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GASEOUS UNIMOLECULAR REACTIONS: THEORY OF THE EFFECTS OF PRESSURE AND OF VIBRATIONAL DEGENERACY

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A theory which gave the high-pressure unimolecular reaction rate as $K_\infty = \nu \exp(-E_0/kT)$ is extended to find the decline of rate with pressure; the gas molecule is again a classical vibrating system which dissociates at a critical extension of an internal co-ordinate. The general rate K is found to be approximately

$$\frac{K}{K_\infty} = \frac{1}{\Gamma(\frac{1}{2}n+\frac{1}{2})} \int_0^\infty \frac{\mathrm{e}^{-x}\, x^{\frac{1}{2}(n-1)}\,\mathrm{d}x}{1+x^{\frac{1}{2}(n-1)}\theta^{-1}},$$

where n is the effective number of normal modes of vibration; θ is proportional to $pT^{-\frac{1}{2}n}$, but depends also on the molecular structure and size. For $n \leqslant 13$, this integral is tabulated, and the pressures at which the rate declines from first order are estimated. The pressure tends to decrease as n increases; for $E_0/kT \sim 40$, it is estimated that only molecules with six or more atoms should show rates approaching K_∞ at normal pressures. The table of K/K_∞ is not carried as far as the 'bimolecular' range, but a precise technique is developed for this region.

The theory is compared with Kassel's classical theory of a molecule of s 'oscillators'. The low-pressure activation energy, and the shape of the curve of $\log K$ against $\log p$, are similar in the two theories if $n = 2s-1$; the absolute values of p for a given rate are also roughly comparable.

Two results are proved, for the present severely classical model, concerning special cases. (i) A pair or triplet of degenerate modes with equal frequencies counts as one in assessing 'n' for the general rate K. (ii) If the dissociation co-ordinate q relates atoms m_1, m_2, and m_1 is replaced by an isotope m_1^*, the high-pressure rate changes in the ratio $\sqrt{\{m_1(m_1^*+m_2)/m_1^*(m_1+m_2)\}}$; for this, the internal potential energy V need not be quadratic, nor need q be isolated in V from other co-ordinates.

1. Introduction

A theory of gaseous unimolecular reactions (Slater 1939, 1948; these papers will be called S and S′) is here extended to investigate the decline of the reaction rate at lower pressures. The theory is based on a classically vibrating molecule which dissociates when a particular internal dimension q reaches a critical value. The high-pressure first-order rate K_∞ found in S′ was $\nu \exp(-E_0/kT)$, where E_0 is the critical energy and ν is a precisely defined average of the normal-mode frequencies of vibration. The present extension to low pressures is essentially a 'collision' theory. The final approximate formula for the rate K at pressure p is

$$\frac{K}{K_\infty} = I_n(\theta) \equiv \frac{1}{\Gamma(\frac{1}{2}n+\frac{1}{2})} \int_0^\infty \frac{\mathrm{e}^{x}\, x^{\frac{1}{2}(n-1)}\,\mathrm{d}x}{1+x^{\frac{1}{2}(n-1)}\,\theta^{-1}}, \tag{1}$$

where the parameter θ is proportional to the collision frequency per molecule, and so to p; n is the number of normal modes contributing to the vibrations in q. The parameter θ is proportional also to $\mu_1\mu_2\ldots\mu_n \left(\sum_1^n \mu_i^2 = 1\right)$, where the μ_i are proportional to the amplitudes of the various normal vibrations as they affect q.

The proper application of the theory is thus to particular molecules of which the vibrational structure is fully known. The numerical illustrations in this paper are confined,

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† Professor Evans had agreed to communicate this paper before his death on 25 December 1952.

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however, to a mythical 'typical' molecule with reasonable values of E_0, T, ν and the μ_i, and values of n up to 13.

As Kassel's theory of unimolecular rates (Kassel 1932) is well known and employs an apparently similar model of the dissociation process, the two theories will be compared at each stage of the argument. It was shown in S′, § 11, that the 'specific dissociation rate' of molecules with a given total energy is, at high pressures, the same in both Kassel's and the present theory. It was indicated also that this did not imply that the theories would agree at low pressures, owing to the different dependence of the dissociation process on the internal energy distribution. It is found here that Kassel's and the present theory give roughly the same trend of rate with pressure if s, the number of 'oscillators' in Kassel's molecule, and n, the number of normal modes on the present theory, are related by

$$n-1 = 2(s-1). \tag{2}$$

Thus in general terms the present theory demands about twice as many effective oscillators as Kassel's, to fit a given K against p curve; but for particular gases the effects of variations in the parameters, particularly the μ_i, may obscure this general trend.

Outline of the argument

The model of dissociation is reviewed in § 2, to remove some earlier obscurities and to introduce the parallel with Kassel. The general rate K is formulated in § 3 (equation (18)) as a multiple integral over the energy distribution in the n modes; its evaluation is deferred until § 6. In reviewing previous high-pressure results in § 4, the opportunity is taken to point out a simple result (equation (32)) concerning isotopic substitutions.

The limiting low-pressure second-order rate K_0 is discussed in § 5, and the relation (2) appears in the comparison of the limiting activation energies. In § 6 the approximation (1) is given for the general rate K, and comparison with a simple approximation to Kassel's classical integral again suggests the relation (2) between the parameters n and s. Illustrative calculations of K in terms of p in § 7 are based on the computed table 3 of the function $I_n(\theta)$ of (1). This table will form a basis for estimating rates for particular gases; but it may have applications in other fields.

Conclusions given in § 8 on the trends of rate with pressure and on appropriate applications of the theory need not be restated here. The last section, § 9, deals with the special case of degenerate vibrations. The theorem is proved that a pair or triplet of degenerate modes with equal frequencies counts as a single mode in assessing the effective number of modes in the breaking co-ordinate. This result is important for symmetrical molecules.

The main mathematics, apart from this theorem, is in the appendices. Appendix 1 gives a numerical method for estimating the low-pressure rate K_0 of § 5. In appendix 2 the general rate K is reduced to the form (1); a note is added on the integral $I_n(\theta)$ in the recent theory of Marcus (1952 *a*, *b*).

2. THE MODEL OF THE DISSOCIATING MOLECULE

The gas molecule is treated classically as an array of point-atoms which vibrate about the equilibrium configuration; the general configuration is described by internal co-ordinates $q_1, q_2, \ldots$ which are zero at equilibrium. Particular co-ordinates may be the extension of the distances between atoms (whether 'bonded' or not), or angles, or Cartesian co-ordinates of atoms referred to axes moving and rotating with the molecule. The potential energy is assumed to be quadratic in the q_s; the internal motion can then be resolved into normal modes $1, 2, \ldots$ with frequencies $\nu_1, \nu_2, \ldots$, energies $\epsilon_1, \epsilon_2, \ldots$ and initial phases $\psi_1, \psi_2, \ldots$. The energies ϵ_i and phases in this classical harmonic model are constant in a free molecule and change only at molecular encounters. A typical internal co-ordinate q is then a function of the time t from the last collision of the form

$$q = \sum_{i=1}^{n} a_i \cos 2\pi(\nu_i t + \psi_i); \quad a_i \equiv \alpha_i \sqrt{\epsilon_i}, \quad \alpha_i \neq 0. \tag{3}$$

The α_i, or 'amplitude factors', are constants characteristic of the co-ordinate q considered; their calculation from the inertial and force constants will be illustrated in a subsequent paper. The number n is at most the total number of normal modes of vibration, but for a particular co-ordinate n may be less than this. For example, if q is a 'symmetry co-ordinate' it will not be affected by some of the modes; again, some modes may affect q so little (that is, they may give such small α_i for the co-ordinate q) that their contribution to (3) may be ignored. Thus n is the number of modes effectively contributing to the co-ordinate q, and so is to be treated as a characteristic of the co-ordinate rather than of the molecule as a whole.

It will be assumed for the present that the frequencies $\nu_1, \nu_2, \ldots, \nu_n$ in (3) are 'independent', that is, linearly independent in the field of rational numbers; this restriction will be lightened in § 9.

The molecule is assumed to dissociate if and when a particular co-ordinate q attains a critically high value q_0; the harmonic motion (3) is assumed to persist up to the moment of rupture. Now with 'independent' $\nu_1, \ldots, \nu_n$, the sum (3) takes in time all values up to $\Sigma |a_i|$, irrespective of the values of the ψ_i. Thus, if the last collision has given the molecule the high energies necessary to satisfy the inequality

$$\Sigma |a_i| \equiv \Sigma |\alpha_i| \sqrt{\epsilon_i} \geqslant q_0, \tag{4}$$

the molecule is 'energized', that is, capable of dissociation; but it will dissociate only if q as a function of t attains the value q_0 before a further collision removes the high internal energy. The chance of dissociation depends therefore both on the behaviour of the function (3) and on the collision frequency; attention is confined in this section to the former factor.

Let $M(\tau)$ be the number of zeros of $q - q_0$ for $0 \leqslant t < \tau$, where for the moment q is defined by (3) as a function of all positive t with the a_i and ψ_i fixed; and let

$$L = \tfrac{1}{2} \lim_{\tau \to \infty} M(\tau)/\tau. \tag{5}$$

For large values of q_0, the function q is for most of the time $(0 < t < \infty)$ less than q_0, and rises briefly to q_0 with the small average frequency L. The fraction of the molecules, with given $a_1, \ldots, a_n$ satisfying (4), for which q rises to q_0 in a short time δt, will be assumed to be $L\delta t$; thus L will be used as the *dissociation frequency* (per molecule). This last assumption is plausible rather than secure. It would be invalidated if, for example, the zeros of $q - q_0$ tended to be 'bunched', with long gaps between the bunches (compare a remark due to Wigner in Pelzer (1933)). This is unlikely for large n. For the over-simple case $n = 2$ it can be inferred from the results of Slater (1950) that high peaks of q are separated by at most three characteristic time intervals. For the general case, 'bunching' of the zeros would make the limit L

an over-estimate of the dissociation frequency. On the other hand, if q tended to rise swiftly to an early peak—as would happen if the ν_i were nearly in simple ratios—then L would be an under-estimate.

