*ABSOLUTE RATE THEORY FOR ISOLATED SYSTEMS AND THE MASS SPECTRA OF POLYATOMIC MOLECULES**

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Studies of the interaction of electrons with atoms and molecules have been of fundamental importance in the development of present-day physical theories. As has been stated so many times, the general problem is now solved "in principle" by the quantum mechanics, but the application of the theory to only the simplest systems has been practicable.[1, 2] In recent years a very large amount of data has been accumulated on the "mass spectra" resulting from the bombardment of molecules by electrons of energy 50 and 70 volts.[3] There is also a significant amount of data on special aspects of the mass spectra of a few polyatomic molecules. A reasonably exact analysis of a mass spectrum would require detailed knowledge of all the electronic states both of the molecule and of all the ions formed from it by removal of electrons and by removal and rearrangement of nuclei. In this paper we present a statistical approach to the problem. Necessarily, assumptions and approximations are required. While this theory is in no way complete, we believe it permits the discussion and coordination of a large amount of the available data in terms of the structure of molecules and ions.

Knowledge of the effect of low-voltage electron bombardment on molecules, besides being of interest in its own right, has varied applications. It has bearing on the relation of molecular structure to chemical reactivity. It is well known that the major fraction of the effect of high energy radiation on matter, including living systems, is due to the low energy secondary electrons.[4] The rate theory presented here should also be applicable to other problems involving isolated systems having a large but finite number of degrees of freedom.

The ionization and dissociation of diatomic molecules by electron impact has by now become quite well understood. Hagstrum[5] has recently discussed in great detail the mass spectra of a number of diatomic molecules, explaining the formation of the several ions and their kinetic energies in terms of Franck-Condon transitions to the various electronic states of the diatomic ions. Another discussion is that of Stevenson[6] who calculated the relative abundance ratios H^+/H_2^+ and D^+/D_2^+ in the mass spectra of hydrogen and deuterium, again using the picture of Franck-Condon transitions to known electronic states. While any discussion of large polyatomic molecules mass spectra must be in accord with these discussions, the direct application of the same methods is impossible.

We start with the following hypothesis, first stated by us at the Oberlin Symposium on Biological Effects of Radiation in 1950 and later elaborated by Wallenstein:[7,8]

Following vertical ionization, the molecule-ion has a certain amount of excitation energy in its electronic and vibrational degrees of freedom, referred to the minimum of its lowest electronic state. Most of the time, this excited molecule-ion does not decompose immediately into ionized and neutral fragments but rather undergoes at least several vibrations. During these vibrations there is high probability of radiationless transitions among the many potential surfaces for the molecule-ion, resulting in a distribution of the excitation energy in completely random fashion. The molecule-ion decomposes only when the nuclei are in the proper configuration and a sufficient amount of vibrational energy has concentrated in the necessary degrees of freedom. The fragments in turn may have sufficient energy to decompose through a similar sequence of events. Rearrangement of the bonds, without dissociation, also may occur in the same fashion.

This hypothesis is based on the early work of Franck and coworkers.[9] It is implicit in the calculations of Stevenson and others on bond energies

TABLE 1

MOLECULE	$\dfrac{\text{C–H BONDS}}{\text{TOTAL BONDS}}$	$\dfrac{C_nH_{2n+1}^+ {}^a}{\text{TOTAL IONIZATION}}$
Propane	0.8	0.08
n-Butane	0.77	0.008
n-Heptane	0.73	0.00002

[a] Calcd. from data in reference 13.

for the processes involved in simple dissociation of the parent molecule-ion at electron voltages near the appearance potential.[10, 11] Similar considerations are also implied in a paper by Langer.[12] The extension of this idea of successive, quasi-equilibrium, unimolecular dissociations to the entire mass spectrum of a molecule is, we believe, new. It is not the complete story; certainly some ionization, especially multiple ionization, will yield immediate dissociation of a non-statistical character. The evidence is that such immediate dissociation follows only a small fraction of the total ionizing collisions.

Let us consider some of the arguments favoring the above hypothesis.

On the contrary assumption that the decomposition of the parent molecule-ion is determined by the location of a particular bond from which the electron is removed, a simple relation should exist between the relative abundance of certain product ions and the number of bonds available in the parent molecule-ion for this type of dissociation. For example, the relative amount of $C_nH_{2n+1}^+$ ions to total ions in a paraffin hydrocarbon mass spectrum should be proportional to the ratio of C–H bonds to total bonds. This is not the case, as may be seen from the data in table 1.

