

Introduction: a brief historical perspective

The statistical theory of unimolecular reactions, now universally known as the “RRKM” theory, has its origins around 1925 when Oscar K. Rice, then a postdoc at Berkeley, became interested in interpreting experimental results on the decomposition of azomethane obtained by Herman C. Ramsperger, another postdoc in the same department. Rice later moved to Cal Tech, where he met Louis S. Kassel, who was working on the same problem. Thus was born what became known as the “RRK” theory.

While building on earlier treatments of unimolecular reactions by Lindemann and Hinshelwood [1, pp. 108ff.], RRK were astute to avoid all dynamical considerations by recognizing that the dissociation of a sufficiently large and suitably energized molecule is basically statistical. They viewed the reacting molecule as an assembly of harmonic oscillators that freely exchange energy; decomposition occurs when by chance a particular critical oscillator accumulates the minimum amount of energy necessary for reaction. RR worked out the problem in terms of classical statistical mechanics [2], whereas Kassel used the discrete combinatorial approach [3].

Since the process of activation (mainly collisional activation at the time) is unlikely to deposit energy directly in the critical oscillator, it can be expected that it will take a while for the requisite amount of energy to find its way into the critical oscillator, time that is longer the larger the number of oscillators in the molecule (“large molecules live longer”). This accounts for the time-lag between activation and decomposition postulated by Lindemann and Hinshelwood and links it to the size of the molecule. However, unlike in Hinshelwood’s theory, the rate constant for decomposition (i.e. the inverse of the lifetime) becomes an increasing function of energy. A few years later, Rice [4] (with Gershinowitz) added the qualitative notion of an “activated complex” (i.e. transition state) as introduced by Eyring [5] in the “absolute reaction-rate theory” which dominated the thinking in the decade before World War II.

It is ironic that the basic idea of the theory survived the ravages of time much better than did the experimental results it sought to explain, for it is now known that the decomposition of azomethane is not a very good reaction on which to test unimolecular theory, afflicted as the reaction is by a free-radical chain [6]. In any event, the state of the technology at the time was such that it was not possible to carry out meaningful experimental tests of the theory, and hence for a time there were no new theoretical developments.

After a hiatus of more than ten years, Rice (who was by then at the University of North Carolina, Chapel Hill) took up the subject of unimolecular reactions again in 1949 when a new postdoc came to Chapel Hill in the person of R. A. Marcus. He introduced the notions of active and adiabatic (essentially rotational) degrees of freedom, as well as quantum considerations, and in general put the notion of the transition state in unimolecular reactions on a firm footing [7]. The circumstances were obviously ripe for a RRK-type unimolecular rate theory incorporating the transition-state concept, for almost at the same time Rosenstock, Wallenstein, Wahrhaftig, and Eyring [8] put forward a theory of mass spectra (known to mass spectrometrists as the QET, or the quasi-equilibrium theory), which, in slightly different language, invoked the same general idea as RRK, a fact not appreciated until many years later [9].

Marcus' improvements did not have an immediate impact since at about the same time a rival, mathematically very elegant, theory due to N. B. Slater [10] came into vogue. Unlike RRK or QET, this theory addressed the problem of the dynamics of reaction: a unimolecular decomposition was seen as the result of a collection of harmonic oscillators coming sufficiently into phase such that the bond extension of a particular oscillator exceeded a critical value and the oscillator dissociated. The time taken to reach this value could be calculated from detailed vibrational analysis of the normal modes. By then the advent of gas chromatography had greatly increased the sensitivity and selectivity of analysis, which encouraged the experimentalists to test Slater's theory. It eventually appeared that his theory predicted thermal rate constants at low pressures that were too small, which was ultimately traced to the unphysical assumption that a decomposing (and therefore highly excited) molecule could be treated as a superposition of normal modes, whereas such a molecule is in reality considerably anharmonic and therefore is able to share energy much more freely [11].