In the present case of 'independent' frequencies, the limit L is independent of the phases $\psi_1, \ldots, \psi_n$. The formula used in S, and again in part of this paper, is an approximation valid for small values of $\Sigma \mid a_i \mid - q_0$, namely,

$$L = \frac{1}{\Gamma(\frac{1}{2}n+\frac{1}{2})} \left(\frac{\Sigma \mid a_i \mid - q_0}{2\pi}\right)^{\frac{1}{2}(n-1)} \left(\frac{\Sigma \mid a_i \mid \nu_i^2}{\mid a_1 a_2 \ldots a_n \mid}\right)^{\frac{1}{2}}. \tag{6}$$

A precise formula (Kac 1943) used in S′ is

$$L = \frac{1}{4\pi^2} \iint_{-\infty}^{\infty} \frac{\cos(q_0 x)}{y^2} \left\{\prod_1^n J_0(a_i x) - \prod_1^n J_0(a_i \sqrt{[x^2 + 4\pi^2 y^2 \nu_i^2]})\right\} \mathrm{d}x \, \mathrm{d}y. \tag{7}$$

This vanishes identically when (4) is not satisfied. The relations of (6) and (7) and other formulae for L will be discussed in another journal.

The critical energy

Only the energy

$$E = \sum_1^n \epsilon_i \tag{8}$$

of the n vibrations effective in the breaking co-ordinate q is of moment. The energies $\epsilon_i = \epsilon_{i0}$ satisfying (4) and having the least sum $E = E_0$ are

$$\epsilon_{i0} = q_0^2 \alpha_i^2 / \alpha^4, \quad \text{where} \quad \alpha^2 \equiv \Sigma \alpha_i^2, \tag{9}$$

so that

$$E_0 = q_0^2 / \alpha^2. \tag{10}$$

This E_0 plays the part of 'critical energy' per molecule, and will be identified later with the high-pressure activation energy; but molecules with $E > E_0$ are not 'energized' unless the distribution $\epsilon_1, \ldots, \epsilon_n$ after the last collision satisfies (4).

Kassel's model

In Kassel's theory (Kassel 1932) the molecule is a system of s 'loosely coupled' oscillators with frequencies which, in the general formulation, are commensurable (in contrast with the linearly independent frequencies assumed here), but, in practical calculations, are taken all equal. Energy is freely transferred between these oscillators all the time, and the molecule dissociates when (some time after a suitably energizing collision) more than a critical energy E_0 (or ϵ_0 in Kassel's notation) wanders into one particular oscillator.

Since these oscillators have frequencies, one is tempted to make them correspond to the n 'effective normal modes' in (3) with $s = n$; but since dissociation is associated with the behaviour of one particular oscillator, one is equally tempted to make the oscillators correspond to the internal (non-normal) co-ordinates such as q itself. Kassel's oscillators have thus a status somewhere between normal and non-normal co-ordinates; they fit best with the picture of a molecule as a collection of localized bonds each represented approximately by an oscillator having a characteristic frequency, with also a 'loose coupling' between the bond-oscillators. This picture has been useful in spite of its inaccuracy; and Kassel's theory likewise is stronger than these remarks might suggest. Without pursuing the foundations any deeper, we shall think of the number of oscillators s and the critical energy E_0 (ϵ_0) of Kassel as corresponding to the n and E_0 of the present theory.

The frequency with which, out of a total energy $E > E_0$, more than E_0 is collected into one of Kassel's oscillators is, in the classical formulation,

$$A(1-E_0/E)^{s-1}, \tag{11}$$

where the arbitrary constant A represents the rate of internal transfer between oscillators. This quantity (11) plays the role of a 'dissociation frequency' L; 'energized molecules' are those for which the energies $\epsilon_1, \ldots, \epsilon_s$ in the s oscillators satisfy

$$\sum_1^s \epsilon_i \equiv E > E_0. \tag{12}$$

3. The general dissociation rate

The following formulation of the dissociation rate at any pressure imitates earlier theories; it is applicable to any model in which the dissociation probability of an energized molecule is determined by the internal energies.

The gas is supposed to be at a suitably high temperature T, and the dissociation to be in a steady but early stage, unaffected by products of reaction. The dissociation rate will be formulated as the average of the 'dissociation frequency' over the distribution of energized molecules; this distribution is found by equating the rate of energization by collision to the sum of the rates of dissociation and de-energization for each elementary range of internal energy.

A '*collision*' will mean an encounter transferring internal energy, or more precisely on the present model, vibrational energy. The collision frequency per molecule, ω, will be assumed to have the classical form

$$\omega = aN, \quad a = 4\sigma^2\sqrt{(\pi kT/m)}, \tag{13}$$

where N is the concentration, m the molecular mass and k Boltzmann's constant. Any 'efficiency-factor' for energy transfer is here absorbed into the effective encounter-diameter σ, but any dependence of σ on T will be neglected.

Attention is confined first to a small 'energized range' $(\epsilon_i, \epsilon_i + \mathrm{d}\epsilon_i)$ $(i = 1, \ldots, n)$, where the internal energies ϵ_i satisfy (4) or, on other models, some other inequality effectively demanding large energy. The number of molecules raised by 'collision' (per unit time and volume) to such a range is assumed to be

$$\omega N \mathrm{e}^{-E/kT} \Pi(\mathrm{d}\epsilon_i/kT), \quad E \equiv \sum_1^n \epsilon_i. \tag{14}$$

This assumption has been discussed by earlier writers, and may be justified on the present model by calculations similar to Kassel's. The 'steady' population in any energized range, however, will not be the 'Boltzmann' distribution $N\mathrm{e}^{-E/kT}\Pi(\mathrm{d}\epsilon_i/kT)$, because of the depletion by dissociation; it will be some smaller number, say $Ng(\epsilon_1, \ldots, \epsilon_n)\,\mathrm{d}\epsilon_1 \ldots \mathrm{d}\epsilon_n$, where g is to be determined. The number of these dissociating per unit time is

$$NgL\,\mathrm{d}\epsilon_1 \ldots \mathrm{d}\epsilon_n, \tag{15}$$

where L is the 'dissociation frequency' discussed in § 2. The number de-energized per unit time is assumed to be

$$\omega Ng\,\mathrm{d}\epsilon_1 \ldots \mathrm{d}\epsilon_n, \tag{16}$$

since it may be assumed that energized molecules are in general de-energized by their next collision.

The assumption that the reaction is 'steady' requires the gain (14) to be equated to the loss (15), (16); hence

$$(L+\omega)\,g=\omega\,\mathrm{e}^{-E/kT}(kT)^{-n}. \tag{17}$$

This determines g as a function of the internal energies (as they occur in E and L), the collision frequency and the temperature. The integration of (15) over the internal energies gives the unimolecular rate-constant K as

$$K=-\frac{1}{N}\frac{\mathrm{d}N}{\mathrm{d}t}=\int\ldots\int gL\,\mathrm{d}\epsilon_1\ldots\mathrm{d}\epsilon_n,$$

or by (17)

$$K=\int\ldots\int\frac{L\,\mathrm{e}^{-E/kT}}{1+L/\omega}\prod_1^n\left(\frac{\mathrm{d}\epsilon_i}{kT}\right), \tag{18}$$

where the integral is over all energized ranges of the ϵ_i.

As in *Kassel's model*, the dissociation frequency (11) depends only on the total energy E, his form of integral corresponding to (18) is naturally a simple integral over E. The preliminary reduction of the general formula (18) for cases where L is a function of E is

$$\underset{E<\Sigma\epsilon_i<E+\mathrm{d}E}{\int\ldots\int}\mathrm{d}\epsilon_1\ldots\mathrm{d}\epsilon_s=\frac{E^{s-1}\,\mathrm{d}E}{(s-1)!}. \tag{19}$$

Thus (18) becomes, using Kassel's form (11) for L and a new variable $x=(E-E_0)/kT$,

$$K=\frac{A\,\mathrm{e}^{-b}}{(s-1)!}\int_0^\infty\frac{x^{s-1}\,\mathrm{e}^{-x}\,\mathrm{d}x}{1+\dfrac{A}{\omega}\left(\dfrac{x}{b+x}\right)^{s-1}},\quad b=\frac{E_0}{kT}, \tag{20}$$

which is equivalent to Kassel's classical formula (1932, p. 103, equation (24)).

In the present model, the more complex forms (6) or (7) of L make the reduction of the integral (18) more complicated. The limiting cases of high and low pressure ($\omega\to\infty$ and 0) will be treated separately before the general case.

4. THE LIMITING FIRST-ORDER RATE

For large values of the concentration, and hence of the collision frequency ω, the rate (18) tends to the first-order rate:

$$K\to K_\infty,\quad K_\infty=\int\ldots\int L\,\mathrm{e}^{-E/kT}\,\Pi(\mathrm{d}\epsilon_i/kT). \tag{21}$$

This integral was treated in S and S′. The remarks (*a*) to (*e*) below are relevant to the present discussion; the note (*f*) is a digression of independent interest.

(*a*) The substitution of Kac's formula (7) for L in (21) gives the precise result (S′)

$$K_\infty=\nu\,\mathrm{e}^{-b}\quad(b=E_0/kT), \tag{22}$$

where

$$\nu=\sqrt{(\Sigma\alpha_i^2\nu_i^2/\alpha^2)}, \tag{23}$$

so that ν is a 'weighted' root-mean-square of the normal mode frequencies. This result predicts that the 'frequency factor' (that is, the rate apart from the exponential e^{-b}) at high concentrations is of the order $10^{13}\,\mathrm{s}^{-1}$ of vibration frequencies.

(*b*) The substitution in (21) of the earlier, approximate, formula (6) for L led in S to the determination of upper and lower bounds to the value of K_∞; these had the right-hand side of (22) as a common dominant term. This result gives confidence in the use of (6) in § 6 below in calculating the rate K at intermediate concentrations.

(*c*) The substitution of Kassel's form (11) for L in (21), or the direct evaluation of (20) with $\omega = \infty$, gives (compare also the discussion in S′, § 11)

$$K_\infty = A\,\mathrm{e}^{-b}, \tag{24}$$

so that Kassel's constant A is determined as the high-pressure 'frequency factor'.

