{1s}q / B_{11}, \quad s = 1, \dots, n, \quad (117)$$

and the energy at  $Q_0$ , which is the least for dissociation, is

$$V(q_{10}, \dots, q_{n0}) = E_0 = Bq^2 / 2B_{11}. \quad (118)$$

This value was also found in (39), where it was noted that  $E_0$  agrees with the value  $q^2 / \alpha^2$  found in 5.2(6). It can be verified also that the configuration (117) corresponds to the minimum normal-mode energies  $\epsilon_{s0}$  of 5.2(4), with the most favorable phases  $\psi_s$  in coordinate  $q_1$ .

We shall use this transition point  $Q_0$  in (iv) below.

**(iii) The velocity in the reaction coordinate.** In the harmonic model with dissociation at  $q_1 = q$ , we naturally take

$$x_1 = q_1 - q \quad (119)$$

as corresponding to the "reaction coordinate" of the transition state (as defined under (56)). The mean velocity  $\langle |\dot{x}_1| \rangle = \langle |\dot{q}_1| \rangle$  for the harmonic model was evaluated in (35) as

$$v = (2\kappa T A_{11} / \pi A)^{\frac{1}{2}} = (2\kappa T g_{11} / \pi)^{\frac{1}{2}}, \quad (120)$$

the second form using the Hamiltonian coefficient  $g_{11}$  of (2). If in the transition-state theory of 6.5 (with the kinetic energy (71) in col coordinates, allowing cross terms) we work out the corresponding mean velocity (73), we find

$$v = (2\kappa T A'_{11} / \pi A')^{\frac{1}{2}} = (2\kappa T g'_{11} / \pi)^{\frac{1}{2}}, \quad (121)$$

in terms of the col-coordinate energy coefficients in (71). In the more usual form 6.6 of transition-state theory (the kinetic energy (96) having no cross terms  $\dot{x}_1 \dot{x}_s$ ), we found in (97)

$$v = (2\kappa T / \pi m)^{\frac{1}{2}}. \quad (122)$$

Thus the effective mass  $m$  in the reaction coordinate corresponds on the harmonic model to

$$m = A / A_{11} = (g_{11})^{-1}. \quad (123)$$

If, for example, the reaction coordinate is the stretch (or contraction)

of the distance between two atoms of mass  $m_a$  and  $m_b$ , then by 3.2(21)

$$g_{11}^{-1} = M_{ab} = m_a m_b / (m_a + m_b). \quad (124)$$

Thus the effective mass in this reaction coordinate is the reduced mass of the atoms it relates.

What is important is not the picturesque language of this last result, but the role of the kinetic energy coefficient  $g_{11}$  in  $v$  and so in the reaction rate. For, if we take the rate  $k^\infty$  in the form (21) or (59), namely,  $\frac{1}{2}P_q v$  or  $\frac{1}{2}P_0 v$ , and make an *isotopic substitution* which leaves the potential energy, and so the (classical) probability  $P_q$  or  $P_0$ , unchanged, then  $k^\infty$  varies as  $v$ , and so, by (120) or (121), as  $\sqrt{g_{11}}$  or  $\sqrt{g_{11}'}$ . For example, if the reaction coordinate is again the distance between  $m_a$  and  $m_b$  and we replace  $m_a$  by an isotope of mass  $m_a^*$ , then the new rate constant  $(k^\infty)^*$  is given by

$$\frac{(k^\infty)^*}{k^\infty} = \frac{v^*}{v} = \left( \frac{g_{11}^*}{g_{11}} \right)^{\frac{1}{2}} = \left( \frac{m_a(m_a^* + m_b)}{m_a^*(m_a + m_b)} \right)^{\frac{1}{2}}, \quad (125)$$

provided, of course, the temperature is the same. This result clearly does not require the potential to be restricted to a harmonic form.<sup>15</sup> Some further cases of isotopic substitution are described in 6.9.

**(iv) Partition functions in the harmonic model.** Here we carry further the analogy in (ii) between the transition point  $Q_0$  of the harmonic model and the saddle point of the transition-state theory. The latter theory began in 6.4 with the transformation (54) to "col coordinates." In the harmonic model the reaction coordinate is  $x_1 = q_1 - q$ , so that our corresponding local coordinates (centered on  $Q_0$ , with position (117)) are

$$x_s = q_s - q_{s0} \quad (s = 1, \dots, n). \quad (126)$$

This is the analog of (54), although here no rotation of axes is introduced.

The harmonic potential  $V$  of (3) becomes in these coordinates

$$V = E_0 + Bq x_1 / B_{11} + \frac{1}{2} \sum_1^n \sum_1^n b_{rs} x_r x_s, \quad (127)$$

so that at dissociation configurations,  $q_1 = q$  or  $x_1 = 0$ , we have

$$V_q = E_0 + V'', \quad (128)$$

where

$$V'' = \frac{1}{2} \sum_2^n \sum_2^n b_{rs} x_r x_s. \quad (129)$$

Moreover the kinetic energy (1) becomes in col coordinates, when  $\dot{x}_1=0$ ,

$$T'' = \frac{1}{2} \sum_2^n \sum_2 a_{rs} \dot{x}_r \dot{x}_s. \quad (130)$$

The energies (129) and (130) correspond to those (compare (89)) used for the modified phase integral  $\Phi_t$  of the complex in the transition-state theory of 6.5. The peculiarity of the present case is that the coefficients in (129) and (130) are the same as those occurring in (1) and (3) for the *normal* molecule in  $q$ -coordinates, because of the absence of rotation in the transformation (126) to  $x$ -coordinates.

We may now annex the classical transition-state results (87) to (94) of 6.5 to the present harmonic model; the results agree, naturally, with our earlier calculation in 6.3. The frequencies  $\nu'_2, \dots, \nu'_n$  of the activated complex (as appearing in (93) and (94)) are those of the dynamical system (129) and (130), and so correspond to the normal molecule with  $q_1$  constrained to a fixed value. These are the frequencies  $\nu'_2, \dots, \nu'_n$  which appeared in (43) above and which were discussed in 3.6. We shall use again shortly the property, mentioned in a footnote in 3.6, that these  $\nu'_i$  have values interlaced with those of the normal frequencies  $\nu_1, \dots, \nu_n$ . Despite their physical unreality, the "frequencies of the complex" have been used widely in considering mechanisms of dissociation. The peculiarity of the harmonic model (which is not necessarily a point in its favor) is that in it these frequencies are determined in such a simple manner.

**(v) Quantum partition functions.** In the original harmonic model the "frequencies of the complex" are represented by the  $\nu'_i$  which were discussed in 3.6 and which were mentioned in a footnote there to be "interlaced" with the normal frequencies  $\nu_i$ . This means that if the sets  $\nu_1, \dots, \nu_n$  and  $\nu'_2, \dots, \nu'_n$  are each in ascending order of magnitude, then

$$\nu_1 \leq \nu'_2 \leq \nu_2 \leq \nu'_3 \leq \nu_3 \leq \dots \leq \nu'_n \leq \nu_n, \quad (131)$$

the equality signs occurring in pairs if two consecutive normal frequencies are equal (e.g.,  $\nu_2 = \nu'_3 = \nu_3$ ).<sup>\*</sup> The pre-exponential factor of the classical rate constant (43) of 6.3 may be arranged in the two ways:

$$\nu = \nu_1 \frac{\nu_2 \nu_3 \dots \nu_n}{\nu'_2 \nu'_3 \dots \nu'_n} = \frac{\nu_1 \nu_2 \dots \nu_{n-1}}{\nu'_2 \nu'_3 \dots \nu'_n} \nu_n. \quad (132)$$

<sup>\*</sup> It will be observed as an interesting consequence of interlacing, that any degenerate (repeated) frequency of the normal molecule is also a frequency of the activated complex.

Comparison of (131) and (132) shows that

$$\nu_1 < \nu < \nu_n, \quad (133)$$

so that  $\nu$  lies in the range of normal frequencies, a result found in 3.6(82) from the initial definition of  $\nu$ .

It is of considerable interest to see if this type of result can be extended to the quantum transition-state formulas of 6.6. Without identifying the activated frequencies  $\nu'_0$  of that section with those of the early harmonic model, let us assume that they are *interlaced* with the normal frequencies as in (131). By arranging differences in the way we arranged ratios in (132), it follows from (131) that for the two energies  $E_0$  and  $E'_0$  of (112),

$$\frac{1}{2}h\nu_1 < E_0 - E'_0 < \frac{1}{2}h\nu_n, \quad (134)$$

so that  $E'_0$  is somewhat less than  $E_0$ .

We now examine the rates (110) and (111), leaving out the exponential factors  $e^{-E_0/\kappa T}$  and  $e^{-E'_0/\kappa T}$ . The functions  $\sinh x$  and  $1 - e^{-x}$  increase with the positive variable  $x$ . Hence if we apply the technique of arrangement as in (132) to the factors of the braces  $\{ \}$  in (110) and (111), we find from the assumption of (131) that

$$2 \sinh (h\nu_1/2\kappa T) < \{ \} < 2 \sinh (h\nu_n/2\kappa T), \{ \} \text{ as in (110), } (135)$$

$$1 - \exp(-h\nu_1/\kappa T) < \{ \} < 1 - \exp(-h\nu_n/\kappa T), \{ \} \text{ as in (111). } (136)$$

These results are quantum analogs of the classical result (133). They yield the following weaker inequalities: from (135), as  $\sinh x > x$ , we have for the rate constant in the form (110)

$$k^\infty > \nu_1 e^{-E_0/\kappa T}; \quad (137)$$

and from (136) if  $h\nu_1/\kappa T$  is sufficiently small we expect for the form (111) that

$$k^\infty > \nu_1 e^{-E'_0/\kappa T}. \quad (138)$$

Also, since  $1 - e^{-x} < x$ , we have from (136) for the form (111)

$$k^\infty < \nu_n e^{-E'_0/\kappa T}. \quad (139)$$

The results (137) and (139) provide firm bounds to the rate, independent of the factor  $\kappa T/h$ . The frequencies  $\nu_1, \dots, \nu_n$  of one molecule may in practice have a wide range, wider for example than the range of  $\kappa T/h$  over the whole unimolecular field, so that our compounded inequalities are not powerful. A main practical significance

of  $\kappa T/h$  is in its relation to individual frequencies  $\nu_i$ , determining whether these are slow and "classical" or fast and "quantal," so that different frequencies may deserve different treatment, especially in molecules containing hydrogen.

*"Loose" complexes:* It is commonly felt that for some reactions the activated complex has a loosened structure; this implies that the activated frequencies  $\nu'_i$  are smaller, and the partition function  $F^\ddagger$  (and the rate  $k^\infty$ ) is therefore larger. The interlaced arrangement (131) is clearly less likely for a loose structure; we might have, for example,  $\nu'_2 < \nu_1 < \nu'_3 < \nu_2 < \nu_3 < \nu'_4 < \dots$ . In such cases the only useful inequality given by the present technique is a lower bound provided by the first inequality in (135) (or (136)). Here, however,  $\nu_1$  is not necessarily the smallest normal frequency; it can be the largest of the  $\nu$ , which leaves a set of  $n-1$  which are respectively larger than the activated frequencies  $\nu'_i$ .

### 6.8 CLASSICAL ANHARMONIC MODELS

I add here an account of two modifications of the harmonic potential (3) by anharmonic (cubic) terms.<sup>14</sup> The first is simple and indicates how the rate and the critical energy are affected. The second modification is tailored to harmonize exactly the previous criterion of dissociation at  $q_1 = q$  with the accepted classical form of transition-state theory.

**(i) A simple anharmonic model.** We return here to the theory as developed in 6.2 and 6.3. Retaining the form (3) of the potential  $V$  for negative values of  $q_1$ , we add a cubic term for positive  $q_1$ :

$$V = \frac{1}{2} \sum_1^n \sum_1^n b_{rs} q_r q_s - B q_1^3 / (3 B_{11} q) \quad (q_1 > 0), \quad (140)$$

where  $B = \|b_{rs}\|$  and  $B_{11}$  is the cofactor of  $b_{11}$ . It is clear that the cubic term should bring in a new parameter; but we choose this to be the critical value  $q$  of  $q_1$ , which in the harmonic model was arbitrary. The form (140) leaves  $V$  and its first and second derivatives continuous, at  $q_1 = 0$ , with the values given by (3) for  $q_1 < 0$ .

There are now two equilibrium points (where  $\partial V / \partial q_1 = \dots = \partial V / \partial q_n = 0$ ), namely, the stable origin  $O$ , and the point  $Q_0$  with coordinates

$$q_{s0} = B_{1s} q / B_{11}. \quad (141)$$

At this point  $\|\partial^2 V / \partial q_r \partial q_s\| = -B < 0$ , and we have a saddle point. Its valley is not in the  $q_1$  direction, however, so that we shall not use tran-

sition-state results, as we continue to take the hyperplane  $q_1 = q$  as the dissociation configuration.

The minimum energy for dissociation occurs at  $Q_0$  and is found from (140) and (141) to be

$$E_0 = \frac{1}{6}Bq^2/B_{11}. \quad (142)$$

It is noteworthy that this is one third of the value (39) found in 6.3 in the harmonic model. It is better, however, to regard  $E_0$  as *given*, so that the critical stretch  $q$  is now  $\sqrt{3}$  times the "harmonic" value. This is in agreement with Evans and Rushbrooke's picture<sup>16</sup> of a greater looseness of the critical configuration for the anharmonic model.

We use the form (21) of the rate constant,  $k^\infty = \frac{1}{2}P_q v$ , which (in the way it was derived in 6.2) does not restrict the form of potential. As we retain the form (1) of the kinetic energy, the mean velocity  $v$  is again (35) as in 6.3, namely,

$$v = (2\kappa T A_{11}/\pi A)^{\frac{1}{2}}. \quad (143)$$

The configurational factor  $P_q$  in the rate constant is (22), which we amend slightly to read

$$P_q = \int \cdots \int_{-\infty}^{\infty} \exp(-V_q/\kappa T) dq_2 \cdots dq_n \\ / \int_{-\infty}^q dq_1 \int \cdots \int_{-\infty}^{\infty} e^{-V/\kappa T} dq_2 \cdots dq_n. \quad (144)$$

The amendment consists in limiting the  $q_1$  range to undissociated states  $(-\infty, q)$ . In 6.7(i) for the harmonic model this refinement was found to be unnecessary in practice, but here it is expedient as well as virtuous, because the cubic term in  $V$  would give divergence at  $q_1 = \infty$ .

In (144),  $V_q$  denotes the potential (140) with  $q_1 = q$ , and in the denominator  $V$  is (140) with the cubic term omitted for  $q_1 < 0$ . To evaluate (144), we make the substitution (36) of 6.3, which gives

$$V = \frac{1}{2}Bx^2/B_{11} + \frac{1}{2} \sum_2^n \sum b_{rs} x_r x_s - \frac{1}{3}Bx^3/(B_{11}q), \quad (145)$$

the last term being absent for  $x < 0$ ; and at  $q_1 = q$

$$V_q = E_0 + \frac{1}{2} \sum_2^n \sum b_{rs} x_r x_s, \quad E_0 \equiv \frac{1}{6}Bq^2/B_{11}. \quad (146)$$

Canceling the  $(x_2, \dots, x_n)$  integrals, we obtain for (144)

$$P_q = \frac{\exp(-E_0/\kappa T)}{I}, \quad I \equiv \int_{-\infty}^q \exp\left\{\frac{-B}{2B_{11}\kappa T}\left(x^2 - \frac{2}{3}\frac{x^3}{q}\right)\right\} dx, \quad (147)$$

where the  $x^3$  term is to be omitted for  $x < 0$ . To evaluate (147), it suffices (assuming  $b = E_0/\kappa T$  is large) to expand the exponential in  $x^3$ . This gives (with the first term as in (41))

$$I = (2\pi\kappa T B_{11}/B)^{1/2} \left\{ 1 + (27\pi b)^{-1/2} + 5/(72b) + \dots \right\}. \quad (148)$$

The first-order rate constant  $\frac{1}{2}P_q v$  of (21), with (143) for  $v$  and (147), (148) for  $P_q$ , is therefore

$$k^\infty = \nu e^{-E_0/\kappa T} \left\{ 1 + (27\pi b)^{-1/2} + 5/(72b) + \dots \right\}, \quad (149)$$

where  $\nu = (2\pi)^{-1}(A_{11}B/AB_{11})^{1/2}$  is the mean frequency 3.6(79), (83), which appeared in the harmonic model in 5.4 and 6.3; the numerator of (149) is in fact the old "harmonic" rate constant.

The main anharmonic effect is thus the changed relation (142) between  $E_0$  and  $q$ . The rate (149) expressed in terms of  $E_0$  does not differ much from the harmonic rate  $\nu e^{-E_0/\kappa T}$ ; with  $b = E_0/\kappa T = 40$ , for example, there is a reduction of about 2 percent. It is seen from (147) and (148) that this reduction is due to the change in the configurational part of the complete phase integral. Although the change is small, it is of a larger order than the harmonic cutoff which was estimated in 6.7(i).

(ii) **An anharmonic model related to the activated complex.** As an alternative anharmonic potential, we try

$$V = \frac{1}{2} \sum_1^n \sum_1^n b_{1s} q_1 q_s - q^{-1} \left\{ \frac{1}{3} b_{11} q_1^3 + \frac{1}{2} q_1^2 \sum_2^n b_{1s} q_s \right\}, \quad (150)$$

where the terms  $\{ \}$  are to be omitted for  $q_1 < 0$ . This form appears artificial and has  $\partial^2 V / \partial q_1 \partial q_r$  discontinuous on the plane  $q_1 = 0$  except at the origin; but it has a col at  $q_1 = q$  with the valley along the  $q_1$  direction. Thus it is the simplest cubic form which suits our original criterion of dissociation at  $q_1 = q$  and also has  $q_1 - q$  as the reaction coordinate in the precise sense of the transition-state theory of 6.4.

The position of the saddle point  $Q_0(q_{10}, \dots, q_{n0})$  is

$$q_{10} = q, \quad q_{s0} = \frac{1}{2} q B_{1s} / B_{11} \quad (s = 2, \dots, n), \quad (151)$$

and the potential at  $Q_0$  is

$$V(q_{10}, \dots, q_{n0}) \equiv E_0 = \frac{1}{8}(BB_{11}^{-1} + \frac{1}{3}b_{11})q^2. \quad (152)$$

In terms of the col coordinates (54), namely,

$$x_s = q_s - q_{s0}, \quad (s = 1, \dots, n) \quad (153)$$

the potential for  $q_1 > 0$  is

$$V = E_0 - \frac{1}{4}(b_{11} + BB_{11}^{-1})x_1^2 + \frac{1}{2} \sum_2^n \sum_2 b_{rs}x_r x_s \\ - \frac{1}{2}q^{-1}x_1^2 \sum_2^n b_{1s}x_s - \frac{1}{3}q^{-1}b_{11}x_1^3. \quad (154)$$

The quadratic terms show that  $Q_0$  is indeed a saddle point and that  $x_1$  is the reaction coordinate as defined under (56) in 6.4.

We may now apply transition-state theory, using the usual harmonic approximation described at the end of 6.5. Thus we retain only quadratic terms in  $V$ , both for the normal molecule (near  $O$  with the  $q_r$  small) and for the complex (near  $Q_0$  with the  $x_r$  small). We have then

$$\text{near } O; T' = \frac{1}{2} \sum_1^n \sum_1 a_{rs}\dot{q}_r\dot{q}_s, \quad V = \frac{1}{2} \sum_1^n \sum_1 b_{rs}q_r q_s, \quad (155)$$

$$\text{near } Q_0; T' = \frac{1}{2} \sum_1^n \sum_1 a_{rs}\dot{x}_r\dot{x}_s, \quad (156)$$

$$V = E_0 - \frac{1}{4}(b_{11} + BB_{11}^{-1})x_1^2 + \frac{1}{2} \sum_2^n \sum_2 b_{rs}x_r x_s. \quad (157)$$

Treating the cross terms  $\dot{x}_1\dot{x}_s$  in  $T'$  as in 6.5, we arrive at the rate constant

$$k^\infty = (\kappa T/h)(F_\ddagger/F)e^{-E_0/\kappa T}, \quad (158)$$

where  $F$  and  $F_\ddagger$  are the classical partition functions as in (92) and (93). Thus

$$k^\infty = \nu e^{-E_0/\kappa T}, \quad \nu = (\nu_1\nu_2 \cdots \nu_n)/(\nu_2' \cdots \nu_n'), \quad (159)$$

where, since the  $b_{rs}$  in (157) are the same as in (155), the activated-complex frequencies  $\nu_2', \dots, \nu_n'$  are those corresponding to the normal molecule with potential (155) but with coordinate  $q_1$  held fixed.

The present model gives, therefore, on this activated-complex treatment, formally the same result as the harmonic model gave in 6.3 or 6.7(iv). The one difference is in the relation (152) of  $E_0$  to  $q$ . To estimate this, suppose that  $b_{12}, b_{13}, \dots, b_{1n}$  are small so that  $B \cong b_{11}B_{11}$ . Then (152) is approximately

$$E_0 = \frac{1}{6}b_{11}q^2 = \frac{1}{6}(B/B_{11})q^2. \quad (160)$$

This agrees with (142) and suggests again that for given  $E_0$  the breaking extension is about  $\sqrt{3}$  times larger in the anharmonic model than in the harmonic.

For those who dare use quantum partition functions in (158), we have here a case where the activated-complex frequencies are known and are interlaced with the normal frequencies. Thus the estimates of magnitude made in 6.7(v) become relevant.

*Accuracy of the approximation:* An obvious point of error in the foregoing treatment is the neglect of the cubic terms in  $V$ , especially in calculating the complete phase integral (or  $F$ ). If we retain these terms, we cannot use the harmonic partition functions; but we can calculate the rate constant  $k^\infty = \frac{1}{2}P_2\nu$  as in (i) above. This gives<sup>14</sup>

$$k^\infty = \nu e^{-E_0/\kappa T} \left/ \left\{ 1 + \frac{(1-c)(1+c)^{\frac{1}{2}}}{4(\pi b)^{\frac{1}{2}}} + \frac{3(1+c)(4-7c+5c^2)}{128b} + \dots \right\} \right., \quad (161)$$

where  $b = E_0/\kappa T$  and  $c = b_{11}B_{11}/(3B)$ . The correction term to  $\nu e^{-E_0/\kappa T}$  in (161) is similar in magnitude (if  $b_{12}, b_{13}, \dots, b_{1n}$  are small) to that in (149) in the earlier model.

This correction presumably represents the sort of error arising in transition-state theory by the common use of the harmonic approximation in the normal potential function, although this is a classical and not a quantum estimate. Concerning the magnitude of the anharmonic effect in (149) or (161), it should also be observed that if we had several cubic terms  $q_1^3, q_2^3, q_3^3, \dots$  in the potential, then the corresponding limitations of the configurational integral (compare (144)) might have a more appreciable effect on the rate, although this is unlikely to change its order of magnitude.

The addition of *quartic terms* to the potential has been studied by Tredgold<sup>17</sup> (the mathematical basis here being related to the work of Stader<sup>18</sup>). This brief study is valuable in indicating the rate of flow of amplitude between two quasi-normal modes due to anharmonicity, and an extension of this type of result to larger systems (if this were possible) would be of importance for general-concentration rates.

## 6.9 CRITICAL COORDINATES AND ISOTOPIC EFFECTS

As an addendum to 6.7(iii) I mention here some further types of critical coordinates, mainly with reference to the effects of isotopic substitution. In 6.7(iii) we regarded  $k^\infty$  as proportional to  $\nu$  and so to  $\sqrt{g_{11}}$  or  $\sqrt{g_{11}'}$ , where  $\frac{1}{2}g_{11}p_1^2$  or  $\frac{1}{2}g_{11}'p_1'^2$  is the energy square term in

the momentum  $p_1$  or  $p_1'$  conjugate to my critical coordinate  $q_1$  or to the transition-state coordinate  $x_1$  respectively. The mass effect on  $\sqrt{g_{11}}$  or  $\sqrt{g_{11}'}$  due to an isotopic substitution gives the whole effect on my model (even with an anharmonic potential), or in "classical" transition-state theory. For the quantum transition-state theory there may be zero-point energy effects as well.

The result (125) found for a single distance as a critical or reaction coordinate is supplemented here by an angular result (iii); the other points discussed are of more importance.

(i) As a general point rather outside the present discussion, it should be observed that the classical isotope effects discussed here are high-concentration effects, which are expected to die out at sufficiently low concentrations.

(ii) If an isotopic change is made not altering the masses involved in the critical coordinate, then clearly  $k^\infty$  is unchanged, since  $g_{11}$  is unaffected.

(iii) If the critical coordinate is the angle  $q_3 = \phi$  subtended at atom  $a$  by atoms  $b$  and  $c$  as in 3.2(24), then the change in  $k^\infty$  for an isotopic substitution of one of these atoms goes as  $\sqrt{g_{33}}$ , where  $g_{33}$  is given by 3.2(25) or (26).

(iv) The typical reaction coordinate  $x_1$  of *transition-state theory* is generally a linear combination of "natural" internal coordinates  $q_1, \dots, q_n$  such as distance and angle variations. Thus we may write  $x_1$  as

$$x_1 = \sum_1^n \gamma_r q_r - c, \quad (162)$$

where the constants  $\gamma_r$  should not involve the atomic masses (compare footnote, p. 116). Let us suppose the motion is described in terms of  $x_1$  and any other independent coordinates  $x_2, \dots, x_n$ , and let  $\frac{1}{2}g_{11}' p_1'^2$  be the square term for the momentum  $p_1'$  conjugate to  $x_1$ , in the energy in terms of these coordinates. Then from (162) it is found that

$$g_{11}' = \sum_1^n \sum_1^n \gamma_r \gamma_s g_{rs}, \quad (163)$$

where  $\frac{1}{2} \sum \sum g_{rs} p_r p_s$  is the energy in the momenta  $p_r$  conjugate to the natural coordinates  $q_r$ . We are not forced here to take for  $x_2, \dots, x_n$  a properly adjusted set of col coordinates as in (54); the result (163) requires merely a knowledge of the reaction coordinate in terms of the  $q_r$ , as in (162).

From (163) we can infer an isotopic effect on  $k^\infty$ , as proportional to

$\sqrt{g_{11}'}$ , by examining what happens to the  $g_{rs}$ , as the  $\gamma_r$  are unaffected. Suppose, for example, the reaction coordinate is

$$x_1 = \gamma_1 q_1 + \gamma_2 q_2 - c, \quad (164)$$

where  $q_1$  and  $q_2$  are the stretches of the distances between atoms  $a, b$  and  $a, c$  respectively. The values of  $g_{11}$ ,  $g_{22}$ , and  $g_{12}$  are in this case given by 3.2(28). Thus for the reaction coordinate (164) we have by (163)

$$k^\infty \sim \sqrt{g_{11}'} = \left\{ \gamma_1^2(m_a^{-1} + m_b^{-1}) + 2\gamma_1\gamma_2 m_a^{-1} \cos(bac) + \gamma_2^2(m_a^{-1} + m_c^{-1}) \right\}^{\frac{1}{2}}. \quad (165)$$

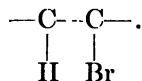
We can infer from this the effect of changing a mass  $m_a$ ,  $m_b$ , or  $m_c$ . A similar result was given for collinear atoms by Bigeleisen and Wolfsberg<sup>19</sup> in connection with "three center" reactions.

(v) A similar analysis may be used in my model. My critical coordinate has been called  $q_1$  throughout; but it was emphasized in 5.1 that it is not necessarily a simple molecular dimension but might be, for example, a combination of distances. If  $q_1, \dots, q_n$  are as in (iv) natural internal distance and angle coordinates, zero at the equilibrium configuration, then my critical coordinate, renamed  $q_0$ , may be a combination of the form

$$q_0 = \sum_1^n \gamma_r q_r, \quad (166)$$

and the critical stretch  $q_0 = q$  would correspond to  $c$  in (162). The amplitude factors 3.4(35) of  $q_0$  are  $\alpha_{0i} = \sum_1^n \gamma_r \alpha_{ri}$ ; the isotope effect would be proportional to  $\sqrt{g_{00}}$ , where  $g_{00}$  (corresponding to a momentum conjugate to  $q_0$ ) would be of the form (163), with the  $\gamma_r$  of (166).

Apart from isotope effects, the fact that a critical coordinate  $q_0$  can be a combination of this nature is of some importance, and this is illustrated in 8.5 below. The point arose also in connection with the work of Maccoll, Green, and P. J. Thomas<sup>20</sup> on the pyrolysis of some organic bromides. A model postulated for the decomposition of *iso*-propyl, *sec*-butyl and *cyclohexyl* bromide was a "four center" elimination of hydrogen bromide. The relevant part of the configurations is



In this we presumably require simultaneous elongations of the CH and CBr bonds (say, of coordinates  $q_1$  and  $q_2$ ), contraction of the HBr

nonbonded distance ( $q_3$ ), and perhaps a change in the CC bond ( $q_4$ ). It does not seem necessary to elaborate the theory in order to cover "simultaneity" of these effects; one might instead just take a breaking coordinate,  $q_0$  of the type (166) with  $\gamma_1, \gamma_2$  positive,  $\gamma_3$  negative, and  $\gamma_5, \gamma_6, \dots$  zero. The fact that the observed  $A$ -factors of the three reactions are between  $10^{12.6}$  and  $10^{13.6} \text{ sec.}^{-1}$ , like vibration frequencies, supports this simple picture. As to the calculation of these  $A$ -factors from the harmonic theory, one might expect that the occurrence of the same "four center" group might make the element  $g_{00}$  roughly the same for the three reactions; variations in the relevant potential energy coefficients might also affect the frequency factor to some extent.

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# Theory of General and Second-Order Rate Constants

THE way the harmonic model was treated in Chapter 5 is well adapted to the extension of the theory from high to general and low concentrations. That treatment was based on a specific rate  $L$  of dissociation of molecules in a given detailed state of internal energy; and this specific rate  $L$  may be combined or contrasted directly with a molecular collision frequency  $\omega$  to determine how the rate constant behaves at lower concentrations (or  $\omega$ -values), where the relative chance of dissociation (as against deactivation) is enhanced. The main hypothesis of the present formulation is that the incidence of dissociation, with its mean frequency  $L$ , is as random as the incidence of collision; this assumption is discussed in 7.1 after we have set up the general rate constant in equation (2).

After this initial formulation of the general rate constant, we concentrate first on very low pressures. It is proved in 7.2 that quasi-unimolecular processes, with continuous energy distributions, do indeed tend toward pure second-order reactions at sufficiently low pressures. In 7.3 analytical and computational methods are given for second-order rate constants; and in 7.4 estimates are made of the orders of magnitude. There is occasion here to discuss collision frequencies and the vibrational amplitudes of normal modes, which affect general as well as low-pressure rate constants in the present model. We also compare the second-order rate constant on this model with the corresponding rate constant on Kassel's model. For a given size of molecule, the latter tends to be much the greater. This is effectively due to the freedom of the internal energy to move between Kassel's "oscillators," as contrasted with the fixed mode-energies of my model; and one suspects that, at low pressures, mobility of energy may be sufficient to move the real rate toward something of Kassel's type.

The remaining five sections are about five fairly distinct developments of the general-concentration rate constant  $k$  of 7.1. In 7.5 we find an approximation to  $k/k^\infty$ , as a function  $I_{\frac{1}{2}(n-1)}(\theta)$  of a parameter  $\theta$  which is proportional to concentration but also involves  $n$ , the number of normal modes. In 7.6 we obtain a general rate constant for molecules having degenerate modes of vibration. In 7.7 it is observed that for a classical Kassel model of  $n$  oscillators,  $k/k^\infty$  is approximately  $I_{n-1}(\theta')$  (with  $\theta'$  resembling the previous  $\theta$ ); the sharp contrast between this and the previous ratio  $I_{\frac{1}{2}(n-1)}(\theta)$  is linked with the earlier findings for low pressures.

The general rate constant  $k$  is linked in 7.8 with the previous high- and low-concentration results by examining the manner in which  $k$  approaches these limiting forms; in particular, the approach to the second order is governed by a factor  $p^{2/(n-1)}$  and so is very gradual for large molecules. Finally, in 7.9 we discuss the comparison of rates at different pressures and temperatures, and in particular the decrease of activation energy with pressure.

Numerical results concerning the behavior of the general rate constant are given in Chapter 8.

### 7.1 THE GENERAL RATE CONSTANT

We continue with the harmonic molecule of Chapter 5, with the assumption of dissociation at a critical stretch  $q$  of coordinate  $q_1$ ; but we now treat lower concentrations  $c$ , at which the equilibrium distribution of energetic molecules is not maintained, and the rate constant  $-c^{-1}dc/dt$  is not at its limiting value  $k^\infty$  but has a general form  $k$  depending on  $c$ . There is no straightforward way of extending the normal transition-state theory to this case. Instead, we adapt to the present harmonic model the form of general rate constant which was set up in 2.3; we shall have to add a discussion of the randomness of dissociation to see how far that form is applicable here.