Largely as a result of the considerable amount of experimental data produced in the laboratory of B. S. Rabinovitch (BSR) from about 1960 onwards, much of it by the then-new technique of chemical activation, it became clear that the purely statistical treatment of "RRKM" (as the theory, with Marcus' additional improvements [12], became known) was the more physically reasonable. Also at this time computers started to appear, and BSR's laboratory developed most of the early

computational routines necessary for practical numerical applications of the theory. As more and more experimental data on a large variety of unimolecular reactions appeared, it became evident that the main RRKM premise, namely complete randomization of energy among internal degrees of freedom prior to dissociation, is violated only in very special circumstances. With the wide-ranging applicability of the RRKM theory thus demonstrated, there appeared in due course a couple of monographs [9, 13] summarizing developments roughly up to 1970.

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The RRK model

“RRK” was historically the first successful model of a unimolecular reaction, being put forward in 1926 by Rice and Ramsperger [1], and, independently and almost simultaneously, by Kassel [2]; hence the abbreviation “RRK.” It conveys all the essential features of a unimolecular reaction, to the point where it is almost semi-quantitatively correct. Although nowadays it has been supplanted by more elaborate versions (known as the RRKM theory and variants thereof), the simplicity of the RRK version has the virtue of bringing into sharp focus the basic assumptions of the theory which perhaps tend to get obscured in the RRKM version. Therefore the exposition of RRK theory has instructional value, in that it lays the foundations on which to build a more elaborate theory.

The presentation below of the RRK theory follows the Kassel discrete-quantum version (sometimes abbreviated to “QRRK”) which has been found useful in modeling multiphoton dissociation (see, e.g., [3–6]). The Rice–Ramsperger version forms the basis of the development given in Chapter 3.

1.1 Isolated molecule

1.1.1 *The model*

Consider an elementary unimolecular process in which a single isolated molecule dissociates, by simple bond rupture, into two fragments. Let us represent the stable (bound) reactant molecule by a collection of harmonic oscillators, say s in number. The reaction, i.e. the bond rupture, will correspond to one particular oscillator – the critical oscillator – dissociating as soon as it has accumulated the necessary energy. The critical oscillator is therefore considered to be a harmonic oscillator with a cut-off (cf. Fig. 2.1).

The process by which oscillators, and the critical oscillator in particular, accumulate energy is left unspecified.

At the simplest level, we shall assume that all the oscillators are of the same frequency ν ; this is the same as if the decomposing molecule were composed of one s -fold-degenerate oscillator of frequency ν . The frequency restriction will be relaxed later.

1.1.2 The probability of dissociation

A suitable excitation process will cause the oscillators to take up energy in the form of quanta, i.e. multiples of $h\nu$ (h is Planck's constant). Suppose that the excitation energy amounts to n quanta; the question of how the n quanta are distributed among the s oscillators now arises. The answer is that, if there is no information (and such was certainly the case around 1930), the only reasonable way to proceed is to assume that *all* ways to distribute the n quanta among the s oscillators are equally probable.

Formulated in this way, the question is identical to a problem in elementary probability, namely the total number of ways n indistinguishable balls can be distributed among s indistinguishable boxes (indistinguishable because obviously neither the quanta nor the oscillators can be distinguished one from the other). The answer can be found as follows: to delimit the s boxes, we need $s - 1$ partitions, represented below by a vertical stroke ($|$), whereas a ball will be represented by a circle (\circ). Imagine the balls and the partitions laid out in a linear array, for example

$\circ \circ \circ | \circ \circ | \circ \circ \circ \circ | \circ | \circ \circ \circ \circ \circ \circ | \circ | \circ \circ | \circ \circ \circ \dots$ etc.

The number of permutations of $s - 1$ partitions and n balls, i.e. of $n + s - 1$ objects, is $(n + s - 1)!$ if the objects are distinguishable; since they are not, we have to divide by the number of permutations of n balls, multiplied by the number of permutations of $s - 1$ partitions, i.e. by $n!(s - 1)!$, so that W_n , the number of ways to put n balls (quanta) into s boxes (oscillators) is

$$W_n = \frac{(n + s - 1)!}{n!(s - 1)!} \quad (1.1)$$

With respect to the problem at hand, Eq. (1.1) represents the number of *states* of an s -fold-degenerate oscillator containing n quanta, or the degeneracy of state n for short.