(*d*) If the *activation energy* E_a is defined as

$$E_a = kT^2\,\partial(\ln K)/\partial T, \tag{25}$$

then both (22) and (24) naturally give

$$E_a = E_0, \tag{26}$$

This determines the 'critical energy' E_0 as the high-pressure activation energy.

(*e*) The critical energy E_0 will be regarded generally as determined experimentally in this way, and not as a quantity to be calculated from the critical extension q_0 by means of (10). Equation (10) can be used for particular gases to estimate q_0 (indicating the degree of distortion of the molecule in the critical configuration) from E_0 and the calculated value of α (9) for the molecule considered.

An isotopic effect

(*f*) The result (32) below is of practical interest. It is a by-product of the extension of Pelzer's method given in S′, § 7; but here there is no need of normal-mode analysis, so that the molecular potential energy is not restricted to quadratic terms.

The molecule is supposed to be described by n internal co-ordinates $q_1, \ldots, q_n$, with $q_1 \equiv q$ as the critical co-ordinate which causes dissociation at the value q_0. The kinetic and potential energies are assumed to be

$$T' = \frac{1}{2}\sum_1^n\sum a_{rs}\dot{q}_r\dot{q}_s, \qquad V = V(q_1, q_2, \ldots, q_n). \tag{27}$$

The high-pressure rate can be formulated (S′, § 7) as

$$K_\infty = vf(E_0, T), \tag{28}$$

where E_0 is a critical energy determined by q_0 and the form of V, and

$$f(E_0, T) = \frac{\frac{1}{2}\int\cdots\int_{-\infty}^{\infty} \exp\{-V(q_0, q_2, \ldots, q_n)/kT\}\,\mathrm{d}q_2\ldots\mathrm{d}q_n}{\int\cdots\int_{-\infty}^{\infty} \exp\{-V(q_1, q_2, \ldots, q_n)/kT\}\,\mathrm{d}q_1\ldots\mathrm{d}q_n},$$

$$v = \frac{\int\cdots\int_{-\infty}^{\infty} \exp(-T'/kT)\,|\dot{q}_1|\,\mathrm{d}\dot{q}_1\ldots\mathrm{d}\dot{q}_n}{\int\cdots\int_{-\infty}^{\infty} \exp(-T'/kT)\,\mathrm{d}\dot{q}_1\ldots\mathrm{d}\dot{q}_n}.$$

This K_∞ is formulated as the rate at which an equilibrium distribution crosses the phase-space hyperplane $q_1 = q_0$ from one side; or it can be regarded as the product of a 'mean transition velocity' v with the concentration $f(E_0, T)$ of 'activated complexes'. From the assumed quadratic form of T' (compare S′, equation (71)),

$$v = \surd(2kTA_{11}/\pi A), \tag{29}$$

where $A = \det(a_{rs})$, and A_{11} is the cofactor of a_{11} in A.

Let the critical co-ordinate q_1 be the extension of the distance between two atoms of masses m_1, m_2; then (Slater 1949)

$$A/A_{11} = m_1 m_2/(m_1+m_2). \tag{30}$$

By (28), (29) and (30)

$$K_\infty = f(E_0, T)\surd\{2kT(m_1+m_2)/\pi m_1 m_2\}. \tag{31}$$

If the atom m_1 is replaced by an isotope of mass m_1^*, and if this leaves the potential energy unchanged, the ratio of the new to the old rate is

$$\frac{K_\infty^*}{K_\infty} = \left(\frac{m_1(m_1^*+m_2)}{m_1^*(m_1+m_2)}\right)^{\frac{1}{2}}. \tag{32}$$

This is the result sought. The same result can be inferred from equations (22) and (34) of S′, under the restrictions that (i) V is quadratic, and (ii) there are no cross-terms $q_1 q_s$ in V (so that rupture occurs at an 'isolated bond'). The derivation given here is independent of both these restrictions; it requires merely that the critical distance for dissociation involve the atom for which an isotope is substituted, and that V be unaltered.

Bigeleisen (1949) has derived on transition state theory a more general expression for K_∞^*/K_∞, containing a factor $\surd(m/m^*)$, where m, m^* denote the 'effective masses' in the dissociation co-ordinate in the two cases; the other factors in his K_∞^*/K_∞ do not arise in the present purely classical and vibrational model. In applications of his formula (for example, Bigeleisen 1952) he has used the 'reduced mass' ratio (32) for $\surd(m/m^*)$ on the basis of S′; this use is strengthened by the present argument.

5. THE LIMITING SECOND-ORDER RATE

For very small values of the collision frequency $\omega = aN$, the general rate (18) approaches the form K_0:

$$K \sim K_0 \quad : \quad K_0 = \omega\Lambda, \tag{33}$$

where

$$\Lambda = \int\ldots\int \mathrm{e}^{-E/kT}\prod_1^n (\mathrm{d}\epsilon_i/kT), \tag{34}$$

the integral being over energized ranges of ϵ_i, that is, on the present theory (combining (4) and (10))

$$\sum_1^n |\alpha_i| \surd\epsilon_i \geqslant \alpha\surd E_0, \tag{35}$$

and on Kassel's model (12), taking $s = n$ for this comparison,

$$\sum_1^n \epsilon_i \equiv E \geqslant E_0. \tag{36}$$

The limiting rate (33) is of second order, and does not depend on the dissociation-frequency function L (although the manner of approach of K to K_0 depends on L). The physical picture is that when collisions are sufficiently rare, almost every 'energized' molecule is given time to reach the critical configuration and dissociate.

Before evaluating (33), the question will be considered whether even on the present theory the energy-boundary (35) should not be replaced by one of the type (36) at very low pressures.

The condition (35) is more stringent than (36), in the sense that the region of ϵ-space ($\epsilon_i \geqslant 0$, $i = 1, \ldots, n$) satisfying (35) is only part of the region (36); as has been remarked, a molecule with energy E exceeding E_0 is not 'energized' on the present theory unless the distribution $\epsilon_1, \ldots, \epsilon_n$ of E between the n effective normal modes satisfies (35). On the picture of strictly harmonic, independent normal modes this distribution was settled by the last collision and does not change between collisions; so that the picture requires the boundary (35). But if cubic and higher terms in the potential energy are added to the quadratic terms of the present model, for example, as perturbations, the picture of independent modes becomes blurred, and as an approximation we have 'nearly independent' modes which can in time redistribute their energies† ϵ_i. Thus molecules satisfying (36) but not (35), immediately after a collision, may eventually reach the distribution (35) if collisions are very rare.

This suggests that the boundary (35) may be approximately correct at low pressures, but that at very low pressures the boundary is more like (36); in this cautious statement it is also borne in mind that there may be symmetry restrictions on energy redistribution even in the anharmonic system. No attempt will be made here to assess the lowness of the pressure at which the boundary (35) is likely to become a poor approximation. The rate (33) will be calculated for the boundary (35) as representing the present model, and (36) as representing Kassel's.

The rate on the present theory

The integral (34) with the boundary (35) is

$$\Lambda = \int \ldots \int_0^\infty \exp\left(-\Sigma \epsilon_i / kT\right) U(\Sigma \,|\, \alpha_i \,|\, \surd \epsilon_i - \alpha \surd E_0) \, \Pi(\mathrm{d}\epsilon_i / kT), \tag{37}$$

where

$$U(t) = 1 \text{ or } 0 \quad \text{according as} \quad t > 0 \text{ or } < 0. \tag{38}$$

With the new parameters μ_i, h and variables x_i defined by

$$\mu_i = |\, \alpha_i \,| / \alpha \qquad (\Sigma \mu_i^2 = 1), \tag{39}$$

$$h^2 = b = E_0 / kT \quad (h > 0), \tag{40}$$

$$x_i^2 = \epsilon_i / kT \qquad (x_i \geqslant 0), \tag{41}$$

(37) becomes

$$\Lambda = \int \ldots \int_0^\infty \exp\left(-\Sigma x_i^2\right) U(\Sigma \mu_i x_i - h) \, \Pi(2x_i \, \mathrm{d}x_i).$$

The formula

$$U(t) = \frac{1}{2\pi\iota} \int_{c-\iota\infty}^{c+\iota\infty} \mathrm{e}^{2zt} \frac{\mathrm{d}z}{z} \tag{42}$$

gives

$$\Lambda = \frac{1}{2\pi\iota} \int_{c-\iota\infty}^{c+\iota\infty} \Phi(z) \, \mathrm{d}z, \tag{43}$$

where

$$\Phi(z) = \mathrm{e}^{-2hz} z^{-1} \prod_1^n \phi(\mu_i z), \tag{44}$$

$$\phi(\mu) = \int_0^\infty \exp\left(-x^2 + 2\mu x\right) 2x \, \mathrm{d}x. \tag{45}$$

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† This corresponds at first sight to Kassel's conception of 'loosely coupled oscillators', but Kassel's redistribution of energy is envisaged as essentially a more rapid process than that considered here; moreover (compare §2 above), Kassel's critical entity for dissociation is the oscillator, not an internal co-ordinate.

The computation of (43) is discussed in appendix 1; the method given there appears necessary if reliable estimates are required, for any values of the μ_i, for the development of bimolecular rates on this theory. If, however, the μ_i are all similar in magnitude, we may proceed more directly by representing (45) by the approximation

$$\phi(\mu) \simeq 2\sqrt{\pi}\,\mu\,\mathrm{e}^{\mu^2}. \tag{46}$$

Then (43) becomes

$$\Lambda = \pi^{\frac{1}{2}(n-1)}\mu_1\mu_2\ldots\mu_n I,$$

where

$$\begin{aligned} I &= \frac{1}{\iota\sqrt{\pi}}\int_{c-\iota\infty}^{c+\iota\infty}(2z)^{n-1}\exp(z^2-2hz)\,\mathrm{d}z \\ &= \frac{\mathrm{d}^{n-1}}{\mathrm{d}(-h)^{n-1}}\mathrm{e}^{-h^2} = \mathrm{e}^{-h^2}\,\mathrm{He}_{n-1}(h), \end{aligned}$$

by one definition of the Hermite polynomial He_n. Hence by (40)

$$\begin{aligned} \Lambda &= \mu_1\mu_2\ldots\mu_n\pi^{\frac{1}{2}(n-1)}\mathrm{e}^{-b}\,\mathrm{He}_{n-1}(\sqrt{b}) \\ &= \mu_1\mu_2\ldots\mu_n(4\pi b)^{\frac{1}{2}(n-1)}\mathrm{e}^{-b}\left\{1-\binom{n-1}{2}\frac{1}{2b}+1\,.\,3\binom{n-1}{4}\frac{1}{(2b)^2}\ldots\right\}. \end{aligned} \tag{47}$$

This is an approximation giving the rate $K_0 = \omega\Lambda$.