Further interesting evidence is obtained from the "total ionization" of a compound, i.e., the total amount of ions formed by a given electron current passing through the compound under specified conditions. There is a tremendous variation in the breakdown patterns among various isomers of a given composition, but the total ionization remains remarkably constant, as shown in table 2. This implies that the probability of removal of a va-

TABLE 2

HYDROCARBON	NUMBER OF ISOMERS	TOTAL IONIZATION (ARBITRARY UNITS)		
		MEAN VALUE	MAXIMUM DEVIATION, %	MEAN DEVIATION, %
C_8H_{18}	18	1.79	10	$3^1/_2$
C_9H_{20}	35	1.94	20	$6^1/_2$
C_6H_8	10^a	1.03	7	4

[a] Including cyclo-olefins, -dienes, and -ynes.

lence electron is essentially independent of the orbital occupied by the electron. The data on stopping power for high energy particles lead to the same conclusion.[17] However, different orbitals will contribute in widely different fashion to the strength of various bonds. Hence, we conclude that after formation but before dissociation of the ion there must be a period during which the energy is distributed throughout the ion.

For the postulated mechanism of energy transfer it is necessary that the density of electronic states for the ion be such that there exist sufficient crossings of the potential surfaces. Consider the propane ion which has nineteen bonding electrons. The number of states corresponding to this system of nineteen electrons all in their ground states is 2^{19}.[1] However, many of these states are degenerate. The number of different eigenvalues, aside from accidental degeneracy, is

$$\frac{n!}{\left(\frac{n +\cdot 1}{2}\right)!\left(\frac{n - 1}{2}\right)!}$$

which for $n = 19$ is of the order of 10^5. These distinct eigenvalues all lie in the range between zero, taken as the lowest state of the ion, and about 100 electron volts, corresponding to the completely antibonding state of the ion. This gives an average spacing between states of about one millivolt. There is, in addition, a still larger number of states corresponding to the various excited states of the separated atoms lying within the same limits. The vibrational energy of such a molecule-ion at room temperature is of the order of one-half electron volt, many times larger than the spacing between states. As the potential surfaces will differ greatly in their dependence on nuclear coordinates, the necessary number of crossings will surely exist.

A consequence of molecular-orbital theory for polyatomic molecules is that a molecule or ion with a half-filled orbital is better described in terms of non-localized molecular orbitals while a molecule containing paired electrons can be described either by non-localized molecular orbitals or by localized valence-orbitals.[18, 19] Thus, a system minus one electron will, in general, have not one much weakened bond but several bonds each weakened to a lesser extent. In particular, the totality of electronic states will not divide into two groups, one completely attractive, the other strongly repulsive in at least one bond direction. Rather, there will be many states which are attractive even though several antibonding electrons are present. In agreement with this, mass spectra show little evidence of fragments arising from strongly repulsive states and so having energies of several volts. This follows from direct measurements[20] and from the symmetrical shape of the mass peaks. Also since mass spectrometers strongly discriminate against ions having appreciable kinetic energy, the constancy of total ionization for isomers indicates that most ions are formed without appreciable kinetic energy.

A most serious gap in any theoretical discussion of mass spectra centers about the problem of energy transfer. One would like to have a distribution function for the fractions of parent ions formed with various amounts of internal excitation energy as a result of electron impact. An attack has been made on this problem only for the hydrogen and helium atoms.[2] However, if one can calculate the breakdown kinetics for parent ions having various internal excitation energies, it will be possible to determine an initial distribution function such that the observed mass spectrum is obtained. Such a distribution function should change in a simple manner for a series of electronically similar molecules such as the paraffin hydrocarbons.

A rate equation applicable to isolated systems may be developed in a fashion analogous to the absolute reaction rate theory of Eyring.[21] Other rate equations using similar reasoning have been discussed by Rice, Ramsperger and Kassel[22] and very recently by Marcus.[23] The liquid drop theory of the nucleus can likewise be treated in principle by this same method.[24]

The behavior of an isolated system is properly described in terms of a microcanonical ensemble,[25] with systems uniformly distributed over all states having energies in the region E to $E + \delta E$ and having nuclear configurations corresponding to the initial chemical structure of the systems. For a reaction to occur, the system must have at least one other stable configuration; since initially the system has a known configuration, each member system of the ensemble can be described as a superposition of many pure states. Consistent with the previously stated hypothesis, it is assumed that the rate of transition of a system among the states is sufficiently

rapid so that the reaction yielding a different configuration has only a negligible effect on the distribution of the unreacted systems among the states. In general, it will be possible to select a "reaction coordinate," and an "activated complex" defined in terms of a saddle point on a potential surface, such that the change in the reaction coordinate describing the motion of the system through the saddle can be taken to be a translational motion.

