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ESTIMATED UPPER BOUNDS TO THE HALF-LIFE
OF THERMAL DECOMPOSITION OF AMMONIA,
HYDROGEN, METHANE, AND PROPANE

by

Dudley Herschbach

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By authority of Dr. J. P. Deschamps, Director, dated 2/11/59

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ABSTRACT

An estimate has been made of the upper bound for the half-time of dissociation at 100 atm for ammonia, methane, and propane at 2800°K and hydrogen at 5000°K. In each case a unimolecular reaction in the homogeneous gas phase was chosen as most suitable for this purpose. Slater's theory has been used to estimate the necessary frequency factors. The upper bounds to the half-time for dissociation range from 3×10^{-7} to 6×10^{-6} sec. Extrapolation of decomposition rate data obtained at ~1000°C and 1 atm pressure gives smaller values for the half-time of dissociation.

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1. Introduction and Summary

Current designs for high-temperature reactors call for pumping a gas at about 100 atm pressure through a pile designed to heat it to about 2800°K within a contact time of the order of a millisecond. The hot gases are then ejected within another millisecond.

Consideration has been given to the problem of the dissociation kinetics of ammonia, hydrogen, methane, and propane. From free energy data, L. R. Sitney of LASL Group K-2 has calculated for several molecules the amounts of the possible decomposition products which would be expected if thermodynamic equilibrium were obtained at the specific temperature (2800°K). Such data for the four molecules considered in this report are listed in Table 1.

TABLE 1

EQUILIBRIUM DATA (2800°K, 100 atm)

Molecule	Equilibrium mixture, molar percentages	$\bar{m}_t^*$ g mole ⁻¹
Ammonia	74.5% H ₂ , 24.5% N ₂ , 1% NH ₃ , 0.5% H	8.53
Hydrogen	98.5% H ₂ , 1.5% H	1.98
Hydrogen**	53.5% H ₂ , 46.4% H	1.53
Methane	66.5% H ₂ , 30% C, 2% C ₂ H ₂ , 0.5% CH ₄ , 0.5% H	5.60
Propane	56.5% H ₂ , 40% C, 2% C ₂ H ₂ , 0.5% C ₂ H ₄ , 0.5% CH ₄ , 0.5% H	6.68

* Mean molecular weight.

** At 5000°K, 100 atm.

In a given application, however, the rate of decomposition will determine whether the equilibrium conditions are actually approached. If the time to reach equilibrium is long compared with the time during which the molecules are actually at the specified temperature, the products and yields may be far different from those of an equilibrium mixture. It is the purpose of this paper to give estimates of the upper limits for the half-life of thermal decomposition for these gases.

The experimental information which bears on the decomposition is reviewed in Section 2. The pyrolysis of hydrocarbons has been studied near 1000°K and at pressures less than 1 atm, but the data have not been adequate for understanding the mechanism, and an extrapolation to 2800°K and 100 atm cannot be justified. There have been no rate measurements of the

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homogeneous decomposition of ammonia and hydrogen.

Theoretical rate formulas apply only to elementary steps involving one, two, or three molecules or atoms. Thus to predict the rate of an over-all reaction, it is necessary to postulate which elementary steps contribute to its mechanism and to estimate the rate of each. This requires so many guesses about the properties of intermediates that the uncertainties rapidly multiply. However, if a series of successive steps is necessary in a mechanism, the slowest determines the over-all rate; if parallel reactions are involved, the fastest is most important. This makes it worthwhile to try to predict an upper bound to the half life τ of the initial step in the decomposition.

The reactions considered for this purpose are listed in Table 2. In each case, a

TABLE 2

REACTIONS CONSIDERED AND PROBABLE UPPER BOUNDS TO THEIR HALF-LIVES
(2800°K, 100 atm)

Reaction	Assumed E_a , kcal mole ⁻¹	τ , sec
$\text{NH}_3 \rightarrow \text{NH}_2 + \text{H}$	105	6×10^{-6}
$\text{H}_2 \rightarrow 2\text{H}$	103	$5 \times 10^{-7} *$
$\text{CH}_4 \rightarrow \text{CH}_3 + \text{H}$	102	1×10^{-6}
		$1 \times 10^{-7} **$
$\text{C}_3\text{H}_8 \rightarrow \text{CH}_3 + \text{C}_2\text{H}_5$	84	3×10^{-7}
		$2 \times 10^{-9} **$

* At 5000°K, 100 atm.