It was essentially assumed in this work that b is large. With the typical experimental value $b = 40$, the last bracket in (47) has the values 0·93, 0·68, 0·38 for $n = 5, 9, 13$. When the μ_i are precisely equal, so that by (39)

$$\mu_i = n^{-\frac{1}{2}}, \tag{48}$$

some values of the non-exponential part of (47) are

$$\text{for } n = 1, 5, 9, 13, \quad \Lambda\mathrm{e}^b = 1,\ 4000,\ 2\times10^6,\ 3{\cdot}5\times10^8. \tag{49}$$

When all of the μ_i are of similar magnitude save that one, μ_n for example, is very small, then in (44) $\phi(\mu_n z)$ may be replaced by unity. This reduces (47) to a similar expression involving the $n-1$ vibrations characterized by $\mu_1, \ldots, \mu_{n-1}$; the nth mode is 'ineffective'. For a more general scatter of the μ_i, the method of appendix 1 appears necessary.

The rate on Kassel's model

The integral (34) is on Kassel's model over the region (12), and becomes after the reduction (19)

$$\Lambda = \frac{\mathrm{e}^{-b}}{(s-1)!}\int_0^\infty (b+x)^{s-1}\,\mathrm{e}^{-x}\,\mathrm{d}x. \tag{50}$$

(This is also given by (20) with ω small.) Hence

$$\Lambda = \frac{b^{s-1}\,\mathrm{e}^{-b}}{(s-1)!}\left\{1+\frac{s-1}{b}+\frac{(s-1)\,(s-2)}{b^2}+\ldots+\frac{(s-1)!}{b^{s-1}}\right\}. \tag{51}$$

The bracket here ranges from 1 to 1·4 for $s = 1$ to 13, if $b = 40$. Typical values of the non-exponential part of (51) for $b = 40$ are

$$\text{for } s = 1, 3, 5, 7, \quad \Lambda\mathrm{e}^b = 1,\ 800,\ 10^5,\ 7\times10^6. \tag{52}$$

Thus for given s or n greater than 1, the rates (51) and (52) are appreciably larger than the previous rates (47) and (49). This confirms a simple inference that can be drawn from the discussion earlier in this section of what is the appropriate energization boundary on the present theory. If at very low pressures the boundary (35) should be changing towards (36), then the Λ of (47) should approach the higher value (51) (with $s = n$). Thus the unimolecular 'constant' $K_0 = \omega\Lambda$ should not decrease proportionately to ω, but more slowly, so that the rate in this region would be between the second and the first order. The variation of rate-order, in going from very high to very low pressures, might thus be of a complex nature. This possibility will not be pursued here.

If (47) and (51) are again taken as representing the present and Kassel's model, the essential difference is in the powers of b. If the value of $n-1$ in (47) is twice the value of $s-1$ in (51), the two formulae give roughly comparable values.

The activation energy

By (25) and (33), the low-pressure activation energy is

$$E_a = kT^2\,\partial(\ln\omega)/\partial T + kT^2\,\partial(\ln\Lambda)/\partial T. \tag{53}$$

As by (13) ω varies as $\sqrt{T}$ for constant concentration N, and as $1/\sqrt{T}$ for constant pressure ($p = NkT$), the contribution of the first term in (53) to E_a is

$$\tfrac{1}{2}kT \;\; (N \text{ constant}), \qquad -\tfrac{1}{2}kT \;\; (p \text{ constant}). \tag{54}$$

This distinction has been emphasized by Johnston (1951). Attention will be concentrated here on the second term in (53). Since $b = E_0/kT$,

$$kT^2\,\partial(\ln\Lambda)/\partial T = -E_0\,\partial(\ln\Lambda)/\partial b.$$

Hence the second term in (53) is on the present theory, if Λ is represented by the approximation (47),

$$E'_a = E_0 - \tfrac{1}{2}(n-1)\,kT\left\{1-\binom{n-2}{2}\frac{1}{2b}+\dots\right\}\Big/\left\{1-\binom{n-1}{2}\frac{1}{2b}+\dots\right\},$$

or, approximately,

$$E'_a = E_0 - \tfrac{1}{2}(n-1)\,kT. \tag{55}$$

The corresponding approximation with the formula (51) of Kassel's model is

$$E'_a = E_0 - (s-1)\,kT. \tag{56}$$

If s and n are related by equation (2), these become the same.

6. The general rate

An approximate simple integral is given to represent the rate (18) on the present theory, and its relations to the high- and low-pressure limiting forms, and to Kassel's formula (20), are noted.

To estimate (18) on the present theory, the approximation (6) is used for the dissociation frequency L (compare § 4 (b)). It is assumed as in § 5 that $b = E_0/kT$ is large, and that the μ_i (39) and the frequencies ν_i are not widely scattered. The n-fold integral (18) may then be simply estimated by an expansion centred on the point of minimal energization ϵ_{i0} (9). A more formal treatment, which appears capable of extension beyond the present restrictions, is given in appendix 2. The approximate formula obtained by either method is

$$K = \nu\,\mathrm{e}^{-b} I_n(\theta), \tag{57}$$

where

$$I_n(\theta) = \frac{1}{\Gamma(\frac{1}{2}n+\frac{1}{2})}\int_0^\infty \frac{x^{\frac{1}{2}(n-1)}\,\mathrm{e}^{-x}\,\mathrm{d}x}{1+x^{\frac{1}{2}(n-1)}\theta^{-1}}. \tag{58}$$

The parameters are (compare (23) and (39))

$$\nu^2 = \Sigma\alpha_i^2\nu_i^2/\alpha^2 = \Sigma\mu_i^2\nu_i^2, \quad b = E_0/kT \tag{59}$$

and

$$\theta = (\omega/\nu)\, b^{\frac{1}{2}(n-1)} f_n, \tag{60}$$

where

$$f_n = (4\pi)^{\frac{1}{2}(n-1)}\,\Gamma(\tfrac{1}{2}n+\tfrac{1}{2})\,\mu_1\mu_2\ldots\mu_n. \tag{61}$$

The parameter θ is thus simply related to the mean vibration and collision frequencies ν and ω; the numerical factor f_n will be discussed later.

At high pressures, ω and θ tend to infinity and I_n to unity, so that

$$K \to \nu\,\mathrm{e}^{-b} = K_\infty. \tag{62}$$

This agrees with the exact high-pressure formula (22). Thus (57) can be written

$$K/K_\infty = I_n(\theta). \tag{63}$$

At very low pressures, ω and θ tend to zero, and K approaches the form

$$K \sim \nu\,\mathrm{e}^{-b}\,\theta/\Gamma(\tfrac{1}{2}n+\tfrac{1}{2}) = \omega\mu_1\mu_2\ldots\mu_n(4\pi b)^{\frac{1}{2}(n-1)}\,\mathrm{e}^{-b}. \tag{64}$$

This is the leading term of the previous $K_0 = \omega\Lambda$ of (33) and (47) or appendix 1 (M).

By its behaviour in these limiting regions, the formula (57) may be expected to give a good indication of the trend of rate with pressure at all except very low pressures.

Simple cases

In the simplest case, $n = 1$ (a simple oscillator, or diatomic molecule), (58) and (60) become

$$I_1(\theta) = 1/(1+\theta^{-1}), \quad \theta = \omega/\nu,$$

and the rate (57) is

$$K = \nu\,\mathrm{e}^{-b}/(1+\nu/\omega). \tag{65}$$

This result is seen to be exact; for in the case of a simple oscillator on the present model, the dissociation frequency $L = \nu$ or 0 according as the energy $\epsilon_1 > E_0$ or $< E_0$. Substituting this L in the original formula (18) for K gives (65). This result shows the characteristic linear relation between $1/K$ and $1/\omega$ (or $1/p$) which obtains when the dissociation probability is *independent* of the excess of energy above E_0.

For $n = 3, 5$, $I_n(\theta)$ can be expressed in tabulated functions, and for $n = 7, 9$ can be reduced to have an integrand with denominator a^2+x^2 (Slater 1941†). The results used here are

$$I_3(\theta) = \theta\{1+\theta\,\mathrm{e}^{\theta}\,\mathrm{Ei}\,(-\theta)\}, \tag{66}$$

$$I_5(\theta) = \tfrac{1}{2}\theta\{1+u(\mathrm{si}\,u\cos u - \sin u\;\mathrm{Ci}\,u)\}, \quad u = \surd\theta, \tag{67}$$

where

$$\{\mathrm{Ei}\,(-\theta),\ \mathrm{si}\,\theta,\ \mathrm{Ci}\,\theta\} = -\int_\theta^\infty \frac{\mathrm{d}y}{y}\{\mathrm{e}^{-y},\ \sin y,\ \cos y\}$$

respectively. These functions are conveniently tabulated in New York W.P.A. (1940).