By hypothesis the critical oscillator will dissociate as soon as it contains m quanta ($m \leq n$), which means that the remaining $s - 1$ oscillators will contain $n - m$ quanta. By an argument similar to the above, we see immediately that the number of ways to put $n - m$ quanta into $s - 1$ oscillators is

$$W_{n-m} = \frac{(n - m + s - 2)!}{(n - m)!(s - 2)!} \quad (1.2)$$

Thus the *probability* that, if s oscillators contain n quanta, one particular (critical) oscillator shall contain (exactly) m quanta is

$$p_{n,m} = \frac{W_{n-m}}{W_n} = \frac{(s-1)(n-m+s-2)!n!}{(n-m)!(n+s-1)!} \quad (1.3)$$

which makes use of the relation $(s-1)! = (s-1)(s-2)!$.

The critical oscillator obviously will dissociate whenever it contains a number of quanta that exceeds the critical threshold of m quanta, i.e. for any number of quanta between m and n . Hence the distribution of Eq. (1.2) has to be summed for all $m \leq n$:

$$W_{n \geq m} = \sum_{i=m}^n W_{n-i} = \sum_{i=m}^n \frac{(n-i+s-2)!}{(n-i)!(s-2)!} \quad (1.4)$$

Let $n-i = y$, hence $0 \leq y \leq n-m$, so that Eq. (1.4) becomes

$$W_{n \geq m} = \sum_{y=0}^{n-m} \frac{(y+s-2)!}{y!(s-2)!} \quad (1.5)$$

This summation can be evaluated by an argument similar to that used in connection with Eq. (1.1) by the device of adding one extra partition that provides an additional box into which to put the $n-m-y$ balls left over after y of them ($0 \leq y \leq n-m$) have been placed into the first $s-1$ boxes. In this way we obtain

$$\sum_{y=0}^{n-m} \frac{(y+s-2)!}{y!(s-2)!} = \frac{(n-m+s-1)!}{(n-m)!(s-1)!} \quad (1.6)$$

and hence the *probability* that, if s oscillators contain a total of n quanta, a particular (critical) one shall contain *at least* m quanta is

$$p_{n \geq m} = \frac{W_{n \geq m}}{W_n} = \frac{(n-m+s-1)!n!}{(n-m)!(n+s-1)!} \quad (1.7)$$

1.1.3 The rate constant and lifetime

In chemical kinetics, the information desired is the rate constant. Before proceeding further it is of interest to consider briefly the wider implication of what in the present instance is the unimolecular rate constant k .

If isolated reactant molecule M decomposes (i.e. disappears) in a unimolecular reaction with rate constant k , this means that

$$-\frac{1}{[M(t)]} \frac{d[M(t)]}{dt} = k \quad (1.8)$$

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where square brackets signify concentrations at time t . This is in fact the definition of a first-order rate constant. The ratio $d[M(t)]/[M(t)]$ is the fraction of molecules decomposing, that is, the probability of decomposition P , so that Eq. (1.8) can be written

$$-\frac{d[M(t)]}{[M(t)]} = k dt = P \quad (1.9)$$

on the assumption that P depends only on the length of the interval dt that M is under observation but is otherwise independent of time. Therefore k represents the probability of decomposition per unit time, likewise independent of time, i.e. independent of the time interval during which the decay of $M(t)$ is measured. Consequently Eq. (1.9) can be integrated directly to yield, with $[M(t = 0)]$ the initial concentration of M ,

$$[M(t)] = [M(t = 0)] \exp(-kt) \quad (1.10)$$

which means that M will decay with a simple exponential time dependence.

Now the probability of M *not* decomposing in dt , i.e. the probability of survival in dt , is $1 - P = 1 - k dt$, and the probability of surviving n such intervals is $(1 - k dt)^n$, given that, by hypothesis, P is independent of time. If we let $n dt = t$, then the probability of survival in $(0, t)$ is

$$P(t) = \lim_{n \rightarrow \infty} (1 - k dt)^n = \lim_{n \rightarrow \infty} \left(1 - k \frac{t}{n}\right)^n = \exp(-kt) \quad (1.11)$$