** Extrapolated from experimental measurements of over-all decomposition rate near 1000°K, and at <1 atm. See Section 2.3.

unimolecular reaction in the homogeneous gas phase was chosen for the following reasons:

1. It is expected to be the slowest of (parallel) homogeneous reactions possible for the initial step. If no faster process occurs, the unimolecular reaction would have to take place. A bimolecular reaction should be more rapid. A heterogeneous reaction is not considered because, even though it has a low activation energy, its frequency factor would be many powers of 10 smaller than those of homogeneous reactions (see first paragraph of Section 2). Also the conditions in the reactor probably favor a homogeneous path.

2. The available experimental evidence strongly confirms that all these decompositions will involve free radical mechanisms, especially at high temperatures. It is well established that reactions involving free radicals have negligible activation energies and are very fast.

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(The rate of recombination for free radicals is an exception, as discussed in the latter part of this section. Thus the initial step which forms the free radicals can be expected to be the slowest of a series.

3. Because the unimolecular reactions chosen all break only one bond and form only free radicals, their energies of activation can be reliably estimated (see Section 3). The largest estimate is selected in keeping with the intention to calculate an upper bound to τ . For unimolecular gas phase reactions, Slater's theory may be used (see Section 4) to calculate the frequency factor at the high concentration limit and the pressure dependence of the rate constant. This theory has given good results in the cases to which it has been applied. As is expected from two of its simplifying assumptions, the theory always predicts the rate constant to be too small at any given pressure (less than experiment by a factor of 4 to 6, typically). Thus it also tends to give an upper bound to τ . Bimolecular reactions could not be treated as satisfactorily, especially their activation energies.

From Statement 3, one should get an upper bound to the τ of the hypothetical reactions of Table 2. Because of Statement 1, it is expected that an upper bound to the τ of the actual initial step will be obtained; because of Statement 2, it is hoped that this may also give an upper bound to the τ for the over-all decomposition.

Of course, without knowing the secondary steps, the final products and their mean molecular weight, $\bar{m}$, cannot be predicted (except for hydrogen). Direct recombination of the initial free radical products is very unlikely, since the recombination of free radicals requires a third body collision to remove energy before the resultant excited molecule merely separates into free radicals again. It is far more probable that the free radicals will attack molecular species, which are present in much greater concentrations. This requires only binary collisions. Some examples of hypothetical mechanisms are given in Section 2.

For hydrogen, the net change will certainly be represented simply by $H_2 \rightarrow 2H$. At $5000^\circ K$ the reaction is very rapid, and thus $\bar{m} = 1.5$, from Table 1.

For ammonia, W. M. Jones of LASL Group CMR-4 suggested that the photochemical reaction be taken as a guide. Here the primary step seems to be $NH_3 \xrightarrow{h\nu} NH_2 + H$. The quantum yield, which summarizes the secondary steps, is found to increase with temperature. So the decomposition is expected to proceed well past the primary step. But as long as two pieces are obtained from each NH_3 molecule, and none of the products other than N_2 (if it is formed) contain more than one N atom, then $\bar{m}$ must be about 8.5, the same value which would be obtained at equilibrium. Products such as N_2H_4 could not persist as long as NH_3 itself at $2800^\circ K$.

Rate studies of the hydrocarbon pyrolysis have left considerable ambiguity in the mechanism,

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but in all cases the activation energy for the over-all decomposition is much less than that needed for a primary split into free radicals. This requires the existence of reaction chains in which the free radicals speed the decomposition by attacking the hydrocarbon. However, the final products near 1000°K are largely heavy compounds containing two carbon atoms. In order to obtain a small $\bar{m}$ at 2800°K , these compounds would have to decompose almost completely into H_2 and solid C. Of course, a new, more direct, path may be possible. Although there is no theoretical or experimental estimate of the speed of such reactions in the homogeneous gas phase, it is probable that they would be very slow.