In principle, the number of states of the system having energy between E and $E + \delta E$, with the system in the initial configuration, can be calculated. If the number of states is large, this number can be represented by a density function: $\rho(E)\delta E$. The activated state will be defined by a total energy between E and $E + \delta E$, with potential energy ϵ_0 and kinetic energy between ϵ_t and $\epsilon_t + \delta\epsilon_t$ in the reaction coordinate. The corresponding number of activated states will be given by $\rho^{\pm}(E, \epsilon_0,\epsilon_t)\rho_t(\epsilon_t)\delta E\text{-}\delta\epsilon_t$. Using the usual expression for translational energy, the density of translational states per length l in the reaction coordinate is

$$\rho_t(\epsilon_t) = \frac{l}{h}\sqrt{\frac{2\mu}{\epsilon_t}}, \tag{1}$$

where μ is the "reduced mass" for the translation. The frequency of crossing the barrier, with v the velocity along the reaction coordinate, is given by

$$\frac{v}{l} = \frac{1}{l}\sqrt{\frac{2\epsilon_t}{\mu}}. \tag{2}$$

Then the unimolecular rate constant is given by one-half the ratio of activated complexes to normal molecule-ions, multiplied by the frequency of crossing the barrier and integrated over all possible values of the translational energy in the reaction coordinate. The factor one-half arises from the equal probability of translation in opposite directions at equilibrium.

$$k = \int_0^{E - \epsilon_0} \frac{\rho^{\pm}(E, \epsilon_0, \epsilon_t)}{\rho(E)} \cdot \frac{1}{h} \, d\epsilon_t. \tag{3}$$

The description of the system as undergoing rapid radiationless transitions between electronic states could be replaced by a more general discussion in which no separation of electronic and nuclear motions is assumed except for the reaction coordinate. Equation (3) is consistent with either view-point.

In the applications which follow, state density functions are calculated for internal rotations and vibrations only. The electronic state density functions are assumed to cancel out. Nuclear motions are taken to be the same in all electronic states of a given ion or activated complex. Making the extreme idealization, the molecule a collection of N weakly coupled harmonic oscillators, the activated complex a collection of $N - 1$ such oscillators, and using the Dirichlet integral[25] one finds

$$k = \frac{1}{h} \int_0^{E-\epsilon_0} \frac{(E - \epsilon_0 - \epsilon_t)^{N-2}(N-1)! \prod\limits_{i=1}^{N-1} \left(\dfrac{1}{h\nu_i^{\ddagger}}\right)}{(N-2)! E^{N-1} \prod\limits_{j=1}^{N} \left(\dfrac{1}{h\nu_j}\right)} d\epsilon_t$$

$$k = \left(\frac{E - \epsilon_0}{E}\right)^{N-1} \frac{\prod\limits_{j=1}^{N} \nu_j}{\prod\limits_{i=1}^{N-1} \nu_i^{\ddagger}} \tag{4}$$

An equation for the rate constant can be derived in a similar manner for the case where the reactant is taken to be a system of $N - L$ weakly coupled harmonic oscillators plus L internal rigid rotors, and the activated complex a system of $N - L^{\ddagger} - 1$ harmonic oscillators plus $L^{\ddagger}$ internal rotors. The equation is

$$k = 2^{(L^{\ddagger} - L)/2} \pi^{L^{\ddagger} - L} \frac{\Gamma[N - (L/2)] \prod\limits_{f=1}^{L^{\ddagger}} I_f^{\ddagger 1/2} \prod\limits_{j=L+1}^{N} \nu_j}{\Gamma[N - (L^{\ddagger}/2)] \prod\limits_{i=1}^{L} I_i^{1/2} \prod\limits_{g=L^{\ddagger}+1}^{N-1} \nu_g^{\ddagger}} \times$$
$$\left(\frac{E - \epsilon_0}{E}\right)^{N - (L/2) - 1} (E - \epsilon_0)^{(L - L^{\ddagger})/2} \tag{5}$$