We return to the form 5.2(1) of the coordinate  $q_1$  as a sum of vibrations, and we assume that the normal frequencies  $\nu_1, \dots, \nu_n$  are *linearly independent* in the sense of 4.1. "Interesting" molecules, in the language of 2.3, are those in which  $q_1$  is capable of reaching  $q$ , and are therefore those for which the normal-mode energies  $\epsilon_i$  satisfy the inequality 5.2(2). Thus the interesting states are classified not by a single discrete number  $r$  as in the main text of 2.3, but by  $n$  (classically continuous) variables  $\epsilon_i$ . The "equilibrium" or high-concentration proportion of molecules in the interesting state  $\epsilon_i = \epsilon_i$  to  $\epsilon_i + d\epsilon_i$  with  $i = 1, \dots, n$  (corresponding to the proportion  $f_r$  in the  $r$ th state in 2.3), is 5.3(10), which we write

$$df = e^{-E/\kappa T} d\epsilon_1 \cdots d\epsilon_n / (\kappa T)^n, \quad E \equiv \sum_1^n \epsilon_i. \quad (1)$$

We represent the specific dissociation rate of these molecules by the function  $L'$  defined as in 5.3(11), namely, the long-time average frequency with which the sum  $q_1$  (5.2(1)) rises to the value  $q$ ; this is, for *l.i.* frequencies, independent of the initial phases  $\psi_i$  in 5.2(1). Finally, we assume (as in the simpler case 2.3(7) rather than 2.3(10)) that there is an effective collision frequency  $\omega$  per molecule, "effective" referring here to changes in vibrational energy.

With the identifications  $df$  of  $f_r$  and  $L'$  of  $k_r$ , the general rate constant 2.3(15) becomes the *basic general rate constant* for the harmonic model:<sup>1</sup>

$$k = \int \omega L' / (\omega + L') df, \quad (2)$$

where  $df$  is given by (1), and the integrations  $d\epsilon_1, \cdots, d\epsilon_n$  are over the interesting states 5.2(2), which may be written, by 5.2(6) and (7),

$$\sum_1^n \mu_i \sqrt{\epsilon_i} \geq \sqrt{E_0} \quad (\epsilon_i \geq 0). \quad (3)$$

**Examination of the formulation.** In the spirit of the second or "direct" formulation of the general rate in 2.3, the element of (2) represents the product of an energization rate  $\omega df$  and an absolute probability  $L' / (\omega + L')$  of dissociation. At the end of 2.3 it was stressed that this absolute probability depends on the incidence of dissociation being random, like that of collision. This randomness will be examined here in a preliminary way.

Consider "interesting" molecules with given mode energies  $\epsilon_1, \cdots, \epsilon_n$  and with the initial phases  $\psi_1, \cdots, \psi_n$  in 5.2(1) randomly (uniformly) distributed over the ranges (0, 1). The proportion of these molecules which pass upward through  $q_1 = q$  in a short time interval  $(t_0, t_0 + \Delta t)$  is

$$\int \cdots \int d\psi_1 \cdots d\psi_n \quad (4)$$

integrated over values such that  $\sum_1^n \alpha_i \sqrt{\epsilon_i} \cos 2\pi(\nu_i t + \psi_i) - q$  has an upward zero in  $(t_0 \leq t \leq t_0 + \Delta t)$ . If we make the change of variables  $\psi_i' = \psi_i + \nu_i t_0$  and  $t' = t - t_0$ , then (4) becomes

$$\int \cdots \int d\psi_1' \cdots d\psi_n', \quad (5)$$

integrated over values such that  $\sum_1^n \alpha_1 \sqrt{\epsilon} \cos 2\pi(\nu_1 t' + \psi_1') - q$  has an upzero in  $(0 \leq t' \leq \Delta t)$ . If  $\Delta t$  is sufficiently small, this integral is (writing  $\psi$  for  $\psi'$ )

$$\int_0^1 \cdots \int_0^1 G_q''(\Delta t; \psi_1, \cdots, \psi_n) d\psi_1 \cdots d\psi_n, \quad (6)$$

where, as in 5.3,  $G_q''(\Delta t; \psi_1, \cdots, \psi_n)$  is the number of upzeros of  $q_1 - q$  in  $(0, \Delta t)$ , with  $q_1$  as in 5.2(1). By the definition 4.1(3) and (4), this last integral is  $L\Delta t$ ,  $L$  being the phase-average frequency, which for *i.e.*  $\nu_{r,s}$  is also the asymptotic frequency  $L'$  by 4.1(11).

We have shown, therefore, that for interesting molecules with given  $\epsilon$ , and a uniform distribution of initial phase the chance of passing (or, the proportion passing) through the dissociation configuration in the interval  $(t, t + \Delta t)$  is  $L'\Delta t$ , independent of  $t$ . This resembles the incidence of collisions, with its probability  $\omega\Delta t$  for interval  $(t, t + \Delta t)$ . Thus the formula  $L' / (\omega + L')$  for the absolute probability of dissociation appears to be justified, and with it the basic rate (2).

This is an oversimplification, for the successive passages of a sum of vibrations  $q_1$  through  $q$  cannot be expected a priori to be random in the same sense as successive collisions are approximately random. We may assume (in ignorance of the distribution of the passages of the sum through  $q$ ) that the hypothesis of randomness is as good a guess as we can make; moreover it corresponds to a hypothesis implicit in all current theories, since they employ factors equivalent to  $k_r / (\omega + k_r)$  in general rates. Thus we shall accept the formula (2) until in Chapter 9 a new approach to reaction theory is developed. This will show that (2) is correct at high and low concentrations but is likely to be only approximate at intermediate concentrations.

## 7.2 EXISTENCE OF A SECOND-ORDER RATE CONSTANT

Before discussing the general rate constant any further, we consider its limiting form at low concentrations. This is a useful preliminary, and the limiting form also has practical significance as a second-order rate.

It is not obvious that a theoretical first-order rate constant, which declines with decreasing concentration, will approach a second-order form even at indefinitely low concentrations. This has been a subject of argument, for example between Benson and Johnston;<sup>2</sup> and the present section will be confined mainly to this question.

There is no difficulty if the "interesting" states have a discrete set of energized lifetimes; for when the interval between effective collisions substantially exceeds the lifetime of the lowest (longest-lived) interesting state, all energized molecules have time to dissociate. At these low

concentrations  $c$ , the number of dissociations is proportional to  $c^2$  and the reaction is of the second order.

If the interesting states are continuous, with specific dissociation frequencies shading off to zero for barely interesting states, the last argument fails, and we have to fall back on mathematics. We shall consider explicitly the model of 7.1, but the argument may immediately be extended to the other theories which use continuous states.

Let\*

$$\Lambda = \int_{L>0} df, \quad (7)$$

where  $df$  is as in (1) and the integral is over positive  $\epsilon$ , for which (3) holds; in words, it is over all interesting states (so that (7) is the high-concentration proportion of interesting molecules). We denote the region of integration by  $L>0$ , rather than by  $L\geq 0$ , to emphasize that the region  $\sum \mu_i \sqrt{\epsilon_i} < \sqrt{E_0}$ , where also  $L=0$ , is excluded. We shall prove for the rate constant  $k$  of (2) that, as the collision frequency  $\omega$  tends to zero,

$$k/\omega \rightarrow \Lambda, \quad (8)$$

so that (as  $\omega$  is proportional to  $c$ ) *the low-concentration rate tends to the second order*. By the form (2) of  $k$ , we have therefore to prove that (over the region  $L>0$ )  $\int L(\omega+L)^{-1}df$  tends to  $\int df$ ; that is, that as  $\omega \rightarrow 0$

$$\omega \int_{L>0} (\omega + L)^{-1} df \rightarrow 0. \quad (9)$$

I follow Johnston's device<sup>2</sup> of dividing the integral into two parts, but first introduce  $\eta$ , a positive number as small as we please. Then with a notation for ranges as in (7),

$$\begin{aligned} \omega \int_{L>0} (\omega + L)^{-1} df &= \omega \int_{0<L\leq\eta} (\omega + L)^{-1} df + \omega \int_{L>\eta} (\omega + L)^{-1} df \\ &< \int_{0<L\leq\eta} df + \omega(\omega + \eta)^{-1} \int_{L>\eta} df \\ &< \int_{0<L\leq\eta} df + \omega(\omega + \eta)^{-1} \Lambda, \end{aligned} \quad (10)$$

since the range  $L>\eta$  is less than that in (7). Now in the last line the first term, which is independent of  $\omega$ , tends to zero with  $\eta$ . Also if we choose a value of  $\omega$  less than  $\eta^2$ , then

\* As the distinction between the phase average  $L$  and the long-time average  $L'$  disappears for *l.i.* frequencies (compare 4.1), I use  $L$  for either from this point on.

$$\omega(\omega + \eta)^{-1} < \eta^2/\eta = \eta,$$

so that the second term in (10) also tends to zero with  $\eta$ , as  $\Lambda$  is certainly less than 1. This establishes the result (9), and so the main result (8).

**Notations and remarks.** It is as well to recall here the original notations of 2.1 for first- and second-order rate constants, which may be applied whether the rate constants are independent of concentration  $c$  or not. The first-order "constant" is  $k_{\text{uni}} \equiv k = -c^{-1}dc/dt$ , and the second-order "constant" is  $k_{\text{bim}} = -c^{-2}dc/dt$ , so that always

$$k_{\text{bim}} = k/c. \quad (11)$$

Since  $\omega$  is proportional to  $c$ , we see by varying  $\omega$  in a general rate constant of the form (2) that  $k$  increases steadily with  $c$ , and so approaches  $k^\infty$  from lower values; while  $k_{\text{bim}}$  increases steadily as  $c$  decreases, and so approaches its limiting second-order value  $k_{\text{bim}}^0$  (as  $c \rightarrow 0$ ) also from lower values.

If we write as in 2.3(8) for the collision frequency

$$\omega = zc, \quad (12)$$

so that (for fixed temperature)  $z$  is independent of the concentration, then  $k_{\text{bim}} = k/c = zk/\omega$  by (11) and (12). Thus the *limiting second-order rate constant* is, by (8) above,

$$k_{\text{bim}}^0 = z\Lambda \quad (13)$$

where  $\Lambda$ , defined by (7), corresponds to the "equilibrium" proportion of interesting molecules.

### 7.3 ANALYSIS OF SECOND-ORDER RATE CONSTANTS

Approximate formulas, (29) and (33) below, are found for the limiting second-order rate constant  $k_{\text{bim}}^0$ , and some attention is paid to the case of unequal amplitude factors  $\alpha_{1i}$ . An alternative second-order rate constant is also given which is common to Kassel's and Hinshelwood's theories.

**Preliminary formulas.** The function  $\Lambda$  in the limiting second-order rate (13) is, by (1), (3), and (7),

$$\Lambda = \int \cdots \int_0^\infty \exp\left(-\sum_1^n \epsilon_i/\kappa T\right) \cdot U\left(\sum_1^n \mu_i \sqrt{\epsilon_i} - \sqrt{E_0}\right) d\epsilon_1 \cdots d\epsilon_n / (\kappa T)^n, \quad (14)$$

where the range of integration has been extended from  $\sum \mu_i \sqrt{\epsilon_i} \geq \sqrt{E_0}$  to *all* positive values of the  $\epsilon_i$ , by introducing the function  $U$ :

$$U(t) = 1 \text{ or } 0 \text{ according as } t > 0 \text{ or } < 0. \quad (15)$$

With positive variables  $x_i$ , and parameter  $\rho$  or  $b$  defined by

$$x_i^2 = \epsilon_i/\kappa T, \quad \rho^2 = b = E_0/\kappa T, \quad (16)$$

we have

$$\Lambda = \int \cdots \int_0^\infty \exp(-\sum x_i^2) U(\sum \mu_i x_i - \rho) \prod (2x_i dx_i). \quad (17)$$

In this we use the integral in a complex  $z$ -plane,

$$U(t) = (2\pi i)^{-1} \int_{c-i\infty}^{c+i\infty} e^{2zt} dz/z \quad (c > 0). \quad (18)$$

This gives a *basic form*

$$\Lambda = (2\pi i)^{-1} \int_{c-i\infty}^{c+i\infty} \Phi(z) dz, \quad (19)$$

where, in this section,

$$\Phi(z) = e^{-2\rho^2 z^{-1}} \prod_1^n \phi(\mu_i z) \quad (20)$$

and

$$\phi(y) = \int_0^\infty \exp(2xy - x^2) \cdot 2x dx \quad (21)$$

$$= 1 + 2y \{1 + H(y)\} / H'(y). \quad (22)$$

Here  $H(y)$  is the error function and  $H'(y)$  its derivative:

$$H(y) = 2\pi^{-1/2} \int_0^y e^{-x^2} dx, \quad H'(y) = 2\pi^{-1/2} e^{-y^2}. \quad (23)$$

There is a tabulation of these functions in parallel columns<sup>3</sup> which is useful for the calculation of  $\phi(y)$ . To give a feeling for  $\phi(y)$  and for reference later, we mention that for *small*  $y$ ,

$$\phi(y) = 1 + y\sqrt{\pi} + 2y^2 + \cdots, \quad (24)$$

and asymptotically for *large*  $|y|$ ,

$$\phi(y) = 2ye^{y^2} \sqrt{\pi} + 1/(2y^2) - 3/(4y^4) + \cdots, \quad (25)$$

and for real positive  $y$ ,

$$1 + 2Y > \phi(y) > \max(1 + Y, 2Y), \quad Y \equiv ye^{y^2}\sqrt{\pi}. \quad (26)$$

**Approximation to  $\Lambda$ .** If the amplitude factors, or the  $\mu_i$ , are roughly similar in magnitude, we may treat all the  $|\mu_i z|$  in (20) as large in the integral (19) by also taking  $c$  large. We may now represent  $\phi(\mu_i z)$  by the first term of (25) and so obtain the *approximation to  $\Lambda$* :

$$\Lambda = \pi^{1(n-1)} \mu_1 \mu_2 \cdots \mu_n I, \quad (27)$$

where

$$\begin{aligned} I &= (i\sqrt{\pi})^{-1} \int_{c-i\infty}^{c+i\infty} (2z)^{n-1} \exp(z^2 - 2\rho z) dz \\ &= (-1)^{n-1} d^{n-1}(e^{-\rho^2})/d\rho^{n-1} = e^{-\rho^2} \text{He}_{n-1}(\rho), \end{aligned} \quad (28)$$

quoting one definition of the Hermite polynomial  $\text{He}_n(\rho)$ . Using (16) and the form of the polynomial, we have for (27)

$$\Lambda = \kappa_n \chi_n(b) b^{1(n-1)} e^{-b} \quad (b = E_0/\kappa T), \quad (29)$$

where  $\kappa_n$  is a numerical factor and  $\chi_n$  a polynomial in  $b^{-1}$ :

$$\kappa_n = (4\pi)^{1(n-1)} \mu_1 \mu_2 \cdots \mu_n, \quad (30)$$

$$\begin{aligned} \chi_n(b) &= 1 - (n-1)(n-2)/(4b) \\ &\quad + (n-1) \cdots (n-4)/\{2!(4b)^2\} - \cdots \end{aligned} \quad (31)$$

This formula (29) is generally used in the rate  $k_{\text{bim}}^0 = z\Lambda$  of (13), although it is an approximation requiring the  $\mu_i$  to be similar in size. Before considering unusually small  $\mu_i$ s, we mention an alternative treatment of  $\Lambda$ .

*Alternative treatment:* The function

$$\psi(z) = \ln \Phi(z) \quad (32)$$

has a saddle point  $z_0$  on the positive real axis (near  $z = \rho$  if  $\rho$  is large), where  $\psi'(z_0) = 0$ . By choosing the path in (19) to be  $z = c + iu = z_0 + iu$  ( $-\infty < u < \infty$ ), and expanding  $\psi(z_0 + iu)$  in a Taylor series, we obtain as a good approximation to (19)

$$\begin{aligned} \Lambda &\cong (2\pi)^{-1} \int_{-\infty}^{\infty} \exp\{\psi(z_0) - \frac{1}{2}u^2\psi''(z_0)\} du \\ &= \Phi(z_0) \{2\pi\psi''(z_0)\}^{-1/2}. \end{aligned} \quad (33)$$

This is the alternative formula; some details are discussed in Appendix

1 of my paper<sup>1</sup> (for example  $\psi''(z_0) \cong 2$  for large  $\rho$ ). We may calculate  $\Lambda$  directly for a reaction in which the  $\mu_i$  and  $\rho$  are known by tabulating the  $\phi(\mu_i z)$  of (22) from error function tables and so finding the saddle point  $z_0$  and interpolating to get (33).

I have verified (as far as the second term in (31)) that in the case of similar  $\mu_i$ , the result (33) agrees with the previous formula (29).

*Small amplitude factors:* We have to consider what use can be made of the approximation (29) when the  $\mu_i$  are widely unequal. If we let one  $\mu_i$ , say  $\mu_n$ , tend to zero, then (30), (29), and the rate constant all vanish; this clearly is fallacious, since the omission of one normal mode would not stop the reaction. If  $\mu_n$  is small, we must not use the first term of (25) to represent  $\phi(\mu_n z)$ , as we did in (27); instead, we must fall back on the saddle point treatment just given, and in evaluating  $\Phi(z_0)$  give special care to the factor  $\phi(\mu_n z_0)$  it contains.

We find in this way that (if  $\mu_1, \dots, \mu_{n-1}$  are similar but  $\mu_n$  is small) there is a crucial value of  $\mu_n$ , which is approximately

$$\mu_n = (\pi b)^{-1/2}. \quad (34)$$

The best use we can make of the formula (29) is to retain  $\mu_n$  if it is larger than this value; if it is smaller, we drop  $\mu_n$  and replace  $n$  by  $n-1$  throughout the formula (29). If a small proportion of the  $\mu_i$  are small like this, we treat them in the same way, although if some of the  $\mu_i$  are as small as  $(\pi b)^{-1/2}$  it would appear that the computation of (33) is superior to (29).

**The limiting rate constant on Kassel's theory.** In Kassel's classical model (compare 2.6), a molecule is "interesting" if it has energy more than  $E_0$  in its  $n$  oscillators; thus the equilibrium high-concentration proportion of interesting molecules is, by 2.4(36),

$$\Lambda' = \int_{E_0}^{\infty} f(E) dE = \{(n-1)!(\kappa T)^n\}^{-1} \int_{E_0}^{\infty} E^{n-1} e^{-E/\kappa T} dE, \quad (35)$$

and the limiting second-order rate constant, exactly analogous to (13), is

$$k_{\text{bim}}^0 = z\Lambda'. \quad (36)$$

It should be remarked here that, if we start with Kassel's *general* rate constant  $k$  of 2.5(79) (compare 2.6(v)), we can prove as in 7.2 that  $k/\omega$  tends to a limit, and this limit is the  $\Lambda'$  of (35). A more obvious remark is that the difference between Hinshelwood's theory and Kassel's disappears at low concentrations, if we identify Hinshelwood's  $E_1$  with Kassel's  $E_0$  (in my notation). Thus the rate constant (36) is

that found for Hinshelwood's theory as 2.4(46), and  $\Lambda'$  here is the  $f_1$  of 2.4(37) with  $E_0$  written for  $E_1$ .

We prefer, however, to write (35), when evaluated, in the form (analogous to the present (29))

$$\Lambda' = \{1/(n-1)!\} \chi_n'(b) b^{n-1} e^{-b} \quad (b = E_0/\kappa T), \quad (37)$$

where (compare 2.4(37))

$$\begin{aligned} \chi_n'(b) = & 1 + (n-1)/b + (n-1)(n-2)/b^2 + \dots \\ & + (n-1)!/b^{n-1}. \end{aligned} \quad (38)$$

The formulas (36) to (38) give the limiting rate.

#### 7.4 PARAMETERS AND COMPARISONS

In an earlier account,<sup>1</sup> I gave only a brief evaluation of the limiting second-order rate constant  $k_{\text{bim}}^0$  and reserved the detailed calculations for the general concentration rate constant  $k$ . In view of the work (see 8.6, 8.7) of Laidler, Schlag, and others, however, it is worthwhile making detailed estimates of  $k_{\text{bim}}^0$ ; this will also provide some parameters useful for actual reactions, for both  $k_{\text{bim}}^0$  and  $k$ . In estimating the order of magnitude of  $k_{\text{bim}}^0$  here, I use the same "typical" values of molecular characteristics (mass, diameter, vibrational amplitudes) as in my earlier work on  $k$ .

The main point of interest is the dependence of  $k_{\text{bim}}^0$  on  $n$ , the number of degrees of freedom. This is compared with results on Kassel's model, and discussion of this striking comparison is a main point of this chapter.

**The collision parameter  $z$ .** The rate  $k_{\text{bim}}^0$  in (13) is the product of a dimensionless number or probability  $\Lambda$  and a collision parameter  $z$ . This parameter will be in no way specialized to the present theory, but we must review briefly its dimensions and calculation.

The number  $\omega$  of collisions per molecule per second is a pure frequency, of dimensions  $\text{second}^{-1}$ , like a first-order rate constant  $k$ . If  $\sigma$  is the "collision diameter,"  $m$  the mass of the molecule in grams, and  $\kappa = 1.38 \times 10^{-16}$  erg/degree is Boltzmann's constant, then the classical kinetic value of  $\omega$  is

$$\omega = 4\sigma^2(\pi\kappa T/m)^{1/2} c \text{ sec.}^{-1} \quad (39)$$

where  $c$  is the concentration, expressed (as is natural in kinetic theory) as the number of molecules per cubic centimeter. If, however,  $c$  is the number of moles per cubic centimeter,

$$\omega = 4\sigma^2(\pi\kappa T/m)^{1/2} N c \text{ sec.}^{-1} \quad (40)$$

where  $\mathbf{N} = 6.025 \times 10^{23}$  is the number of molecules in a mole.

The parameter  $\mathbf{z} = \omega/c$  of (12) is of dimensions second<sup>-1</sup>·concentration<sup>-1</sup>, like a second-order rate constant  $k_{\text{bim}}$ ; so its value depends on the concentration unit. Thus, corresponding to (39), we have

$$\mathbf{z} = 4\sigma^2(\pi\kappa T/m)^{\frac{1}{2}} \text{ cc. molecule}^{-1} \text{ sec.}^{-1} \quad (41)$$

(the purist could object to the inclusion of "molecule<sup>-1</sup>" here, but it makes for clarity); and corresponding to (40),

$$\mathbf{z} = 4\mathbf{N}\sigma^2(\pi\kappa T/m)^{\frac{1}{2}} \text{ cc. mole}^{-1} \text{ sec.}^{-1} \quad (42)$$

In applying these formulas to reaction rates, it is common to reduce  $\omega$  and  $\mathbf{z}$  by an efficiency factor, which is likely to be important, generally speaking, for small rather than for complicated molecules.

*Typical values of  $\mathbf{z}$ :* I use the illustrative values, with  $m^* = m\mathbf{N}$  the molecular weight,

$$\sigma = 5 \times 10^{-8} \text{ cm.}, \quad m^* = 50, \quad T = 700^\circ\text{K.} \quad (43)$$

These give (41) and (42) the values (which may be scaled by the factor  $\sigma^2(T/m^*)^{\frac{1}{2}}$  for particular cases)

$$\begin{aligned} \mathbf{z} &= 6.05 \times 10^{-10} \text{ cc. molecules}^{-1} \text{ sec.}^{-1} \\ &= 3.61 \times 10^{14} \text{ cc. mole}^{-1} \text{ sec.}^{-1}. \end{aligned} \quad (44)$$

**Characteristic parameters.** We examine next the parameters in the form (29) of the factor  $\Lambda$  of the rate (13); as (29) is itself an approximation, we must handle the detail with some care to retain confidence in the order of magnitude of the results.

*Amplitude factors:* The product  $\mu_1\mu_2 \cdots \mu_n$  in the parameter  $\kappa_n$  of (30) depends on the number and scatter of the amplitude factors  $\alpha_i$ , (compare 5.2(7) and (8)). Since  $\sum_1^n \mu_i^2 = 1$ , the product is greatest when the  $\mu_i$  are equal, at  $\mu_i = n^{-\frac{1}{2}}$ ; and it is convenient to introduce a parameter  $m_n$  such that

$$\mu_1\mu_2 \cdots \mu_n = m_n n^{-\frac{1}{2}n}, \quad m_n \cong 1 \text{ for } \begin{array}{l} \text{equal} \\ \text{unequal} \end{array} \text{ amplitudes.} \quad (45)$$

In practice the amplitudes are unequal, and we require some realistic idea of the effect of this without a full calculation, at this point, for particular gases. If the largest amplitude is  $a$  times the smallest and the  $\alpha_i$ , (or  $\mu_i$ ) are in geometrical progression, then

$$m_n = \{a(a^q - 1)n/(a^{q+2} - 1)\}^{\frac{1}{2}n}, \quad q \equiv 2/(n - 1). \quad (46)$$

In a couple of early analyses of vibrations, I observed that there was a

fairly even spread of amplitudes, with the largest about five times the smallest. This suggests that we may fairly reasonably use (46) with  $a=5$ . This gives the values\*

$$m_{3,5,7} = .337, .238, .162; \quad m_{9,11,13} = .110, .0747, .0505. \quad (47)$$

(N.B.: For  $n=1$ , the parameter  $m_n$  here, like  $\kappa_n$ ,  $f_n$ ,  $\chi_n$ ,  $\Lambda e^b$  in Table 7.4 and  $\Lambda'e^b$  in (53), is equal to 1.)

In the following results (see Table 7.4), we give one or both of the cases

$$\text{eq: equal } \mu_i, \quad m_n = 1; \quad \text{uneq: unequal } \mu_i, \quad m_n \text{ as (47),} \quad (48)$$

which represent respectively an extreme and a "realistic" situation.

TABLE 7.4  
PARAMETERS AND PRE-EXPONENTIAL FACTORS

$n$	$\kappa_n$		$f_n$		$\chi_n(b)$	$\Lambda e^b$ (uneq)
	(eq)	(uneq)	(eq)	(uneq)		
3	2.42	.814	2.42	.814	.988	32
5	2.82	.672	5.65	1.34	.925	990
7	2.19	.355	13.1	2.13	.820	$1.9 \times 10^4$
9	1.27	.140	30.4	3.35	.682	$2.4 \times 10^5$
11	.587	.0438	70.4	5.26	.530	$2.4 \times 10^6$
13	.226	.0114	163	8.22	.381	$1.8 \times 10^7$

$\kappa_n = f_n / \Gamma(\frac{1}{2}n + \frac{1}{2}) = (4\pi)^{(n-1)/2} \mu_1 \mu_2 \cdots \mu_n$ , with the  $\mu_i$  equal or unequal as in (45), (47), and (48).  $\chi_n(b)$  and  $\Lambda$  are as in (29) and (31) with here  $b=40$ .

*The parameters  $\kappa_n$  and  $f_n$ , and  $\chi_n(b)$ :* When we have to give a numerical value to  $b = E_0/\kappa T$  in any illustrations, we use the typical experimental value

$$b = E_0/\kappa T = 40. \quad (49)$$

The polynomial  $\chi_n(b)$  of (31) is only slightly temperature-dependent in a practical reaction; some values for  $b=40$  are given in Table 7.4 above. The more important parameter  $\kappa_n$  of (30) is independent of  $T$ , and this is tabulated for the two cases of (48). It is also useful to give

\* The range  $a=5$  in (46) implies that the *smallest*  $\mu_i$  is of the order  $1/5$ . This is appreciably larger than the critical value  $(4\pi b)^{-1/2}$  of (34) (which is 0.045 when  $b=40$ ), so that the procedure of dropping small  $\mu_i$ s, discussed in 7.3, is not required.

The value found for cyclopropane (after dropping an exceptionally small  $\mu_i = 0.015$ ; see 8.6) was  $m_{13} = 0.033$ ; this is of the same order as  $m_{13}$  in the illustration (47).

here the modified form  $f_n$  (which will appear in the general rate constant  $k$  later):

$$f_n \equiv \Gamma(\frac{1}{2}n + \frac{1}{2})\kappa_n \equiv \Gamma(\frac{1}{2}n + \frac{1}{2})(4\pi)^{\frac{1}{2}(n-1)}\mu_1 \cdots \mu_n. \quad (50)$$

**The rate constant.** Turning now to the rate constant  $k_{\text{bim}}^0 = z\Lambda$ , we calculate the "pre-exponential" factor  $\Lambda/e^{-b}$  of (29), using the "realistic" values  $\kappa_n$  unreq, and the values of  $\chi_n(b)$ , with also  $b=40$  in  $b^{\frac{1}{2}(n-1)}$ . The results, given in the last column of Table 7.4, show a *fairly rapid increase of the pre-exponential factor with  $n$* ; this is of course due to the power of  $b$  occurring in the rate constant.

An alternative appearance may be given to the rate in the following way. The factor multiplying  $b^{\frac{1}{2}(n-1)}e^{-b}$  in  $\Lambda$  ((29)) is, by (50),  $f_n\kappa_n/\Gamma(\frac{1}{2}n + \frac{1}{2})$ . In Table 7.4,  $f_n$  unreq  $\cdot \kappa_n$  ranges from 1 to 3 as  $n$  goes to 13. Thus for this "realistic" case (and moderate  $n$ s) we have within a factor of 3,

$$k_{\text{bim}}^0 = z\Lambda, \quad \Lambda = \{b^{\frac{1}{2}(n-1)}/\Gamma(\frac{1}{2}n + \frac{1}{2})\}e^{-b}. \quad (51)$$

This formula would be exact for slightly smaller values of  $m_n$  than (47) but would be an overestimate for still smaller values.

**Comparison with Kassel's model.** The limiting second-order rate constant corresponding to Kassel's (and Hinshelwood's) theory is  $k_{\text{bim}}^0 = z\Lambda'$ , where  $\Lambda'$  is given without approximation by (37). The polynomial  $\chi_n'(b)$  of (38) increases slowly with  $n$ ; when  $b=40$  it is 1.17 for  $n=7$ . If we replace it by unity, the rate becomes

$$k_{\text{bim}}^0 = z\Lambda', \quad \Lambda' = \{b^{n-1}/\Gamma(n)\}e^{-b}. \quad (52)$$

If we include  $\chi_n'(b)$ , the values of the pre-exponential factor of (37) are, with  $b=40$ ,

$$\Lambda'/e^{-b} = \left. \begin{array}{cccccc} \text{for } n = & 2 & 3 & 4 & 5 & 6 & 7 \end{array} \right\} \cdot (53)$$

$$\Lambda'/e^{-b} = 41 \quad 840 \quad 1.2 \times 10^4 \quad 1.2 \times 10^5 \quad .97 \times 10^6 \quad .67 \times 10^7$$

This shows a much more rapid increase with  $n$  than the last column of Table 7.4 because of the doubled power of  $b$  in  $\Lambda'$ ; indeed the values of  $\Lambda'$  in (53) for  $n=2, 3, \dots, 7$  are quite close to those of  $\Lambda$  in Table 7.4 for  $n=3, 5, \dots, 13$ . From these figures, and more simply from a comparison of the approximate formulas (51) and (52), we see that

*The second-order rate constant is much the same for a "Slater" model of  $n_S$  modes of vibration as for a "Kassel" model of  $n_K$  oscillators, if*

$$n_S - 1 = 2(n_K - 1). \quad (54)$$

The absolute fit is not close and depends on the amplitude factors, which appear only in my model. But the striking parallel is between the main temperature-dependent factors,  $b^{1/(n-1)}e^{-b}$  and  $b^{n-1}e^{-b}$  of  $\Lambda$  and  $\Lambda'$ , which are reconciled by the choice (54) of  $ns$ .

**Discussion of the comparison.** We make three cumulative points out of this comparison.

(i) A naïve view of the relation (54) is that the criterion of dissociation in my theory is the accumulation of *amplitude* in a coordinate, as against the accumulation of *energy* in an oscillator in Kassel's theory; amplitude goes as the square root of energy, so that to obtain a stated value of the rate constant about twice as many contributors or modes are required in the former case as in the latter.