The τ 's obtained from the Slater theory calculations and the assumed energies of activation are listed in Table 2. The complete theory was applied to NH_3 and H_2 , but approximations were made in treating the hydrocarbons. It is emphasized again that these numbers may have limited significance for the actual reactor process. All that can be expected is that they represent upper bounds for the τ of the initial step in the homogeneous gas phase decomposition at uniform temperature and pressure.

2. Experimental Information and Speculative Mechanisms

In this section, the experimental information which bears on the mechanism of the decomposition is briefly reviewed. Only the key literature references are cited. The data are not sufficient to definitely establish mechanisms, although some general features are clear. However, one must be very cautious when extrapolating mechanisms, because steps which were negligible under "normal" conditions can become important under extreme conditions and thereby greatly alter the over-all kinetics. For example, if the rates of two steps are compared in terms of the parameters of the Arrhenius equation for rate constant

$$k = A \exp(-E/RT)$$

we have

$E_2 - E_1, -1$ kcal mole	k_1/k_2 at 1000°K	k_1/k_2 at 2800°K
5	$12 A_1/A_2$	$2.4 A_1/A_2$
10	$150 A_1/A_2$	$8.5 A_1/A_2$
20	$22000 A_1/A_2$	$35 A_1/A_2$
30	$3.3 \times 10^6 A_1/A_2$	$210 A_1/A_2$

If, for example, $A_2/A_1 = 2000$ and $E_2 - E_1 = 30$ kcal, it is seen that Reaction 2 would be a completely unimportant path compared with Reaction 1 at 1000°K ($k_1/k_2 = \sim 10^3$), whereas at 2800°K it would be much more rapid than Reaction 1 ($k_1/k_2 = \sim 0.10$). This is a reason why the decomposition should not be expected to be predominantly heterogeneous. Even though a

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heterogeneous reaction has a much lower E, its A is generally found to be many orders of magnitude smaller than those for homogeneous reactions. At 2800°K and 100 atm, the number of gas phase collisions, w, experienced by a molecule is of the order of 10^7 within a milli-second, while it has been estimated by B. B. McInteer of LASL Group CMR-4 that a molecule will collide with the confining walls only about 100 times.

2.1 Ammonia

Hinshelwood reports (Ref. 1, p. 224) that the homogeneous decomposition was immeasurably slow at 1000°C, and calculated that the total energy of activation required therefore probably must be greater than 80 kcal.

Funke² asserted that he observed NH_3 to decompose fairly rapidly at 900°C in an ammonia-illuminating gas flame, and found the NH 3360 Å band was weakly emitted. Since the brass tubes had an estimated temperature of only 300°C next to the flames, he assumed that the reaction must occur in the gas phase and not at the wall. By sending continuous light through a long row of these flames, he was able to observe a diffuse absorption line at 3360 Å. He failed to find this spectrum when he heated NH_3 in an oven up to 1750°C, but stated that again the decomposition of NH_3 had begun by 900°C.

Frank and Reichardt³ were able to detect the absorption spectrum of the NH radical (estimated concentration 0.1 to 1%) when they flowed NH_3 at 1 atm through a beryllium oxide tube heated to 2000°C (cross-section, 1.3 cm²; distance at maximum temperature, 1 to 2 cm). The spectrum became more intense with increasing flow rate, but rapidly faded away when the flow rate was decreased below 40 cm/sec. Below 1800°C, the absorption line was no longer observed.

Hinshelwood has studied (Ref. 1, pp. 43, 189, 221) the heterogeneous decomposition of NH_3 on various surfaces. On tungsten, at 850°C, he found the reaction was zero order in NH_3 , and the rate was 0.12 mm/sec with an activation energy of 39 kcal.

In the photochemical decomposition of NH_3 , the primary step is believed to be

rather than

The evidence is reviewed in Ref. 4, p. 363, and Ref. 5, p. 375, and possible mechanisms for secondary steps are discussed. The quantum yield is found to increase with temperature. The mean life of H atoms was estimated to be so short (10^{-2} to 10^{-3} sec, decreasing with increasing pressure) as to indicate that they were removed from the homogeneous phase by some

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process much more rapid than third body recombination. Some evidence has been found for the formation of hydrazine as an intermediate, but the yield decreased rapidly as the temperature was increased above 300°C. The emission spectrum of NH_2 has been observed when NH_3 was illuminated at wavelengths below 1650 Å.