In other words, $P(t) = \exp(-kt)$ is the probability of lifetime t . A lifetime that obeys Eq. (1.11) is said to be random, for reasons that will appear shortly. Normalized to unity, $P(t)$ becomes

$$P'(t) = k \exp(-kt) = -\frac{dP(t)}{dt} \quad (1.12)$$

which can be shown (Problem 1.1) to be the rate referred to the number of molecules present initially, rather than at time t , as in Eq. (1.8). A further ramification is the subject of Problem 1.2. The average lifetime $\langle t \rangle$, using the usual definition of an average, turns out to be the reciprocal of k :

$$\langle t \rangle = \int_0^{\infty} t P'(t) dt = \frac{1}{k} \quad (1.13)$$

1.1.4 The Kassel rate constant

Returning to the problem on hand, with Eq. (1.7) for the probability, and in view of the consequence of Eq. (1.9), according to which the rate constant k represents the

probability of decomposition per unit time, we can now write for the rate constant

$$k_{n \geq m} = A p_{n \geq m} = A \frac{(n - m + s - 1)! n!}{(n - m)! (n + s - 1)!} \quad (1.14)$$

where, since the probability $p_{n \geq m}$ is dimensionless, there appears a proportionality constant A of dimension s^{-1} . This is also the dimension of frequency, so that A can be interpreted as the characteristic frequency with which oscillators exchange quanta of energy. Since most oscillator frequencies are about 10^{13} s^{-1} , we can expect A to be of the same order of magnitude.

It is worthwhile to stop here and ponder the meaning of Eqs. (1.7) and (1.14). The derivation is based on the assumption that there exists a large collection of reactant molecules with a distribution of quanta such that every possible distribution is represented with equal probability. In other words, $p_{n \geq m}$ measures the probability that a molecule chosen at random will have the specified property, which is reflected in the lifetime represented by Eq. (1.11). The implication is that $p_{n \geq m}$, and hence the rate constant $k_{n \geq m}$, measures an *average* property of decomposing molecules.

The second assumption is that $p_{n \geq m}$ and the underlying distribution are achieved whatever the excitation process. This means that, if, at the moment of excitation, the distribution is different (e.g. most molecules contain all n quanta in only a few of the s oscillators), then by the time the collection of molecules actually dissociates all possible distributions are equally represented. The implication is that (1) there is some mechanism for the redistribution of quanta among the oscillators, and (2) there is a time-lag between excitation and dissociation that allows the redistribution to take place. Thus $1/k_{n \geq m}$ may be interpreted as the average time-lag, i.e. average lifetime of an excited molecule (Eq. (1.13)).

The putative existence of a mechanism for the redistribution of quanta (or randomization as it is often called) means that the oscillators cannot be strictly harmonic since harmonic oscillators are unable to exchange quanta. The oscillators must therefore be considered perturbed (e.g. anharmonic), sufficiently so that a redistribution of quanta may take place, but not enough to invalidate the calculation that leads to the probability of dissociation $p_{n \geq m}$. The exact mechanism of the perturbation need not be specified since it does not appear anywhere explicitly.

1.1.5 The energy dependence

Equation (1.14) is not always useful for calculations because the factorials quickly become very large even for relatively small values of n . If the factorials are developed and common terms dropped, we get

$$p_{n \geq m} = \frac{(n - m + 1)(n - m + 2) \dots (n - m + s - 1)}{(n + 1)(n + 2) \dots (n + s - 1)} \quad (1.15)$$

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Assuming that $s - 1 \ll n - m$, which in a large molecule corresponds to the classical limit, Eq. (1.15) reduces to a simpler, but less realistic, version of Eq. (1.7):

$$p_{n \geq m} \approx \left(\frac{n - m}{n} \right)^{s-1} \quad (1.16)$$

Problems 1.3 and 1.4 explore an alternative approach using Stirling's approximation to the factorials. If it is more convenient to work in terms of energies rather than quanta, let $E = nh\nu$ and $E_0 = mh\nu$, where E is now the excitation energy and E_0 is the critical energy for dissociation. On combining Eqs. (1.15) and (1.16) we have

$$k(E) = A \left(1 - \frac{E_0}{E} \right)^{s-1} \quad (1.17)$$

where $k(E)$ is now the unimolecular rate constant (s^{-1}) in terms of energy. Equation (1.17) is known as the Kassel form of the unimolecular rate constant. A more elaborate version of $k(E)$ is the subject of Chapter 3.