(ii) The relation (54) is, however, less important than the consideration that for a given molecule, with presumably  $n_S = n_K = n$  (normal modes being as numerous as oscillators), the rate is much faster on Kassel's than on my model; and this is because  $\Lambda' \gg \Lambda$ . The "Kasselian" parameter  $\Lambda'$  of (35), the equilibrium probability of energy more than  $E_0$  in  $n$  oscillators, is (referring right back to 2.4(31)–(36))

$$\Lambda' = \int \cdots \int_{\sum \epsilon_i = E_0} \exp\left(-\sum_1^n \epsilon_i / \kappa T\right) d\epsilon_1 \cdots d\epsilon_n / (\kappa T)^n, \quad (55)$$

whereas the parameter  $\Lambda$  of (7) or (11) in the present model is

$$\Lambda = \int \cdots \int_{\sum \mu_i \sqrt{\epsilon_i} \geq \sqrt{E_0}} \exp\left(-\sum_1^n \epsilon_i / \kappa T\right) d\epsilon_1 \cdots d\epsilon_n / (\kappa T)^n. \quad (56)$$

The boundary of integration in (56) touches the "plane" boundary  $\sum \epsilon_i = E_0$  of (55) at the point  $\epsilon_i = \epsilon_{i0} = \mu_i^2 E_0$  (compare 5.2(9)); otherwise it lies wholly outside this plane. Thus the smaller region of integration makes  $\Lambda$  less than  $\Lambda'$ , the effect increasing markedly with the dimension  $n$  of the integration.

The essence of the argument (compare 5.2) is that on my model the molecule must not merely have energy at least  $E_0$  (like Kassel's) to be interesting, but must also have the energy distributed in a restrictive way between the normal modes. As no redistribution of internal energy is allowed, this cuts down the equilibrium chance  $\Lambda$  of "interest" below  $\Lambda'$ ; more strictly it cuts down the rate of "energization,"  $\omega\Lambda$ , below  $\omega\Lambda'$ .

(iii) Whether one uses classical or quantal mechanics, there is no redistribution of energy between the modes of a harmonic system with linearly independent frequencies. But real molecules are not harmonic, and anharmonicity blurs the normal modes into approximate

modes between which the energy can move. If we allow anharmonicity to creep in, then at sufficiently low concentrations in a big enough vessel almost any molecule with energy more than  $E_0$  will (before it hits another or the vessel wall) have time to redistribute its energy to satisfy  $\sum \mu_i \sqrt{\epsilon_i} > \sqrt{E_0}$  and so dissociate. We therefore expect the rate to become  $k_{\text{bim}}^0 = z\Lambda'$  eventually, with  $\Lambda'$  as in Kassel's theory.

The big question here (which I raised earlier<sup>1</sup> and which Laidler and Gill<sup>4</sup> are seriously working on) is at what concentration  $c$  this effect of anharmonicity will appear. It would seem that, so long as we treat the molecule as having even approximate modes of vibration, a theoretical attack on this question should be in the spirit of the work of Tredgold mentioned at the end of 6.8. We shall continue, however, to develop the harmonic model, which has been found useful at high and moderate concentrations.

### 7.5 THE GENERAL RATE INTEGRAL

We take up the general-concentration rate constant  $k$  of (1) and (2). This  $n$ -fold integral over  $\epsilon_1, \dots, \epsilon_n$  will be reduced approximately to the simple integral (78) below. I found this originally by simple-minded expansions near the critical point  $\epsilon_{c0}$  of 5.2(9); but the present method,<sup>1</sup> suggested by Professor H. E. Daniels, is more powerful and capable of extension. Some comments are added on the result and on the simple case  $n=1$  of one oscillator.

**Notations and formulas.** We denote the Gamma function by a factorial sign, even for complex values. The formula used is, with  $\mathbf{R}$  denoting real part,

$$z! = \Gamma(z+1) = \int_0^\infty e^{-x} x^z dx \quad (\mathbf{R}(z) > -1). \quad (57)$$

A factor  $1/\sqrt{-1}$  before an integral, for example  $i^{-1} \int \dots dz$ , will imply this is a *path integral* from  $z=c-i\infty$  to  $c+i\infty$  with  $\mathbf{R}(z) > 0$ ; the constant  $c$  may be changed in successive forms of an integral. This notation enters through two transforms, of (inverse) Mellin<sup>5</sup> and Laplace types, which are the basis of the work. These are

$$1/(1+x) = (2i)^{-1} \int x^{-z} (\sin \pi z)^{-1} dz \quad (0 < \mathbf{R}(z) < 1), \quad (58)$$

$$t^s U(t) = s!(2\pi i)^{-1} \int p^{-s-1} e^{pt} dp, \quad (59)$$

where  $U(t)$  is as in (15).

**The rate constant and its reduction.** The rate constant (1)–(3) is by (15)

$$k = \int \cdots \int_0^\infty \omega L(\omega + L)^{-1} \cdot e^{-E/\kappa T} U(\sum \mu_i \sqrt{\epsilon_i} - \sqrt{E_0}) d\epsilon_1 \cdots d\epsilon_n / (\kappa T)^n \quad (60)$$

$$= \int \cdots \int_0^\infty \omega L(\omega + L)^{-1} \cdot \exp\left(-\sum_1^n x_i^2\right) U(\sum \mu_i x_i - \rho) \prod_1^n (2x_i dx_i), \quad (61)$$

where  $x_i$ , and  $\rho$  are as in (16).

To find  $k^\infty$  in 5.4 we used for  $L$  Kac's formula 4.3(16); this does not seem feasible here, so we use my approximation 4.6(79). The parameters in that formula become, in the present variables (16),

$$a_i = |\alpha_{1i}| \sqrt{\epsilon_i} = \alpha \mu_i x_i (\kappa T)^{\frac{1}{2}}, \quad a = \sum a_i, \quad \text{and} \quad q = \alpha \sqrt{E_0} = \alpha \rho (\kappa T)^{\frac{1}{2}}.$$

Thus 4.6(79) becomes

$$L = \frac{1}{m!} \left( \frac{\sum \mu_i x_i - \rho}{2\pi} \right)^m \left( \frac{\sum \mu_i \nu_i^2 x_i}{\mu_1 x_1 \cdots \mu_n x_n} \right)^{\frac{1}{2}} \quad (62)$$

where

$$m \equiv \frac{1}{2}(n - 1). \quad (63)$$

Before inserting (62), however, we write in (61)

$$\omega L(\omega + L)^{-1} = (2i)^{-1} \int L^z \omega^{1-z} (\sin \pi z)^{-1} dz, \quad (64)$$

which is (58) with  $x = \omega/L$ . We now insert (62); this gives in (61) a factor  $(\sum \mu_i x_i - \rho)^{mz} U(\sum \mu_i x_i - \rho)$ , to which we apply the transform (59), and a power of  $\sum \mu_i \nu_i^2 x_i$ , which is treated similarly. We have then (using (63))

$$k = 4^{m\frac{1}{2}i-1} \int \omega^{1-z} A^z (\sin \pi z)^{-1} (\frac{1}{2}z)! (mz)! F(z) dz, \quad (65)$$

where

$$A^{-1} = (2\pi)^m m! (\mu_1 \mu_2 \cdots \mu_n)^{\frac{1}{2}}, \quad (66)$$

$$F(z) = (2\pi i)^{-1} \int q^{-1-\frac{1}{2}z} dq \cdot (2\pi i)^{-1} \int p^{-1-mz} e^{-\rho p} \Psi dp, \quad (67)$$

$$\Psi = \prod_1^n \psi \{ \mu_i (p + \nu_i^2 q) \}, \quad \psi(y) \equiv \int_0^\infty \exp(xy - x^2) x^{1-\frac{1}{2}z} dx; \quad (68)$$

the variables  $x_i$  in (61) become the  $x$ s of the integrals in  $\Psi$ .

We assume as in 7.3 that  $\rho = \sqrt{(E_0/kT)}$  is fairly large. If the spread of the  $\mu_i$  is not wide, we require  $\psi(y)$  only for large  $\mathbf{R}(y)$  in all the factors of  $\Psi$ , so that (compare (25)) we may write

$$\psi(y) \cong \sqrt{\pi(y/2)^{1-\frac{1}{2}z}} e^{1/2 y^2}. \quad (69)$$

Thus in (68)

$$\begin{aligned} \Psi \cong \pi^{1/n} \prod \left\{ \frac{1}{2} \mu_i (p + \nu_i^2 q) \right\}^{1-\frac{1}{2}z} \\ \cdot \exp \left\{ \frac{1}{4} (p^2 + 2\nu^2 p q + q^2 \sum \nu_i^2 \mu_i^2 \nu_i^2) \right\}, \end{aligned} \quad (70)$$

where as before  $\nu^2 = \sum \mu_i^2 \nu_i^2$ .

At this point we replace the last  $\nu_i^2$  in the exponential and in the product  $\prod$  by  $\nu^2$ ; in this one process we assume that the frequencies can effectively be replaced by this mean value. Now (70) becomes

$$\pi^{1/n} \{ \mu_1 \mu_2 \cdots \mu_n [\frac{1}{2}(p + \nu^2 q)]^n \}^{1-\frac{1}{2}z} \exp \left\{ \frac{1}{4} (p + \nu^2 q)^2 \right\}, \quad (71)$$

and we write (67) as

$$\begin{aligned} F(z) = \pi^{1/n} (\mu_1 \cdots \mu_n)^{1-\frac{1}{2}z} \frac{e^{-b}}{2\pi i} \int \frac{e^{\nu^2 \rho q} dq}{q^{1+\frac{1}{2}z}} \\ \cdot \frac{1}{2\pi i} \int \frac{e^{1/2 u^2 \{ \frac{1}{2}(p + \nu^2 q) \}^{n(1-\frac{1}{2}z)}}}{p^{1+mz}} dp, \end{aligned} \quad (72)$$

where

$$u = p + \nu^2 q - 2\rho, \quad b = \rho^2. \quad (73)$$

In the last integral of (72), the variable  $p$  is changed (with a lateral shift of the path) to  $u$ ; and in that integrand we replace powers of  $p$  and of  $p + \nu^2 q$  by powers of  $2\rho$  to obtain the leading term. This leaves for the  $u$ -integration

$$(2\pi i)^{-1} \int e^{1/2 u^2} du = 1/\sqrt{\pi}, \quad (74)$$

and the  $q$ -integration in (72) is, by (59),

$$(2\pi i)^{-1} \int e^{\nu^2 \rho q} q^{-1-\frac{1}{2}z} dq = (\nu^2 \rho)^{1/2} / (\frac{1}{2}z)! \quad (75)$$

Substituting these results in (72), we now have for (65)

$$k = \{ \nu e^{-b} / (2m!) \} \int \theta^{1-z} (mz)! (\sin \pi z)^{-1} dz, \quad (76)$$

where

$$\theta = (\omega/\nu) m! (4\pi b)^m \mu_1 \mu_2 \cdots \mu_n. \quad (77)$$

Finally in (76) we replace  $(mz)!$  by the formula (57) and then recognize the right-hand side as containing an integral of type (58); thus

$$\begin{aligned} k &= \{ \nu e^{-b} / (m!) \} \int_0^\infty e^{-x} dx (2i)^{-1} \int x^{mz} \theta^{1-z} (\sin \pi z)^{-1} dz \\ &= \frac{\nu e^{-b}}{m!} \int_0^\infty \frac{x^m e^{-x} dx}{1 + x^m \theta^{-1}}, \end{aligned} \quad (78)$$

which is the approximate formula for the rate.

**The result.** As the precise high-concentration rate constant 5.4(23), namely,

$$k^\infty = \nu e^{-b} \quad (b = E_0/\kappa T), \quad (79)$$

is a factor of (78), we write the result, with suffix  $n$  reminding us of the number of normal modes,

$$(k/k^\infty)_n = I_{\frac{1}{2}(n-1)}(\theta), \quad (80)$$

where\*

$$I_m(\theta) = \frac{1}{m!} \int_0^\infty \frac{x^m e^{-x} dx}{1 + x^m \theta^{-1}} \quad (m! \equiv \Gamma(m+1)), \quad (81)$$

and  $\theta$  is (77), or with the notation (50),

$$\theta = (\omega/\nu) f_n b^{\frac{1}{2}(n-1)}, \quad f_n = \Gamma(\frac{1}{2}n + \frac{1}{2}) (4\pi)^{\frac{1}{2}(n-1)} \mu_1 \cdots \mu_n. \quad (82)$$

Thus  $\theta$  is proportional to the collision frequency  $\omega$ , and so to the concentration or pressure.

**Comments.** Deferring numerical calculations until the next chapter, we comment briefly on the reliability of formula (80).

*At high concentrations*,  $\omega$  and  $\theta$  tend to infinity, so that

$$I_m(\theta) \rightarrow 1. \quad (83)$$

\* **N.B.** In two papers<sup>1,2</sup> I denoted the present  $I_{\frac{1}{2}(n-1)}(\theta)$  by  $I_n(\theta)$ . The present notation is simpler, but it must be remembered that in (81)  $m$  may be a half-integer.

Thus the approximate formula for  $k$  tends exactly to the precise  $k^\infty$ . This is an unjustifiably good result in view of (a) the use of the approximation (62) for  $L$  and (b) the drastic picking out of leading terms in the analysis leading to (80). The convergence of  $k$  to the exact  $k^\infty$  suggests that for large  $\theta$  the errors due to (a) and to (b) effectively cancel out.

At low concentrations,  $\omega$  and  $\theta$  tend to zero. Now from (81)

$$1 - m!\theta^{-1}I_m(\theta) = \theta \int_0^\infty e^{-x}(\theta + x^m)^{-1}dx, \quad (84)$$

and this will be shown in 7.8 to tend to zero with  $\theta$  for  $m \geq 1$ . Thus for small  $\theta$

$$I_m(\theta) \cong \theta/m!, \quad (85)$$

and (80)–(82) give then

$$k \cong \nu e^{-b}\theta/m! = \omega \kappa_n b^{\frac{1}{2}(n-1)}e^{-b},$$

where  $\kappa_n$  is as in (30) or (50). This corresponds to a limiting second-order rate constant,  $k_{\text{lim}}^0 = k/c = kz/\omega$ , of the form

$$k_{\text{lim}}^0 = z\kappa_n b^{\frac{1}{2}(n-1)}e^{-b}. \quad (86)$$

This is the previous result  $z\Lambda$  of (29), except that it lacks the factor  $\chi_n(b)$ , which is of the order of unity (compare Table 7.4).

The lack of this factor indicates the error of the rate formula (80) for small  $\theta$  or  $\omega$ . It is clearly connected with the approximations (b) mentioned after equation (83), for the errors induced by (a), the approximate form of  $L$ , must fade out at low concentrations. The errors of type (b) increase with  $n$ ; this does not increase their importance, since only for small  $n$  are we likely to approach the second-order region in experiments.

This comparison with the second-order rate constant indicates that the critical value (34) for discarding a *small amplitude factor* may roughly be applied in the general as well as in the second-order rate constant.

**The case  $n = 1$ .** Here  $m = \frac{1}{2}(n-1) = 0$ , and (81) and (82) become

$$I_0(\theta) = 1/(1 + \theta^{-1}), \quad \theta = \omega/\nu, \quad (87)$$

so that

$$k = \omega\nu(\omega + \nu)^{-1}e^{-b}. \quad (88)$$

This result is *exact*; for the specific rate of a simple oscillator of fre-

quency  $\nu_1 = \nu$  is  $L = \nu$  if the energy  $\epsilon$  exceeds  $E_0$ ; and if we put  $L = \nu$  in (2), with  $df = e^{-\epsilon/\kappa T} d\epsilon/\kappa T$ , we obtain (88). The result is in fact of the form

$$k^\infty/k = 1 + (\nu/\omega), \quad (89)$$

which was found in 2.4 to hold when interesting molecules have only one specific rate. As, however, vibration frequencies are much larger than collision frequencies in gases, the result (89) indicates that diatomics, represented by simple oscillators, will not show unimolecular behavior.

### 7.6 DEGENERATE VIBRATIONS\*

The rate we have been discussing was based on the assumption in 7.1 that the normal frequencies  $\nu_1, \dots, \nu_n$  were linearly independent. We must pay some attention, however, to degenerate vibrations—normal modes of equal frequency—such as occur in symmetrical molecules.

As a sample case, suppose that for the  $n$  modes affecting the critical coordinate  $q_1$ ,

$$\nu_1, \nu_2, \dots, \nu_{n-1} \text{ are } l.i. \text{ and } \nu_n = \nu_{n-1}. \quad (90)$$

The critical coordinate is still of the form 5.2(1), namely (writing  $\alpha_i$  for  $\alpha_{1i}$ ),

$$q_1 = \sum_1^n a_i \cos 2\pi(\nu_i t + \psi_i), \quad a_i \equiv \alpha_i \sqrt{\epsilon_i}. \quad (91)$$

With  $\nu_{n-1} = \nu_n$  different choices of the normal coordinates  $Q_{n-1}$  and  $Q_n$  of 3.4(35) are possible, but it can be shown from the general theory of vibrations that these choices leave invariant the combination

$$(\alpha_{n-1}^2 + \alpha_n^2)^{\frac{1}{2}} = \alpha'_{n-1}. \quad (92)$$

Assuming that the phases  $\psi_{n-1}$  and  $\psi_n$  of the degenerate vibrations are random, we shall prove that

*the general rate constant  $k$  for the system (90) is as for a molecule of  $n-1$  modes, of frequencies  $\nu_1, \dots, \nu_{n-1}$ , and amplitude factors  $\alpha_1, \dots, \alpha_{n-2}, \alpha'_{n-1}$ .* (93)

\* The present type of degeneracy, arising from symmetry and having equal frequencies, is more important in practice than the "generalized degeneracy" discussed in 2.5 (type (ii) between 2.5(74) and (75)) and the type mentioned at the end of 2.6, where the frequencies were merely in whole number ratios. The mathematical problems of general rate constants in these cases would be much more formidable.

After proving this, we add some comments and generalizations.

**Proof of (93).** Since  $\nu_n = \nu_{n-1}$ , we may write (91) as the sum of  $n-1$  terms,

$$q_1 = \sum_1^{n-2} a_i \cos 2\pi(\nu_i t + \psi_i) + R \cos 2\pi(\nu_{n-1} t + \psi), \quad (94)$$

where  $\psi$  is an appropriate phase and

$$R = \{a_{n-1}^2 + a_n^2 + 2a_{n-1}a_n \cos 2\pi(\psi_{n-1} - \psi_n)\}^{1/2}. \quad (95)$$

The asymptotic frequency  $L = L(a_1, \dots, a_{n-2}, R)$  with which the sum (94) rises to  $q$  is independent of the phases  $\psi_1, \dots, \psi_{n-2}$  and  $\psi$ , but depends (through  $R$ ) on  $\psi_{n-1} - \psi_n$ . "Interesting" molecules are those for which  $q_1$  can reach  $q$ , so that they have

$$\sum_1^{n-2} |a_i| + R - q > 0. \quad (96)$$

This is a condition involving  $\epsilon_1, \dots, \epsilon_n$  and  $\psi_{n-1} - \psi_n$ ; but to simplify the exposition we regard the interesting states as having  $\epsilon_1, \dots, \epsilon_n, \psi_{n-1}$  and  $\psi_n$  (separately) as classifying parameters. Assuming that  $\psi_{n-1}$  and  $\psi_n$  are uniformly distributed, we have as the analog of the rate constant (2):

$$k = \int \int_0^1 \int \dots \int_0^\infty \omega L(\omega + L)^{-1} \cdot e^{-E/\kappa T} d\epsilon_1 \dots d\epsilon_n d\psi_{n-1} d\psi_n (\kappa T)^{-n}, \quad (97)$$

where the integration is extended over the full ranges of all variables by noting that  $L=0$  where (96) is not satisfied. (For limiting low concentrations, we insert in (97) a factor  $U\left(\sum_1^{n-2} |a_i| + R - q\right)$  corresponding to the  $U$ -factor in (14).)

To deal first with the degenerate modes, we write (97) as

$$k = \int \dots \int_0^\infty \exp\left(-\sum_1^{n-2} \epsilon_i/\kappa T\right) d\epsilon_1 \dots d\epsilon_{n-2} (\kappa T)^{2-n} \cdot k', \quad (98)$$

where

$$k' = \int \int_0^\infty d\epsilon_{n-1} d\epsilon_n (\kappa T)^{-2} \int \int_0^1 d\psi_{n-1} d\psi_n M(R) \cdot \exp\left\{-\left(\epsilon_{n-1} + \epsilon_n\right)/\kappa T\right\}, \quad (99)$$

and as a temporary notation

$$M(R) \equiv \omega L(\omega + L)^{-1}, \quad L \equiv L(a_1, \dots, a_{n-2}, R). \quad (100)$$

Referring back to (91), (94), and (95), we may write  $R$  as

$$R = (X^2 + Y^2)^{\frac{1}{2}}, \quad X = x_{n-1} + x_n, \quad Y = y_{n-1} + y_n, \quad (101)$$

where

$$(x_i, y_i) = \alpha_i \sqrt{\epsilon_i} (\cos, \sin) 2\pi\psi_i, \quad i = n-1, n. \quad (102)$$

Changing from variables  $\epsilon_i, \psi_i$  to  $x_i, y_i$ , we have for (99)

$$k' = \int \cdot \int_{-\infty}^{\infty} M(R) \prod_i \{ \exp [ -(x_i^2 + y_i^2) / \alpha_i^2 \kappa T ] dx_i dy_i / \pi \alpha_i^2 \kappa T \}. \quad (103)$$

This has the form of the *expectation value* of a function of  $R = (X^2 + Y^2)^{\frac{1}{2}}$  over a Gaussian distribution of two "vectors"  $(x_i, y_i)$  with sum  $(X, Y)$ ; the corresponding mean squares of each of  $x_i$  and  $y_i$  are  $\frac{1}{2}\kappa T \alpha_i^2$ , so that the corresponding mean squares of  $X$  and  $Y$  are  $\frac{1}{2}\kappa T (\alpha_{n-1}^2 + \alpha_n^2)$ , or  $\frac{1}{2}\kappa T \alpha_{n-1}^2$  by (92). Thus (103), as an expectation over the joint distribution, is

$$k' = \int \int_{-\infty}^{\infty} M(R) \exp \{ -(X^2 + Y^2) / \alpha_{n-1}^2 \kappa T \} dX dY / \pi \alpha_{n-1}^2 \kappa T. \quad (104)$$

Changing from  $(X, Y)$  to polar coordinates  $(R, \theta)$  and writing

$$R = \alpha_{n-1}' \sqrt{\epsilon_{n-1}},$$

we obtain

$$k' = \int_0^{\infty} M(\alpha_{n-1}' \sqrt{\epsilon_{n-1}}) \exp (-\epsilon_{n-1} / \kappa T) d\epsilon_{n-1} / \kappa T. \quad (105)$$

Here  $\epsilon_{n-1}$  is not (physically) the energy  $\epsilon_{n-1}$  appearing in (91), but a variable of integration.

Using (105) in the rate (97) or (98), we have finally as the rate constant for "degenerate" molecules

$$k = \int \cdot \cdot \cdot \int_0^{\infty} \omega L(\omega + L)^{-1} \cdot \exp \left( - \sum_1^{n-1} \epsilon_i / \kappa T \right) d\epsilon_1 \cdot \cdot \cdot d\epsilon_{n-1} / (\kappa T)^{n-1}, \quad (106)$$

where, by (100),  $L = L(a_1, \dots, a_{n-2}, \alpha'_{n-1}\sqrt{\epsilon_{n-1}})$  is the dissociation frequency as for a molecule with

$$q_1 = \sum_1^{n-1} a_i \cos 2\pi(\nu_i t + \psi_i), \quad a_{n-1} = \alpha'_{n-1}\sqrt{\epsilon_{n-1}}.$$

This establishes the result (93).

**Comments.** The *limiting first-order rate constant*  $k^\infty$  for this degenerate case is (106) with  $\omega/(\omega+L)$  omitted; it is therefore calculated as in Chapter 5, with  $n-1$  for  $n$ , and is

$$k^\infty = \nu \exp(-q^2/\alpha^2\kappa T) \quad (107)$$

where (compare (93))

$$\alpha^2 = \sum_1^{n-2} \alpha_i^2 + \alpha'^2_{n-1}, \quad \alpha^2\nu^2 = \sum_1^{n-2} \alpha_i^2\nu_i^2 + \alpha'^2_{n-1}\nu_{n-1}^2. \quad (108)$$

By (92) these forms are

$$\alpha^2 = \sum_1^n \alpha_i^2, \quad \alpha^2\nu^2 = \sum_1^n \alpha_i^2\nu_i^2. \quad (109)$$

These are the same as for  $n$  distinct frequencies; so that  $k^\infty$  is not affected in form by degeneracy.

The *limiting second-order rate constant*,  $k_{\text{bim}}^0$ , calculated as in 7.3, gives the approximate result (29), with  $n$  replaced now by  $n-1$  and the product  $\mu_1\mu_2 \dots \mu_n$  by  $\mu_1\mu_2 \dots \mu'_{n-1}$ , where

$$\mu'_{n-1} = \alpha'_{n-1}/\alpha. \quad (110)$$

Remembering from 7.4 that  $k_{\text{bim}}^0$  tends to increase with  $n$ , we infer that the effect of degeneracy is to decrease  $k_{\text{bim}}^0$ . The reason for this is that the sum of two vibrations of different (incommensurable) frequencies takes all values up to the sum of the amplitudes, while the sum of two degenerate vibrations has a fixed amplitude, which is less than the sum of the two amplitudes except for one particular phase relation. Thus degeneracy reduces the chance of a critical distortion, especially at low concentrations where there are almost no collisions to change the phase relation. It would be wrong, however, to say that when we have a degenerate pair of modes we can completely discard one mode as not affecting the rate; for there are at least two ways in which both of the modes contribute. In the first place, the exponential factor  $\exp(-q^2/\alpha^2\kappa T)$  contains in  $\alpha^2$  contributions from both the modes, and also in the weighting of the mean frequency  $\nu$  both modes contribute.

The general rate constant  $k$  shows a fall-off of  $k/k^\infty$  as for  $n-1$  modes instead of  $n$ ; this (as later calculations indicate) means that the fall-off will set in at rather higher concentrations in the degenerate case.

**Generalizations.** The arguments of this section show that a set of more than two degenerate modes again behaves as a single mode (with amplitude the root sum square) for forming  $k$ . As a more realistic case, if there are several pairs of degenerate modes, with frequencies  $\nu_1, \nu_2, \dots$ , then each pair contributes 1 to the effective value of  $n$  in the general rate.\*

The extreme case, in which all the normal modes have the same frequency  $\nu$ , does not occur for any real polyatomic molecule. But it is amusing to observe that in this case the general rate constant would reduce to the form (88) as for a diatomic molecule with  $n=1$ .

### 7.7 COMPARISON WITH KASSEL'S CLASSICAL RATE

The approximation found in 7.5 for the general rate will now be compared briefly with the classical form of Kassel's rate constant. This classical form (compare (v) in "Points in Kassel's theory" in 2.6) is given by 2.5(79)–(82), namely,

$$\frac{k}{k^\infty} = \frac{1}{(n-1)!} \int_0^\infty \frac{x^{n-1} e^{-x} dx}{1 + (A/\omega) \{x/(b+x)\}^{n-1}}, \quad k^\infty = A c^{-b}, \quad (111)$$

where  $b = E_0/kT$  and  $n$  is the number of oscillators.

It is worth remarking that the rate constant (111) was set up in 2.5 as the extension of an Arrhenius  $k^\infty$  to general concentrations, on the hypothesis that we may treat  $k_E$ , the specific rate for total energy  $E$ , as basic and ignore the differential effect on  $k$  of more detailed specifications of the internal molecular processes. This treatment of  $k_E$  as basic led Giddings and Eyring,<sup>7</sup> for example, to the form (111) (with  $A = \nu_1 \cdots \nu_n/\nu_2' \cdots \nu_n'$  as in 6.5(94)) as an extension of classical transition-state theory to general concentrations. It also led Benson<sup>8</sup> to (111) (with  $A = \nu$  as in Chapter 5) as representing my theory, on the assumption that my specific rate  $L(\epsilon_1, \dots, \epsilon_n)$  could be averaged over distributions  $\epsilon_1, \dots, \epsilon_n$  of  $E = \sum \epsilon_i$  before considering the dependence of the process on concentration. In both these treatments  $k_E$  appears essentially as an average, so that (111) (as resulting from 2.5(75) based on  $k_E$ ) does not appear to be a correct formulation;<sup>9</sup> we feel happier with Kassel's use if only for the reason that in his model  $k_E$  defies

\* B. S. Rabinovitch and K.-W. Michel find some support for this result in a forthcoming paper (J. Amer. Chem. Soc.).

analysis into "detailed contributions" and is thus a basic concept. It should be added, however, that Kassel prefers to regard (111) (which is similar also to Rice and Ramsperger's rate) as the limiting form of his quantum rate; but we stick here to classical forms and defer quantum forms until a later chapter.

Treating (111) now as Kassel's formula, we remark that for the large values of  $b$  experimentally common, we may risk replacing  $b+x$  in the denominator by  $b$ . This reduces (111) to the *approximate form*

$$(k/k^\infty)_n = I_{n-1}(\theta'), \quad \theta' \equiv (\omega/A)b^{n-1}, \quad (112)$$

where  $I_{n-1}(\theta')$  is precisely the function defined in (81). It will be seen from the calculations in 8.4 below that (112) is a moderate approximation to (111), although it is not so good as I may have led people to suppose.

**The comparison.** Representing my model and Kassel's by the respective approximations (80) and (112), we see that the decline  $(k/k^\infty)_n = I_{\frac{1}{2}(n-1)}(\theta)$  is the same function of  $\theta$  on my model as  $(k/k^\infty)_n = I_{n-1}(\theta')$  is of  $\theta'$  on Kassel's, provided the numbers  $n_s$  of my modes and  $n_K$  of his oscillators are related by

$$n_s - 1 = 2(n_K - 1). \quad (113)$$

We see also that this relation makes the parameters  $\theta = (\omega/\nu)f_n b^{\frac{1}{2}(n-1)}$  of (82) and  $\theta' = (\omega/A)b^{n-1}$  of (112) agree if (i) we identify the high-concentration parameters  $\nu$  and  $A$  and (ii) we ignore the factor  $f_n$  of  $\theta$ . The "realistic" sample values of  $f_n$  in Table 7.4 were of the order 1 to 10; this is a small range compared with the powers of  $b \approx 40$  that occur in  $\theta$  or  $\theta'$ , so that  $f_n$  is of relatively minor importance.

Since  $\theta$  and  $\theta'$  involve the collision frequency  $\omega$  in the same way, we conclude that the decline of rate with concentration (or pressure) is comparable on the two models, if we relate  $n_s$  and  $n_K$  by (113). An exact agreement is not to be expected; in the first place the use of the approximation (112) for (111) slightly affects the shape of the curve of decline, and in the second place variations in the parameter  $f_n$  (involving the vibrational parameters in my theory) may shift my curve of decline along the pressure axis appreciably.

These comparisons agree with those made for second-order rate constants in 7.4, where equation (54) was the present relation (113); and the reasons for the contrast between  $n_K$  and  $n_s$  (for a given value of the rate) were discussed there.

A more important aspect of this comparison (as also in 7.4) is that if for a particular gas we take  $n_s = n_K = n$ , then the forms of  $(k/k^\infty)_n$  are

markedly different on the two models. It will be seen from the calculations of the next chapter (compare 8.3) that, if we stick to *one* theory, then the decline of rate constant  $k$  with  $\omega$  or with concentration  $c$  is spread over a rather larger range of  $\log c$  when  $n$  is larger; more importantly, the first-order rate constant is effectively maintained to lower concentrations the larger  $n$  is. Thus, for example, for a molecule of 7 "oscillators," the Kassel fall-off is much the same as my theory would give for 13 normal modes; and my fall-off for 13 modes occurs at appreciably lower concentrations than my fall-off for 7 modes. Hence the decline toward the second-order reaction occurs (for  $n_K = n_S$ ) at lower concentrations on Kassel's theory. This accords with the result of 7.4 (compare particularly equation (53) and Table 7.4, last column) that the limiting second-order rate is higher on Kassel's theory for a given  $n$ . The reason is (as in 7.4) the greater range of available energy distributions for dissociation when energy is allowed to pass freely between the oscillators; thus for given  $n$  and concentration, the Kassel rate is the greater.

*Degenerate vibrations:* There is a striking dissimilarity between the role of degenerate vibrations in the two models. In my model the shape  $k/k^\infty = I_{\frac{1}{2}(n-1)}(\theta)$  of the curve of decline is determined, by 7.6, by the number  $n$  of distinct vibration frequencies, whereas in Kassel's model the corresponding parameter is the number of oscillators and these (especially in the usual quantum version) are *all* of equal frequency. The result, noted at the end of 7.6, that for  $n$  degenerate modes my model gives the same  $k/k^\infty$  as for one oscillator, emphasizes the contrast between the physical pictures. For my "phase-interference accumulation of extension in a nonnormal coordinate," differences of vibration frequencies are the root cause of the accumulations; for Kassel's accumulation of energy in an oscillator, equality of frequencies greatly helps the necessary energy transfers.