Comparison with Kassel's theory

The result (57) has a close affinity with a simple approximation to Kassel's formula (20). This approximation, valid for large b, not too large s nor too small ω, consists in

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† In this early form of the theory no accurate high-pressure formula was available, and a more elaborate integral was computed for K, to which the present $I_n(\theta)$ then served as a check.

replacing $b+x$ by b in the denominator of (20). This gives (writing ν for Kassel's constant A, as before)

$$K = \frac{\nu\,\mathrm{e}^{-b}}{\Gamma(s)}\int_0^\infty \frac{x^{s-1}\,\mathrm{e}^{-x}\,\mathrm{d}x}{1+x^{s-1}/\theta'}, \qquad \theta' = \frac{\omega}{\nu}\,b^{s-1}. \tag{68}$$

This tends to Kassel's high-pressure formula (24) as ω tends to infinity, and to the form of the first term of the low-pressure formula (51) as ω tends to zero. In terms of the function defined in (58), (68) can be written

$$K = \nu\,\mathrm{e}^{-b} I_n(\theta'), \tag{69}$$

with

$$n-1 = 2(s-1), \tag{70}$$

so that

$$\theta' = (\omega/\nu)\,b^{\frac{1}{2}(n-1)}. \tag{71}$$

Comparing this with (57) shows that in the present approximation,

Kassel's rate for a molecule with s oscillators is the same in form as the present theory gives for $n = 2s-1$ *normal modes.* (72)

The one difference, namely, the factor f_n occurring in the parameter θ, (60) of the present theory, and not in θ' (71), will be estimated below.

The mathematical basis of the contrasted n and s in (72) is to be seen in the formulae (6) and (11) for L in the two theories. The physical basis is obscure, because of the quite different approaches to the formulation of L; the contrast may be connected with the fact that the present criterion for dissociation is accumulation of extension or amplitude, not of energy.

The factor f_n

To complete the comparison with Kassel's theory, and to lighten the calculations of the next section, the numerical factor f_n (61) in θ will be estimated.

For the dissociation of a particular gas, the product $\mu_1 \ldots \mu_n = \alpha_1 \ldots \alpha_n \alpha^{-n}$ in f_n can be calculated from the vibrational structure; but here typical values are sought to represent an unspecified molecule. The product $\mu_1 \ldots \mu_n$ has its maximum value, $n^{-\frac{1}{2}n}$, when $\mu_1 = \ldots = \mu_n = n^{-\frac{1}{2}}$; this maximum decreases strongly as n increases. For general values of the μ_i, it is convenient to introduce a molecular characteristic, λ, between 0 and 1, by the definition

$$\mu_1 \mu_2 \ldots \mu_n = \lambda n^{-\frac{1}{2}n}. \tag{73}$$

An estimate of λ is required. In preliminary calculations on two or three molecules, involving a hydrogen in the critical co-ordinate, it was found that the μ_i were fairly evenly distributed, with the greatest about five times the least; this is also within the range of μ_i, for which the present rate-approximations appear reliable (as judged by tests on the two methods, of § 5 and of appendix 1, for estimating K_0). Let it be supposed, then, as a simple illustration that $\mu_1, \mu_2, \ldots, \mu_n$ are in geometrical progression with $\mu_1 = 5\mu_n$, so that a simple formula can be set up for λ (73) in terms of n. The values of λ found in this way are given in table 1, together with the values of f_n (61), (α) for $\lambda = 1$ (that is, for $\mu_1 \ldots \mu_n = n^{-\frac{1}{2}n}$) and ($\beta$) for the illustrative λ's of this table.

The more representative results (β) indicate that for $n \leqslant 13$, f_n may be expected to be roughly of the order of unity.

It follows that for a moderate spread of the μ_i, the parameter θ (60) of the present theory is not far from that ((68) and (71)) attributed to Kassel, with $n-1 = 2(s-1)$. Thus, having similar parameters in $I_n(\theta)$, the two theories will show roughly the same decline of rate with absolute pressure. This is a mere suggestion of comparable orders of magnitude; the pressures for a given value of the rate will in fact differ by the factor f_n.

TABLE 1. VALUES OF λ, AND f_n: (α) FOR $\lambda=1$, (β) FOR THESE λ

n	3	5	7	9	11	13
f_n (α)	2·4	5·6	13	30	70	163
λ	0·34	0·24	0·16	0·11	0·075	0·050
f_n (β)	0·8	1·3	2·1	3·3	5·3	8·2

The comparison with Kassel's theory may be concluded at this point; the comparison of the parameters has to a limited extent strengthened the formal similarity noted in (72).

7. NUMERICAL VALUES OF THE GENERAL RATE

The formula $I_n(\theta)$ (58) for K/K_∞ depends solely on n, the number of modes, and θ. As by (60) θ is proportional to the collision frequency ω, and so to the pressure p at constant temperature T, the theory in the present approximation predicts a single characteristic curve of $\log_{10} K/K_\infty$ against $\log_{10} p$ for each n; the sole effect of changing to a different temperature, or to a different gas with the same n, is to translate the curve parallel to the $\log_{10} p$ axis. A table of $I_n(\theta)$ thus gives the shape of the curves for all cases where the present approximations are reliable; but the absolute position of the curve on the pressure scale requires an estimation of the ratio θ/p for the gas and temperature under consideration. (The calculation of a K/K_∞ table is not made superfluous by the previous comparison with Kassel's theory; for Kassel used his exact quantal or classical formulae, and calculated K/K_∞ afresh for the characteristics s, A, E_0, T of each reaction he treated.)

A table of $I_n(\theta)$ is given in (*b*) below, preceded in (*a*) by general estimates of θ/p for various n. It would be misleading to give the table first, since the increase of $I_n(\theta)$ with n might suggest that K/K_∞ increases with n for fixed p; in fact, it tends to decrease owing to changes in the p/θ ratio. This point is made clear in (*c*) below, by giving the 'transition pressures' for specified values of K/K_∞. In (*d*) a note is added on temperature effects.

The appraisal of these results is deferred until § 8.

(*a*) *The relation of p to θ*

The parameter θ (60) is related to p through the collision frequency ω. In the assumed form (13) of ω,

$$k = 1{\cdot}38\times 10^{-16}\,\text{erg/deg.},\quad m = 1{\cdot}66\times 10^{-24} m^*\,\text{g},\quad N = 9{\cdot}72\times 10^{18} p/T,$$

where m^* is the molecular weight, and p is in mm of mercury. Thus (13) is

$$\omega = 6{\cdot}28\times 10^{23}\sigma^2 (m^*T)^{-\frac{1}{2}} p\ \ \text{s}^{-1}, \tag{74}$$

and the general formula for θ/p is, by (60),

$$\frac{\theta}{p} = \frac{6{\cdot}28\times 10^{23}}{\surd(m^*T)}\,\frac{\sigma^2 f_n}{\nu}\,b^{\frac{1}{2}(n-1)}. \tag{75}$$

In the following, the illustrative values used are

$$m^* = 50,\quad \sigma = 5\times 10^{-8}\,\text{cm},\quad \nu = 5\times 10^{13}\,\text{s}^{-1},\quad T = 700^\circ\,\text{K},\quad b = 40. \tag{76}$$

Values of f_n were given in table 1. From these and (75) and (76), the ratios p/θ of table 2 were calculated. They refer, like the f_n of table 1:

(α) to $\lambda = 1$ (73), so that $\mu_1\mu_2\ldots\mu_n$ is maximum and p/θ is minimum for varying μ_i;

(β) to the λ's listed in table 1, so that the μ_i have a moderate spread, and the p/θ ratios are more 'representative' than those of (α).

It is seen that for these illustrative values, p/θ decreases markedly as n increases.

Table 2. Ratios p/θ: (α) minimum, (β) 'representative'

n	3	5	7	9	11	13
p/θ (α)	$6{\cdot}15\times10^4$	658	7·09	0·0765	$8{\cdot}26\times10^{-4}$	$8{\cdot}92\times10^{-6}$
p/θ (β)	$1{\cdot}83\times10^5$	2770	43·7	0·694	0·0111	$1{\cdot}77\times10^{-4}$

(b) *Computed values of* $I_n(\theta)$

The integral $I_n(\theta)$, representing K/K_∞, was computed for $n = 3, 5, \ldots, 13$ from (58) and the special formulae (66) and (67). Some results for regular increments of $\log_{10}\theta$ are given in table 3. The numerical integration has been rounded to three figures, since check calculations of $I_n(\infty)$ gave 1·000... with some error in the next decimal.

Table 3. $I_n(\theta)=\dfrac{1}{\Gamma(\frac{1}{2}n+\frac{1}{2})}\displaystyle\int_0^\infty \frac{x^{\frac{1}{2}(n-1)}\mathrm{e}^{-x}\,\mathrm{d}x}{1+x^{\frac{1}{2}(n-1)}\theta^{-1}}$

n ... $\log_{10}\theta$	3	5	7	9	11	13
−2	0·0096	0·0044	—	—	—	—
−1	0·0835	0·0282	0·0101	—	—	—
0	0·404	0·189	0·0619	0·0154	—	—
1	0·844	0·579	0·258	0·0789	0·0180	—
2	0·981	0·904	0·632	0·280	0·0821	0·0178
3	0·998	0·988	0·912	0·627	0·269	0·0751
4	—	0·999	0·988	0·897	0·587	0·239
5	—	—	0·999	0·985	0·864	0·525
6	—	—	—	0·998	0·975	0·811
7	—	—	—	—	0·997	0·957
8	—	—	—	—	—	0·994

Table 4. $I_n(\theta_5)=0{\cdot}950$, $I_n(\theta_{50})=0{\cdot}50$

n	3	5	7	9	11	13
θ_5	37·1	213	2000	$2{\cdot}58\times10^4$	$4{\cdot}19\times10^5$	$8{\cdot}20\times10^6$
θ_{50}	1·56	6·65	46·3	448	5550	$8{\cdot}33\times10^4$
θ_5/θ_{50}	24	32	43	58	75	98

In table 4 are given the values θ_5 and θ_{50} of θ for which $I_n(\theta) = 0{\cdot}950$ and 0·50 respectively. These correspond to the pressures at which (for constant T) the rate has declined by 5 and 50 % respectively from the high-pressure limit; they will be called *transition pressures*.

It is easily visualized from table 3 that increasing n causes a lateral shift of the curve of I_n (or $\log_{10} I_n$) against $\log_{10}\theta$, together with a fairly slow change of shape of the curve. (The direction of the shift has no physical significance, because of the change in the p/θ ratio with n.) Similarly, in table 4, θ_5 and θ_{50} change markedly with n; the significant quantity, namely, the ratio θ_5/θ_{50}, increases slowly. The overall increase in θ_5/θ_{50} from $n = 3$ to $n = 13$ is, however, by a factor 4; this indicates a more gradual decline of rate with relative pressure for more complex molecules.