Equation (5) is used in cases such as the following: For internal excitation high enough to cause decomposition of propane ions, it is very probable that the two methyl groups rotate freely about their C–C bonds. Appearance potential measurements indicate that the formation of $C_3H_6^+$ ion is accompanied by the formation of a hydrogen molecule, rather than two hydrogen atoms.[26] If one assumes the two lost hydrogens to have come from adjacent carbon atoms rather than the same one, then it is probable that in the activated complex the free rotation of one methyl group will have changed to a torsional vibration because of the formation of a weak H---H bond, as shown below.
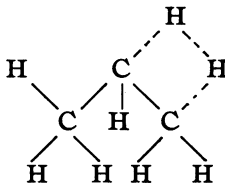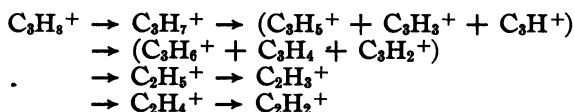

The discussion so far has been for a single reaction only. If there are several competing reactions the theory should be equally applicable. One need only make the assumption that the rate of interchange of energy among the degrees of freedom of the reactant is sufficiently rapid so that the

formation of activated complexes for one reaction does not appreciably affect the rate of formation of activated complexes for other reactions.

Using the considerations outlined above, we have made calculations in an attempt to reproduce the mass spectrum of the propane molecule. A simple computation shows that there is a time interval of roughly 10^{-5} seconds between formation of an ion in the electron beam and the acceleration of the ion in the ion gun of the mass spectrometer. Ions formed during this time interval by unimolecular decomposition of the parent propane ions will be detected at their expected place on the mass scale. Any decomposition occurring later will, in general, result in loss of the ions from the collected ion current, due to the ion-optical characteristics of the spectrometer. The one exception to this rule, metastable ions, will be discussed later.

Using the following breakdown scheme for the principal ions observed in the propane mass spectrum,

$$C_3H_8^+ \rightarrow C_3H_7^+ \rightarrow (C_3H_5^+ + C_3H_3^+ + C_3H^+)$$
$$\rightarrow (C_3H_6^+ + C_3H_4 + C_3H_2^+)$$
$$\rightarrow C_2H_5^+ \rightarrow C_2H_3^+$$
$$\rightarrow C_2H_4^+ \rightarrow C_2H_2^+$$

the relative amount of unimolecular decomposition along various competing reaction paths for a time $t = 10^{-5}$ seconds has been calculated as a function of the internal excitation energy of the parent ion.

The activation energies were calculated from appearance potentials, ionization potentials and thermal data.[8] The frequencies and moments of inertia were estimated from data on their neutral counterparts (propane ion data from molecule data, for example) and the same values used for the activated complexes derived from them, except where obvious changes were indicated. The latter has already been illustrated for the activated complex for the reaction

$$C_3H_8^+ \rightarrow C_3H_8^{+\ddagger} \rightarrow C_3H_6^+ + H_2,$$
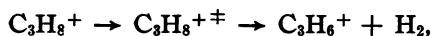
where a methyl group free rotation in the excited ion was assumed to have become a torsional vibration in the activated complex. A further example is the reaction

$$C_3H_8^+ \rightarrow (C_2H_5\text{---}CH_3)^{+\ddagger} \rightarrow C_2H_5^+ + CH_3.$$
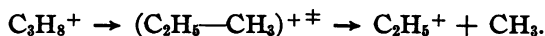
Here the activated complex is essentially a propane ion with one C–C bond stretched to several times the equilibrium separation. One may reasonably assume that this bond stretching results primarily in a decrease of the rocking frequencies of the loose methyl group in the activated complex.

The results of this calculation are shown in the breakdown graphs of

figures 1 and 2.   These graphs show the relative amounts of fragment ions formed from a parent ion with given excitation energy at the end of 10^{-5} seconds.   The two graphs were calculated and plotted for two different possible activated complexes associated with the formation of the propyl ion.   The other activated complexes were the same.