### 7.8 THE APPROACH OF RATE CONSTANTS TO LIMITING FORMS

In 7.2 it was proved that a general rate constant  $k$  tends to a second-order form at low concentrations. Here we examine from a theoretical angle the manner of approach of the rate constant to its high- and low-concentration limiting forms; this is also of some practical significance. The general formulas with which we begin are put in terms of the specific rate  $L$  and distribution element  $df$  of the harmonic model (compare 7.1 above), but these formulas may be extended to other models by suitable replacements of  $L$  and  $df$ .

**General formulas.** We take the general rate constant  $k$  in the form (2), with a corresponding "second-order" rate constant  $k_{\text{bim}} = k/c$ ; thus

$$k = \int' \omega L(\omega + L)^{-1} df, \quad k_{\text{bim}} = z \int' L(\omega + L)^{-1} df, \quad (114)$$

where  $\int'$  denotes *integration over interesting states* and  $z = \omega/c$ . The limiting forms at high and low concentrations are

$$k^\infty = \int' L df, \quad k_{\text{bim}}^0 = z \int' df, \quad (115)$$

so that

$$k^\infty - k = \int' L^2(\omega + L)^{-1} df, \quad k_{\text{bim}}^0 - k_{\text{bim}} = z \int' (1 + L/\omega)^{-1} df. \quad (116)$$

The interesting quantities near high and low concentrations are the (fractional) *deficiencies*  $1 - (k/k^\infty)$  and  $1 - (k_{\text{bim}}/k_{\text{bim}}^0)$  respectively. For the former, when  $\omega$  or  $c$  is very large, we have approximately from (116)

$$1 - (k/k^\infty) \cong \omega^{-1} \int' L^2 df / \int' L df. \quad (117)$$

This indicates that *small* deficiencies are linear in  $c^{-1}$ ; but it is not a very useful formula, since for large molecules, which are more likely than small ones to get close to  $k^\infty$  at not too high concentrations, the approximation made in (117) is not accurate beyond very small decreases of the rate constant.

The low-concentration deficiency defies any visual estimate corresponding to (117), since the second integral in (116), with  $\omega$  small, has a delicate region of just-interesting states where  $L$  also is small. We leave this until we have examined the high-concentration deficiency.

**The approach to  $k^\infty$ .** If we treat the first integral in (116) (with (62) for  $L$ ) by the method of 7.5, or if alternatively we represent  $k/k^\infty$  by  $I_{\frac{1}{2}(n-1)}(\theta)$  as in (80), we find the formula

$$1 - (k/k^\infty) = (m!)^{-1} \int_0^\infty x^{2m}(\theta + x^m)^{-1} dx, \quad (118)$$

where  $m = \frac{1}{2}(n-1)$  and  $\theta$  is as in (77). For large  $\theta$  this becomes, if we neglect  $x^m$  in the denominator,

$$1 - (k/k^\infty) \cong (2m)!/(m!\theta), \quad (119)$$

although this is clearly not a good approximation (except for  $1 - (k/k^\infty)$  very small) for large  $m$ . Using the form (82) of  $\theta$ , we have as representing (117)

$$1 - (k/k^\infty) = \left\{ \frac{(2m)!}{m!b^m} \right\} \frac{1}{f_n} \frac{\nu}{\omega} \quad (m = \frac{1}{2}(n - 1)). \quad (120)$$

This shows clearly the role of the ratio  $\nu/\omega$  of vibration to collision frequency in the fall-off. For large  $b$ , the other predominant factor  $(2m)!/(m!b^m)$  decreases markedly as  $n$  increases; thus the concentration  $c$  (being proportional to  $\omega$ ), at which we have, say, a 5 percent deficiency, tends also to decrease as the number  $n$  of independent modes increases.

The corresponding formula to (120) for the Kassel rate (111) is

$$1 - (k/k^\infty) \cong \frac{(2m)!}{m!b^m} \cdot \frac{A}{\omega} \quad (m = n - 1). \quad (121)$$

**The approach to  $k_{\text{bim}}^0$ .** If we treat the second integral in (116) also by the method of 7.5, we find

$$k_{\text{bim}}^0 - k_{\text{bim}} = z(4\pi b)^m \mu_1 \cdots \mu_n e^{-b} K_m(\theta) \quad (m = \frac{1}{2}(n - 1)), \quad (122)$$

where

$$K_m(\theta) = \theta \int_0^\infty e^{-x} (\theta + x^m)^{-1} dx. \quad (123)$$

The coefficient of  $K_m(\theta)$  in (122) is the approximation (86) which the method of 7.5 gave for  $k_{\text{bim}}^0$ , so that it is clearly appropriate to regard it here as representing  $k_{\text{bim}}^0$ . Thus the deficiency is

$$1 - (k_{\text{bim}}/k_{\text{bim}}^0) = K_m(\theta), \quad (124)$$

namely, the function  $K_m(\theta)$ . A little reflection shows that this result is effectively contained in equations (84) and (85).

*The deficiency  $K_m(\theta)$ :* If  $m > 1$ , we put  $x = y\theta^{1/m}$  in (123), obtaining

$$K_m(\theta) = \theta^{1/m} \int_0^\infty \exp(-y\theta^{1/m}) dy / (1 + y^m). \quad (125)$$

For sufficiently small  $\theta$  we may omit the exponential and so obtain (without further approximation)

$$K_m(\theta) \cong \theta^{1/m} \int_0^\infty dy / (1 + y^m) = \theta^{1/m} u_m, \quad (126)$$

where  $u_m = (\pi/m) \operatorname{cosec}(\pi/m)$  is of the order of unity. Hence from (82)

$$K_m(\theta) \cong u_m b (f_n \omega / \nu)^{1/m}. \quad (127)$$

This shows that (i) the deficiency is proportional to  $b = E_0/\kappa T$  and not to a varying power of  $b$ ; and (ii) the deficiency is proportional to  $\omega^{2/(n-1)}$  or  $c^{2/(n-1)}$ . For example, if  $n = 13$ , the deficiency is proportional to the sixth root of  $c$ . The approach to the second-order rate constant is thus a very prolonged affair for moderately large molecules, and we can hardly hope to find pure second-order reactions in such cases.

The case  $m = 1$  ( $n = 3$ ) gives rather similar results. Writing  $x + \theta = y$  gives in (123) in this case

$$K_1(\theta) = \theta e^\theta \int_\theta^\infty e^{-y} y^{-1} dy = -\theta e^\theta \operatorname{Ei}(-\theta) \quad (128)$$

where  $\operatorname{Ei}(-\theta)$  is the "exponential integral." This gives for small  $\theta$

$$K_1(\theta) \cong \theta \ln(1/\theta) \quad (129)$$

$$= (bf_3\omega/\nu) \ln(\nu/bf_3\omega), \quad (130)$$

by (82). Since as  $\theta$  decreases,  $\ln(1/\theta)$  increases more slowly than any negative power  $\theta^{-\epsilon}$  of  $\theta$ , the result shows that the deficiency is nearly proportional to  $b\omega$ ; and this resembles (127).

The low-concentration deficiency on Kassel's rate is similar to (127) but with  $m = n - 1$  instead of  $\frac{1}{2}(n - 1)$ .

## 7.9 TEMPERATURE EFFECTS AND ACTIVATION ENERGY

So far we have considered variations of concentration or pressure. We now examine the effects of varying the temperature as well, and also (as in the determination of activation energy) small temperature variations keeping concentration or pressure fixed.

**Combined effects.**<sup>1</sup> We use the approximation (80) for  $k/k^\infty$ . This depends, for given  $n$ , solely on the parameter  $\theta$ , which by (82) is proportional to  $\omega(E_0/\kappa T)^m$ , where (as before)

$$m = \frac{1}{2}(n - 1). \quad (131)$$

The collision frequency  $\omega$ , treated as in 7.4, is proportional to  $c\sqrt{T}$ , or equivalently to  $p/\sqrt{T}$ , since the pressure  $p$  is proportional to concentration  $c$  and to temperature  $T$ . Hence

$$\theta \sim c/T^{m-\frac{1}{2}} \sim p/T^{m+\frac{1}{2}}. \quad (132)$$

If we choose, for varying  $T$ , values of  $p$  proportional to  $T^{m+\frac{1}{2}}$  (or values of  $c$  proportional to  $T^{m-\frac{1}{2}}$ ), then we have  $\theta$  constant and so  $k/k^\infty$

constant. This is not convenient to test, however, for it implies measuring  $k^\infty$  as well as  $k$  at each temperature.

It is more practicable to take just two temperatures,  $T_1$  and  $T_2$ , and to measure  $k$  for ranges of pressure reaching to  $k^\infty$  at each temperature. Then we expect the same value of  $k/k^\infty$  at pairs of pressures  $p_1$  and  $p_2$  (at temperatures  $T_1$  and  $T_2$  respectively) such that  $p_1/p_2 = (T_1/T_2)^{m+1} = (T_1/T_2)^{1/n}$ ; for these correspond to the same  $\theta$ . If then we plot  $k/k^\infty$ , or  $\log k/k^\infty$ , against  $\log p$ , the curves for the two temperatures should be the same, but with the curve for the higher temperature  $T_1$  (say) shifted along the  $\log p$  axis by a distance

$$\Delta \log p = \frac{1}{2}n \log (T_1/T_2). \quad (133)$$

For not too small  $n$  this shift is appreciable.

**Activation energy.** We define the activation energy  $E_a$ , as in 2.8, as

$$E_a = \kappa T^2 \partial \ln k / \partial T, \quad (134)$$

keeping either  $c$  or  $p$  constant. This proviso is immaterial for the pure first-order rate constant  $k^\infty$ . As  $k^\infty$  is of the Arrhenius form  $\nu \exp(-E_0/\kappa T)$ , we have as in 2.8 at high concentrations

$$E_a^\infty = E_0. \quad (135)$$

For general concentrations, with the approximation (80) for  $k$  and the notation (131),

$$\begin{aligned} E_a &= \kappa T^2 \partial \ln k^\infty / \partial T + \kappa T^2 \partial \ln I_m(\theta) / \partial T \\ &= E_0 + \kappa T^2 (\partial \theta / \partial T) d \ln I_m(\theta) / d\theta. \end{aligned} \quad (136)$$

In the second term, by (132),

$$T \partial \theta / \partial T = - (m \mp \frac{1}{2}) \theta, \quad (137)$$

where the *upper and lower signs* refer to the cases of constant concentration and constant pressure respectively, as in 2.8(105)–(107). These alternative terms ( $\pm \frac{1}{2}\theta$ ) contribute to  $E_a$  the “collisional activation energy”  $E_{coll}$  which was treated separately in 2.8, but we shall retain their contribution in  $E_a$  for completeness here.

Writing  $I_m(\theta)$  ((81)) as

$$I_m(\theta) = (\theta/m!) \int w e^{-x} dx, \quad w \equiv x^m (\theta + x^m)^{-1} \quad (138)$$

(all integrals here being from 0 to  $\infty$ ), we see that in (136)

$$\theta d \ln I_m(\theta) / d\theta \equiv A_m(\theta) = \int w^2 e^{-x} dx / \int w e^{-x} dx. \quad (139)$$

An alternative form of this function, equally suitable for computation, is obtained by integrating  $\int w^2 e^{-x} dx$  by "parts"; this is

$$A_m(\theta) = m^{-1} \left\{ m + 1 - \int w x e^{-x} dx / \int w e^{-x} dx \right\}. \quad (140)$$

It is seen from either form that, as  $\theta$  decreases from infinity to zero,  $A_m(\theta)$  increases from a lower limit zero to an upper limit unity.

The activation energy (136) is, by (137) and (139),

$$E_a = E_0 - (m \mp \frac{1}{2}) \kappa T A_m(\theta), \quad (141)$$

and from the last observation this decreases with pressure from  $E_0$  in the first-order region to  $E_0 - (m \mp \frac{1}{2}) \kappa T$  in the second-order region. If, for example, we are making "constant pressure" measurements of  $E_a$  and so take the lower sign in (111), the total decrease is  $\frac{1}{2} n \kappa T$ . This effect has to be borne in mind when we attempt to estimate the critical energy  $E_0$  from observed values of  $E_a$  in a region where the reaction is of intermediate order (where we suspect  $k$  is well below  $k^\infty$ ).

On Kassel's model, with the rate constant  $k$  of (111) represented by the approximation (112), the activation energy is as in (141), but with  $m = n - 1$  instead of  $\frac{1}{2}(n - 1)$ . The exact low-pressure  $E_a$  (apart from the "collisional" term) for this model was given in 2.8(118); and this reminds us that the present results are approximations. A closer approximation to the low-pressure  $E_a$  on my theory can be obtained by differentiating the form (13) and (29) of  $k_{\text{lim}}^0$ .

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## Numerical Results and Comparisons

THE relative decline  $k/k^\infty$  of the rate constant was found in 7.5 to be approximately  $I_{\frac{1}{2}(n-1)}(\theta)$ , with  $\theta$  a parameter proportional to concentration  $c$  (or pressure  $p$ ) and  $n$  the number of effective normal modes. We use this result now to study the decline of the rate constant numerically. There are three main items: (i) the calculation of  $I_m(\theta)$ , which gives the shape of the curve of  $\log k/k^\infty$  against  $\log \theta$  or  $\log c$ ; (ii) the ratio  $c/\theta$  (or  $p/\theta$ ), which gives the absolute concentration at which  $k/k^\infty$  has a given value; and (iii) the application of these results to specific reactions.

(i) Methods of calculating  $I_m(\theta)$  are described in 8.1. Prominence is given to an "asymptotic" method, because this may have other applications and also because it gives some feeling for the behavior of  $I_m(\theta)$ ; actually, direct numerical integration with an automatic machine is nowadays more accurate. Calculated values are given in 8.2. The value of  $\log \theta$ , at which  $I_m(\theta)$  declines appreciably from unity, increases by about 1 for an increase of 1 in  $m$ . The over-all decline of  $I_m(\theta)$  is the more spread out on the  $\log \theta$  scale the larger  $m$  is, so that more complex molecules are expected to require a larger range of  $\log c$  to show the transition from near first- to near second-order kinetics.

(ii) Numerical formulas (30) and (31) are given in 8.3 for  $c/\theta$  and  $p/\theta$ . These ratios depend on the temperature, the molecular mass and "diameter" and vibrational characteristics; they are also proportional to  $b^{-\frac{1}{2}(n-1)}$ , where  $b = E_0/kT$ . The ratios are then calculated for the mythical "typical" molecule we used in the illustrations in 7.4, with the number  $n$  of modes the one variable parameter. Despite the increase, noted in (i) above, of  $\log \theta$  with  $m$  for a given value of  $k/k^\infty$ , the factor  $b^{-\frac{1}{2}(n-1)}$  in  $c/\theta$  tends to make the absolute value of  $c$  for given  $k/k^\infty$  decrease as  $n$  increases. Thus more complex molecules approach the first-order limit  $k/k^\infty = 1$  generally at lower concentrations than simple molecules. These tendencies are illustrated by graphs of

log  $k/k^\infty$  for the "typical" molecule; the positions of the curves on the concentration axis would of course need adjustment for specific molecules with other values of the parameters.

(iii) As an illustrative rather than a definitive calculation, I work out in 8.5 the decline of the rate constant for nitril chloride, using the vibrational analysis of 3.8; this is compared with an estimated position of an experimental  $k/k^\infty$  plot (the estimate being of the value of  $k^\infty$ ). In 8.6 I summarize briefly my early calculations on the isomerization of cyclopropane (which stand now in need of revision using new vibrational data) and add notes on recent work. In 8.7 there are notes on the related investigations of Laidler and Gill, which center on a theoretical transition from my rate toward a Kassel type at very low concentrations.

There are two other short sections: 8.4 contains a comparison of values of Kassel's rather more complicated integral for  $k/k^\infty$ , with values of  $I_m(\theta)$ ; and 8.8 gives numerical illustrations of the decline of activation energy with concentration, based on the theoretical formula of 7.9; with the increase in experimental accuracy this effect may increase in significance.

### 8.1 METHODS OF CALCULATING THE RATE INTEGRAL

I describe methods of calculating the integral 7.5(81), namely,

$$I_m(\theta) = \frac{1}{m!} \int_0^\infty \frac{x^m e^{-x} dx}{1 + x^m \theta^{-1}}, \quad m! \equiv \Gamma(m + 1), \quad (1)$$

which can be put also into the forms

$$I_m(\theta) = \frac{\theta}{m!} \left\{ 1 - \int_0^\infty \frac{e^{-x} dx}{1 + x^m \theta^{-1}} \right\} \quad (2)$$

$$= 1 - \frac{1}{m!} \int_0^\infty \frac{x^{2m} e^{-x} dx}{\theta + x^m}. \quad (3)$$

As in the harmonic model the decline of rate constant is  $k/k^\infty = I_m(\theta)$  with  $m = \frac{1}{2}(n-1)$ , we require that  $m$  be integral or half-integral. I first give precise formulas for  $m = 1$  and 2 and then a general asymptotic method which has other applications; finally I comment on numerical methods.

**The cases  $m = 1$  and 2.** The exponential, sine, and cosine integrals are respectively

$$\text{Ei}(-\theta), \text{si}\theta, \text{Ci}\theta = - \int_\theta^\infty y^{-1} dy \{ e^{-y}, \sin y, \cos y \}, \quad (4)$$

and these have been well tabulated.<sup>1</sup> In terms of these functions

$$I_1(\theta) = \theta + \theta^2 e^\theta \text{Ei}(-\theta), \quad (5)$$

as follows from (2) with  $x + \theta = y$ ; and<sup>2,3</sup>

$$I_2(\theta) = \frac{1}{2}\theta \{1 + u(\text{si } u \cos u - \sin u \text{Ci } u)\}, \quad u \equiv \sqrt{\theta}. \quad (6)$$

This result may also be found from (2) by expressing  $(u^2 + x^2)^{-1}$  in partial fractions and using simple contour integrals to get

$$\int_0^\infty e^{-x}(u^2 + x^2)^{-1} dx = u^{-1} \int_0^\infty (u + x)^{-1} \sin x dx.$$

Similar methods reduce  $I_3$  and  $I_4$  to have only  $x^2$  in the denominator, but not to tabulated functions.

**A general method.** Marcus<sup>3</sup> estimated  $I_3(\theta)$  by a simple method similar to the way Stirling's formula for the Gamma function is sometimes approached, and this seemed to deserve generalization for similar integrals. Stirling's formula, as far as the terms which interest us, is

$$m! \cong m^m e^{-m} (2\pi m)^{1/2} \{1 + 1/(12m) + 1/(288m^2)\}. \quad (7)$$

To obtain this we may write  $m!$  (7.5(57)) as

$$\int_0^\infty \exp \{f(x)\} dx \quad (8)$$

where

$$f(x) = -x + m \ln x, \quad (9)$$

and observe that  $f(x)$  has a strong maximum (if  $m$  is reasonably large) at  $x = x_0 = m$ . Expanding  $f(x) = f(x_0 + y)$  by Taylor's theorem and treating the range in  $y$  as  $(-\infty, \infty)$  instead of  $(-x_0, \infty)$  in (8), we have

$$\int_0^\infty e^f dx = \exp(f_0) \int_{-\infty}^\infty \exp(f_0'' y^2/2) \cdot \exp\{f_0''' y^3/3! + \dots + f_0^{(6)} y^6/6!\} dy, \quad (10)$$

where  $f_0 \equiv f(x_0)$ ,  $f_0' \equiv (df/dx)_{x_0} = 0$ ,  $f_0'' = -m^{-1}$ ,  $\dots$ . If now we expand the last exponential,  $\exp\{\dots\}$ , as far as  $y^6$  and integrate, we obtain Stirling's formula to the approximation (7).

Generalizing this, we may have in (8) some other function  $f(x)$  which (like (9)) has a unique strong maximum at some positive value  $x = x_0$ ,

and we expand as before. It is convenient to represent the derivatives  $f^{(r)}(x_0)$  in terms of functions  $\psi_r(x_0)$  defined as

$$\psi_r = (-x_0)^{r-1} f^{(r)}(x_0) / (r-1)! \quad (11)$$

so that  $\psi_1 = 0$  and in the particular case (9)  $\psi_2 = \psi_3 = \dots = 1$ . Expanding (10), we obtain the *asymptotic formula*

$$\int_0^\infty e^f dx \cong \exp \{f(x_0)\} (2\pi x_0 / \psi_2)^{1/2} (1 + C_1 + C_2), \quad (12)$$

where the correction terms are

$$C_1 = (10\psi_3^2 - 9\psi_2\psi_4) / (12x_0\psi_2^3) \quad (13)$$

$$C_2 = (1540\psi_4^2 + 2016\psi_2^2\psi_3\psi_5 + 945\psi_2^2\psi_1^2 - 720\psi_2^3\psi_6 - 3780\psi_2\psi_3^2\psi_4) / (288x_0^2\psi_2^6). \quad (14)$$

In the case (9), when  $x_0 = m$ , this reduces to Stirling's formula.

**The rate integral.** We apply this result to (1), which we write

$$I_m(\theta) = J(\beta) / m!, \quad \beta \equiv 1/\theta, \quad (15)$$

$$J(\beta) = \int_0^\infty e^{f(x)} dx, \quad f(x) \equiv -x + m \ln x - \ln(1 + \beta x^m). \quad (16)$$

In this case,

$$f'(x) = -1 + m/(x + \beta x^{m+1}),$$

so that the maximum of  $f(x)$  occurs at  $x = x_0 = m - \epsilon$ , say, where

$$\theta = x_0^{m+1} / (m - x_0) = (m - \epsilon)^{m+1} / \epsilon, \quad \epsilon \equiv m - x_0. \quad (17)$$

By successive differentiations we find the functions (11) to be, in terms of  $\epsilon$ ,

$$\begin{aligned} \psi_2 &= 1 + \epsilon, & \psi_3 &= 1 - \frac{1}{2}(m-3)\epsilon + \epsilon^2, \\ \psi_4 &= 1 + (m^2 - 6m + 11)\epsilon/6 - (m-2)\epsilon^2 + \epsilon^3, \\ \psi_5 &= 1 - (m-5)(m^2 - 5m + 10)\epsilon/24 + (7m^2 - 30m + 35)\epsilon^2/12 \\ &\quad - \frac{1}{2}(3m-5)\epsilon^3 + \epsilon^4, \\ \psi_6 &= 1 + (m^4 - 15m^3 + 85m^2 - 225m + 274)\epsilon/120 \\ &\quad - \frac{1}{4}(m-3)(m^2 - 4m + 5)\epsilon^2 + \frac{1}{4}(5m^2 - 18m + 17)\epsilon^3 \\ &\quad - (2m-3)\epsilon^4 + \epsilon^5. \end{aligned} \quad (18)$$

We have now for (16), as represented by the form (12),

$$J(\beta) = \frac{x_0^m e^{-x_0}}{1 + \beta x_0^m} \left( \frac{2\pi x_0}{m+1-x_0} \right)^{\frac{1}{2}} (1 + C_1 + C_2), \quad (19)$$

where  $C_1$  and  $C_2$  are given by (13), (14), and (18). Finally, in (15) we represent  $m!$  by Stirling's formula (7) and so reach the *asymptotic formula for  $I_m(\theta)$* :

$$I_m(\theta) \cong (1 - \epsilon/m)^{m+3/2} \frac{e^\epsilon}{(1 + \epsilon)^{\frac{1}{2}}} \frac{\{1 + C_1 + C_2\}}{\{1 + 1/(12m) + 1/(288m^2)\}}. \quad (20)$$

To compute  $I_m(\theta)$  for given  $\theta$ , we have first to solve (17) for  $\epsilon$ ; alternatively we may assign  $\epsilon$  instead of  $\theta$ . To obtain the "order of magnitude" of  $I_m(\theta)$  quickly, we drop the correction terms  $\{ \} / \{ \}$  in (20), although the inclusion of  $C_1$  and  $1/(12m)$  is necessary to obtain a reasonably close estimate.

*Related integrals:* If we apply the above method to the integral in (3), the leading term of the formula corresponding to (20) gives a useful indication of  $1 - I_m(\theta)$  for large  $\theta$ .

More important applications of the above general method are to the activation energy integrals 7.9(139) or (140) and to the new rate integrals in Chapter 9.

**Direct numerical integration.** There is little to choose, if moderately precise values are required, between the full formula (20) and direct numerical integration of  $I_m(\theta)$ ; and nearly all the following results in 8.2 were obtained by quadrature. If it were necessary again to use desk machines, one should note the superiority of Weddle's rule for this type of integral (compare Buckingham<sup>4</sup>). The values of  $I_1(\theta)$  and  $I_2(\theta)$  were found from (5) and (6) using tables; some of these values could be checked from the direct tabulation of  $I_1$  and  $I_2$  included in a recent paper by Dingle.<sup>5</sup>

### 8.2 NUMERICAL VALUES OF $I_m(\theta)$

Calculated values of  $I_m(\theta)$  are given in Table 8.2(a). Some of these, for  $m$  and  $\log \theta$  both integers, come from my earlier table,<sup>6</sup> to which I later added the cases  $m=6$  ( $\log \theta$  half-integral),  $m=6\frac{1}{2}$ , 7 ( $\log \theta$  integral). The remaining values for half-integral  $m$  or  $\log \theta$  are mainly due to E. W. Schlag.<sup>7</sup> I am indebted to W. Barrett for a complete recalculation of the table amending four entries and adding a useful number.

Powell<sup>8</sup> has a table of similar size of the function which is in the



present notation (my  $m$  is his  $s$  and vice versa):

$$k/k^\infty = \frac{1}{m!} \int_0^\infty \frac{x^m e^{-x} dx}{1 + x^m/(m!s)} \quad (21)$$

This is  $I_m(\theta)$  with

$$\theta = m!s \quad (\text{my notation}). \quad (22)$$

This he has calculated for (my)  $m = 1, 2, \dots, 8$  and  $\log s = -5.5$  to  $5.0$ . The relation (22) makes a direct comparison difficult but greatly increases the available number of values of  $I_m(\theta)$ .

In Table 8.2 (b) I list values  $\theta_5$  and  $\theta_{50}$  for which  $I_m(\theta) = 0.95$  and  $0.50$

TABLE 8.2(b)  
FIVE AND 50 PERCENT POINTS OF  $I_m(\theta)$

$m$	$\theta_5$	$\theta_{50}$	$\theta_5/\theta_{50}$
0	19	1.0	19
1	37	1.56	24
2	213	6.65	32
3	2000	46.3	43
4	$2.6 \times 10^4$	450	58
5	$4.2 \times 10^5$	5550	76
6	$8.2 \times 10^6$	$8.33 \times 10^4$	98

$$I_m(\theta_5) = 0.95, I_m(\theta_{50}) = 0.50.$$

respectively. These correspond to the pressures at which the rate constant has declined by 5 per cent and 50 per cent from the high-pressure limit; for given  $m$ ,  $\theta_5/\theta_{50}$  is the direct ratio of these pressures.

It is seen from the tables that the behavior of  $I_m(\theta)$  in terms of  $\log \theta$  changes only slowly with  $m$ ; there tends to be a *bigger spread* of  $\log \theta$  for a given decline of  $I_m(\theta)$  as  $m$  increases, so that for large  $n$  the fall-off of the rate constant is more gradual than for small  $n$ . The main effect noticeable in the tables is that, for corresponding values of  $I_m(\theta)$ ,  $\theta$  increases by a factor of the order of 10 for an increase of unity in  $m$ ; in particular, the value of  $\theta_5$  increases in roughly this way.

### 8.3 THE DECLINE OF RATE CONSTANT WITH PRESSURE

We begin by calculating the ratio of the parameter  $\theta$  to concentration or pressure, using some of the detail and the typical molecular quantities introduced in 7.4. This enables us to estimate how the decline of the rate constant with pressure depends on the complexity of the molecule; the main trends are summarized at the end of the section.

**The parameter  $\theta$ .** We state the combined results of 7.5 and 7.6 for the decline of the rate constant and recall the meaning of the various quantities. The decline is given in terms of the function  $I_n(\theta)$  of (1) by

$$k_{\nu} = I_{\nu(n-1)}(\theta), \quad (23)$$

where  $n$  is the number of *distinct* vibration frequencies  $\nu_1, \nu_2, \dots, \nu_n$ . The parameter  $\theta$  is 7.5(82), namely,

$$\theta = (\omega/\nu)f_n b^{\frac{1}{2}(n-1)}, \quad (24)$$

where

$$\nu = \sqrt{\left(\sum_1^n \mu_i \nu_i^2\right)}. \quad \mu_i = |\alpha_{1i}| / (\sum \alpha_{1i}^2)^{\frac{1}{2}}. \quad (25)$$

We recall from 7.6 that if, for example,  $\nu_n$  is the frequency of a pair of degenerate modes the corresponding amplitude factor  $\alpha_{1n}$  is to be the composite amplitude of the two modes, formed as in 7.6(92).

The other parameters in (24) are

$$f_n = (4\pi)^{\frac{1}{2}(n-1)} \Gamma(\frac{1}{2}n + \frac{1}{2}) \mu_1 \mu_2 \cdots \mu_n, \quad (26)$$

and, for a reaction at temperature  $T$ ,

$$l = E_0/\kappa T = E_0'/R'T, \quad (27)$$

where  $E_0$  is the critical energy per molecule in ergs (with  $\kappa = 1.38 \times 10^{-16}$ ) or  $E_0'$  the energy per mole in calories (with  $R' = 1.987$ ). Finally, the collision frequency per molecule, which was discussed in 7.4, is

$$\omega = zc, \quad z = 4N\sigma^2(\pi RT/m^*)^{\frac{1}{2}}, \quad (28)$$

where, with the concentration  $c$  in moles per cubic centimeter,  $N = 6.025 \times 10^{23}$ ,  $R = 8.314 \times 10^7$  ergs deg. $^{-1}$  mole $^{-1}$ , and  $\sigma$  is the molecular collision diameter in centimeters and  $m^*$  the molecular weight.

We now express  $\theta$  in terms of  $c$  or of the pressure  $p$  in millimeters of mercury; we assume as for a perfect gas that

$$c = 1.603 \times 10^{-5} p/T. \quad (29)$$

The general results from (24), (28), and (29) are then

$$\theta/c = 3.894 \times 10^{28} \sigma^2 (T/m^*)^{\frac{1}{2}} (f_n b^{\frac{1}{2}(n-1)}/\nu), \quad (30)$$

$$\theta/p = 6.243 \times 10^{23} \sigma^2 (Tm^*)^{-\frac{1}{2}} (f_n b^{\frac{1}{2}(n-1)}/\nu). \quad (31)$$

One of these formulas, combined with the table of  $I_n(\theta)$ , enables us to predict  $k/k^\infty$  as a function of  $c$  or  $p$  for a gas of known molecules, if we

can analyze the vibrations and guess what is the critical coordinate and what the value of  $\sigma$ .

If, on the other hand, we take a general view of these formulas, we see that if the other parameters remain much the same but we increase  $n$ , then  $\theta/c$  or  $\theta/p$  increases by a factor  $b$  for an increase of 2 in  $n$  (or 1 in  $m$ ), so that  $c$  or  $p$  decreases by  $1/b$  for given  $\theta$ . This suggests that the pressure at which  $k/k^\infty$  declines will tend to decrease as  $n$  increases; for this factor  $1/b$  (for  $\Delta m = 1$ ) will generally outweigh the increase of about 10 in  $\theta$  for a given decline of  $I_m(b)$ , which was noted at the end of 8.2.

**Illustrative values.** We use the same illustrative values for a "typical molecule" (independently of  $n$ ) as in 7.4(43) and (49) for second-order rate constants, namely,

$$\sigma = 5 \times 10^{-8} \text{ cm.}, \quad m^* = 50, \quad T = 700^\circ\text{K}, \quad b = 40. \quad (32)$$

For the one additional parameter, the mean frequency, we take

$$\nu = 5 \times 10^{13} \text{ sec.}^{-1} \quad (33)$$

These give for (30) and (31)

$$\theta/c = 7.286 f_n b^{1/2(n-1)}, \quad \theta/p = 1.668 \times 10^{-7} f_n b^{1/2(n-1)}. \quad (34)$$

Finally, we represent the vibrational parameter  $f_n$  of (26) by the two values  $f_n(\text{eq})$  and  $f_n(\text{uneq})$  of Table 7.4. The former (compare 7.4(45) and (48)) is the maximum  $f_n$  for all possible amplitudes, and the latter is intended to represent typical distributions of the amplitudes; the ratios  $f_n(\text{uneq})/f_n(\text{eq}) = m_n$  were given in 7.4(47). Thus for given  $\theta$  or  $k/k^\infty$ , using  $f_n(\text{eq})$  in (34) gives us the *least possible* concentration or pressure for this rate, and using  $f_n(\text{uneq})$  suggests a more "realistic" concentration or pressure, provided of course the other parameters are as in (32) and (33).