(*c*) *The decline of rate with pressure*

The estimates p/θ of table 2 could be used to convert table 3 into a table of K/K_∞ against $\log_{10} p$ for the various values of n. This, however, would over-emphasize or 'crystallize' the results for a special set of p/θ ratios; it is better to estimate the best n and p/θ ratio for any particular gas that is studied, and then construct a graph of K/K_∞ against $\log_{10} p$ from the corresponding column of table 3.

It will be a sufficient indication here of the general dependence of K/K_∞ on n if the p/θ ratios of table 2 are used to convert the θ_5, θ_{50} of table 4 into the corresponding 'transition pressures' of 5 and 50 % decline of K; this will suggest rough orders of magnitude. The results are shown in table 5, (α) for $\lambda = 1$, (β) for the λ of table 1. The results (α) indicate the minimum (for varying μ_i, and also for $\sigma \leqslant 5 \times 10^{-8}$) pressures at which the rate is 5 or 50 % down; the results (β) again are more 'representative' estimates. The ratios p_5/p_{50} are of course equal to the θ_5/θ_{50} of table 4.

Comments are made in § 8 on these 'transition pressures'. The sensitivity of absolute pressure estimates to changes in b as well as in f_n (compare the form (75) of p/θ) must be kept in mind.

TABLE 5. 'TRANSITION' PRESSURES (MM) OF 5 AND 50 % DECLINE: (α) AND (β) AS IN TABLES 1 AND 2

	n	3	5	7	9	11	13
(α)	p_5	$2{\cdot}3 \times 10^6$	$1{\cdot}4 \times 10^5$	$1{\cdot}4 \times 10^4$	2000	350	73
	p_{50}	$9{\cdot}6 \times 10^4$	4400	330	34	4·6	0·74
(β)	p_5	$6{\cdot}8 \times 10^6$	$5{\cdot}9 \times 10^5$	$8{\cdot}7 \times 10^4$	$1{\cdot}8 \times 10^4$	4650	1450
	p_{50}	$2{\cdot}9 \times 10^5$	$1{\cdot}8 \times 10^4$	2000	310	62	15

(*d*) *Temperature effect*

For any particular gas, the parameter θ determining K/K_∞ is by (75) proportional to $pb^{\frac{1}{2}(n-1)}\,T^{-\frac{1}{2}}$, and so to $pT^{-\frac{1}{2}n}$. Thus for one gas K/K_∞ has the same value for pairs of values (p, T) such that $pT^{-\frac{1}{2}n}$ is constant. If, for example, plots are made of $\log_{10}(K/K_\infty)$ against $\log_{10} p$, (1) at a temperature T_1 and (2) at a higher temperature T_2, then the curve (2) is the curve (1) shifted in the direction of increasing $\log_{10} p$ by an amount

$$\Delta \log_{10} p = \tfrac{1}{2} n \log_{10}(T_2/T_1), \tag{77}$$

since for the higher temperature the same K/K_∞ occurs at the higher pressure.

If $T_1 = 700°\,\mathrm{K}$, $T_2 = 750°$, $n = 13$, this shift is approximately $\Delta \log_{10} p = 0{\cdot}2$. This is of an order which could be tested by experiment.

Some comparisons of this nature with early experimental data were made by Kassel (1932, chapter x).

8. CONCLUSIONS

Concerning the central problem of the variation of rate with pressure at constant temperature, some 'general and particular trends' are listed here which are apparent in the foregoing theory and illustrative calculations. Some applications of the theory are then foreshadowed.

General trends

(i) The general shapes of $\log_{10} K$ against $\log_{10} p$ curve are naturally similar to those of earlier theories in which the dissociation probability increases with energy.

(ii) For fixed values of $b = E_0/kT$, m^*, σ as in § 7, the 'transition pressures' p_5 and p_{50}, of 5 or 50 % decline of K, tend to decrease as n increases (table 5). This suggests that the more complex the molecule, the lower will be the pressure at which the first-order rate is approached. But this general trend may be contradicted in specific instances; for example, of two gases the one with larger n may have the larger transition pressures if it has the smaller E_0.

(iii) The ratio p_5/p_{50} increases with n. This means that once K has begun to decline from K_∞, its subsequent decline with decreasing $\log_{10} p$ is the slower the larger n is. This 'trend' admits no exceptions if the approximations of § 6 are valid; for $p_5/p_{50} = \theta_5/\theta_{50}$, and this ratio (given in table 4) depends by the nature of $I_n(\theta)$ solely on n.

(iv) For a given gas, the pressure at which K/K_∞ has any assigned value increases with temperature (§ 7 (*d*)).

Particular trends

(v) Table 5 suggests that, for conditions roughly simulated by the constants used in § 7, gases will show first-order rates under two atmospheres only if n is at least 10, or more probably at least 12 (compare parts (α) and (β) of the table). First-order rates would appear for smaller n, however, in cases where b is appreciably larger than the value 40 used in § 7.

(vi) Smaller molecules should show rates between first and second order at normal ranges of pressure.

(vii) As for non-linear molecules the number n is at most $3N-6$, where N is the number of atoms, the trend (v) implies that (with $b \sim 40$) first-order rates would normally be observed only if N is at least about 6.

(viii) As by § 6 the present theory gives much the same K/K_∞ for n modes as Kassel's theory does for s oscillators, with $s-1 = \frac{1}{2}(n-1)$, it would be expected that Kassel's theory, fitted to particular gases, would require s to be at most half the available number $3N-6$ of degrees of freedom. In the examples in his book, s tends to be nearer two-thirds of this number; but this discrepancy is not conspicuous, and in any case a review of both old and recent data seems desirable.

Fields of application

(ix) The field to which the theory is best suited is the dissociation of molecules of which the vibrational structure has been fully analyzed; the constants $\alpha_1, \ldots, \alpha_n$ and ν are then calculable, and the rate K can be estimated, 'absolutely', as a function of pressure; the critical energy is however assumed as an empirical constant and there is uncertainty in the assignment of the appropriate collision diameter σ.

(x) For complex molecules of less well-known vibrational structure, it may be possible to deduce how many normal modes are effectively concerned in some likely breaking coordinate. The theoretical shape of the K against $\log_{10} p$ curve can then be inferred, and its position estimated for a conventional spread of the amplitude factors.

(xi) More reliable estimates of the *relative* behaviour of related molecules may be attempted. For example, (*a*) one may estimate the relative 'transition pressures' of molecules which are neighbours in homologous series by inferring the effective differences in n, without much attention to other detail; or (*b*) one may estimate the relative transition pressures of molecules differing only by an isotope at the critical co-ordinate.

(xii) Some comparisons of the types (ix) to (xi) (*a*) with early experimental data have been made. In view, however, of recent experiments and criticisms of the interpretation of early data, some fresh comparisons have been initiated.

9. Degenerate vibrations

This section deals with an important special case. So far the normal frequencies $\nu_1, \ldots, \nu_n$ have been all linearly independent, and so have certainly been all different. This excluded the phenomenon of degenerate vibrations in symmetrical molecules, which have pairs or triplets of normal modes with equal frequencies. The question arises: do the three degenerate modes of a triplet, for example, count as 3 in assessing the 'effective number' of normal modes in a breaking co-ordinate? The answer is, no; the general rate integral reduces to a form in which each degenerate set of modes is represented by a single mode with an enhanced 'amplitude factor', so that the effective number of modes is the number of distinct frequencies. This result is exact, if an additional assumption is admitted concerning the initial phases.

The precise result for a triplet of degenerate modes is the following. Let the breaking co-ordinate q contain n modes in all, so that it is of the form (3), but with

$$\nu_1 = \nu_2 = \nu_3, \quad \nu_3, \nu_4, \ldots, \nu_n \text{ independent,} \tag{78}$$

and let

$$\alpha' = \sqrt{(\alpha_1^2 + \alpha_2^2 + \alpha_3^2)}. \tag{79}$$

Then

the general reaction rate is as if there were $n-2$ modes with amplitude factors $\alpha', \alpha_4, \ldots, \alpha_n$ and frequencies $\nu_3, \nu_4, \ldots, \nu_n$. (80)

This theorem will be proved by an application of 'random-walk' theory, and some comments added.

By (78) the expression (3) can be written in the present case

$$q = a\cos 2\pi(\nu_3 t + \psi) + \sum_4^n a_i \cos 2\pi(\nu_i t + \psi_i), \tag{81}$$

where

$$a^2 = \left(\sum_1^3 a_s \cos 2\pi\psi_s\right)^2 + \left(\sum_1^3 a_s \sin 2\pi\psi_s\right)^2, \tag{82}$$

and, as in (3),

$$a_i = \alpha_i \sqrt{\epsilon_i} \quad (i = 1, \ldots, n). \tag{83}$$

In the case where $\nu_1, \ldots, \nu_n$ were all 'independent', the dissociation frequency L defined by (5) was a function of $a_1, \ldots, a_n$ and q_0, and independent of $\psi_1, \ldots, \psi_n$ (compare (7)). For the frequencies (78), L depends also on $\psi_1 - \psi_2$ and $\psi_2 - \psi_3$; or, if the form (3) of q is replaced by (81), L is a function of a (involving $a_1, a_2, a_3, \psi_1, \psi_2, \psi_3$ by (82)), $a_4, \ldots, a_n$ and q_0:

$$L = L(a, a_4, \ldots, a_n; q_0). \tag{84}$$

The formulation in § 3 of the rate K must be adjusted for this new dependence of L on phase. An 'energized molecule' is now one with energies $\epsilon_1, \ldots, \epsilon_n$ and phases ψ_1, ψ_2, ψ_3 such that q can attain the critical values q_0; this requires, by (81),

$$a + \sum_4^n |a_i| \geqslant q_0, \tag{85}$$

the ϵ_i, ψ_s entering this inequality through (82) and (83). An 'elementary energized range' is now a range $(\epsilon_i, \epsilon_i + \mathrm{d}\epsilon_i)$, $(\psi_s, \psi_s + \mathrm{d}\psi_s)$ satisfying (85). It is now assumed that the initial phases ψ_1, ψ_2, ψ_3 in the gas are uniformly distributed over the range $(0, 1)$, so that the equilibrium number of energized molecules in an elementary range would be (compare § 3) $N\,\mathrm{e}^{-E/kT} \prod_1^n (\mathrm{d}\epsilon_i/kT)\,\mathrm{d}\psi_1\,\mathrm{d}\psi_2\,\mathrm{d}\psi_3$. The additional factor $\mathrm{d}\psi_1\,\mathrm{d}\psi_2\,\mathrm{d}\psi_3$ now appears in equations (14) to (16) of § 3, and the rate (18) is replaced by

$$K = \int \ldots \int \frac{L\,\mathrm{e}^{-E/kT}}{1 + L/\omega} \prod_1^n \frac{\mathrm{d}\epsilon_i}{kT} \prod_1^3 \mathrm{d}\psi_s. \tag{86}$$

The integral may be taken for $\epsilon_i = (0, \infty)$, $\psi_s = (0, 1)$, since $L = 0$ where (85) is not satisfied. (For the low-pressure integral corresponding to (37) the factor $U\left(a + \sum_4^n |a_i| - q_0\right)$ must be inserted.)