At this point the arbitrary nature of the calculation is surely apparent. One is dealing with many more parameters than unknowns.   However, this much can be stated: |In so far as vibrational frequencies and moments of inertia are concerned, their function as arbitrary parameters is very much restricted by criteria of self-consistency among the various activated com-
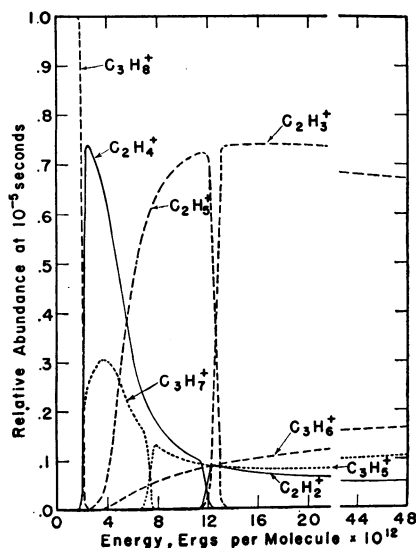

FIGURE 1

Fraction of the several fragment ions formed from propane ions in 10^{-5} seconds as a function of internal excitation energy.
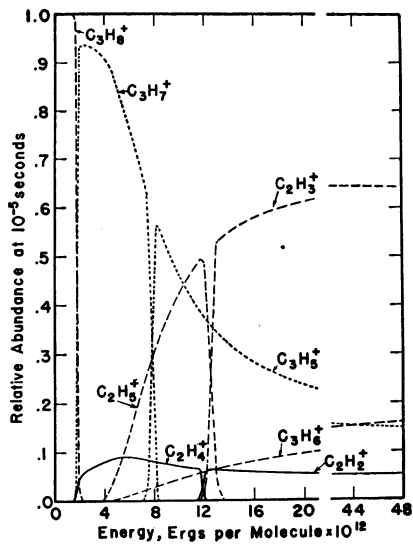
FIGURE 2

Same as figure 1, but calculated assuming a different activated complex for the formation of the propyl ion.

plexes and also by what might be termed consistent analogy to the values experimentally obtained on the corresponding neutral molecules.

The energies of activation are essentially experimental quantities, differences in appearance potentials.   Their validity in use as activation energies hinges on the validity of the view-point which considers the mass spectrum of a large molecule in terms of a rate theory such as given above. We have been able to deduce breakdown schemes for both normal butane and isobutane and have calculated energies of activation which, in so far as they parallel the breakdown scheme for propane, are in good agreement:[27]

As previously discussed, theory has not yet provided a distribution func-

tion for internal excitation for polyatomic molecules. The probability of obtaining ions with no internal excitation is essentially zero because the minima on the potential surfaces of the molecule and the molecule-ion will, in general, have different equilibrium internuclear distances. The amount of fragmentation observed in mass spectra, "stopping power" measurements for high energy particles[28] and the relatively small amount of double ionization in mass spectra[29] all indicate that the mean of this distribution function is in the range of five to ten electron volts and that the function drops off quite rapidly for much higher energies. We have tried the following extremely simple distribution functions: (i) Unit probability in the range 0–20 $\times$ 10^{-12} ergs/molecule; zero probability above 20 $\times$ 10^{-12}. (ii) Unit probability in the range 0–16 $\times$ 10^{-12}; 0.5 probability in the range 16–20 $\times$ 10^{-12}; zero probability above 20 $\times$ 10^{-12}. (iii) Probability 0.9 in the range 0–4 $\times$ 10^{-12} ergs/molecule; 1.0 in the range 4–14 $\times$ 10^{-12}; 0.5 in the range 14–20 $\times$ 10^{-12}; 0.0 above 20 $\times$ 10^{-12}. (1 $\times$ 10^{-12} ergs/molecule = 0.624 electron volt.)

With these distribution functions and the results shown in figure 1 the following mass spectra are obtained by graphical integration.

DISTRIBUTION FUNCTION			MASS SPECTRUM					
	$C_3H_8^+$	$C_3H_7^+$	$C_3H_6^+$ $C_3H_5^+$ C_3H^+	$C_2H_6^+$ $C_2H_4^+$ $C_2H_2^+$	$C_2H_5^+$	$C_2H_4^+$	$C_2H_3^+$	$C_2H_2^+$
(i)	0.102	0.064	0.059	0.062	0.249	0.161	0.272	0.031
(ii)	0.114	0.071	0.056	0.057	0.277	0.178	0.220	0.027
(iii)	0.111	0.074	0.056	0.056	0.300	0.185	0.194	0.024
Experimental	0.090	0.071	0.103	0.042	0.310	0.183	0.122	0.027

Total ionization normalized to unity.   Experimental peaks omitted total 0.052.

The agreement between the experimental values and those calculated for distribution function (iii) is remarkably good, inasmuch as with but one exception the parameters first estimated for the activated complexes were used in the calculation. Under these circumstances, the agreement is somewhat fortuitous but still indicative of the validity of the theory.