In Table 8.3 I give the values of  $p/\theta$  calculated from (34) (with  $b=40$ ) for  $f_n(\text{eq})$  and  $f_n(\text{uneq})$ .

We are now able to estimate  $k/k^\infty$  as a function of pressure (or concentration) by combining these  $p/\theta$  values with the tables in 8.2, putting  $m = \frac{1}{2}(n-1)$  in those tables. The results are represented—

(i) By two columns in Table 8.3 showing the values of  $p_{50}$ , the pressure at which  $k/k^\infty = \frac{1}{2}$ , for the present illustrative values (32) and (33). These  $p_{50}$ 's come from the  $\theta_{50}$ 's of Table 8.2(b); the corresponding  $p_b$ 's could be written down as  $p_{50}(\theta_b/\theta_{50})$  from that table.

(ii) By Fig. 8.3, some curves of  $\log(k/k^\infty)$  against  $\log p$  for odd values of  $n$ . These are based on the ratios  $p/\theta$  of Table 8.3 for  $f_n(\text{uneq})$ , the "realistic" case.

TABLE 8.3  
VALUES OF  $p/\theta$  AND PRESSURES OF 50 PERCENT DECLINE

$n$	$p/\theta$ ( $\alpha$ )	$p/\theta$ ( $\beta$ )	$p_{50}$ ( $\alpha$ )	$p_{50}$ ( $\beta$ )
3	$6.2 \times 10^4$	$1.84 \times 10^5$	$9.7 \times 10^4$	$2.9 \times 10^5$
5	$6.6 \times 10^2$	$2.8 \times 10^3$	$4.4 \times 10^2$	$1.8 \times 10^4$
7	7.15	$4.4 \times 10$	$3.3 \times 10^2$	$2.0 \times 10^3$
9	$7.7 \times 10^{-2}$	$7.0 \times 10^{-1}$	$3.5 \times 10$	$3.1 \times 10^2$
11	$8.3 \times 10^{-4}$	$1.1 \times 10^{-2}$	4.6	$6.2 \times 10$
13	$9.0 \times 10^{-6}$	$1.8 \times 10^{-4}$	$7.5 \times 10^{-1}$	$1.5 \times 10$

$p/\theta$  is calculated from (34), using the values ( $\alpha$ )  $f_n(\text{eq})$  and ( $\beta$ )  $f_n(\text{uncq})$  from Table 7.4. The values of  $p_{50}$  are  $(p/\theta)\theta_{50}$  with  $\theta_{50}$  from Table 8.2(b) and  $n = 2m + 1$ . In all cases  $p$  is in mm. of mercury.

**Examination of the results.** In looking at these results, we must distinguish between firm conclusions, which are independent of the illustrative parameters of (32), and trends, suggested by the results of using these parameters but liable to be upset to some extent by results for particular gases with particular values of the parameters.

(i) One firm conclusion is that the curve of decline (of  $\log k/k^\infty$  against  $\log \theta$  or  $\log p$ ) changes shape quite slowly with  $n$  but tends to be more spread out—a more gentle decline—for larger  $n$ , corresponding to more complicated molecules. This is seen in the graphs and also in the  $\theta_5/\theta_{50}$  ratios. It is also in harmony with the result 7.8(127), namely, the slowness of approach to  $k_{\text{bim}}^0$  for large  $n$ .

(ii) The second-order behavior is in fact approached too slowly to be clearly visible in the range of the tables, or in Powell's table,<sup>8</sup> although Kassel<sup>9</sup> has given calculations reaching this range.

(iii) There is a clear trend, shown in the graphs and in the values of  $p_{50}$  in Table 8.3, for the pressure, at which the rate constant declines, to decrease as  $n$  increases. This trend may be expected to be reliable only for comparisons of molecules with considerably different  $n$ s; but if, for example, two molecules have  $n$  differing by unity, the larger  $n$  may correspond to a higher pressure for decline, owing to changes in the parameters, in particular the energy or temperature. To put this another way, changes in the  $p/\theta$  ratio due to changes in the parameters may shift the curve of decline more than the "typical" shift due to a small change in  $n$ . The direction of these  $p/\theta$  shifts is easily inferred from (31).

(iv) The most striking feature of the illustrative results is that the pressures at which the limiting first-order rate constant is approached are very high when  $n$  is small. Thus for  $p_{50}$  to be under one atmosphere,

Table 8.3 suggests that  $n$  should be at least 8. Since for a nonlinear molecule of  $N$  atoms the number of distinct frequencies  $n$  is

$$n \leq 3N - 6, \quad (35)$$

this suggests that we need at least five atoms. For molecules up to this size we expect the reaction to be of quasi-unimolecular type, or rather (when few distinct frequencies are involved) "quasi-bimolecular."

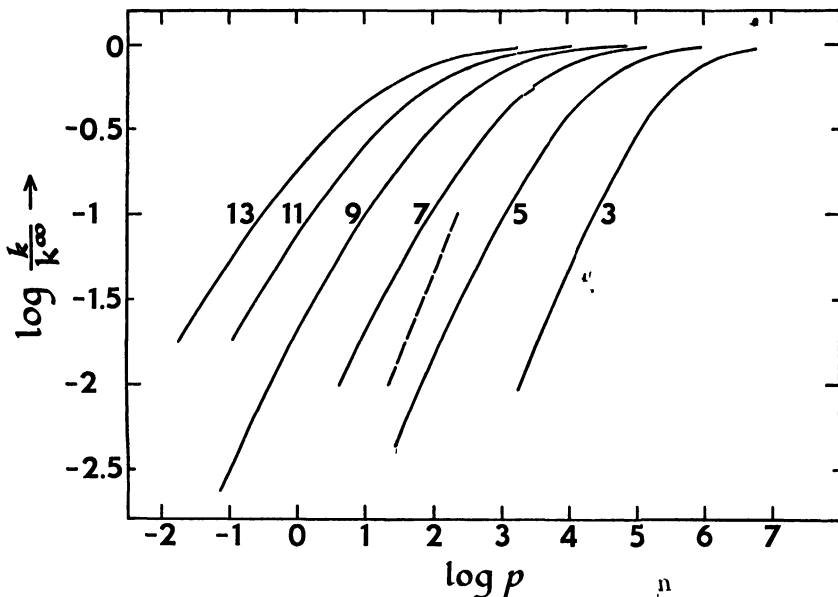


Fig. 8.3.—Theoretical curves for  $n=3$  to 13.  $p$  is in mm. The broken line shows the unit (bimolecular) slope.

#### 8.4 NOTE ON COMPARISONS WITH KASSEL'S RATE

It was observed in 7.7 that by a simple approximation Kassel's classical formula for  $k/k^\infty$  could be expressed as the integral  $I_m$  which we have been using here. It is well at this point to scrutinize this approximation, since my previous comparison<sup>6</sup> gave the impression that the  $k/k^\infty$  curves of my theory (based on  $I_m$ ) are an adequate representation of Kassel's, and vice versa.

The accurate formula 7.7(111) for a molecule of  $n=m+1$  Kassel oscillators is

$$\frac{k}{k^\infty} = g_m(\theta) = \frac{1}{m!} \int_0^\infty \frac{x^m e^{-x} dx}{1 + \theta^{-1} \{x/(1 + xb^{-1})\}^m}, \quad (36)$$

where

$$\theta = (\omega/A)b^m, \quad b = E_0/kT. \quad (37)$$

The approximation we made in 7.7 was to drop the last term  $x b^{-1}$ . This reduces (36) to  $I_m(\theta)$ , which is the integral (1) representing  $k/k^\infty$  in my theory, although the number of frequencies in my case is  $n=2m+1$ , and  $\theta$  contains an extra factor  $f_n$  (7.5(82)), which is only roughly of the order of unity.

In Table 8.4 we compare values of  $\mathcal{G}_m(\theta)$  and  $I_m(\theta)$  for  $m=2, 4$  and  $6$ , using in  $\mathcal{G}_m(\theta)$  the representative value  $b=40$ . It is seen that the ratio  $\mathcal{G}_m/I_m$  rises appreciably above unity, to about 1.4 for  $m=6$ , although this would not be very noticeable on the usual logarithmic plot. The

TABLE 8.4  
COMPARISON OF  $I_m(\theta)$  AND  $\mathcal{G}_m(\theta)$  (KASSEL'S MODEL)

log $\theta$	$I_2(\theta)$	$\mathcal{G}_2(\theta)$	$I_4(\theta)$	$\mathcal{G}_4(\theta)$	$I_6(\theta)$	$\mathcal{G}_6(\theta)$
7					.957	.987
6					.811	.913
5			.985	993	.525	.670
4			.897	939	.239	.331
3	.988	.991	.627	.707	.075	.107
2	.904	.919	.280	.334	.018	.025
1	.579	.608	.079	.095		
0	.189	.202	.0154	.0182		
-1	.034	.036				

order of magnitude of the  $\theta$  value (for given  $m$ ) at which the rate perceptibly declines is, however, the same for  $\mathcal{G}_m$  and  $I_m$ .

We conclude that  $I_m(\theta)$  is a useful approximation, either for estimating (for not too large  $m$ ) the decline of rate constant on Kassel's theory or for general comparisons of the theories as in 7.7. For accurate values of  $k/k^\infty$  on Kassel's theory one should use (36); other examples of the calculation will be found in Kassel's book.

### 8.5 THE DECOMPOSITION OF NITRYL CHLORIDE

The decomposition of nitryl chloride may serve as a reasonably simple illustration of the application of the present theory. The calculations here are in fact intended to be illustrative rather than definitive; and this seems the proper course while H. S. Johnston (who has been assisted by H. F. Cordes, M. Volpe, and G. Casaletto)<sup>10,11,12</sup> is pursuing his thorough study. I am indebted to him for new experimental material (only a small part of which is used here) and to D. R. Herschbach for theoretical rate calculations based on his vibrational analysis, which was mentioned in 3.8. I shall in fact use my own related analysis as given in 3.8.

The decomposition involves the processes



our interest is in the (slow) unimolecular process (38), for which the rate constant  $k$  is half the over-all recorded value.

**The critical coordinate.** In default of a knowledge of the full potential surface we have to assume some reasonable form of critical coordinate. This clearly will involve a stretch of the NCl distance (compare Fig. 3.8), but it is also likely that a lateral (in-plane) distortion of the NCl line will be favorable to decomposition. As this implies a lessening of a ClO distance, the critical coordinate may accordingly be taken as  $q_1$ , the NCl stretch, minus some fraction of  $q_3$ , a ClO stretch. The rate is not very sensitive to the weighting of the combination; so for simplicity I take the critical coordinate, called here  $q_0$ , to be

$$q_0 = q_1 - q_3. \quad (40)$$

It is a simple matter to calculate the amplitude factors of other combinations from Table 3.8.

**The decline of the rate constant.** By 7.5(80), the decline is  $k/k^\infty = I_{\frac{1}{2}(n-1)}(\theta)$ , where  $\theta$  is proportional to the concentration  $c$ . All five normal modes are involved in the coordinate  $q_0$  of (40); thus the *shape* of the curve of decline, of  $\log k/k^\infty$  against  $\log c$ , is that of the curve of  $\log I_2(\theta)$  against  $\log \theta$ , and this can be read off Table 8.2(a). The shape changes inappreciably (as we shall see) if we take  $n=4$ , with the curve  $I_{\frac{1}{2}}(\theta)$ .

To estimate the absolute value of  $c$  for a given decline of rate, we need the  $\theta/c$  ratio (30) for appropriate values of the parameters there involved. These fall into two groups, independent of and dependent on the choice of critical coordinate.

The *independent parameters* in (30) are  $\sigma^2$ ,  $T$ , and  $m^*$ , arising from the collision parameter  $\mathbf{z}$ . I take

$$\sigma = 6.7 \times 10^{-8} \text{ cm.}, \quad m^* = 81.5, \quad T = 273 + 147^\circ. \quad (41)$$

The value of  $T$  is to suit later experimental comparisons, and the value of  $\sigma$  ( $\pm 0.6$  angstroms) is from Hawes's virial coefficient measurements.<sup>13</sup> From (41) we have for (30), with  $c$  again in moles per cubic centimeter,

$$\theta/c = 3.97 \times 10^{14} f_n b^{\frac{1}{2}(n-1)} / \nu. \quad (42)$$

The *critical energy*  $E_0$  should, of course, be regarded as determinable (like the critical coordinate) from the energy surface, but in practice

we take it from experiment as the high-pressure activation energy. Adopting Herschbach's estimate of  $E'_0 = 29.5$  kcal. for this, we have at  $T = 420^\circ$

$$b = E_0/\kappa T = E'_0/R'T = 35.35. \quad (43)$$

The *vibrational parameters* in (30), depending on the choice of critical coordinate, are  $n$ ,  $f_n$ , and  $\nu$ . For the coordinate (40),  $n=5$ . If we write (40) in terms of the normal coordinates  $Q_i$ , as

$$q_0 = \sum_1^5 \alpha_{0i} Q_i, \quad (44)$$

then the *amplitude factors*  $\alpha_{0i}$  of  $q_0$  are, in terms of the  $\alpha_r$ , of 3.8(123) (the amplitudes of the  $q_i$ )

$$\alpha_{0i} = \alpha_{1i} - \alpha_{3i}, \quad i = 1, \dots, 5. \quad (45)$$

These are, from Table 3.8 together with  $\alpha = \sqrt{(\sum \alpha_{0i}^2)}$ , all in units  $10^{-3}$  cm. erg $^{-1/2}$ ,

$$\alpha_{0i} = -.59, 1.85, 2.09, -.29, -2.72; \quad \alpha = 3.95. \quad (46)$$

The corresponding  $\mu_i = |\alpha_{0i}|/\alpha$  and *mean frequency*  $\nu = \sqrt{(\sum \mu_i^2 \nu_i^2)}$  (with the frequencies  $\nu_i$  as in Table 3.8) are

$$\mu_i = .149, .468, .529, .073, .688; \quad \nu = 1.65 \times 10^{13} \text{ sec.}^{-1}. \quad (47)$$

This frequency  $\nu$  (which is not very sensitive to the exact choice of critical coordinate) is also the *theoretical pre-exponential or A-factor* of the rate constant  $k^\infty$ . Experimental measurements of  $k^\infty$  have not been achieved, but extrapolation from high concentrations suggests an A-factor of the order  $5 \times 10^{12}$  sec. $^{-1}$ ; this figure is not at present considered to be very reliable.

The *product of the  $\mu_i$*  in (47) is 0.00185, so that the parameter  $f_n$  of (26), with  $n=5$ , is

$$f_5 = 0.585. \quad (48)$$

(For equal amplitudes the product would be  $5^{-5/2} = 0.0179$ , and the parameter  $f_5(\text{eq}) = 5.65$  as in Table 7.4; so the effect of inequality is here quite marked.)

Finally the  $\theta/c$  ratio (42) becomes, by (43), (47), and (48)

$$\theta/c = 1.76 \times 10^4, \quad c/\theta = 5.7 \times 10^{-5}. \quad (49)$$

The *decline of rate  $k/k^\infty$*  is  $I_2(\theta)$  with this  $c/\theta$  ratio. This gives from

Table 8.2(a), beginning with  $\theta = 10^{3/2}$ ,

$$\left. \begin{array}{cccccc} c & 1.8 \times 10^{-3} & 5.7 \times 10^{-4} & 1.8 \times 10^{-4} & 5.7 \times 10^{-5} & 1.8 \times 10^{-5} \\ k/k^\infty & .78 & .58 & .36 & .19 & .085 \end{array} \right\} \cdot (50)$$

*Omission of a small amplitude:* According to 7.3 and 7.5, modes with relatively small amplitude factors should be omitted from the calculations; and although  $\mu_4$  in (47) is above the critical value 7.3(34), let us see what happens if we drop the corresponding mode  $i=4$  and recalculate as for a system of  $n=4$  modes. The rooted sum  $\alpha$  changes very little, as do  $\mu_1, \mu_2, \mu_3, \mu_5$ ; the mean frequency  $\nu$  drops to  $1.51 \times 10^{13}$ , because of the omission of the fastest frequency  $\nu_4$ . The product of the  $\mu_s$  rises sharply to 0.0257, and (48) changes to  $f_4 = 1.524$ . The ratio (42) becomes

$$\theta/c = 0.84 \times 10^4, \quad c/\theta = 1.19 \times 10^{-4}. \quad (51)$$

The decline  $k/k^\infty$  is now  $I_{11}(\theta)$  with these  $\theta$ s, and Table 8.2(a) gives

$$\left. \begin{array}{cccccc} c & 1.2 \times 10^{-3} & 3.8 \times 10^{-4} & 1.2 \times 10^{-4} & 3.8 \times 10^{-5} & 1.2 \times 10^{-5} \\ k/k^\infty & .73 & .51 & .29 & .14 & .055 \end{array} \right\} \cdot (52)$$

These results are in fact very close to (50).

**Comparison with experiment.** Casaletto<sup>12</sup> made careful measurements of the intermediate pressure rate, including many at 117°C which have been plotted as  $k/k^\infty$  values after the estimation of  $k^\infty$ . Although I have been warned that the  $k^\infty$  estimate may not be good, I have ventured to reproduce these results in Fig. 8.5 as a  $\log k/k^\infty$  against  $\log c$  plot. I have also marked on the figure the theoretical points (50) and (52), for  $n=5$  and (omitting the small amplitude) for  $n=4$ . The two theoretical curves  $n=5$  and 4 would be so close together that they could not both be drawn in distinctly, and this is physically reasonable. It is also a useful general reminder that the *shape* of the fall-off changes only slowly with  $n$ , and that the *position* of the fall-off on the concentration axis need not change with  $n$  in particular cases.

The theoretical points lie close to the experimental curve, and it should be remarked that once we have agreed on a critical coordinate the theoretical points are determinate (apart from changes in the collision diameter). One should not be too much impressed by this agreement, however. If the extrapolation from experiments to  $k^\infty$  proves to be an underestimate, then the experimental points for  $\log k/k^\infty$  will some day move bodily downward. Moreover we shall shortly discuss a symmetry consideration which should shift the theoretical points to

the right (on the concentration scale). These two changes are in the same general direction (southeast), so a measure of agreement may survive.

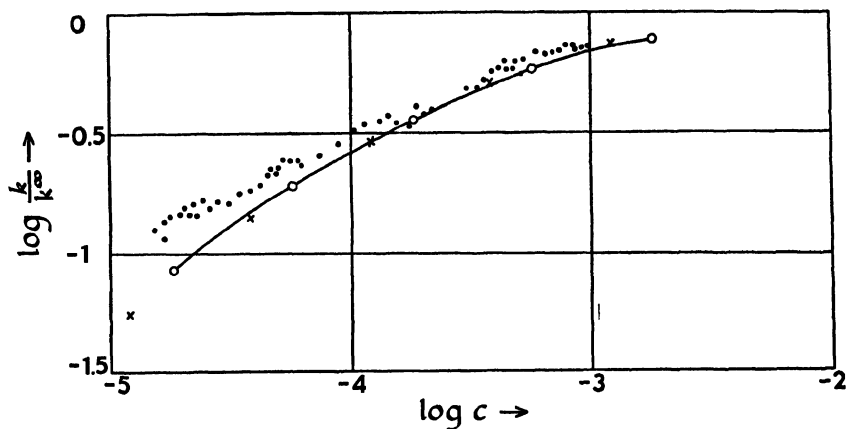


FIG. 8.5. Nitryl chloride decomposition at 147° C. . . . experiment; o o o theory,  $n=5$  (with curve); x x x,  $n=4$ . The concentration  $c$  is in moles per cc.

**The second-order rate constant.** For small  $n$  (where the factor  $\chi_n(b)$  of 7.3(31) is near unity), the limiting second-order rate constant is approximately 7.5(86), which may be written (compare 7.4(50))

$$k_{\text{lim}}^0 = z \left\{ f_n / \Gamma(\frac{1}{2}n + \frac{1}{2}) \right\} b^{1(n-1)} e^{-b}. \quad (53)$$

From (24) and (28),  $\theta/c = z\theta/\omega = z f_n b^{1(n-1)}/\nu$ ; so in (53) the "pre-exponential factor"  $k_{\text{lim}}^0 e^b$  is  $\nu/\Gamma(\frac{1}{2}n + \frac{1}{2})$  times  $\theta/c$ . Using the value (49) of  $\theta/c$  for nitryl chloride with  $n=5$ , we find for the pre-exponential factor

$$k_{\text{lim}}^0 e^b = 1.45 \times 10^{17} \text{ cc. mole}^{-1} \text{ sec.}^{-1}. \quad (54)$$

The experimental value was estimated by Cordes and Johnston at  $5.8 \times 10^{16}$ ; the agreement is reasonable.

**Symmetry considerations.** I have kept the argument simple by ignoring an obvious symmetry effect connected with the breaking coordinate. If a high value  $q$  of the combination  $q_0$  of (40) causes dissociation, so must the same value  $q$  of the combination

$$q'_0 = q_1 - q_5, \quad (55)$$

since  $q_0$  and  $q'_0$  are similarly related to the two oxygens in Fig. 3.8; thus  $q'_0$  is equally a breaking coordinate. By Table 3.8,  $q_0$  and  $q'_0$  have the same amplitude factors in modes 1, 2, and 3 but opposite ones in 4 and 5, indicating an (antisymmetric) opposition of phase; so for states with

appreciable energies  $\epsilon_4$  and  $\epsilon_5$ ,  $q_0$  and  $q_0'$  will take turns at reaching high peaks. This implies that, if  $L$  is the frequency (for given  $\epsilon_4$ ) with which  $q_0$  reaches  $q$ , then the frequency with which  $q_0$  or  $q_0'$  reaches  $q$  is  $2L$ , and this is for the most important molecular states the effective dissociation frequency. This would not be the case, of course, for molecules with little or no energy in modes 4 and 5, but in view of the largeness of the amplitude factor in mode 5 these molecules are probably relatively unimportant.

These considerations suggest that we should replace the high-concentration and general rate constants  $k^\infty$  and  $k$  found earlier in this section by  $k_2^\infty$  and  $k_2$ , where (compare 5.3(16) for  $k^\infty$  and 7.1(1) and (2) for  $k$ )

$$k_2^\infty = \int 2Ldf, \quad k_2 = \int 2\omega L/(\omega + 2L)df. \quad (56)$$

Comparing these formulas we see, first, that

$$k_2^\infty = 2k^\infty, \quad (57)$$

so that the limiting rate is doubled. Secondly, the new decline of rate constant is (compare the procedure in 7.5)

$$(k_2/k_2^\infty) = \int \frac{1}{2}\omega L/(\frac{1}{2}\omega + L)^{-1}df / \int Ldf \quad (58)$$

$$= I_{\frac{1}{2}(n-1)}(\theta_2), \quad (59)$$

where  $I$  is 7.5(81) and  $\theta_2$  is the  $\theta$  of 7.5(82) with  $\omega$  replaced by  $\frac{1}{2}\omega$ . Since  $\omega \sim c$ , this means that in place of (49) we have

$$\theta_2/c = 0.88 \times 10^4 \quad c/\theta_2 = 1.14 \times 10^{-4}; \quad (60)$$

that is, for a given decline ( $k_2/k_2^\infty$ ) we now have to have *twice* the concentration of the earlier treatment. Thus, as was foreshadowed above, this symmetry consideration shifts the curve of decline to higher values of the concentration, through a distance  $\Delta \log c = \log 2$ .

It may be seen that the limiting second-order rate constant is unchanged by these symmetry considerations. This is expected, for when a molecule has unlimited time to dissociate it is immaterial whether  $q_0$  or  $q_0'$  reaches  $q$  first.

## 8.6 THE ISOMERIZATION OF CYCLOPROPANE

The first paper M. G. Evans sponsored to the Royal Society was the theory of Chapter 5; the last papers were those on the theory of Chapter 7 and its application to cyclopropane,<sup>14</sup> together with the experi-

mental paper of Pritchard, Sowden, and Trotman-Dickenson.<sup>15</sup> At the suggestion of F. S. Dainton, I had calculated the rate of isomerization of cyclopropane for comparison with the experiments of Chambers and Kistiakowsky<sup>16</sup> and of Corner and Pease.<sup>17</sup> When I called on M. G. Evans early in May 1952 to tell him of the results, he silenced me until he had assembled a quorum including H. C. Longuet-Higgins, H. O. Pritchard, and A. F. Trotman-Dickenson. By this device he had the theoretical and experimental results revealed simultaneously, and he also enticed Longuet-Higgins into a fruitful interest. Some generalized results for degenerate vibrations (7.6) and isotopic substitutions also emerged at this meeting.

The main interest on that occasion lay in the confronting of the first absolute calculation of a declining unimolecular rate constant with its experimental determination over an unusually wide pressure range. In retrospect it seems that the agreement we then found is unjustifiably close. For this reason I shall merely summarize here the main heads of my previous account, noting where the investigation should be recast or worked over. The topics are: the reaction mechanism, the vibrational analysis, and the high- and general-concentration rates. Some notes are added concerning recent isotopic and other experiments.

**The reaction mechanism.** The isomerization is to propylene,  $\text{CH}_3\text{—CH=CH}_2$ . Let us represent the cyclopropane molecule as a horizontal triangle of carbon atoms  $\text{A}^{\text{C}}\text{B}$ , with hydrogens  $\bar{\text{a}}^{\text{C}}\bar{\text{b}}$  above and  $\text{a}^{\text{C}}\text{b}$  below near the corresponding carbon corners.

One initial step suggested was the rupture of a carbon-carbon link. I tried (at the end of my paper) such a link AB as a critical coordinate; but, involving only three vibrations effectively, this gave a wildly high concentration of initial decline of  $k/k^\infty$ . It is, I think, generally felt now that the initial step cannot be merely such a rupture.

It had been suggested by Chambers and Kistiakowsky that a hydrogen might migrate, for example,  $\bar{\text{c}}$  move toward A, with then rupture of AB and doubling of the BC bond, giving propylene. I accordingly took as critical coordinate the *diminution* (from the value in the equilibrium configuration) of a distance from a hydrogen to a nonadjacent carbon, such as a move of  $\bar{\text{c}}$  toward A. There are 12 equivalent coordinates of this type, namely,  $\text{A}\bar{\text{b}}$ ,  $\text{Ab}$ ,  $\text{A}\bar{\text{c}}$ ,  $\text{Ac}$ , and those resulting from cyclic permutations of the letters. It may be thought crude to represent what may be a complicated potential "col" merely by an extreme value of one interatomic distance; but this coordinate (for example  $\text{A}\bar{\text{b}}$ ) involves all the 21 modes of vibration, and if we refined the model by adding moderately small multiples of other internal distances into the critical coordinate this would modify the effective

“amplitude factors”  $\alpha_i$ , probably without basically altering the nature of the decline of the rate constant.

**Vibration analysis.** I based my calculations of amplitude factors on Saksena's study<sup>18</sup> and used his assignments of frequencies and force constants. It is clear that this work should be repeated on the basis of the recent investigations of Lord and others<sup>19,20</sup> on  $C_3H_6$  and  $C_3D_6$ . Like Saksena, I used local Cartesians to combine into symmetry coordinates. One can in fact see the symmetry coordinates most simply in terms of twenty-one independent distances, namely, the distances in the ABC triangle (which effectively forms a coordinate base triangle) and the eighteen distances  $\bar{a}A$ ,  $\bar{a}B$ ,  $\bar{a}C$  relating the hydrogens to this base. That these include the twelve critical distances is a minor advantage, and this coordinate system is at present the subject of a more general investigation. As an example, the symmetry coordinates of the fully symmetric vibration species are the cyclic sums of distances  $\sum BC$ ,  $\sum(A\bar{a} + Aa)$ , and  $\sum(A\bar{b} + A\bar{c} + Ab + Ac)$ .

The symmetry of cyclopropane is  $D_{3h}$ ; the twenty-one modes include seven pairs of degenerate vibrations. In the full solution for the twelve critical coordinates  $A\bar{b}$ , there are phase differences of two kinds between the coordinates: (i) phase changes of  $\pm 2\pi/3$  in the degenerate modes as one goes around the basic triangle (for example, from  $A\bar{b}$  to  $B\bar{c}$ ) and (ii) phase changes of  $\pi$  between pairs such as  $A\bar{b}$  and  $Ab$ , or  $A\bar{b}$  and  $A\bar{c}$ . These do not occur in the fully symmetric modes, and have a varying incidence in the other symmetry species. One may picture the twelve critical coordinates dipping to their minimum value like a circle of chickens pecking corn in the old-fashioned toy—one at a time.

**The first-order rate constant.** Owing to these phase effects, the contributions of the twelve critical coordinates add up to give a high concentration rate  $k^\infty$  twelve times that for one coordinate. The mean frequency 5.4(22) I found for a single coordinate was  $\nu = 3.33 \times 10^{13}$  sec.<sup>-1</sup>; hence the  $A$ -factor of  $k^\infty$  is  $4.0 \times 10^{14}$ . The accepted experimental value is about  $15 \times 10^{14}$ .

The critical distortion  $q$  in a coordinate is related to the critical energy by 5.2(6), namely,  $q = \alpha \sqrt{E_0}$ . My analysis gave  $\alpha = \sqrt{\sum_1^{21} \alpha_i^2} = 5.44 \times 10^{-3}$  cm.erg<sup>-1/2</sup>; experiment has given  $E_0$  as 65 k.cal/mole or  $4.5 \times 10^{-12}$  erg/molecule. Thus the critical distortion  $q$  is  $1.15 \times 10^{-8}$  cm. This is about half the equilibrium  $A\bar{b}$  distance. This is physically reasonable as a critical distortion, although it is rather a large distortion for the use of harmonic vibrations.

**The decline of the rate constant.** The symmetry considerations involved in the calculation of the decline of rate with pressure are here much more difficult to handle than in 8.5, owing to the presence of

seven pairs of degenerate modes as well as twelve alternative critical coordinates. The formula I reached after a detailed examination of the phases was<sup>14</sup>

$$k = 12 \int \cdot \int L(1 + 2L/\omega)^{-1} \exp\left(-\sum_1^{14} d\epsilon_i/\kappa T\right) \prod_1^{14} (d\epsilon_i/\kappa T). \quad (61)$$

Here  $L$  is the frequency with which *one* critical coordinate, for example  $q_1$  the diminution of  $\overline{A\bar{b}}$ , would reach  $q$ , with  $q_1$  taken as

$$q_1 = \sum_1^{14} \alpha_i \sqrt{\epsilon_i} \cos 2\pi\nu_i t, \quad (62)$$

and the summation taken over the fourteen *distinct* frequencies, with enhanced amplitude factors for the degenerate modes as in 7.6(92). The most that can be claimed for (61) (which was the subject of helpful criticism from F. E. Harris) is that with its factor 2 it represents the best simple approximation at not too low pressures, clearly it converges to a multiple of the correct second-order rate at very low pressures.

Of the fourteen reduced amplitude factors  $\mu_i = |\alpha_i|/\alpha$  in (62),  $\mu_5 = 0.015$  was negligibly small in my old vibrational analysis, so that unless a recalculation affects  $\mu_5$  appreciably we have effectively a system with  $n = 13$  distinct frequencies.\* The shape of the curve of decline is therefore given by  $I_6(\theta)$  of Table 8.2(a). This shape was indistinguishable at any point from Pritchard, Sowden, and Trotman-Dickenson's mean experimental curve of  $\log k/k^\infty$  against  $\log p$ , over the range 200 to 0.05 mm. of  $p$  and 0.9 to 0.075 of  $k/k^\infty$ . This range, incidentally, does not approach the second-order region, where we expect (61) to be unreliable.

Finally, the  $\theta/p$  ratio (31) was calculated, estimating (as explained in my paper<sup>14</sup>) the collision diameter at  $\sigma = 5 \times 10^{-8}$  cm., so that the theoretical  $k/k^\infty$  values could be plotted on the absolute pressure scale. It was found that the theoretical pressures for given declines were  $3\frac{1}{2}$  times the experimental. This "scale-error" is of course sensitive to the estimate of collision diameter; it might also be affected by a recalculation of the amplitude factors.

**Isotopic and "hot" cyclopropane.** Three other types of cyclopropane reaction should be mentioned because of their implications for the development of rate theory.

(i) *Isotopic studies:* Weston<sup>21</sup> found that when one hydrogen is replaced by tritium, the  $A$ -factor of  $k^\infty$  decreased. This would be ex-

\* The inclusion of  $\mu_5$  (giving  $n$  its maximum value 14) was in fact tried and found to have only a small effect. This effect would of course change if a recalculation of the vibrations made  $\mu_5$  appreciably larger.

pected classically (from 6.9) if the critical coordinates involve the isotope, as in the above "hydrogen migration," although his effect was about twice as large as I expected. Lindquist and Rollefson,<sup>22</sup> on the other hand, found an increased  $A$ -factor. From his work on trans-cyclopropane- $d_2$ , Schlag<sup>7</sup> inferred a decreased factor. Further studies, especially on  $C_3D_6$ , would be useful.