The integration of (86) will first be performed for ϵ_1, ϵ_2, ϵ_3, ψ_1, ψ_2, ψ_3. Leaving out the 'factor'

$$\int \ldots \int \prod_4^n \{\exp(-\epsilon_i/kT)\,\mathrm{d}\epsilon_i/kT\}, \tag{87}$$

the integral (86) is

$$\int \ldots \int f(a) \prod_1^3 \{\exp(-\epsilon_s/kT)\,(\mathrm{d}\epsilon_s/kT)\,\mathrm{d}\psi_s\}, \tag{88}$$

where (compare (82) to (84))

$$f(a) = L/(1 + L/\omega). \tag{89}$$

In (88) the ϵ_s, ψ_s are replaced by new variables

$$\begin{matrix} x_s \\ y_s \end{matrix} = \alpha_s \left(\frac{2\epsilon_s}{kT}\right)^{\frac{1}{2}} \begin{matrix} \cos \\ \sin \end{matrix}\, 2\pi\psi_s \quad (s = 1, 2, 3), \tag{90}$$

so that

$$R^2 \equiv (\Sigma x_s)^2 + (\Sigma y_s)^2 = 2a^2/kT \tag{91}$$

by (82) and (83). Then (88) becomes

$$\int \ldots \int_{-\infty}^{\infty} f\{R\surd(\tfrac{1}{2}kT)\} \prod_1^3 \exp\left(-\frac{x_s^2 + y_s^2}{2\alpha_s^2}\right) \frac{\mathrm{d}x_s\,\mathrm{d}y_s}{2\pi\alpha_s^2}. \tag{92}$$

If (x_s, y_s) are components of three coplanar vectors, R is the length of the vector sum $\mathbf{R} = (X, Y) = (\Sigma x_s, \Sigma y_s)$. Now (92) is the expectation of a function f of R over a normal ('Gaussian') distribution of x_s, y_s, each with standard deviation α_s $(s = 1, 2, 3)$. For such a distribution, the sums X, Y each have normal distributions with standard deviation α' given by (79). The expectation (92) thus becomes, in terms of the distribution of the length R,

$$\int_0^\infty f\{R\surd(\tfrac{1}{2}kT)\} \exp(-R^2/2\alpha'^2)\, R\,\mathrm{d}R/\alpha'^2 = \int_0^\infty f(\alpha'\surd\epsilon_3) \exp(-\epsilon_3/kT)\,\mathrm{d}\epsilon_3/kT, \tag{93}$$

where

$$\epsilon_3 = \tfrac{1}{2}kTR^2/\alpha'^2;$$

this 'energy' is not to be identified physically with the original ϵ_3.

The rate (86) now becomes, by (87) to (89) and (93),

$$K = \int \dots \int \frac{L}{1+L/\omega} \exp\left(-\sum_3^n \frac{\epsilon_i}{kT}\right) \prod_3^n \frac{d\epsilon_i}{kT}, \tag{94}$$

where, by (84), (89) and (93), $L = L(\alpha' \sqrt{\epsilon_3}, a_4, \dots, a_n; q_0)$. This K is the rate as for a breaking co-ordinate of $n-2$ modes, namely,

$$q = \alpha' \sqrt{\epsilon_3} \cos 2\pi(\nu_3 t + \psi) + \sum_4^n \alpha_i \sqrt{\epsilon_i} \cos 2\pi(\nu_i t + \psi_i), \tag{95}$$

with α' given by (79). This proves the theorem (80).

The result applies equally to a pair of degenerate modes, and to any number of sets of degenerate modes in q.

Comments

(i) When the modes 1, 2 and 3 have equal frequencies, the corresponding amplitude factors α_1, α_2, α_3 are to some extent arbitrary; this corresponds to arbitrariness in the choice of the degenerate normal co-ordinates Q_1, Q_2, Q_3 (compare S′, equation (7)). But for different choices it can be shown that the sum $\alpha_1^2+\alpha_2^2+\alpha_3^2$ is invariant; thus the 'enhanced amplitude' α' (79) is invariant.

(ii) In the high-pressure limit where ω tends to infinity, the integral (94) can be evaluated by the methods of S′ and gives

$$K_\infty = \nu\, e^{-b}, \quad b = E_0/kT, \tag{96}$$

with

$$\alpha^2 = \alpha'^2 + \sum_4^n \alpha_i^2, \quad E_0 = q_0^2/\alpha^2,$$

$$\nu^2 = \left(\alpha'^2 \nu_3^2 + \sum_4^n \alpha_i^2 \nu_i^2\right)/\alpha^2.$$

By (79)

$$\alpha^2 = \sum_1^n \alpha_i^2,$$

$$\nu^2 = \sum_1^n \alpha_i^2 \nu_i^2/\alpha^2 \quad (\nu_1 = \nu_2 = \nu_3),$$

so that these constants α, E_0, ν agree with the earlier formulae (9), (10) and (23). Thus (96) is the same as the rate K_∞ (22) found for n independent frequencies. It can be shown that the formula (22) is true for any n frequencies (for example, with rational ratios) provided a random distribution of phase is assumed.

(iii) In the approximate evaluation of the rate (94) at general or low pressures the constants ν, E_0 (compare (ii) above) play the same role as before; the factor

$$\mu_1 \mu_2 \dots \mu_n = \alpha_1 \alpha_2 \dots \alpha_n \alpha^{-n}$$

of §§ 5 to 7 is of course replaced by

$$\alpha' \alpha_4 \alpha_5 \dots \alpha_n \alpha^{-(n-2)}$$

by the theorem.

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PHILOSOPHICAL TRANSACTIONS OF THE ROYAL SOCIETY A MATHEMATICAL, PHYSICAL & ENGINEERING SCIENCES

APPENDIX 1. THE LOW-PRESSURE INTEGRAL

A saddle-point method is sketched for the integral (43) to (45); notes are added on computation and on analytical details. It is assumed throughout that $b = h^2$ is large and n not too large; in examples h^2 has been about 40 and n up to 13.

The method. In (44) let

$$\psi(z) = \ln \Phi(z) = -2hz - \ln z + \sum_1^n \ln \phi(\mu_i z). \qquad \text{(A)}$$

This function has a unique minimum on the real positive axis, at z_0, say, and here the derivatives ψ''', ψ^{iv} are small compared with ψ'' (compare the details below). In the integral (43) take $c = z_0$, so that the path of integration is $z = z_0 + \iota y$, $y = (-\infty, \infty)$. With the Taylor expansion

$$\psi(z_0 + \iota y) = \psi_0 - \tfrac{1}{2} y^2 \psi_0'' - \tfrac{1}{6} \iota y^3 \psi_0''' + \tfrac{1}{24} y^4 \psi_0^{\text{iv}} \dots$$

(the suffix 0 indicating the value at $z = z_0$, where $\psi' = 0$), the integral (43) becomes

$$\Lambda = \frac{\Phi_0}{2\pi} \int_{-\infty}^{\infty} \exp\left(-\tfrac{1}{2} y^2 \psi_0'' - \dots\right) \mathrm{d}y.$$

The terms beyond y^3 in the exponential may be neglected; the term in ιy^3 yields a cosine factor which may be replaced by unity to a fair approximation. This gives the formula sought, namely

$$\Lambda = \Phi_0 / \surd(2\pi \psi_0''). \qquad \text{(B)}$$

The computation. For a given molecule with known values of the μ_i and h, it is simple to tabulate $\psi(z)$ for real positive z, and to find the minimum point z_0, and hence ψ_0 and ψ_0'' by interpolation. To tabulate $\psi(z)$ it is observed that in (45)

$$\phi(\mu) = 1 + 2\mu\{1 + H(\mu)\}/H'(\mu), \qquad \text{(C)}$$

where $H(\mu) = 2\pi^{-\frac{1}{2}} \int_0^{\mu} \mathrm{e}^{-x^2}\,\mathrm{d}x$ is the error function and $H'(\mu)$ its derivative; these are tabulated side-by-side in New York W.P.A. (1941).