There is some evidence from studies with isotopically labeled molecules[30] that the kinetics summarized in figure 2 are preferable to those shown in figure 1. Similar calculations based on the results of figure 2 do not yield nearly as good agreement with experiment but do indicate that suitable adjustment of parameters would permit agreement to be obtained.

To eliminate the arbitrary features of this theory more data are required. Most useful would be the complete mass spectra for propane and the butanes for several electron voltages in the range 15 to 40 volts. The maximum excitation energy available for the parent ions is the electron energy minus the ionization energy of the molecule. The above voltage range would give a variation in the high-energy cut-off of the distribution function between 6 and 50 $\times$ 10^{-12} ergs/molecule and corresponding variations in

the mean value of the excitation energy. It is hoped that such data will be available shortly and that the validity of this theory can then be definitely demonstrated.

Several others aspects of mass spectra are explainable in terms of this theory, namely, temperature dependence, metastable transitions and isotope effects.

The essential feature of temperature effects in mass spectra is the marked decrease of parent ion intensity with increasing temperature.[31] Fragment ion intensity changes are much smaller and may have either sign. In terms of this theory, increased temperature shifts the energy distribution function maximum to slightly higher values and causes it to rise less steeply from its near-zero value at zero energy. As may be seen from figures 1 or 2, this results in a smaller relative abundance of the parent ion in the calculated mass spectrum. Changes in intensities of other mass peaks will depend upon how the change in the energy distribution function affects the integrals of the product of the distribution function with the relative breakdown curves such as are given in figures 1 and 2.

Careful scanning of the mass spectrum of many molecules at non-integral mass values has revealed the presence of numerous diffuse peaks.[32] These peaks result from decompositions of ions into smaller ions and neutral fragments in the time interval occurring between the exit of the ions from the electrostatic accelerating field and their entry into the magnetic analyzing field. Their intensity is rarely greater than one per cent of maximum peak intensity in a typical mass spectrum. In terms of the proposed theory their significance is twofold. All metastable transitions involve decompositions which are similar to those transitions proposed here as the decomposition reactions by means of which the mass spectrum of a typical molecule is formed.[33] This is substantiation in the sense that the proposed decompositions, arrived at by consideration of the energies involved, do actually occur to at least some extent. Furthermore, the energy distribution function will yield a small fraction of excited ions having an amount of internal excitation which will give rise to decompositions with a half-life centered about the value 10^{-6} seconds, the experimental value measured by Hipple.[34] The theory presented here implies that metastable ions of all half-lives should exist. The experimental value quoted above was actually determined by the geometry and fields of the mass spectrometer used and does not indicate that metastable ions of other half-lives are absent. Quantitative calculations of metastable peak heights and comparison with experiment will also be undertaken as soon as suitable data are available.

As can readily be seen from the rate equation derived above, a detailed discussion of isotope effects would require a much better knowledge of physical parameters such as frequencies, moments of inertia and activation

energies than is presently available. However, one interesting series of experiments can be quite simply discussed. Introducing a deuterium atom into a hydrocarbon speeds up the dissociation of any one of the remaining hydrogens. However, this deuterium comes off less readily than did the hydrogen it replaced.[30]

The expression in the rate equation for the density of states of a collection of harmonic oscillators does not take the zero-point energy of the oscillators into account, since the expression is a derivative. Following Marcus,[23] we call the internal vibrational energy minus the zero-point energy the "non-fixed" energy. It is clear then that the internal energy E in the rate equation refers to this non-fixed energy rather than to the total vibrational energy. In terms of this quantity then, the replacement of other hydrogens by deuterium atoms results in increased non-fixed energy. Hence the rate of decomposition will increase if all other conditions are kept the same; in other words a hydrogen atom will now come off more easily. However, substitution of the given hydrogen atom by a deuterium atom results in a slower decomposition rate (or probability) because of a decrease in the "frequency factor" of the rate equation and an increase in the activation energy necessary to break the C–D bond.[35]

Summary.—The mass spectra of polyatomic molecules have been discussed in terms of a series of quasi-equilibrium unimolecular decompositions. An absolute rate theory for isolated systems having a large but finite number of degrees of freedom has been presented. The application of the rate theory to such a decomposition scheme for propane gives results in agreement with experiment. Due to the large number of parameters and approximations this agreement is not conclusive indication of the validity of the theory. Additional qualitative supporting evidence is also presented. The theory will serve as a basis for further calculations and experiment.

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