(ii) *Geometrical isomerization*: In addition to the "structural" isomerization to propylene we have been discussing, there is in the case of cyclopropane- $d_2$  a "geometrical" isomerization between its *trans* and *cis* forms. This was fully studied by Schlag<sup>7</sup> (see also Rabinovitch, Schlag, and Wiberg<sup>23</sup>). He found a decline of  $k/k^\infty$  for the geometrical isomerization corresponding to a value (on my theory) of  $n = 1.4$ . This suggests a critical coordinate or coordinates heavily involving the H or D nuclei (in some way like the structural isomerization); whether or not this involves also a definite ring rupture and recyclization is a vexed question.

(iii) "*Hot*" cyclopropane: Frey and Kistiakowsky<sup>24,25</sup> formed "hot" cyclopropane from a combination of methylene and ethylene; this then isomerized to propylene after an abnormally short life because of high initial vibrational energy. This process (like mass spectrometer reaction measurements) presumably depends on the specific rates for molecules in a narrow range of total energy. The inferred lifetimes of the hot molecules did not agree with the classical average specific rate (for example 5.5(37)) for their estimated energy content; two possible reasons are the inadequacy of the classical formula, or some specialization of the "hot" energy distribution, making a plain average over the normal modes inappropriate for the average rate.

### 8.7 THE WORK OF LAIDLER AND GILL

Gill and Laidler have been carrying out a considerable set of vibrational analyses (in particular, of the "amplitude factors" required in the present theory) in conjunction with a program of calculating reaction rates. These analyses include ozone,<sup>26</sup> nitrous oxide,<sup>27</sup> hydrogen peroxide,<sup>28</sup> and ethyl chloride; and these cases and ethane, nitrogen pentoxide, and cyclopropane have been included in an interesting general paper.<sup>29</sup> The work is a comparison of the declining and second-order rate constants as predicted respectively by my theory and by the Kassel or Hinshelwood theory, with a careful look in the latter cases at the plausibility of the appropriate number of oscillators. This leads in the general paper to a new formulation of low-concentration rates, which will be sketched later in this section.

For the three little molecules first mentioned, attention centers on

the pure second-order rate constant, for which the approximation (53) is used as representing my model. In the case of ozone, with an O—O distance as critical, the second-order rate constant calculated on my theory is found to agree with Benson and Axworthy's analysis of observations.<sup>30</sup> For nitrous oxide, my second-order rate is found to be too low by a factor of 10, and for hydrogen peroxide by a factor of about 30 (using an OH critical distance), whereas the Hinshelwood-Kassel rate can be made right by using two oscillators for  $N_2O$  and omitting one of the six for  $H_2O_2$ . The restriction to two (Kassel) oscillators for  $N_2O$  is held to be plausible because only stretching modes of vibration are thought likely to be involved. Similarly for the dissociation of ethane into methyl radicals, a restriction to nine (Kassel) oscillators (necessary to keep near the "observed" rate) is consistent with a restriction to symmetrical vibrations. For the larger molecules, my theory makes on the whole a better showing.

It will be realized from these comparisons that an attempt is being made in this work to identify the set of Kassel oscillators with my set of normal modes of the critical coordinate; and this is a deliberate development of the arguments (ii) and (iii) at the end of 7.4 above. The basic idea is that my model, of effectively independent normal modes, is valid at fairly high concentrations; at lower concentrations there are transfers of energy between the modes, so that the critical coordinate may be able to gather enough amplitude to burst, even although the initial energization had not satisfied my usual condition of distribution, equation 5.2(2). This wandering of energy will carry the low concentration rate from my form toward the larger value given by Kassel's rate for the same number of "oscillators." Laidler and Gill plausibly suggest that this wandering of energy is more likely to be important in smaller molecules, where dissociation implies higher excitation per normal mode; and this seems on the whole to correspond to the more Kasselian rates of the smaller molecules.

The new formulation of rates (mentioned above) proposed by Laidler and Gill allows for this extra step of transfer of energy between modes, while retaining my ultimate criterion of dissociation by the accumulation of extension in a (nonnormal) coordinate. Thus the reversible steps are (i) collision-energization in Kassel's sense (to obtain total energy more than  $E_0$ ) and (ii) the transfer of energy between modes until my condition 5.2(2) is satisfied; this is followed after the usual time lag, of order  $1/L$ , by dissociation, unless another collision or alternatively an unfavorable internal rearrangement occurs. At high or moderately high pressures, the direct process of collision-excitation to states satisfying 5.2(2) will presumably predominate over this two-

stage excitation, and the rate will approach my form. At low pressures, step (i) will direct us toward a Kassel rate; but to determine the respective spheres of interest of the two types of process, we require more knowledge of the rate of energy transfer between the nearly distinct normal modes.

### 8.8 THE VARIATION OF ACTIVATION ENERGY WITH PRESSURE

The variation of activation energy  $E_a'$  with pressure is given on the present theory by 7.9(141), which with the energies in calories per mole is

$$E_a' = E_0' - \frac{1}{2}nR'TA_m(\theta), \quad m = \frac{1}{2}(n - 1), \quad (63)$$

where  $E_0'$  is the limiting high-pressure activation energy,  $n$  the effective number of modes,  $\theta$  the usual parameter proportional to pressure, and

TABLE 8.8  
THE ACTIVATION-ENERGY FUNCTION  $A_m(\theta)$

$\log \theta$	$A_1(\theta)$	$A_7(\theta)$
7		.150
6		.285
5	.013	.428
4	.081	.556
3	.245	.663
2	.452	.747
1	.638	
0	.774	
-1	.834	

$A_m(\theta)$  the function 7.9(139). This function rises from 0 to 1 as  $\theta$  falls from infinity to zero, so that  $E_a'$  declines by an amount  $\frac{1}{2}nR'T$ .

I give in Table 8.8 calculated values of  $A_m(\theta)$  for  $n=9$  and 15 or  $m=4$  and 7; from these the decline of  $E_a'$  may be inferred. As  $\log \theta$  declines, the rise of  $A_m(\theta)$  (or decline of  $E_a'$ ) first gathers momentum and then tails off. It will be seen by comparison with the corresponding  $I_m(\theta)$  values of Table 8.2(a) that the decline of  $E_a'$  is most marked in the region where  $k/k^\infty = I_m(\theta)$  is of the order 0.5 to 0.1.

These calculations were performed partly in conjunction with some experiments of Trotman-Dickenson and Steel<sup>31</sup> on the decomposition of azomethane. Although there are difficulties of interpretation in this case, it seems very likely that for straightforward quasi-unimolecular reactions the predicted decline of activation energy with pressure will be confirmed by appropriate experiments; for a decline of activa-

tion energy of this type was shown in 2.8(112) to be an inevitable theoretical consequence of models in which the specific chance of dissociation increases with molecular energy; and models of this sort seem to be necessary to give a reasonably close representation of the decline of rate constant with pressure.

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## A New Approach to Rate Theory

THE purpose of this chapter is to see what happens if we discard the hypothesis of "random incidence of dissociation." We shall thereby put the harmonic model on a firmer basis and shall also obtain a formal way of extending transition-state theory from high- to general-concentration rate constants.

A basic hypothesis in most quasi-unimolecular reaction theories is that, although "interesting" molecules of given energies have precise *average* mean lives before dissociation, their individual dissociations are "random" events like the collisions which energize and de-energize them; the decline of the rate constant then depends on the ratios of these mean lives to the mean times between collisions. It is clear, however, that if we knew the precise classical state (of coordinates and momenta, or of normal-mode energies and phases in the harmonic case) of an interesting molecule, then we should know the precise time,  $s$  say, it requires to reach the dissociation configuration; and at a concentration where the collision frequency is  $\omega$ , the absolute chance of dissociation would be  $e^{-\omega s}$ , the chance of no collision in time  $s$ . A new reaction rate constant is accordingly set up as the integral of this probability over the collisional rate of production of interesting molecules in the various relevant states. This integration over fully detailed states corresponds to the usual integration (for example in Kassel's theory) over much more broadly defined states, combined with an assumption of random incidence of dissociation; it is clearly not inevitable that the results will agree.

The new general rate constant  $k$  is set up in 9.1 as an integral of  $\omega e^{-\omega s}$  (with  $s$  a function of the  $qs$  and  $ps$ ) over a  $q, p$  phase-space distribution, and in 9.2  $k$  is transformed into an integral over a critical surface. It is clear that (with the usual assumption of randomness of phase, or of uniformity of distribution of the initial  $q, p$  phase points of given energy) in the extreme cases of high and low concentrations

the distribution of lifetimes is irrelevant to the limiting rate constants  $k^\infty$  and  $k_{\text{bim}}^0$ ; at very low concentrations, if a molecule is at all able to dissociate, it has time to do so, while at very high concentrations it has so little time that only the mean frequency of dissociation matters. It is found in 9.2 that the new rate constant is indistinguishable, at high concentrations, from that of transition-state theory (formulated as a flow through a critical surface); and it would seem that this new rate may be regarded as a correct generalization of transition-state theory to general concentrations.\*

In 9.3 we revert to the harmonic oscillator model, with the states characterized by the normal-mode energies and phases. Here the average of  $\omega e^{-\omega\psi}$  over the phases  $\psi$ , may be replaced by  $L(1 - \langle e^{-\omega\tau} \rangle)$  where, as in earlier chapters,  $L$  is the mean frequency with which a coordinate as a sum of  $n$  vibrations reaches the critical value  $q$ , and  $\langle e^{-\omega\tau} \rangle$  is the average of  $e^{-\omega\tau}$  over a long sequence of gaps  $\tau$  between the occurrences of the critical value  $q$  of the coordinate (as a continuous mathematical function of the time). This new reaction rate constant converges at high and low concentrations to the rates of Chapter 5 and 7.2(13) respectively; its determination at intermediate concentrations demands for  $\langle e^{-\omega\tau} \rangle$  a knowledge of the distribution of gaps between the upward crossings of the vibrational sum through the value  $q$ .

In 9.4 we find the effects of assuming that the distribution of gaps is of Gamma type, proportional to  $\tau^{u-1}e^{-uL\tau}$ , with a parameter  $u$ . The limiting case  $u \rightarrow \infty$  corresponds to regular (equal) gaps, and this gives the fastest possible dissociation rate at any concentration. The other limiting case  $u = 1$  corresponds to "random" (free-path) gaps and reproduces the results of Chapter 7; this very probably gives the slowest rate for all reasonable gap distributions. As the rate constant  $k$  converges to the old forms at high and low concentrations, we are thus left with a "bounded uncertainty" of the rate constant in the intermediate range, in default of a precise knowledge of the gap distribution. Some numerical illustrations are given in 9.5, indicating that this uncertainty is not in fact very large.

Finally, in 9.6 there are some mathematical and computational results on the actual distributions of gaps of sums of vibrations. It will

\* Normal unimolecular transition-state theory is concerned only with what happens on the boundary, and so makes no use of the lifetimes of molecules from collision-energization to dissociation. Thus it appears to lack the tools for an extension to general-concentration rates. Giddings and Eyring<sup>1</sup> attempted to remedy this by using a calculated specific rate  $k_E$  for molecules of total energy  $E$  (which may also be deduced from 2.5(63)) in a Kassel-type general rate 2.5(78). This is an oversimplification, for the dissociation probability in the transition state does not depend solely on the total energy.

be seen that, for small numbers  $n$  of modes and large critical values  $q$ , the distribution is heavily bunched around certain gap lengths. For  $n$  of the order 5 or more, there are enough points of bunching to make a representation by Gamma-type distributions reasonable. The parameter  $u$  of the equivalent distribution tends to fall sharply as  $q$  rises from zero; but a value of the order  $u = 2$  or less seems plausible for high peaks.

### 9.1 A NEW GENERAL RATE

We formulate here, in equation (5), a new general expression for a reaction rate in terms of classical mechanics.<sup>2</sup>

The internal state of a molecule at any instant is described theoretically by the values of a set of general coordinates  $q_1, \dots, q_n$  and momenta  $p_1, \dots, p_n$ , or equivalently by the position of a representative point  $Q$  with coordinates  $(q_1, \dots, p_n)$  in the phase space. We suppose (much as in 6.4) that there is a  $(2n - 1)$ -dimensional hypersurface HS with equation

$$\eta(q_1, q_2, \dots) = 0 \quad (1)$$

such that if  $Q$  lies on HS the molecule is just dissociating. It is natural to think that the specification (1) of HS involves only the  $q$ s and not the  $p$ s, so that dissociation depends only on configuration (and an appropriate direction of motion); this was in fact the model used in 6.4, and a similar restriction may be assumed (for convenience rather than of necessity) to hold here. Undissociated and dissociated states correspond to points  $Q$  with  $\eta < 0$  and  $\eta > 0$  respectively, and so on the "one side" or the "other side" of HS; it may be preferred to regard them as "inside" or "outside" a surface in pure  $q$  space.

The classical velocity  $(\dot{q}_r, \dot{p}_s)$  of the phase point representing a molecule is  $(\partial H / \partial p_r, -\partial H / \partial q_s)$  in terms of the Hamiltonian  $H(q_1, \dots, p_n)$ , thus in the absence of extraneous effects or collisions the future behavior is determined by the present state  $(q, p)$ . We may therefore divide points  $Q$ , describing undissociated molecules, into *two classes*: those whose Hamiltonian motions eventually carry  $Q$  through HS and those for which  $\eta < 0$  always. The former points represent the *interesting* molecules, capable of dissociation; the latter we may again call *uninteresting*.

Starting at an interesting point  $Q$ , we proceed along the unique Hamiltonian path of motion which after a definite time interval will for the first time cross HS. Let

$$s = s(q_1, \dots, p_n) \quad (2)$$

be this time interval as a function of the position of the initial  $Q$ . Then a molecule initially at  $Q$  will dissociate at time  $s$  if it is not disturbed before this.

We must now allow for disturbances. We assume, as in earlier theories and chapters, that interesting molecules are rare (because of a high energy requirement), so that if they suffer collision they cease to be interesting. The incidence of collisions is assumed, as in 2.3, to be *random*, so that the chance of a molecule colliding in any time element  $\Delta t$  is  $\omega \Delta t$ , where  $\omega$  is called the mean frequency of collision per molecule. It follows as in 2.3(19) that the chance that no collision occurs to a molecule in time  $(0, t)$  is  $e^{-\omega t}$ . Thus *the absolute probability of dissociation of an interesting molecule initially in state  $q_1, \dots, p_n$  is*

$$\exp \{ -\omega s(q_1, \dots, p_n) \}, \quad (3)$$

since this is the chance of avoiding collision in the time  $s$  which it needs to dissociate. This is an absolute probability, not a probability per unit time.

The over-all dissociation rate is formed by combining this probability with a more orthodox expression for the rate of production of interesting molecules. At a given temperature of the gas, let  $f(q_1, \dots, p_n) \cdot dq_1 \cdots dp_n$  be the equilibrium proportion which would be in states  $(q_1, q_1 + dq_1) \cdots$  if dissociation were inhibited, or the actual proportion in a very high concentration of dissociating gas. Relying on the discussion in 2.3 around a similar formula 2.3(11), we assume that for general values of the concentration  $c$ , the number of molecules entering an interesting range  $dq_1, \dots, dp_n$  per second, through collisions, is

$$c\omega f(q_1, \dots, p_n) dq_1 \cdots dp_n \quad (4)$$

(this is as if the energization process is unaffected by what goes on in the rare interesting states). Out of this number (4), the proportion  $e^{-\omega s}$  succeed in dissociating, so that the number (per second) dissociating after entering the range  $dq_1, \dots, dp_n$  is  $c\omega f e^{-\omega s} dq_1 \cdots dp_n$ . Hence the total proportion of molecules dissociating per second, *the first-order rate constant*, is

$$k = \int \cdots \int \omega \exp \{ -\omega s(q_1, \dots, p_n) \} f(q_1, \dots, p_n) dq_1 \cdots dp_n, \quad (5)$$

the integral being over all interesting states  $q, p$ .

This is the new formula in its most general form, applicable, for example, when the variables are action and angle variables as in 9.3 below. For the present we are thinking of ordinary  $qs$  and  $ps$  with a Hamil-

tonian  $H(q_1, \dots, p_n)$ . In this case  $f(q_1, \dots, p_n)$  is  $\exp(-H/\kappa T)/\Phi$ , where  $\Phi$  is the phase integral 2.4(27). Thus the rate constant (5) is

$$k = \Phi^{-1} \int \dots \int \omega \exp \{ -\omega s - H/\kappa T \} dq_1 \dots dp_n, \quad (6)$$

where

$$\Phi = \int \dots \int \exp(-H/\kappa T) dq_1 \dots dp_n. \quad (7)$$

The integral (6) is over interesting states; the integral (7) is over "uninteresting states" as well, but in view of the discussion 6.7(i) it should be confined (in the  $q$  integration), formally at least, to all undissociated states.

## 9.2 GENERAL AND LIMITING FORMS AND THE ACTIVATED COMPLEX

Some of the sting of novelty of the new rate constant will be removed here by finding that its behavior at very low and high concentrations is quite conventional; we also (by a contact transformation) reduce it to a semblance of order at intermediate concentrations.

To simplify comparisons with earlier developments in this book, we revert for a while to the criterion that dissociation occurs when a particular coordinate  $q_1$  reaches a high value  $q$ ; thus the hypersurface (1) becomes

$$\eta \equiv q_1 - q = 0. \quad (8)$$

**Low concentrations.** When the concentration  $c$  is small, so is the collision frequency  $\omega = zc$ ; and ultimately we may ignore the factor  $e^{-\omega s}$  in (5) or (6). Thus the rate tends to the form

$$k \cong \omega \Lambda, \quad \Lambda = \Phi^{-1} \int \dots \int e^{-H/\kappa T} dq_1 \dots dp_n, \quad (9)$$

the last integral being over the interesting states, so that  $\Lambda$  is the "equilibrium" proportion of interesting molecules. This corresponds to a second-order rate constant  $k_{\text{bim}} = k/c$ , namely,

$$k_{\text{bim}}^0 = z\Lambda, \quad (10)$$

which is the limiting form found earlier in 7.2.

**General concentrations.** Here we find a contact transformation (as defined in 6.1) useful. Consider an element  $dq_1 \dots dp_n$  of phase

space around a general "interesting" point  $Q$ , for which the transition time is  $s(q_1, \dots, p_n)$ ; and suppose that for the various points of the element the transition time has the range  $s$  to  $s+ds$ . If we follow the Hamiltonian path from  $Q$ , we arrive at a point  $Q'$  ( $q, q'_2, \dots, p'_n$ ) on the critical surface. We apply a contact transformation to the neighborhood of  $Q$ , which transforms  $Q$  into  $Q'$ ; this will transform the element  $dq_1 \dots dp_n$  at  $Q$  into an element  $dq'_1 \dots dp'_n$  at  $Q'$ . As the contact transformation corresponds to the natural motion from  $Q$  to  $Q'$  in time  $s$ , and as there is a range  $ds$  of transition times for the original element, the first factor of the element at  $Q'$  is

$$dq'_1 = \dot{q}'_1 ds, \quad (11)$$

where  $\dot{q}'_1 = \partial H / \partial p'_1$  is the velocity in coordinate  $q_1$  at  $Q'$ . The rest  $dq'_2 \dots dp'_n$  of the new element is an element of the critical surface (here  $q_1 = q$ ) itself.

In the contact transformation the value of the Hamiltonian  $H$  is preserved, and also the extension  $dq_1 \dots dp_n = dq'_1 \dots dp'_n$  (this may also be regarded here as Liouville's Theorem). Thus the contribution of the element  $dq_1 \dots dp_n$  to the rate integral (6) is expressed as

$$\Phi^{-1} \omega \exp \{ -\omega s - H(q, q'_2, \dots, p'_n) / \kappa T \} \dot{q}'_1 ds dq'_2 \dots dp'_n. \quad (12)$$

We apply a similar transformation to each element of (6), so that the integration is now over the critical surface and over  $s$ . It is seen that original elements at points  $Q$  on one trajectory which "terminates" at a critical point  $Q'$  ( $q, q'_2, \dots, p'_n$ ) give contributions differing only in the values of  $s$ ; that for these elements  $s$  ranges from 0 to  $s_1$ , namely the time since this trajectory previously crossed the critical surface (with negative  $\dot{q}_1$ ); and that this maximum life  $s_1$  is a function of the terminal position  $q'_2, \dots, p'_n$ . The  $s$  integration (which must accordingly be performed first) of (12) is

$$\int_0^{s_1} \omega e^{-\omega s} ds = 1 - \exp \{ -\omega s_1(q'_2, \dots, p'_n) \}. \quad (13)$$

Dropping the primes which now adorn all the variables, we have now for the rate constant as the integral of (12)

$$k = \Phi^{-1} \int \dots \int \dot{q}_1 \{ 1 - \exp(-\omega s_1) \} \exp(-H_q / \kappa T) dq_2 \dots dp_n, \quad (14)$$

where  $\dot{q}_1$  and  $H_q$  denote  $\partial H / \partial p_1$  and  $H$ , both evaluated at  $q_1 = q$ , so that  $\dot{q}_1$ ,  $s_1$ , and  $H_q$  are all functions of  $q_2, \dots, p_n$ . It is seen also from

the way we set up the formula by going *forward* along the paths that the range of integration is limited to values for which  $\partial H/\partial p_1 > 0$ .

This is the general rate as an integral over the critical surface; it involves the awkward function  $s_1$ , which is the maximum possible lifetime of a molecule dissociating in state  $(q, q_2, \dots, p_n)$ .

**High concentrations.** For all (or certainly for very nearly all) critical states,  $\exp(-\omega s_1)$  tends to zero at high concentrations, where  $\omega \rightarrow \infty$ . Thus the rate constant (14) approaches the pure first-order form

$$k^\infty = \Phi^{-1} \int \dots \int_{q_1 > 0} \dot{q}_1 \exp(-H_q/\kappa T) dq_2 \dots dp_n. \quad (15)$$

This is Pelzer's formula 6.1(20) in its most general form, with no restriction of the potential to a quadratic form or of the kinetic energy to be independent of the  $q_s$ . It may equally be regarded as the classical equivalent (for our critical surface) of the (first-order) activated-complex rate constant. Thus the general rate constant (6) may be regarded as a way of extending transition-state theory to general concentrations; it is (to my mind) hard to see any other valid way, short of a generalized integro-differential equation of transport.

*An alternative approach* to (15) may be made from the original form (6) of the rate. If  $q_1$  is near the boundary  $q$ , the transition-time from  $q_1$  to  $q$  is approximately

$$s = (q - q_1)/\dot{q}_1 \quad (\dot{q}_1 > 0). \quad (16)$$

If  $\omega$  in (6) is large, only small values of  $s$  are important; we may assume that these arise from points  $q_1$  near  $q$  with  $\dot{q}_1 > 0$ , and use (16) as a first approximation to  $s$ . The integration of (6) for  $q_1$  is then approximately

$$\int^q \omega \exp \left\{ -\frac{\omega(q - q_1)}{\dot{q}_1} - \frac{H}{\kappa T} \right\} dq_1 = \dot{q}_1 \exp(-H_q/\kappa T); \quad (17)$$

the lower limit for  $q_1$  is unspecified but gives a negligible contribution for large  $\omega$ . If we use (17), we see that it reduces (6) to the high-concentration rate constant (15).

It is possible that by replacing (16) by a considerably more elaborate approximation to  $s$  in terms of  $\dot{q}_1, \ddot{q}_1, \dots$ , we might evaluate (6) well enough to show the nature of the fall-off of  $k$  with  $\omega$  at moderately high concentrations.

**A general critical surface.** If the critical surface is not of the simple

form (8) but of the general form (1), we may still use the contact transformation. This gives for the rate constant (6)

$$k = \Phi^{-1} \int v_n (1 - e^{-\omega s_1}) \exp(-H_0/\kappa T) d\sigma, \quad (18)$$

where  $d\sigma$  denotes the element of the  $(2n-1)$ -dimensional critical surface,  $v_n$  the velocity of the phase point at  $d\sigma$ , resolved perpendicular to  $d\sigma$ ,  $H_0$  the value of  $H$  on the boundary, and  $s_1$  the time back to the previous crossing of the boundary; the integration is over the regions  $d\sigma$  for which  $v_n$  has the one appropriate sign.

The limiting form of (18) as  $\omega \rightarrow \infty$  and  $e^{-\omega s_1} \rightarrow 0$  corresponds to the activated-complex rate constant  $k^\infty$  with a general critical surface.

### 9.3 THE HARMONIC OSCILLATOR MODEL

We now apply these ideas specifically to the model of Chapters 5, 7, and 8, namely, a molecule with strictly harmonic vibrations, dissociating when a coordinate  $q_1$  reaches the value  $q$ . We can make better progress by using normal-mode energies and phases (as in Chapters 5 and 7) rather than  $q, p$  phase space (as in Chapter 6). The basic rate constant (23) below could in fact be regarded as the general form (6) with action and angle variables representing the  $ps$  and  $qs$ ; but it is less confusing to reformulate the rate from the initial ideas of 9.1. We shall then proceed to convert the rate (23) into the more useful form (33).

**The basic rate constant.** If  $\epsilon_1, \dots, \epsilon_n$  are the normal-mode energies and  $\psi_1, \dots, \psi_n$  the initial phases in the modes, the equilibrium or high-concentration proportion of molecules in an elementary range is, as in 5.3(14),

$$e^{-E/\kappa T} \prod_1^n \{d\epsilon_i d\psi_i / (\kappa T)\}, \quad E = \sum_1^n \epsilon_i, \quad 0 \leq \psi_i < 1. \quad (19)$$

The time behavior of coordinate  $q_1$  in an undisturbed molecule is, as in 5.2(1),

$$q_1 = \sum_1^n \alpha_{1i} \sqrt{\epsilon_i} \cos 2\pi(\nu_i t + \psi_i), \quad (20)$$

and the molecule is *interesting* if  $q_1$  can reach  $q$ , namely, if

$$\sum_1^n |\alpha_{1i}| \sqrt{\epsilon_i} \geq q, \quad (21)$$

provided we again assume the frequencies are *l.i.* Let

$$s = s(\epsilon_1, \dots, \psi_n) \quad (22)$$

be the smallest positive time  $t$  at which the function (20) attains the value  $q$ ; then  $s$ , as in 9.1, is the time an undisturbed molecule requires to dissociate, and the absolute probability of dissociation is  $e^{-\omega s}$ .

The rate of production (4) of interesting molecules in a given range is in the present case  $\omega$  times the first expression in (19). Hence *the general rate constant* corresponding to (5) is

$$k = \int \dots \int \omega e^{-\omega s} e^{-E/\kappa T} \prod_1^n (d\epsilon_i d\psi_i / \kappa T), \quad (23)$$

the integration being over  $\epsilon_i$ , satisfying (21) and over phases  $\psi_i$  from 0 to 1.

**The phase integration.** Just as the rate (23) is really (6) given a "new look," so we can convert it to a form analogous but somewhat superior to (14) by considering the phase integrations  $d\psi_i$ . For this we introduce the function (which by (22) depends also on the  $\epsilon_i$ )

$$\phi(\omega) = \int_0^1 \dots \int_0^1 \omega e^{-\omega s} d\psi_1 \dots d\psi_n. \quad (24)$$

The rate (23) then becomes, *with the prime denoting integration over the range* (21),

$$k = \int \dots \int' \phi(\omega) e^{-E/\kappa T} d\epsilon_1 \dots d\epsilon_n / (\kappa T)^n. \quad (25)$$

We are assuming again that the frequencies  $\nu_i$  in (20) are *l.i.*, so that (24) as a phase-averaged property of the sum  $q_1$  of (20) may be replaced by a long-time average property (compare the end of 4.1). To be specific, (24) is the phase average of  $\omega e^{-\omega s}$ , where  $s$  is the time to the first upzero of  $q_1 - q$  for given phases  $\psi_i$  in (20). For a long-time average we drop the phases, and consider therefore the function

$$f(t) = \left( \sum_1^n \alpha_i \sqrt{\epsilon_i} \cos 2\pi \nu_i t \right) - q; \quad (26)$$

and we define  $s' = s'(t)$  to be the time *from* a given value of  $t$  to the next upzero of  $f(t)$ . The relevant long-time average is of the function  $\omega \exp \{ -\omega s'(t) \}$ . Equating this to the phase average (24), we have

$$\phi(\omega) = \lim_{T \rightarrow \infty} T^{-1} \int_0^T \omega \exp \{ -\omega s'(t) \} dt. \quad (27)$$

Let  $t_1, t_2, \dots$  be the times of the successive upzeros of  $f(t)$ . By our definition

$$\text{if } t_r \leq t < t_{r+1}, \text{ then } s'(t) = t_{r+1} - t. \quad (28)$$

Hence

$$\begin{aligned} \phi(\omega) &= \lim_{m \rightarrow \infty} t_m^{-1} \sum_{r=1}^m \int_{t_r}^{t_{r+1}} \omega \exp \{ -\omega(t_{r+1} - t) \} dt \\ &= \lim_{m \rightarrow \infty} t_m^{-1} \sum_r^m [1 - \exp \{ -\omega(t_{r+1} - t_r) \}] \\ &= \lim (m/t_m) \left[ 1 - \lim \left\{ m^{-1} \sum_r^m e^{-\omega \tau_r} \right\} \right], \end{aligned} \quad (29)$$

where  $\tau_r = t_{r+1} - t_r$  is the *gap* between the  $r$ th and  $(r+1)$ th upzeros. By the result 4.1(10) the *asymptotic frequency of upzeros* (we write  $L$  for  $L'$  as there is here no distinction) is

$$L = \lim_{m \rightarrow \infty} (m/t_m). \quad (30)$$

Also the *asymptotic average over the gaps* is

$$\langle e^{-\omega \tau} \rangle = \lim_{m \rightarrow \infty} m^{-1} \sum_r^m e^{-\omega \tau_r}. \quad (31)$$

Thus finally

$$\phi(\omega) = L(1 - \langle e^{-\omega \tau} \rangle). \quad (32)$$

To obtain a corresponding result by sticking to phase averages (without introducing asymptotic averages) is possible but more intricate.

**The result.** Inserting (32) gives for the rate constant (25)

$$k = \int \dots \int' L(1 - \langle e^{-\omega \tau} \rangle) e^{-E/\kappa T} d\epsilon_1 \dots d\epsilon_n / (\kappa T)^n. \quad (33)$$

If  $\omega$  is very large,  $\langle e^{-\omega \tau} \rangle$  is negligible, and we recover the same limiting rate constant as in Chapter 5, namely,

$$k^\infty = \int \dots \int L e^{-E/\kappa T} d\epsilon_1 \dots d\epsilon_n / (\kappa T)^n = \nu \exp(-E_0/\kappa T). \quad (34)$$

In view of this it will be useful later to write (33) as

$$k = k^\infty - \int \dots \int' L \langle e^{-\omega \tau} \rangle e^{-E/\kappa T} d\epsilon_1 \dots d\epsilon_n / (\kappa T)^n, \quad (35)$$

the second term showing the decrement at falling concentration.

If  $\omega$  is very small,

$$\langle e^{-\omega\tau} \rangle \cong 1 - \omega \langle \tau \rangle = 1 - \omega/L \quad (36)$$

(compare (38) and (39) below), so that the rate constant (33) approaches the form

$$k = \omega \int \cdots \int' e^{-E/\kappa T} d\epsilon_1 \cdots d\epsilon_n / (\kappa T)^n, \quad (37)$$

which is the limiting second-order form found in Chapter 7.

These results confirm again that the new theory agrees with the old in the limiting cases of high and low concentration.

#### 9.4 RATE CONSTANTS FOR DIFFERENT ASSUMED GAP DISTRIBUTIONS

To perform the integration of the rate constant (33), we need an expression for the average  $\langle e^{-\omega\tau} \rangle$  as a function of the energies  $\epsilon_i$ , and for this we need the statistical distribution of the gaps  $\tau_r$ . Some evidence as to the nature of this distribution (mainly for the important region where  $\sum |\alpha_{1i}| \sqrt{\epsilon_i - q}$  is relatively small) will be presented in 9.6. Meanwhile we examine here what the rate constant  $k$  would look like for different assumed distributions of the gaps; these will include the conventional "random" distribution and a regular distribution, as extreme cases of Gamma-type distributions which may cover a near approach to the real situation.