Consider now the physical implications of Eq. (1.17). Since the rate constant $k(E)$ is by definition positive, Eq. (1.17) implies that $k(E) = 0$ for $E < E_0$. At the other extreme, as $E \rightarrow \infty$, $k(E) \rightarrow A$, which means that the rate constant cannot exceed the rate at which oscillators exchange energy. At intermediate energies, $k(E)$ will be an increasing function of energy, the rate constant with the *smallest* s being numerically largest (Fig. 1.1). Hence, at the same excitation energy, the average lifetime (given by $1/k(E)$) of a small molecule (small s) is shorter than the average lifetime of a large molecule (large s). Physically this means that, in

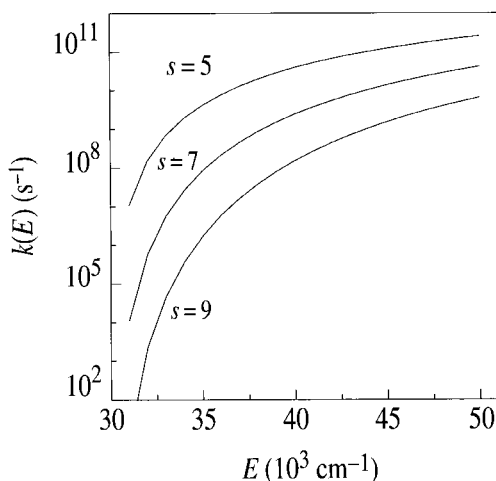


Fig. 1.1. An illustration of the energy dependence of $k(E)$ given by Eq. (1.17) at three values of the parameter s , assuming that $E_0 = 30\,000\text{ cm}^{-1}$ and $A = 10^{13}\text{ s}^{-1}$.

a large molecule, it takes longer for the energy to “find” its way into the critical oscillator, since there are many more ways to distribute a given energy. In short, “a large molecule lives longer.” These are the principal characteristics of the RRK rate constant which are also found in every more elaborate version of unimolecular rate theory.

Note in particular that the rate constant is a function only of energy E and of the complexity of the molecule as represented by the parameter s . Implicit is the notion that the development is valid only insofar as the oscillators exchange energy at a rate ($A \text{ s}^{-1}$) that is faster than the rate at which the molecule actually dissociates. No reference is made anywhere to the dynamics of the dissociation process, which is avoided by the use of probabilistic arguments.

1.1.6 Non-degenerate oscillators

In any real molecule, oscillators are not all of the same frequency, and the problem of how to modify the preceding development then arises. The simplest way is to replace the individual frequencies ν_i ($i = 1, \dots, s$) by some kind of average. Which average? It appears that the answer depends to some extent on the use one wishes to make of the RRK formulation. In infrared laser multiphoton dissociation, for example $\text{SF}_6 \rightarrow \text{SF}_5 + \text{F}$ [3, 4], it is useful to work with quanta rather than energies. In such cases some [5] argue in favor of the arithmetic-average frequency $\langle \nu \rangle = \sum_i \nu_i / s$ as most appropriate, whereas others [6] favor the geometric average

$$\langle \nu \rangle = \left(\prod_{i=1}^s \nu_i \right)^{1/s} \quad (1.18)$$

where s is defined, as before, as the total number of oscillators. In either case, if the total energy is E , the corresponding (average) quantum is then $\langle n \rangle = E / (h \langle \nu \rangle)$. Thus the essence of the previous development is preserved, with ν and n merely replaced by averages.

1.2 Molecule in a thermal system

1.2.1 Lifetimes and collisions

So far we have considered only the somewhat artificial case of the decomposition of an isolated molecule. In a more realistic situation such as a thermal reaction, molecules undergo collisions that affect their survival probability.

Collisions being random, if the collision frequency is ω , the probability of collision in t , $t + dt$ is ωdt , and the probability of *no* collision in $0, t$ is $\exp(-\omega t)$, using the same argument as that which led to Eq. (1.11). If decomposition is also random,