Analytical details. (i) For positive μ, $\phi(\mu)$ (45) is monotonic. It has the expansion for small μ

$$\phi(\mu) = 1 + \surd\pi\,\mu + 2\mu^2 \dots, \qquad \text{(D)}$$

and asymptotically for large μ (the source of the approximation (46))

$$\phi(\mu) \simeq 2\surd\pi\,\mu\,\mathrm{e}^{\mu^2} + \frac{1}{2\mu^2} - \frac{3}{4\mu^4} + \dots. \qquad \text{(E)}$$

Also

$$\phi'(\mu) = \{(1 + 2\mu^2)\,\phi - 1\}/\mu. \qquad \text{(F)}$$

(ii) *The minimum of* $\psi(z)$ (z is real and positive in this subsection). From (A) and (F),

$$\psi'(z) = f(z)/z, \quad f(z) \equiv 2z^2 - 2hz + n - 1 - M(z), \qquad \text{(G)}$$

where

$$M(z) = \sum_1^n 1/\phi(\mu_i z) \quad \left(\sum_1^n \mu_i^2 = 1\right). \qquad \text{(H)}$$

As by (3) and (39) the μ_i lie strictly between 0 and 1, it can be inferred that, for large h, $f(z)$ has a unique zero at $z = z_0$ near h. If physically unreal distributions of the μ_i, such as $\mu_1 \approx 1$, μ_2, ..., $\mu_n \approx 0$, are excluded, then $M(z)$ is small near $z = h$ compared with the first three terms of $f(z)$ in (G). Hence the root z_0 is nearly

$$z_0 = \tfrac{1}{2}\{h + \surd(h^2 - 2n + 2)\} = h(1 - \epsilon - \epsilon^2 \dots), \quad \epsilon \equiv (n-1)/2h^2. \qquad \text{(J)}$$

For the derivatives of $\psi(z)$ at z_0,

$$\left.\begin{aligned}\psi'_0 &= 0,\\ \psi''_0 &= z_0^{-1}(4z_0-2h-M'_0)\approx 2(1-\epsilon-2\epsilon^2),\\ \psi'''_0 &\approx 4\epsilon(1+3\epsilon)/h, \quad \psi^{\text{iv}}_0\approx -12\epsilon(1+4\epsilon)/h^2,\end{aligned}\right\} \tag{K}$$

(neglecting the small derivatives M'_0, M''_0, ..., which can be expressed in terms of the $\phi(\mu_i z_0)$ by (F)). This confirms the relative magnitudes to be as stated after equation (A). The rough approximation $\psi''_0 = 2$ suggested by (K) shows that the order of magnitude of the result (B) is

$$\Lambda \approx \Phi_0/2\sqrt{\pi}. \tag{L}$$

(iii) *The case of similar* μ_i. If the μ_i are similar in size, all the $\phi(\mu_i z_0)$ in (B) may be represented approximately by the first term of (E). Then, since $\Sigma\mu_i^2 = 1$,

$$\Phi_0 = \exp(z_0^2-2hz_0)\,\mu_1\ldots\mu_n z_0^{n-1}(2\sqrt{\pi})^n.$$

Using (J) and (K) the result (B) becomes, as far as the terms of order ϵ^2,

$$\Lambda = \mu_1\mu_2\ldots\mu_n(4\pi h^2)^{\frac{1}{2}(n-1)}\,\mathrm{e}^{-h^2}\left\{1-\frac{(n-1)\,(n-2)}{4h^2}\right\}, \tag{M}$$

which agrees with the approximation (47) found in § 5 for similar μ_i.

Appendix 2. The general rate

The approximate formula (57) and (58) for the general rate is obtained here, and a note is added on the integral (58) as it appears in the work of Marcus.

The special notations will be used:

$$\tfrac{1}{2}(n-1) = m, \quad \Gamma(s+1) = s!, \tag{N}$$

where n is the number of normal modes; s is any variable. Also, integral signs preceded directly by $1/\iota$ imply paths from $c-\iota\infty$ to $c+\iota\infty$, with $c\geqslant 0$. The transform formulae to be used are

$$\frac{L}{1+L/\omega} = \frac{1}{2\iota}\int\frac{L^z\omega^{1-z}\,\mathrm{d}z}{\sin\pi z} \quad (0<\mathbf{R}(z)<1), \tag{O}$$

$$t^sU(t) = \frac{s!}{2\pi\iota}\int\frac{\mathrm{e}^{pt}}{p^{s+1}}\,\mathrm{d}p. \tag{P}$$

The rate integral (18) to be evaluated over the range (4) may be written

$$K = \int\ldots\int_0^\infty \frac{L\exp\left(-\sum\limits_1^n x_i^2\right)}{1+L/\omega}\,U\left(\sum_1^n\mu_i x_i - h\right)\prod_1^n(2x_i\,\mathrm{d}x_i), \tag{Q}$$

by the use of (38) to (40) and the variables x_i of (41). The approximation (6) to L is, with the present variables and notation,

$$L = \frac{1}{m!}\left(\frac{\Sigma\mu_i x_i - h}{2\pi}\right)^m\left(\frac{\Sigma\mu_i\nu_i^2 x_i}{\Pi\mu_i x_i}\right)^{\frac{1}{2}}. \tag{R}$$

Formula (O) is inserted in (Q), the order of integration is reversed, and then (R) is inserted for L, with the powers of $(\Sigma\mu_i x_i - h)$ and $(\Sigma\mu_i\nu_i^2 x_i)$ replaced by the appropriate transforms of the type (P). The result is

$$K = \frac{2^n}{2\iota}\int\frac{\omega^{1-z}A^z}{\sin\pi z}(\tfrac{1}{2}z)!\,(mz)!\,\mathrm{d}z\,\frac{1}{2\pi\iota}\int\frac{\mathrm{d}q}{q^{\frac{1}{2}z+1}}\,\frac{1}{2\pi\iota}\int\frac{\mathrm{e}^{-hp}}{p^{mz+1}}\prod_1^n\phi\{\mu_i(p+\nu_i^2 q)\}\,\mathrm{d}p, \tag{S}$$

where $A^{-1} = (2\pi)^m m! \surd(\mu_1 \ldots \mu_n)$, and (in contrast with the simpler integral (45) of the same type)

$$\phi(\mu) = \int_0^\infty \exp(\mu x - x^2)\, x^{1-\frac{1}{2}z}\, \mathrm{d}x. \tag{T}$$

For large h and only a moderate spread of the μ_i, $\phi(\mu)$ will be required for large $\mathbf{R}(\mu)$, so that approximately (compare (46))

$$\phi(\mu) = \surd\pi\, (\tfrac{1}{2}\mu)^{1-\frac{1}{2}z}\, \mathrm{e}^{\frac{1}{4}\mu^2}. \tag{U}$$

This is used in equation (S), with the relations $\Sigma\mu_i^2 = 1$, $\Sigma\mu_i^2\nu_i^2 = \nu^2$. The resulting factor $\Pi(p+\nu_i^2 q)$ in equation (S) is represented by $(p+\nu^2 q)^n$, and the exponent $p^2+2\nu^2 pq+\Sigma\mu_i^2\nu_i^4 q^2$ by $(p+\nu^2 q)^2$; this is an approximation requiring the ν_i alone to be of similar magnitude.

After these reductions of $\Pi\phi\{\ \}$, the part of equation (S) after '$\mathrm{d}z$' can be written

$$(\mu_1 \ldots \mu_n)^{1-\frac{1}{2}z}\, \pi^{\frac{1}{2}n}\, \mathrm{e}^{-h^2} \frac{1}{2\pi\iota}\int \frac{\mathrm{e}^{\nu^2 hq}\, \mathrm{d}q}{q^{\frac{1}{2}z+1}} \frac{1}{2\pi\iota}\int \frac{\mathrm{e}^{\frac{1}{4}u^2}}{p^{mz+1}} \{\tfrac{1}{2}(p+\nu^2 q)\}^{n(1-\frac{1}{2}z)}\, \mathrm{d}p, \tag{V}$$

where
$$u = p+\nu^2 q - 2h. \tag{W}$$

In the last integral, the variable p is replaced by u (shifting the path of integration), and the powers of p and $p+\nu^2 q$ are represented by powers of $2h$; this gives the leading term in an expansion which could be carried further. The integrals for q (using (P)) and u are then

$$\frac{1}{2\pi\iota}\int \frac{\mathrm{e}^{\nu^2 hq}}{q^{\frac{1}{2}z+1}}\, \mathrm{d}q = \frac{(\nu^2 h)^{\frac{1}{2}z}}{(\frac{1}{2}z)!}, \quad \frac{1}{2\pi\iota}\int \mathrm{e}^{\frac{1}{4}u^2}\, \mathrm{d}u = \frac{1}{\surd\pi}.$$

The integral (equation (S)) is now, with the notation of (60) and (61),

$$K = \frac{\nu\, \mathrm{e}^{-b}}{m!} \frac{1}{2\iota}\int \frac{\theta^{1-z}(mz)!\, \mathrm{d}z}{\sin \pi z} = \frac{\nu\, \mathrm{e}^{-b}}{m!}\int_0^\infty \mathrm{e}^{-t}\, \mathrm{d}t \frac{1}{2\iota}\int \frac{t^{mz}\, \theta^{1-z}\, \mathrm{d}z}{\sin \pi z},$$

or, by (O),
$$K = \frac{\nu\, \mathrm{e}^{-b}}{m!}\int_0^\infty \frac{t^m\, \mathrm{e}^{-t}\, \mathrm{d}t}{1+t^m\theta^{-1}}.$$

This is the result (57) and (58), if the special notations (N) are now removed.

Note on $I_n(\theta)$ in Marcus's theory

An integral of the form (58) occurs in a unimolecular rate formula of Marcus (1952*a*), namely,

$$\frac{1}{\Gamma(1+\frac{1}{2}r)}\int_0^\infty \frac{\mathrm{e}^{-x}\, x^{\frac{1}{2}r}\, \mathrm{d}x}{1+ax^{\frac{1}{2}r}},$$

the parameter a being inversely proportional to the pressure. In the notation (58) this integral is $I_{r+1}(1/a)$, so that it has the same pressure dependence as (58) since the parameter θ of the present theory varies as the pressure. The formal resemblance is close, but the interpretation is quite different; Marcus's r represents the number of 'non-adiabatic rotations of the activated complex' and is not related to vibrational degrees of freedom.

In a companion paper Marcus (1952*b*) evaluates the equivalent of $I_5(\theta)$ by sine and cosine integrals, and approximates to $I_7(\theta)$ by a method akin to the present appendix 1. His method could be extended to higher values of n, but it does not lend itself to the computation of $I_n(\theta)$ for regular increments of $\log_{10}\theta$. The numerical quadrature used for $n > 5$ in table 3 appears to be as simple for this purpose.

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