*Preliminary formulas:* The mean gap  $\langle \tau \rangle$  according to our long-time averaging is

$$\begin{aligned} \langle \tau \rangle &= \lim_{m \rightarrow \infty} \left( \frac{\sum_1^m \tau_r}{m} \right) = \lim_{m \rightarrow \infty} \{ (t_{m+1} - t_1) / m \} \\ &= \lim_{m \rightarrow \infty} (t_m / m), \end{aligned} \quad (38)$$

where, as in 9.3,  $t_m$  is the total time to the  $m$ th upzero. Comparing this result with the form (30) of the asymptotic frequency  $L$  of upzeros gives

$$\langle \tau \rangle = 1/L. \quad (39)$$

For convenience we treat the distribution of gaps as continuous and write  $h(\tau)d\tau$  for the proportion of gaps, out of an indefinitely long se-

quence, which have lengths between  $\tau$  and  $\tau+d\tau$ . Two conditions  $h(\tau)$  must satisfy are, using (39),

$$\int_0^{\infty} h(\tau) d\tau = 1, \quad \langle \tau \rangle = \int_0^{\infty} \tau h(\tau) d\tau = 1/L. \quad (40)$$

The average we require is

$$\langle e^{-\omega\tau} \rangle = \int_0^{\infty} e^{-\omega\tau} h(\tau) d\tau. \quad (41)$$

It is clear that the distribution  $h(\tau)$ , and consequently  $\langle e^{-\omega\tau} \rangle$ , will depend on the amplitudes of the vibrations; and even the statistical type of  $h(\tau)$  may change with the amplitudes, and so with the energies  $\epsilon_*$ . Such a change of type would introduce into the integration of the rate (33) complications which we shall not fully investigate.

We now examine some forms of  $h(\tau)$ .

(i) "Random" distribution: by this I mean the distribution

$$h(\tau) = Le^{-L\tau}. \quad (42)$$

It corresponds to the assumption that the incidence of dissociation is "random" (like the assumed incidence of collisions), so that the probability of occurrence in any element of time  $dt$  is  $Ldt$ . The plausibility of this assumption was discussed in 7.1, and it appears almost inevitable in most theories of the decline of the rate constant.

For the distribution (42) we have in (41)

$$\langle e^{-\omega\tau} \rangle = L \int_0^{\infty} \exp \{ -(\omega + L)\tau \} d\tau = L/(\omega + L), \quad (43)$$

so that the rate constant (33) is

$$k = \int \cdots \int' \omega L(\omega + L)^{-1} e^{-E/\kappa T} d\epsilon_1 \cdots d\epsilon_n / (\kappa T)^n. \quad (44)$$

This is precisely the general rate constant of Chapter 7; this emphasizes the status of "random dissociation" in that formulation, as in other theories having a denominator of the type  $\omega + k_B$  in the rate integral.

(ii) *Regular gaps*: For a single oscillator or diatomic molecule the gaps would be all the same, namely, the period of oscillation. Such a simple system does not interest us, but the assumption for a general molecule that the gaps (for given energies  $\epsilon_*$ ) are effectively all of the same length  $\tau = 1/L$  provides an important limiting case. With equal

gaps,  $\langle e^{-\omega\tau} \rangle = e^{-\omega/L}$ , so that the rate constant in the forms (33) and (35) is

$$k = \int \cdots \int' L(1 - e^{-\omega/L})e^{-E/\kappa T} d\epsilon_1 \cdots d\epsilon_n / (\kappa T)^n \quad (45)$$

$$= \nu \exp\left(-\frac{E_0}{\kappa T}\right) - \int \cdots \int' L \exp\left\{-\frac{\omega}{L} - \frac{E}{\kappa T}\right\} \frac{d\epsilon_1 \cdots d\epsilon_n}{(\kappa T)^n}.$$

This is the *largest possible rate constant*, at given  $\omega$ , for all conceivable distributions  $h(\tau)$  of the gaps. To prove this, we observe that for  $m$  positive numbers  $x_1, \cdots, x_m$  with a fixed sum  $mx$ , the average

$$\langle \exp(-x_i) \rangle \equiv m^{-1} \sum_1^m \exp(-x_i) \text{ is least when the } x_i \text{ are all equal,}$$

the value then being  $e^{-x}$ . Thus for a set of unequal intervals  $\tau_r$  with mean  $1/L$ , the average of  $\exp(-\omega\tau_r)$  is greater than  $\exp(-\omega/L)$ . It follows that the general rate constant (35), at any value of  $\omega$ , is less than (45); hence the "regular gap" rate (45) is greater than that given by any other distribution of the gaps.

(iii) *Gamma-type distributions*: The general Gamma-type distribution, with mean  $\langle \tau \rangle = 1/L$  and parameter  $u$ , is

$$h_u(\tau) = (uL)^u \tau^{u-1} e^{-uL\tau} / \Gamma(u) \quad (1 \leq u < \infty). \quad (46)$$

Our earlier cases were the *extremes*, (i)  $u=1$  and (ii)  $u \rightarrow \infty$ . For (46)

$$\langle e^{-\omega\tau} \rangle = (1 + \omega/uL)^{-u}, \quad (47)$$

so that the rate constant (33) or (35) is

$$k = \int \cdots \int' L \{1 - (1 + \omega/uL)^{-u}\} e^{-E/\kappa T} d\epsilon_1 \cdots d\epsilon_n / (\kappa T)^n \quad (48)$$

$$= \nu e^{-E_0/\kappa T} - \int \cdots \int' L(1 + \omega/uL)^{-u} e^{-E/\kappa T} d\epsilon_1 \cdots d\epsilon_n / (\kappa T)^n.$$

A binomial expansion shows that  $(1 + \omega/uL)^u$  increases with  $u$ . Thus if in (48) we assume that  $u$  is constant (independent of the  $\epsilon_i$ ), then the greater the constant value we assume, the greater the rate constant  $k$  is for given  $\omega$  or concentration. Even if we assume in (48) that  $u$  is variable (depending on the  $\epsilon_i$ , or perhaps merely on the function  $L$  of the  $\epsilon_i$ ), then this rate is greater than that for  $u=1$ , namely, the random-gap or conventional rate (44) of (i); and this rate (48) is less than that for  $u \rightarrow \infty$ , namely, the regular gap rate (45) of (ii).

As it will be seen later that we may reasonably approximate to the behavior of some vibrational sums by Gamma-type distributions (per-

haps with a variable parameter  $u$ ), it follows that the conventional rate constant (44) is very probably a lower bound to the real value; and we have shown earlier that, whatever the gap distribution, the regular-gap rate constant (45) is an upper bound. All distributions give the *same* limiting high- and low-concentration rates; so we are left with a bounded uncertainty at intermediate concentrations.

### 9.5 APPROXIMATE VALUES OF THE DECLINE OF RATE CONSTANT

The general rate constant (48) for a Gamma-type distribution of gaps is reduced here to an approximate simple integral, and this is used to obtain some numerical estimates of the decline of the rate constant with concentration for the case of  $n=11$  modes. The results suggest that for moderately complex molecules the nature of the gap distribution has a secondary (although not inappreciable) effect on the shape of the decline.

**The approximation to the rate.** Treating the parameter  $u$  as fixed, we approximate to the rate (48) by the method of 7.5, with again the approximation 7.5(62) for  $L$ . In 7.5 we were in fact handling the case  $u=1$  (the "random gap" case) of (48); and accordingly the inverse Mellin transform 7.5(58) has to be replaced by the more general form

$$\frac{1}{(1+x)^u} = \frac{1}{2i} \int_{c-i\infty}^{c+i\infty} \frac{(1-z)(2-z) \cdots (u-1-z)}{\Gamma(u) \sin \pi z} x^z dz \quad (0 < c < u). \quad (49)$$

Proceeding as in 7.5, we find for (48), with  $k^\infty = \nu e^{-b}$ ,  $b = E_0 / \kappa T$ ,  $m = \frac{1}{2}(n-1)$ , and  $m! \equiv \Gamma(m+1)$ ,

$$\begin{aligned} k/k^\infty &= \frac{1}{m!} \int_0^\infty \left\{ 1 - \left( \frac{ux^m}{\theta + ux^m} \right)^u \right\} x^m e^{-x} dx \\ &= 1 - \frac{1}{m!} \int_0^\infty \left( \frac{ux^m}{\theta + ux^m} \right)^u x^m e^{-x} dx. \end{aligned} \quad (50)$$

This is the required formula, with  $\theta$  the same parameter 7.5(77) as before, proportional to  $\omega$  or concentration.

The corresponding result for the "regular-gap" rate constant (45) (equivalent to  $u \rightarrow \infty$  in (50)) is

$$\begin{aligned} k/k^\infty &= \frac{1}{m!} \int_0^\infty \{ 1 - \exp(-\theta x^{-m}) \} x^m e^{-x} dx \\ &= 1 - (m!)^{-1} \int_0^\infty \exp(-x - \theta x^{-m}) x^m dx. \end{aligned} \quad (51)$$

These formulas may be evaluated by methods discussed in 8.1; of the two forms of each of (50) and (51) the first is sometimes preferable except for large  $\theta$ .

**Numerical examples.** In Table 9.5 we give some values of  $k/k^\infty$  as a function of the parameter  $\theta$  for the case of  $n=11$  vibrational modes. It may be recalled from Table 8.3 that for the illustrative molecular quantities there employed the pressure (in mm. mercury) was about  $\theta/100$  for  $n=11$ .

The three columns of  $k/k^\infty$  in Table 9.5 refer to the cases:

(a) "Random" gaps ( $u=1$ ); this is the rate as in Chapters 7 and 8, and the values are from Table 8.2(a).

(b) Gamma-type gap distribution with  $u=2$  (results calculated from

TABLE 9.5  
THE DECLINE OF RATE CONSTANT

log $\theta$	$k/k^\infty$		
	(a) Random	(b) $u=2$	(c) Regular
6	.975	.991	.995
5	.864	.905	.938
4	.587	.631	.679
3	.269	.290	.327
2	.082	.088	.095

The gap distributions used in (a), (b), and (c) are explained in the text. The number of modes is  $n=11$  ( $m=5$ ).

equation (50)). This representation of gaps has a degree of plausibility in view of some of the results in 9.6 below.

(c) "Regular" gaps ( $u \rightarrow \infty$ ), with results calculated from (51). Insofar as (51) is a reliable approximation, these values of  $k/k^\infty$  are the maximum possible for any gap distribution.

**Remarks on the results.** The spread between the columns of  $k/k^\infty$  is seen to be moderately small and on the more usual logarithmic scale would seem quite small; it is roughly of the order found in 8.4 for the spread between the accurate and approximate forms of Kassel's rate constant. In the present table the decline of the rate constant sets in at rather lower  $\theta$ s (or concentrations) as we pass from the random to the regular case; but we may infer for  $n$  of the order of 11 that it is  $n$  rather than the gap distribution which governs the concentration at which the decline becomes marked.

The results for  $u=2$  lie nicely between the extreme "random" and

“regular” cases, and we may regard them as a reasonable approximation to the real situation. The general impression from this work is that gap distribution effects are likely to be of secondary importance among the factors determining the rate, but they deserve inclusion in a refined theory. The *limiting* first- and second-order rate constants are independent of the distribution, but the manner of transition and approach to the limits are not.

### 9.6 NOTES ON THE DISTRIBUTION OF GAPS

The distribution of the gaps  $\Delta t$  between the zeros of a sum

$$f(t) = \sum_1^n a_i \cos 2\pi(\nu_i t + \psi_i) - q \quad (52)$$

is a difficult and interesting problem, with applications outside the present chemical theory. Following the work of S. O. Rice,<sup>3</sup> M. S. Longuet-Higgins<sup>4</sup> has developed results for the type of case where  $q$  is zero and  $n$  infinite. We are concerned with the very different situation where  $\sum |a_i| - q$  is usually small compared with  $q$  (since few molecules have energies making  $\sum |\alpha_i| \sqrt{\epsilon_i}$  much larger than the critical stretch), and also  $n$  is moderately small. I give here a solution for  $n=2$  and a conjecture (well supported) for larger  $n$ , and I examine the validity of the Gamma-type distributions of 9.4.

For convenience we take the amplitudes  $a_i$  positive and *the largest frequency to be*  $\nu_n = 1$ . We assume  $\nu_1, \dots, \nu_n$  are *l.i.*, so that we omit the phases  $\psi_i$  and consider the long-time behavior of  $f(t)$ . (There is a corresponding “phase-average” problem for unrestricted  $\nu_i$ .)

**High peaks.** Assuming that  $2\pi^2 h^2 \equiv \sum a_i - q$  is small, we see from 4.6 that (52) has a pair of zeros (an upzero followed by a downzero) near certain integral values  $r$  of  $t$ , and these integers  $r$  are the solutions of the inequality (compare 4.6(76))

$$\phi(\{\nu_i r\}) \equiv \sum_1^{n-1} a_i \{\nu_i r\}^2 - A_r^{-1} \left( \sum_1^{n-1} a_i \nu_i \{\nu_i r\} \right)^2 < h^2, \quad (53)$$

where

$$A_r \equiv \sum_1^n a_i \nu_i^2, \quad \{x\} \equiv x \text{ minus nearest integer.} \quad (54)$$

We are interested in the gaps  $\tau = \Delta t$  between successive *upzeros* of (52); we represent these fairly adequately by the corresponding gaps  $\Delta r$  between successive solutions of (53). The mean gap is  $\langle \tau \rangle = \langle \Delta r \rangle = 1/L$ ,

where  $L$  is the asymptotic frequency of upzeros; for the representation 4.6(73) of  $f(t)$ ,  $L$  is precisely 4.6(78).

For the case  $n=2$ , 4.6(78) gives  $L=2h\sqrt{(A_1/a_1a_2)}$ , and (53) may be written

$$\{\nu_1 r\}^2 < L^2/4. \quad (55)$$

I solved this<sup>5</sup> in terms of the continued fraction for  $\nu_1$ , but Florek<sup>6</sup> has put the result more simply. Let  $R_1$  and  $R_2$  be the smallest positive integers satisfying

$$-L < \{\nu_1 R_2\} < 0 < \{\nu_1 R_1\} < L. \quad (56)$$

Then the *only* gaps  $\Delta r$  between successive solutions of (55) are

$$\Delta r = R_1, R_2, R_1 + R_2, \quad (57)$$

and these occur in numbers asymptotically proportional to

$$L - \{\nu_1 R_1\} : L + \{\nu_1 R_2\} : \{\nu_1 R_1\} - \{\nu_1 R_2\} - L. \quad (58)$$

Thus there are two basic gaps  $R_1, R_2$  between the upzeros of  $f(t)$ , the sum  $R_1+R_2$  also occurring when the increment of  $|\{\nu_1 r\}|$  due to a change  $R_1$  or  $R_2$  would overshoot the range in (55). This is very much a discrete distribution, and it would be only slightly smudged if we incorporated the small fractional parts of  $\Delta t$  in the gaps.

For the case  $n=3$ , the inequality (53) represents the points  $P_r$  with coordinates  $x = \{\nu_1 r\}$ ,  $y = \{\nu_2 r\}$  which lie inside the ellipse  $\phi(x, y) = h^2$ . If  $r$  and  $r+\Delta r$  give successive upzeros, so will  $s$  and  $s+\Delta r$  if the points  $P_r$  and  $P_s$  are close together in the ellipse (allowing for certain internal boundary conditions), since the vectors  $\overrightarrow{P_r P_{r+\Delta r}}$  and  $\overrightarrow{P_s P_{s+\Delta r}}$  are equal. Thus we can demarcate areas  $\alpha_1, \alpha_2, \dots$  of the ellipse such that gaps of lengths  $R_1, R_2, \dots$  arise from points  $P_r$  in  $\alpha_1, \alpha_2, \dots$  respectively. As the points  $P_r$  are uniformly dense in the ellipse (compare 4.6), the asymptotic numbers of gaps  $R_1, R_2, \dots$  are proportional to the areas. This is a practicable method, although its theoretical basis is not complete.

A general conjecture based on these investigations is that for a sum (52) of  $n$  terms with the upzeros represented by (53) (as for small  $\sum a_i - q$ ) there are  $n$  basic gaps  $\Delta r = R_1, \dots, R_n$ , together with a limited set of combination gaps of the type  $\sum \lambda_u R_u$ , the  $\lambda_u$  being non-negative integers. This conjecture is supported by all the results which have been obtained, for  $n=3$  to 7 and various frequencies, by running the inequality (53) on the computers at Manchester and

Leeds Universities.\* To mention two examples, both with the  $a_i = 1$  and  $\nu_n = 1$ ,

$$(i) \quad n = 3, \quad \nu_1 = \sqrt{133} - 11, \quad \nu_2 = 3\pi - 9, \quad q = 2.75;$$

the gaps for  $r \leq 51,102$  are 19, 28, 45 (basic) and 47, 73, 92, 120 (combination gaps), occurring respectively 94, 92, 85, 470, 97, 122, and 21 times.

(ii)  $n = 7$ ,  $q = 6$ ,  $\nu_i =$  fractional part of  $\sqrt{N}$ , with  $N = 2, 3, 5, 7, 11, 73$ ; up to  $r = 111,286$  there are seven basic gaps and thirty-six combinations ( $\Delta r = 22$  and  $2,397$  occur 12 and 5 times respectively). These numbers indicate the desirability of a statistical treatment for larger  $n$ .

**Gamma-type distributions.** For  $n \geq 5$  the gap lengths become sufficiently numerous for us to attempt to represent them by a continuous distribution. How best to do this requires further investigation, but a moderate fit can be obtained with the Gamma-type distribution (46). For example (ii) above, the theoretical mean gap calculated from 4.6(79) is  $\langle \tau \rangle = 1/L = 927$ ; if we assume a distribution (46) with  $u = 2$ , this implies (from the relations (59) below of the moments) that  $\langle \tau^2 \rangle^{\frac{1}{2}} = 1,135$ ,  $\langle \tau^3 \rangle^{\frac{1}{3}} = 1,337$ . The run mentioned in (ii) above was rather short for reliable statistics but gave  $\langle \tau \rangle$ ,  $\langle \tau^2 \rangle^{\frac{1}{2}}$ ,  $\langle \tau^3 \rangle^{\frac{1}{3}}$  as 912, 1155, 1324, in moderate agreement. I think that in the chemical problem it is reasonable to assume a Gamma-type distribution of gaps with  $u$  about 2, although, for very small ( $\sum a_i$ ) -  $q$ ,  $u$  is probably effectively less than 2 and so nearer to the "random" case  $u = 1$ .

**General values of  $q$ .** For values of  $q$  not near the limit  $\sum a_i$ , we naturally use the exact form (52) of  $f(t)$  and measure the exact gaps  $\tau = \Delta t$  between upzeros, and not integer approximations. In this case machine computations give us samples from a truly continuous distribution  $h(\tau)d\tau$ , although for small  $n$  there is again a noticeable bunching of  $h(\tau)$  as  $q$  rises.

For the Gamma-type distribution (46), the relations between the moments  $m_1 = \langle \tau \rangle = 1/L$ ,  $m_2 = \langle \tau^2 \rangle$ ,  $\dots$ , are

$$m_2/m_1^2 = 1 + u^{-1}, \quad m_3/m_1m_2 = 1 + 2u^{-1}, \quad m_4/m_1m_3 = 1 + 3u^{-1}, \quad (59)$$

where  $u$  is the parameter of the distribution. We may test the distribution of a sample run of  $\tau$ s for a given  $f(t)$  by calculating  $u$  from the observed sample values of  $m_1$  and  $m_2$  from the first relation (59), and then seeing how close the observed  $m_3$  and  $m_4$  are to the values predicted by the other relations of (59).

\* I am grateful for the cooperation of R. A. Brooker and A. S. Douglas in these universities, and for the extensive work undertaken by A. J. Mitchell.

This test was applied to  $f(t)$  with  $n=7$  and with the  $a_i$  and  $\nu_i$  as in example (ii) above, for  $q=0, 0.9, 1.8, 2.7, 3.6$ . For runs of about 200 gaps in each case, it was found that the observed and the predicted values of  $m_3^{\ddagger}$  and of  $m_4^{\ddagger}$  agreed (to about  $\frac{1}{2}$  and 1 per cent respectively), so that the Gamma-type appears a reasonable representation. The estimated values of  $u$  for these five  $q$ s were respectively

$$u = 6.75, 5.9, 4.8, 3.2, 2.2. \quad (60)$$

These values of the parameter show a striking change in the distribution with increasing  $q$ . The first four large values of  $u$ , however, represent cases where  $\sum a_i > 2q$ . These are almost wholly irrelevant to the chemical problem, since very few molecules indeed have energies such that the breaking coordinate could reach twice its critical value.

The tentative conclusion from this work is that we may fairly confidently treat the distribution of gaps as approximately of Gamma type, with a parameter  $u$  about 2, and not very far removed from the usually assumed "random" distribution. This tentative conclusion must await confirmation by a proper mathematical analysis of the gaps. All this, of course, refers to the strictly harmonic model; if we wish to treat more general potentials, we must return to the phase-space or "transition-state" form (14) or (18) of the general rate constant  $k$ .

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## Quantum Harmonic Oscillator Models

AN attempt is made in this concluding chapter to come a little closer to reality by treating the harmonic oscillator model (apart from collisional effects) quantum mechanically. Three desirable properties of a quantum unimolecular theory are (a) a logical or well-principled structure, (b) computable formulas for not too small molecules, and (c) results agreeing with experiment. The present models, like the others I have met, are deficient in one or another of these properties, but they should be viewed as trial steps, possibly in the right direction.

The model in 10.1 makes no claim to be logical, although it may be roughly right. It is a combination of a quantized distribution of normal-mode energies with the classical dissociation probability  $L$  of earlier chapters. In an earlier attempt to evaluate  $k^\infty$  on this model, I found something like a transition-state formula, with a mixture of classical and quantum partition functions. I have discarded this here in favor of a better approximation, although this merely shows that the general-concentration rate constant  $k$  is probably close to that of the classical model of Chapter 7.

The rest of the chapter is on the thesis that, if dissociation results from passage through a critical configuration, the molecule should be described in terms of coordinates and momenta, and not mode energies, as primary observables. For this description I use Moyal's statistical quantum theory;<sup>1</sup> this is peculiarly simple for the harmonic model, since the phase-space distribution elements in this case behave classically, although the equilibrium distribution as a whole has nonclassical parameters. The high-concentration rate constant  $k^\infty$  is accordingly set up in 10.2 as the quasi-classical flow of this distribution through dissociation (although I have to ignore any effect of the cutoff in the distribution at the critical configuration). In 10.3  $k^\infty$  is expressed in terms of matrices and series. More importantly it is found that the activation energy  $E_a^\infty$  is dependent on temperature; and the removal

of a factor  $\exp(-E_a^\infty/\kappa T)$  from  $k^\infty$  leaves us with an  $A$ -factor suggesting (although quasi-thermodynamic notions are avoided) a negative entropy of activation.

In 10.4  $k^\infty$  is reformulated in terms of the variables  $\epsilon_i$  and  $\psi_i$ , which are the mathematical expressions for the normal-mode energies and phases in terms of the coordinates and velocities  $Q_i$  and  $\dot{Q}_i$ ; as the latter are still the primary observables, the  $\epsilon_i$  have continuous probability distributions. The classical-deterministic behavior of the elements of the distribution now enables us to use the classical concepts of specific dissociation probabilities of interesting conditions (or "states"). Thus in 10.4,  $k^\infty$  appears as the average, over the continuous distribution of the  $\epsilon_i$ , of the mean dissociation frequency  $L$ ; this is analogous to the classical calculation in Chapter 5. Similarly in 10.5 we extend this to the general-concentration rate constant  $k$ , both for the assumption (as in Chapter 7) of "random incidence" of dissociation and also (as in Chapter 9) for the refined model involving specific lifetimes; this is a new development.

The various forms of rate constant (for high or low concentrations, and for medium concentrations with "random" or with specialized lifetime distributions) all approach the corresponding classical forms at high temperatures. Without appealing to this result, however, we are able in 10.6 to extend previous methods of calculation to estimate (at any temperature) the quantum rate constant  $k$ , or the decline  $k/k^\infty$ . It is also noted how the new parameters in the quantum rates influence comparisons with the classical theory, and this is briefly illustrated by the case of nitril chloride. In the concluding remarks, some dubious and unsatisfactory features of the present quantum model are mentioned. The model has enough good points to suggest that one might at this stage try to strengthen it by reassessing the basic distribution, so as to make some allowance for energy considerations.

### 10.1 A HYBRID THEORY

The high-concentration rate constant  $k^\infty$  was formulated in 5.3 as the dissociation frequency  $L$  averaged over the *classical* equilibrium distribution 5.3(10) of normal-mode energies  $\epsilon_i$ . Dr. J. Bigeleisen suggested that we should replace this by the discrete quantum energy distribution, retaining the classical form of  $L$ . This is in the spirit of activated-complex theory, in which quantum partition functions are combined with classical motion and energy in the reaction coordinate. I once stated<sup>2</sup> the form of  $k^\infty$  corresponding to Bigeleisen's suggestion but did not develop it. Here we formulate the general-concentration

rate constant  $k$  for this model, although the investigation will not be very deep.

**The formulation.** In quantum theory the possible results  $\epsilon'_i$  of measuring the energy  $\epsilon_i$  of an oscillator or normal mode of classical frequency  $\nu_i$  are

$$\epsilon'_i = (m_i + \frac{1}{2})h\nu_i, \quad m_i = 0, 1, 2, \dots, \quad (1)$$

and in an assembly at temperature  $T$  the proportion of oscillators with conceptually measurable energy  $\epsilon'_i$  is

$$(1 - u_i)u_i^{m_i}, \quad u_i \equiv \exp(-h\nu_i/\kappa T). \quad (2)$$

For an assembly of "harmonic" molecules, the equilibrium distribution of vibration energy (considered as observable) is the product of these expressions for the normal modes  $i=1, 2, \dots, n$ . We assume now that the specific dissociation rate for energies  $\epsilon'_i$  is represented by  $L(\epsilon'_1, \dots, \epsilon'_n)$ , the classical frequency with which the critical coordinate  $q_1$  would attain the value  $q$ , as in Chapters 5 and 7. Combining this with the quantal energy distribution, we have for the general rate constant analogous to 7.1(2)

$$k = \left\{ \prod_1^n (1 - u_i) \right\} \cdot \sum_{m_1} \dots \sum_{m_n} \{ u_1^{m_1} \dots u_n^{m_n} \omega L(\epsilon'_1 \dots) / [\omega + L(\epsilon'_1 \dots)] \}, \quad (3)$$

with the  $\epsilon'_i$  given by (1), and the summation extended over all  $m_i$  for which  $L > 0$ . Here  $L$  is regarded as a function of the energies; if, for example, Kac's formula 4.3(16) is used, the parameters there are  $a_i = |\alpha_i| \sqrt{\epsilon'_i}$ . The limiting first- and second-order forms of (3) are (with  $\omega = zc$  the collision frequency)

$$k^\infty = \left\{ \prod_1^n (1 - u_i) \right\} \sum \dots \sum \{ u_1^{m_1} \dots u_n^{m_n} L(\epsilon'_1, \dots) \}, \quad (4)$$

$$k_{\text{bim}}^0 = z \left\{ \prod_1^n (1 - u_i) \right\} \sum \dots \sum u_1^{m_1} \dots u_n^{m_n}, \quad (5)$$

again summed over integers  $m_i$  for which

$$L(\epsilon'_1, \epsilon'_2, \dots) \equiv L \left\{ (m_1 + \frac{1}{2})h\nu_1, (m_2 + \frac{1}{2})h\nu_2, \dots \right\} > 0. \quad (6)$$

**An approximate evaluation.** We observe that in (2)

$$(1 - u_i)u_i^{m_i} = \int_{m_i, h\nu_i}^{(m_i+1)h\nu_i} \exp(-\epsilon_i/\kappa T) d\epsilon_i/\kappa T, \quad (7)$$

a simple identity which may be viewed as relating the quantum distribution to the classical phase integral. This enables us to write the rate constant (3) as

$$k = \sum_{m_1} \cdots \sum_{m_n} \omega L(\epsilon'_1, \cdots) \{\omega + L(\epsilon'_1, \cdots)\}^{-1} \cdot \prod_1^n \int_{m_i, h\nu_i}^{(m_i+1)h\nu_i} \exp(-\epsilon_i/\kappa T) d\epsilon_i/\kappa T, \quad (8)$$

the summation obeying (6). The *second-order rate constant* (5) may be written similarly; but we prefer to lump the integrations and write it

$$k_{\text{bim}}^0 = z \int \cdots \int e^{-E/\kappa T} d\epsilon_1 \cdots d\epsilon_n / (\kappa T)^n, \quad E \equiv \sum_1^n \epsilon_i, \quad (9)$$

where the boundary of integration has to be pieced together from the ranges and summation as in (8), using (6). The inequality (6) is by 5.2(2) equivalent to

$$\sum_1^n |\alpha_{1i}| (m_i h\nu_i + \frac{1}{2} h\nu_i)^{\frac{1}{2}} - q > 0. \quad (10)$$

We can construct "minimal sets"  $m'_1, \cdots, m'_n$  of nonnegative integers which satisfy (10) but would not do so if any nonzero member of a set were decreased by unity. If in the positive part  $P$  ( $\epsilon_1 \geq 0, \cdots, \epsilon_n \geq 0$ ) of a Euclidean space ( $\epsilon_1, \cdots, \epsilon_n$ ) we draw all the hyperplanes  $\epsilon_i = m'_i h\nu_i$  for all minimal sets  $m'_i$ , these will enclose a region  $R$  of  $P$ . It will be seen that the integrals (8) and (9) are over  $P$  excluding the region  $R$ .  $R$  is bounded by parts of the coordinate planes ( $\epsilon_i = 0$ ) and a "rough" surface  $S$  composed of orthogonal plane facets, and this (with the exterior parts of the coordinate planes) is the boundary of integration in (8) and (9).

The approximation suggested for  $k_{\text{bim}}^0$  is to replace the boundary  $S$  by the smooth surface

$$\sum_1^n |\alpha_{1i}| \sqrt{\epsilon_i} - q = 0. \quad (11)$$

With this approximation, which appears reasonably good, the second-order rate constant (9) agrees exactly with the classical formula 7.2(13).

In the *general rate* (8),  $L$  is to be evaluated at the midpoint  $\epsilon'_i = (m_i + \frac{1}{2})h\nu_i$  of the ranges shown in the integrals. The natural approximation here is to extend the integration over the factor  $\omega L/(\omega + L)$ ,

replacing in  $L$  the  $\epsilon_i'$  by the current variables  $\epsilon_i$ , of integration. This gives for (8)

$$k = \int \cdots \int \omega L(\epsilon_1, \cdots) \{ \omega + L(\epsilon_1, \cdots) \}^{-1} \cdot e^{-E/\kappa T} d\epsilon_1 \cdots d\epsilon_n / (\kappa T)^n. \quad (12)$$

We may again replace the boundary  $S$  of integration by (11); this appears a better approximation the larger  $\omega$  is, since  $L(\epsilon_1, \cdots) = 0$  on (11), and  $L$  is small near the boundary. The effect of replacing  $L(\epsilon_i', \cdots)$  by  $L(\epsilon_i, \cdots)$  in the integral may be examined at high concentrations and not too low temperatures by expanding

$$L(\epsilon_i', \cdots) - L(\epsilon_i, \cdots),$$

using Kac's formula for  $L$ ; the error here appears to be moderately small and (as might be expected on general principles) tends to zero at high temperatures

Since (12) with the boundary (11) is the general classical rate constant 7.1(2), we find that in the present approximations the hybrid classical-quantum rate of (3) is the same as the classical rate. This sort of result is not new; for example, the high-concentration rate constant 2.6(89) of Kassel's quantum theory is the same as on his classical theory at all temperatures.

## 10.2 COORDINATE AND VELOCITY DISTRIBUTIONS

The hybrid nature of the theory of 10.1 lay in the combination of a discrete quantal energy distribution with a classical transition frequency. If in fact dissociation is determined by measuring a velocity of transition through a configuration ( $q_1 = q$ ), we are concerned primarily with distributions of coordinates and velocities (or momenta) rather than of energy, which becomes a secondary characteristic. The formulation of  $k^\infty$  now to be described began, in fact, as an adaptation of the method at the end of 6.3, the adaptation consisting in replacing the classical Gaussian coordinate distribution by the quantum distribution (due originally to Bloch<sup>3</sup>) and replacing the velocity distribution similarly. It occurred to me afterward, however, that this procedure could be regarded as an application of Moyal's statistical treatment of quantum theory,<sup>1</sup> which was worked out for the harmonic oscillator by Bartlett and Moyal.<sup>4</sup> Before the formulation of  $k^\infty$  is begun, some relevant ideas and formulas of Moyal will be mentioned.

In Moyal's work the behavior of a phase-space probability distribution  $F(Q, P; t)$  of a quantum system with Hamiltonian  $H(Q, P)$  is determined by the equation (equivalent in its consequences to Schrödinger's equation)

$$\frac{\partial F}{\partial t} = \frac{4\pi}{h} \left[ \sin \frac{h}{4\pi} \left( \frac{\partial}{\partial P_F} \frac{\partial}{\partial Q_H} - \frac{\partial}{\partial P_H} \frac{\partial}{\partial Q_F} \right) \right] H(Q, P) F(Q, P; t), \quad (13)$$

where a subscript  $F$  or  $H$  indicates whether the operator is to affect  $F$  or  $H$  respectively. For the harmonic oscillator, with  $H$  quadratic in  $Q$  and  $P$ , only the linear terms in the expansion of the sine are of effect, so that (13) becomes (compare also Wigner<sup>6</sup>)

$$\frac{\partial F}{\partial t} = \frac{\partial H}{\partial Q} \frac{\partial F}{\partial P} - \frac{\partial H}{\partial P} \frac{\partial F}{\partial Q}. \quad (14)$$

This is as in *classical* mechanics; so that a phase-space distribution of oscillator probability has the same deterministic behavior in quantum as in classical mechanics (compare also the work of Coulson and Rushbrooke<sup>6</sup>).

These probability distributions refer primarily to a single dynamical system (e.g., one oscillator), but Moyal and Bartlett extended the results to statistical mechanical assemblies. For convenience we take the Hamiltonian of an oscillator of frequency  $\nu, \equiv \lambda/(2\pi)$  to be  $H = Q_i^2 + \frac{1}{4}\lambda_i P_i^2$ ; also for convenience we replace the momentum  $P_i$  by the coordinate velocity  $\dot{Q}_i = \frac{1}{2}\lambda_i P_i$ , so that the energy takes the form standard in this book (compare 3.5(62))

$$\epsilon_i = \dot{Q}_i^2 + \dot{Q}_i^2/\lambda_i, \quad (\lambda_i = 4\pi^2\nu_i^2). \quad (15)$$

The result of Bartlett and Moyal, converted to this notation, for a Maxwell-Boltzmann equilibrium assembly at temperature  $T$  is that the proportion of oscillators with  $Q_i$  and  $\dot{Q}_i$  in given small ranges  $dQ_i$  and  $d\dot{Q}_i$  is

$$(4\pi^2\sigma_i^2\nu_i)^{-1} \exp \left\{ -(Q_i^2 + \dot{Q}_i^2\lambda_i^{-1})/2\sigma_i^2 \right\} dQ_i d\dot{Q}_i, \quad (16)$$

where

$$2\sigma_i^2 = \frac{1}{2}h\nu_i \coth(h\nu_i/2kT). \quad (17)$$

The distribution (16) is seen to correspond to a Gaussian distribution of  $Q_i$  (being that of Bloch<sup>3</sup>) and an independent Gaussian distribution of  $\dot{Q}_i$ ; the mean squares are

$$\langle \dot{Q}_i^2 \rangle = 2\sigma_i^2, \quad \langle Q_i^2 \rangle = \lambda_i\sigma_i^2. \quad (18)$$

It is seen from (17) that the product  $\sigma_i \cdot \sigma_i \sqrt{\lambda_i}$  exceeds the Heisenberg limit  $\hbar/4\pi$  at all positive temperatures. This is for the assembly; but it is also a consequence of Moyal's theory that the Uncertainty Principle is obeyed by the phase-space distributions for the individual systems.

The mean energy of an oscillator of the assembly, as calculated from measurements of  $Q_i$  and  $\dot{Q}_i$ , is

$$\begin{aligned} \langle \epsilon_i \rangle &= \langle \dot{Q}_i^2 \rangle + \langle Q_i^2 \rangle / \lambda_i = 2\sigma_i^2 \\ &= \frac{1}{2}\hbar\nu_i \coth(\hbar\nu_i/2\kappa T) = \frac{1}{2}\hbar\nu_i + \hbar\nu_i / \{ \exp(\hbar\nu_i/\kappa T) - 1 \}. \end{aligned} \quad (19)$$

This agrees with the mean energy  $\langle \epsilon_i' \rangle$  (including zero-point energy) in an assembly of oscillators which have directly measurable and so quantized energies  $\epsilon_i'$ . This agreement is in fact inherent in the way Bartlett and Moyal set up their representation of a "Maxwell-Boltzmann" assembly,\* but it is important to observe that in our original assembly, with  $Q_i$  and  $P_i$  as the primary observables, it is not to be thought that we can measure energies independently, so that our  $\epsilon_i$  are not quantized. For our original assembly, the calculated mean square deviation of the energy is  $\langle Q_i^2 + \dot{Q}_i^2 / \lambda_i - \langle \epsilon_i \rangle \rangle^2 = \langle \epsilon_i \rangle^2$ ; whereas for an assembly with measured and so discrete energies  $\epsilon_i' = (n_i + \frac{1}{2})\hbar\nu_i$ , the deviation is smaller,<sup>4</sup> namely,  $\langle \epsilon_i' - \langle \epsilon_i' \rangle \rangle^2 = \langle \epsilon_i' \rangle^2 - (\frac{1}{2}\hbar\nu_i)^2$ . This dual role of  $\frac{1}{2}\hbar\nu_i$ , as zero-point energy and as diminution of the scatter for discrete energies, may be important in a reassessment of the present application to kinetics.

**Application to molecules.** We consider the vibrating molecule as a combination of  $n$  normal modes or oscillators  $Q_1, \dots, Q_n$ ; the coordinate  $q_1$  and velocity  $\dot{q}_1$  are then given by 3.4(35) as

$$q_1 = \sum \alpha_{1i} Q_i, \quad \dot{q}_1 = \sum \alpha_{1i} \dot{Q}_i. \quad (20)$$

In an equilibrium assembly these sums, being compounded of independent Gaussian distributions, have themselves Gaussian distributions, that of  $\dot{q}_1$  being independent of that of  $q_1$ . The mean squares, from (17), (18), and (20), are

$$\begin{aligned} \langle q_1^2 \rangle &\equiv \sigma^2 = \sum \alpha_{1i}^2 \sigma_i^2 = \frac{1}{2}\kappa T \sum \alpha_{1i}^2 y_i \coth y_i, \\ \langle \dot{q}_1^2 \rangle &\equiv \sigma^2 = \sum \alpha_{1i}^2 \lambda_i \sigma_i^2 = \frac{1}{2}\kappa T \sum \alpha_{1i}^2 \lambda_i y_i \coth y_i, \end{aligned} \quad (21)$$

\* The *mathematical* framework of energy eigenfunctions remains beneath the continuous  $(Q, P)$  distribution of probability of a single system, and similarly the Maxwell-Boltzmann energy distribution  $\exp(-\epsilon_i'/kT)$  beneath the assembly distribution. An essential feature of Moyal's argument is that the distribution of a variable depends on the choice of basic observables, so that when energy is not a primary observable its calculable values correspond to a continuum with a larger scatter than when it is observable and discrete.

where for convenience we write

$$y_i = hv_i/(2\kappa T). \quad (22)$$

For these distributions, the proportion of molecules having  $q_1$  in the range  $q$  to  $q+dq_1$  is  $P_q dq_1$ , where

$$P_q = (2\pi\sigma^2)^{-\frac{1}{2}} \exp(-q^2/2\sigma^2); \quad (23)$$

also the mean absolute value of the velocity  $\dot{q}_1$  is (from the usual relation of mean and mean square in a Gaussian distribution)

$$\langle |\dot{q}_1| \rangle = (2/\pi)^{\frac{1}{2}} (\dot{q}_1^2)^{\frac{1}{2}} = (2/\pi)^{\frac{1}{2}} \dot{\sigma}. \quad (24)$$

**The first-order rate constant.**<sup>2</sup> For the present equilibrium distribution the proportion of the distribution flowing per second from configurations with  $q_1 < q$  to  $q_1 > q$  (compare 6.2) is

$$P_q \int_0^\infty \dot{q}_1 P(\dot{q}_1) d\dot{q}_1 = \frac{1}{2} P_q \langle |\dot{q}_1| \rangle. \quad (25)$$

We now turn suddenly to the dissociation problem, assuming that dissociation occurs at the configuration  $q_1 = q$ . At high concentrations we assume that we have effectively the equilibrium distribution, even right up to these configurations; so that the flow (25) represents the *first-order rate constant*. We have then by (23) and (24)

$$k^\infty = \dot{\sigma} (2\pi\sigma)^{-1} \exp(-q^2/2\sigma^2), \quad (26)$$

with  $\sigma$  and  $\dot{\sigma}$  as in (21).

For use in (21) here and later, we remark that for  $|y| < \pi$

$$y \coth y = 1 + y^2/3 - y^4/45 + 2y^6/945 - y^8/4725 \dots \quad (27)$$

As  $T \rightarrow \infty$ , the  $y_i \rightarrow 0$  in (22), and  $y_i \coth y_i \rightarrow 1$ , so that in (17)  $\sigma_i^2 \rightarrow \frac{1}{2} \kappa T$ , the classical value used in 6.3, and in (21)  $\sigma$  and  $\dot{\sigma}$  approach the corresponding classical forms. The present theory then merges with the classical theory of 6.3. This is useful support, although of course it is not sufficient in itself to validate the present theory.

### 10.3 CALCULATION OF THE FIRST-ORDER RATE CONSTANT

We find here some more useful or illuminating forms of the rate constant (26). The factor  $\dot{\sigma}/(2\pi\sigma)$  is expressed first as a mean frequency, and  $\sigma$  and  $\dot{\sigma}$  are then given in matrix and series forms. The exponential factor  $\exp(-q^2/2\sigma^2)$  of the rate is then examined and proved to be smaller than  $\exp(-E_a^\infty/\kappa T)$ , where  $E_a^\infty$  is the activation energy; we shall return to this point in 10.6.

**The quantum mean frequency.** Positive weighting factors  $\mu_i$  (analogous to the classical  $\mu_i$  of 5.2(7) and approaching them at high temperatures) are defined in conjunction with (21) as

$$\mu_i = |\alpha_{1i}| \sigma_i / \sigma \quad \left( \sum_1^n \mu_i^2 = 1 \right). \quad (28)$$

A quantum mean frequency is defined as

$$\nu = \sqrt{(\sum \mu_i^2 \nu_i^2)} = \nu / (2\pi\sigma), \quad (29)$$

the second form following from (21). Thus the first-order rate constant (26) is

$$k^\infty = \nu \exp(-q^2/2\sigma^2). \quad (30)$$

As a mean,  $\nu$  lies between the least and greatest of the vibration frequencies  $\nu_i$ , although it changes gradually with temperature because of the behavior of the  $\sigma_i$ . It approaches the classical mean  $\nu$  of 5.4(22) when either (a)  $T \rightarrow \infty$  or (b) the frequencies  $\nu_i$  tend toward equality.

**Matrix formulas.** The mean squares in (17) and (21) may be written

$$\sigma_i^2 = \frac{1}{2} \kappa T \phi(\lambda_i), \quad \sigma^2 = \frac{1}{2} \kappa T \sum \alpha_{1i}^2 \phi(\lambda_i), \quad \dot{\sigma}^2 = \frac{1}{2} \kappa T \sum \alpha_{1i}^2 \lambda_i \phi(\lambda_i), \quad (31)$$

where

$$\phi(x^2) \equiv (\hbar x / 2\kappa T) \coth(\hbar x / 2\kappa T). \quad (\hbar \equiv h/2\pi). \quad (32)$$

Returning to the kinetic and potential energy matrices  $\mathbf{a}$  and  $\mathbf{b}$  of Chapter 3, with also  $\mathbf{c} = \mathbf{a}^{-1}\mathbf{b}$ ,  $\mathbf{h} = \mathbf{b}^{-1}$ , we recall the matrix equation 3.4(59). The (1, 1) element of this equation is

$$\sum_i \alpha_{1i}^2 \lambda_i^m = (\alpha \lambda^m \alpha')_{11} = 2(\mathbf{c}^m \mathbf{h})_{11}. \quad (33)$$

Thus when we may legitimately expand  $\phi(\lambda_i)$  in a power series (compare (27) and (32)), we have in (31)

$$\sigma^2 = \kappa T \{ \phi(\mathbf{c}) \mathbf{h} \}_{11}, \quad \dot{\sigma}^2 = \kappa T \{ \mathbf{c} \phi(\mathbf{c}) \mathbf{h} \}_{11}. \quad (34)$$

This enables us to express the rate (30) in terms of the energy matrices (the high-temperature limiting or classical form being 6.3(42)). The formula (34) for  $\sigma^2$  is related to one of Higgs;<sup>7</sup> it is also of interest in electron diffraction measurements as the value of  $\langle q_1^2 \rangle$  when  $q_1$  is the extension of an interatomic distance.

**Expansions.** From (27), when  $y_i = h\nu_i/(2\kappa T) < \pi$  for all the frequencies, we may expand (31) as

$$\begin{aligned}\sigma^2 &= \frac{1}{2}\kappa T \sum \alpha_{i1}^2 (1 + y_i^2/3 - \dots) \\ &= \frac{1}{2}\kappa T \alpha^2 (1 + \gamma^2 \langle \nu^2 \rangle / 3 - \gamma^4 \langle \nu^4 \rangle / 45 + \dots),\end{aligned}\quad (35)$$

$$(\dot{\sigma}/2\pi)^2 = \frac{1}{2}\kappa T \alpha^2 (\langle \nu^2 \rangle + \gamma^2 \langle \nu^4 \rangle / 3 - \gamma^4 \langle \nu^6 \rangle / 45 + \dots),\quad (36)$$

where  $\alpha^2 = \sum \alpha_{i1}^2$ ,  $\langle \nu^m \rangle = \sum \alpha_{i1}^2 \nu_i^m / \alpha^2$ , and  $\gamma = h/(2\kappa T)$ . The expansions use the classically weighted moments of the frequencies; in particular,  $\langle \nu^2 \rangle$  is the classical mean frequency 5.4(22).

**Activation energy.** When  $T$  is so large that  $\gamma^2$  is negligible in (35), the exponent in the rate constant (30) is

$$q^2/(2\sigma^2) = q^2/(\alpha^2 \kappa T) = E_0/\kappa T,\quad (37)$$

where  $E_0 = q^2/\alpha^2$  is the critical energy, or high-concentration activation energy, of the classical theory. Although we have not introduced the concept of critical energy in the present quantum theory, it is natural to introduce the experimental parameter called activation energy by the operational definition  $E_a^\infty = \kappa T^2 d \ln k^\infty/dT$  of 2.8. Using the exact form (21) of  $\sigma^2$  but neglecting the small temperature change of  $\nu$ , we have then for the rate (30) (since from (22)  $T dy_i/dT = -y_i$ )

$$\frac{E_a^\infty}{\kappa T} = -T \frac{d}{dT} \left( \frac{q^2}{2\sigma^2} \right) = \frac{q^2}{2\sigma^2} \frac{1}{\chi},\quad (38)$$

where

$$\chi = \chi(T) = \sum \alpha_{i1}^2 y_i \coth y_i / \left( \sum \alpha_{i1}^2 y_i^2 \operatorname{cosech}^2 y_i \right).\quad (39)$$

This function is calculable from the vibrational parameters, so that (38) may be regarded as determining the critical stretch  $q$  in terms of measurements of  $E_a^\infty$ . It is clear that in this theory  $E_a^\infty$  changes with temperature.\*

Using (38), we may now write the rate constant (30) as

$$k^\infty = \nu e^{S'/\kappa} \exp(-E_a^\infty/\kappa T),\quad (40)$$

where

$$S' = \frac{E_a^\infty}{T} - \frac{\kappa q^2}{2\sigma^2} = \frac{E_a^\infty}{T} (1 - \chi).\quad (41)$$

\* In regarding the activation energy as an experimental parameter to be used in theoretical calculations, I have in mind the usual observational restriction of unimolecular reactions to a quite narrow temperature range, where the variation of  $E_a^\infty$  is not likely to be very considerable.

Since  $y \coth y > y^2 \operatorname{cosech}^2 y$ , it follows from (39) that  $\chi > 1$ , so that  $S'$  is essentially negative. Thus the rate constant (40) is essentially smaller than  $\nu \exp(-E_a^\infty/\kappa T)$ .

#### 10.4 AN ALTERNATIVE FORMULATION

We set up in (15) below a new form of the high-concentration rate constant. This could be obtained from the form (26) by the reverse of the mathematical transformation used in 6.1, but we prefer to view the problem afresh in order to introduce concepts that will be needed later for general-concentration rates.

Continuing to regard  $Q_i$  and  $\dot{Q}_i$  as the primary observables for an oscillator, we introduce auxiliary mathematical variables  $\epsilon_i$  and  $\psi_i$  as

$$\epsilon_i = Q_i^2 + \dot{Q}_i^2/\lambda_i, \quad \psi_i = (2\pi)^{-1} \tan^{-1} \{ -\dot{Q}_i/(Q_i\sqrt{\lambda_i}) \}. \quad (42)$$

Transforming the distribution (16) into these variables, we find that the fraction  $F(\epsilon_i, \psi_i)d\epsilon_i d\psi_i$  of oscillators with  $\epsilon_i$  and  $\psi_i$  ( $0 \leq \psi_i < 1$ ) in given small ranges has

$$F(\epsilon_i, \psi_i) = F(\epsilon_i) = (2\sigma_i^2)^{-1} \exp(-\epsilon_i/2\sigma_i^2); \quad (43)$$

this distribution is independent of  $\psi_i$ .

For the molecules, regarded as sets of vibrators, the motion of the elements of the phase-space distribution evolves continuously as in classical mechanics (from (14) as reached by Moyal). Thus an element of the distribution (not to be considered as composed of individual molecules) at  $(\epsilon_i, \psi_i)$  at  $t=0$  evolves into an element at  $(\epsilon_i, \psi_i + \nu_i t)$  at time  $t$ . The corresponding values of the critical molecular coordinate are

$$q_1 = \sum \alpha_{1i} \sqrt{\epsilon_i} \cos 2\pi\psi_i, \quad q_1 = \sum \alpha_{1i} \sqrt{\epsilon_i} \cos 2\pi(\nu_i t + \psi_i). \quad (44)$$

Thus the proportion of the distribution, with given  $\epsilon_i$  and random  $\psi_i$ , which passes outward through the configuration  $q_1 = q$  per second is  $L$ , the frequency of upward zeros of the function  $(\sum \alpha_{1i} \sqrt{\epsilon_i} \cos 2\pi\nu_i t) - q$ .

Assuming again that the equilibrium distribution is present right to the boundary, the first-order rate constant as the average of  $L$  over the distribution (43) is

$$k^\infty = \int \cdots \int_0^\infty L(\epsilon_1, \cdots, \epsilon_n) \prod_1^n F(\epsilon_i) d\epsilon_i. \quad (45)$$

This integral may be evaluated by the method of 5.4, using Kac's formula for  $L$ . The result is (26), or equivalently (30) with the quantum form of  $\nu$ .

This method is close to that in 10.1; the essential difference is the direct use of continuous variables instead of the discrete  $\epsilon'_i$  of 10.1.

### 10.5 THE GENERAL-CONCENTRATION RATE CONSTANT

The following extension to general concentrations is based on the second or "direct" formulation (around 2.3(18)) in 2.3, although we shall also bring in the "refined" ideas of Chapter 9.

In the coordinate-velocity space  $(Q_1, \dots, \dot{Q}_n)$ , we define "interesting" configurations as those connected by *classical* dynamical orbits with the dissociation configuration, as in 9.1. If the gas were not dissociating, the number of molecules near a given interesting configuration would be  $cd_f$ , with  $c$  the concentration and  $d_f$  the product of elements (16) for  $i=1, \dots, n$ . The number losing interest through collisions would be  $\omega c d_f$  per second; by "detailed balancing" the same number would be rendered interesting. We assume as before that collisions throw the same number  $\omega c d_f$  into an interesting range in the actual dissociating gas. Expressing this number in terms of the auxiliary variables  $\epsilon_i, \psi_i$  of (42), we say that the number

$$\omega c \prod_1^n F(\epsilon_i) d\epsilon_i \quad (46)$$

enter, per second, interesting configurations near  $\epsilon_i$ , with random values of the  $\psi_i$ .

The following three paragraphs discuss two alternative procedures and the difficulty of generalizing to anharmonic systems.

(i) If we ignore for the moment the work of Chapter 9 and revert to the earlier assumption that in the classical picture the incidence of dissociation is "random," then we obtain the same random incidence in the quantum model, owing to the corresponding behavior of quantum and classical phase-space elements. This gives as before for the proportion of the molecules (46) which do dissociate the ratio  $L/(\omega+L)$ . Thus the *general rate constant* is, with  $F(\epsilon_i)$  as in (43),

$$k = \int \dots \int \omega L (\omega + L)^{-1} \prod_1^n F(\epsilon_i) d\epsilon_i, \quad (47)$$

which is the form of  $k$  we shall mostly use.

(ii) It is clear that, by appealing to the correspondence of behavior of the quantum and classical elements of harmonic oscillator distributions, we could have followed the refined method of Chapter 9. Thus

for the present model we should arrive at a rate constant of the form 9.3(33), namely,

$$k = \int \cdots \int L(1 - \langle e^{-\omega\tau} \rangle) \prod_1^n F(\epsilon_i) d\epsilon_i, \quad (48)$$

where  $\tau$  has its previous significance as a time gap. This is the most general form of  $k$  available on the present theory.

(iii) In accordance with this last remark, it should be observed that to formulate a quantum theory of this type for *anharmonic systems* would be a much deeper problem, for in this case Moyal's equation (13) would not reduce to (14), and we could not appeal to the classical behavior as a reliable guide to the behavior of the quantum distribution. Thus, for example, we could not directly adapt a general rate of the type 9.1(6) to the quantum model; in addition to the problem of the choice of the quantum  $q$ ,  $p$  distribution, we should have to recalculate the parameter  $s$  (the "time to dissociation") in accordance with the behavior (13) of the "anharmonic" distribution. There is scope here for some heavy research.

#### 10.6 APPROXIMATIONS, COMPARISONS, AND CONCLUDING REMARKS

We shall find here an approximation to the general rate constant (47) and shall mention a corresponding result for the form (48). The former approximation is then compared with the earlier classical theory, and there are some concluding remarks concerning possible modifications and the general position of the theory. First of all, however, an exact comparison (50) is made between the classical and the present quantum rate.

*The general rate constant (47) is, by (43),*

$$k = \int \cdots \int \omega L(\omega + L)^{-1} \prod_1^n \{ \exp(-\epsilon_i/2\sigma_i^2) d\epsilon_i/2\sigma_i^2 \}. \quad (49)$$

Comparing this with the general classical "harmonic" rate constant 7.1(1) and (2) we see that

*the present quantum rate becomes the previous classical rate when we give the mean squares  $\langle Q_i^2 \rangle = \sigma_i^2$  their limiting high temperature form  $\frac{1}{2}\kappa T$ .* (50)

This correspondence extends to the limiting constants  $k^\infty$  (compare the end of 10.2) and  $k_{\text{bim}}^0$ .

The approximations of 7.5 for the general classical rate constant may accordingly be adapted to the quantum rate constant (49) by replacing  $\kappa T$  by  $2\sigma_i^2$  in the appropriate places. The essential step here is to re-define the positive variables  $x_i$  and parameters  $\rho$ ,  $b$  in 7.3(16) as

$$x_i^2 = \epsilon_i/2\sigma_i^2, \quad \rho^2 = b = q^2/2\sigma^2. \quad (51)$$

The region of nonzero  $L$ , namely,  $\sum \alpha_{1i} \sqrt{\epsilon_i} > q$ , becomes in these new variables  $2^{\frac{1}{2}} \sum \alpha_{1i} \sigma_i x_i > q$ . With the  $\rho$  of (51) and the quantum  $\mu_i$  of (28), the region is

$$\sum_1^n \mu_i x_i - \rho > 0. \quad (52)$$

In terms of the variables  $x_i$ , the rate (49) is now formally identical with the exact classical form 7.5(61).

We now proceed to approximate precisely as in 7.5, using my approximation for  $L$ . The corresponding final results are

$$k = k^\infty I_m(\theta), \quad k^\infty = \nu e^{-b} = \nu \left( \sum \mu_i^2 \nu_i^2 \right) e^{-q^2/2\sigma^2}, \quad (53)$$

where  $m = \frac{1}{2}(n-1)$ ;  $I_m(\theta)$ ,  $\theta$ ,  $f_n$  are 7.5(81), (82) with now  $\mu_i = |\alpha_{1i}| \sigma_i/\sigma$ ; and  $\sigma_i$  and  $\sigma$  are given by (17) and (21).

The refined form (48) of the quantum rate constant bears the same correspondence (50) to the "refined classical rate" 9.3(33). Thus if we again assume a gap distribution of the type 9.4(46), we find for the rate constant (48) of 10.5

$$k = \int \cdots \int L \{ 1 - (1 + \omega/uL)^{-u} \} \prod_1^n \exp(-\epsilon_i/2\sigma_i^2) d\epsilon_i/2\sigma_i^2, \quad (54)$$

which corresponds to 9.4(48). Approximating as in 9.5, we find for the quantum form (54) that  $k/k^\infty$  is given by 9.5(50), where now  $\theta$  incorporates the quantum  $\mu_i$ , and  $b = q^2/2\sigma^2$ . This is the furthest point we shall reach in this proliferation of rate formulas.

The reliability of the approximations in 7.5 for the quantum rate (49) has not been deeply studied. A main point in 7.5 was that the  $\mu_i$  should not be too disparate. For the present function (17),  $\sigma_i$  increases with  $\nu_i$  (roughly as  $\sqrt{\nu_i}$  at the highest frequencies), so that we might expect a larger spread of the  $\mu_i = |\alpha_{1i}| \sigma_i/\sigma$ . On the other hand the amplitudes  $\alpha_{1i}$  tend to be smaller for the larger frequencies, so that this tends to reduce the spread of the quantum  $\mu_i$ .

**Comparison of the quantum and classical declines of rate constant.** Since the approximation  $I_m(\theta)$  to  $k/k^\infty$  is the same function in the classical and quantum theories, the predicted shape of curve of  $\log(k/k^\infty)$

against  $\log \theta$  or  $\log c$  is the same in both theories. There may, however, be a considerable difference in the ratio  $c/\theta$  on the two theories, and so a difference in the absolute concentrations at which the rate constant declines. The main source of this difference is the factor  $b^{1/(n-1)}$  in  $\theta$  (compare 7.5(82)). In the classical theory we identify  $b = E_0/\kappa T$  by using for  $E_0$  the experimental high-concentration activation energy  $E_a^\infty$ . In the quantum theory  $b = q^2/2\sigma^2$  was found in (38) to be  $\chi \cdot E_a^\infty/\kappa T$ , where  $\chi$ , the function (39), is greater than unity. Thus the quantum  $b$  (for given  $E_a^\infty$ ) is greater than the classical, and the quantum  $\theta/c$  is the greater. Consequently the concentration for a given value of  $k/k^\infty$  tends to be smaller in the quantum case than in the classical.

*Nitryl chloride:* Dr. D. R. Herschbach kindly gave me his draft calculations of the quantum rate for this molecule, and I have repeated them on the basis of the analysis given in 3.8 and 8.5. Corresponding to the classical values 8.5(47), the "quantum"  $\mu_i$  are .54, .44, .43, .095, and .56, having a product 3.0 times that of the classical case. The quantum mean frequency  $\nu$  is  $2.54 \times 10^{13}$  sec.<sup>-1</sup>, and the parameter  $\chi$  of (39) is 2.2 for the temperature  $T = 420^\circ$  used in 8.5. From these values it is found that the  $\theta/c$  ratio is 9.5 times as great in the quantum case as in the classical, or 4.5 times if we omit the one small amplitude in both cases. Thus the concentrations for a given  $k/k^\infty$  are somewhat smaller in the quantum case.

**Concluding remarks.** Although we do not find any great difference in the fall-off of rate constant in this example, the position of the present quantum theory is much less happy for the high-concentration rate constant  $k^\infty$ . As was seen in 10.3, a temperature-dependent activation energy  $E_a^\infty$  is predicted, or equivalently a curvature of the plot of  $\log k^\infty$  against  $1/T$ . This curvature is of a size which should be just detectable for the cyclopropane isomerization, and this may be tested experimentally. A further difficulty is the factor  $e^{S'/\kappa}$  in (40), which brings the theoretical  $A$ -factor below the order of magnitude of vibration frequencies. This suggests a serious inadequacy in the present theory. This might be associated with anharmonic quantum effects and with the scant attention we paid to energy in the formulation.

H. S. Johnston and M. Wolfsberg have stressed to me on different occasions that there should be superimposed on the criterion of "dissociation at a critical configuration" some criterion of having enough energy. H. C. Longuet-Higgins suggested that the difficulty (as in a similar formulation which he and P. W. Higgs<sup>8</sup> tried out) is in the lack of attention paid to zero-point energy; for the rate constant does not go absolutely to zero at  $T = 0$ . If, for example, we remove the zero-

point energy  $\frac{1}{2}h\nu$ , from the expression (17) for  $2\sigma$ ,<sup>2</sup> (and the remarks after (19) on energy dispersion may be relevant to this idea) and carry this modification through the subsequent work, we obtain a rate constant  $k^\infty$  which does tend to zero at  $T=0$ . Moreover this modification would in the case of nitryl chloride change the parameter  $\chi$  of (39) from 2.2 to 1.1, so that the factor  $e^{S'/k}$  in (40) comes much closer to unity.

Although the present model of dissociation as a flow of a quantum but not quantized distribution is to my mind attractive, this discussion suggests that it stands in need of modification, perhaps by an ergodic restriction of the dimensionality of the phase-space distribution or by some exclusion of the zero-point part of the distribution. This alternative raises difficulties of fundamental principles; without too much attention to these the construction of pictures of rate processes is much eased.

I have been concerned mainly with simple models driven mathematically to yield a reasonable amount of information. The time seems almost ripe for a much more complete synthesis of the essential factors in gas kinetics, including collision processes; and in this the mathematics may have to be driven a good deal harder.

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# Subject and Symbol Index

Symbols occurring repeatedly with the same meaning are listed here, generally with the page numbers of their first appearance or main definition. *Italic* numbers give all the pages on which certain symbols are used with a special meaning.

Greek-letter symbols are arranged according to the initial letters of their English spelling.

- $a_i$ , amplitude of  $i$ th vibration, 71  
 $a = \sum a_i$ , 77  
 $A_p = \sum a_i \nu_i^2$ , 83  
 $a_{rs}$ , kinetic energy coefficient, 44  
 $a_{r'}$ , in col coordinates, 111  
 $\mathbf{a}$ ,  $A$ ,  $A_{r'}$ , see Notations  
 $A$  for pre-exponential, see  $A$ -factor  
 $A_m(\theta)$ , activation energy function, 162  
 $\alpha_{r'}$ , amplitude factor, 55  
 $\alpha^2 = \sum a_i^2$ , 88  
 $\alpha$ , matrix  $\{\alpha_{r'}\}$ ;  $\alpha'$ , transpose, 53  
 $\alpha = t$  minus nearest integer, 83  
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 $b_1 = E_1/\kappa T$ , 22  
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 $\mathbf{b}$ ,  $B$ ,  $B_{r'}$ , see Notations

- Balancing, detailed, 17, 30  
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- c*, gas concentration (generally of molecules, but in numerical formulas, moles per cubic centimeter)  
*c*, positive constant in limits of integrals, 139-140, 147, 201  
 $\mathbf{c} = \mathbf{a}^{-1}\mathbf{b} = \mathbf{g}\mathbf{b}$  (matrix), 54  
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- E*, energy of molecule  
 $E_0$  (per molecule) or  $E'_0$  (per mole),  
   critical classical energy for dissociation; *also* Arrhenius parameter, 13  
 $E'_0$ , minimum quantum energy, 119, 124  
 $E_1$ , critical energy in Hinshelwood's theory, 20  
 $E_a$ ,  $E_a^\infty$ , general and high-concentration activation energy, 37, 35  
 $\bar{E}_a$ ,  $E_{a,01}$ , mean value and collisional part of  $E_a$ , 37  
 $\epsilon_n$ , energy in normal mode, 55  
 $\epsilon_{n,0}$ , minimum critical  $\epsilon_n$ , 88  
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 $f(E)dE$ , equilibrium proportion with energy ( $E$ ,  $E+dE$ ), 21, 25  
 $f_r$ , *r*-state equilibrium probability, 16  
 $f_n$ , reaction parameter for molecule of *n* frequencies, 145  
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 $g_r$ , proportion in  $r$ th state at general concentration, 16  
 $g_{rr}$ , Hamiltonian coefficient, 44  
 $g_{r'}$ , in col coordinates, 111  
 $\mathbf{g} = \{g_{r'}\} = \mathbf{a}^{-1}$ , matrix, 41  
 GeO, geometrical operation, 49  
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 $\log$ , logarithm to base 10  
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 $\|a_{rs}\| = A$ , determinant  
 $A_{rs}$ , cofactor of  $a_r$ , in  $A$   
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