An entirely speculative series of steps which may represent some of the important processes occurring in the thermal decomposition at 2800°K is as follows, where M represents the container wall:

The mechanism indicated here has some features in common with the Rice-Herzfeld free radical mechanisms, which have had some success in explaining the thermal decomposition of hydrocarbons (see Section 5.3). Reaction 1 was chosen as the first step rather than 1a, partly because of the experimental observations mentioned above (which are not conclusive), but mainly from steric considerations. The bimolecular step, $2\text{NH}_3 \longrightarrow 2\text{NH}_2 + \text{H}_2$, may well be the actual process. Reactions 2 reflect two general ideas. First, the reactive free radicals formed initially are more likely to attack NH_3 , which is present in much greater concentration, than to recombine as in the reactions 2a. Secondly, when NH_3 or NH_2 collides with other molecules, it is more likely that H's will be involved than N's. Reactions 3 also express this idea, and are examples of steps which may well occur when the concentration of free radicals has grown relatively large. Exchanges such as illustrated by 3a are also likely then.

2.2 Hydrogen

There is some photochemical evidence which bears on a collisional mechanism for activation (Ref. 4, p. 267). It is found that when a trace of Xe is introduced into H_2 and the mixture is illuminated with the Xe resonance line at 1469 Å, decomposition of the H_2 occurs. In this case there seems to be no doubt that the mechanism is

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Since a rare gas is involved, there is no reason to consider the possibility of the formation of an intermediate compound. The mechanism of energy transfer is a "collision of the second kind," in which the transferred energy raises the H_2 molecule to a repulsive state causing dissociation within one vibration period. By a "collision of the second kind" is meant a collision which permits a photoactivated molecule or atom to return to the normal state because the previously absorbed energy is converted into translational or vibrational energy of both of the colliding atoms or molecules.

In the thermal decomposition of H_2 , the activation is also provided by collisions. There appear to be only two possible mechanisms for the initial process in the homogeneous decomposition:

Unimolecular, with M representing H_2 or the wall (see Section 4)

Bimolecular

Here the right-hand side is written to express a true bimolecular process in which one H comes from each of the colliding H_2 molecules. If both H's come from one H_2 , the reaction is really unimolecular with $c \gg b$. In either case, the rate would be second order, since for H_2 , the unimolecular reaction would certainly be in its low concentration limit region even at 100 atm (see Sections 4 and 5.2 and Fig. 1 in Section 4). The practical difference between these mechanisms is that the activation energy for the true bimolecular process could be much lower. For example, if we consider the decomposition of HI, it is found to be bimolecular with $E = 44$ kcal, whereas the unimolecular process would require for E about 71 kcal (Ref. 1, p. 224).

The secondary steps include

Since the recombination is relatively slow until the equilibrium concentration of H is built up, the rate of attainment of equilibrium is essentially that of the initial decomposition.

2.3 Methane and Propane

Rate studies of the thermal decomposition of hydrocarbons have been made up to about $1300^\circ K$ at low pressures (10 to 760 mm). Steacie⁶ gives a thorough critical discussion both

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of the experimental results and of possible mechanisms. All of the reactions appear to be mainly homogeneous and of roughly the first order. The rate constants are found to decrease with decreasing pressure, but there is little regularity in the falling-off. Thus despite a general resemblance to an elementary unimolecular process (see Section 4), the reactions are certainly complex and perhaps of varying order. The falling-off of the observed rate constants has led to the custom of extrapolating rate constants to high pressures (a few atmospheres). This tacitly assumes that the over-all reaction is unimolecular, not merely first order, so the meaning of the extrapolation is not very clear. In all cases free radicals have been detected and it is established that free radical steps must be important features of the mechanisms, especially at high temperatures. The activation energy for the over-all reaction is always found to be much less than that expected for a primary split into free radicals, but the assumption of free radical chains can account for this. Since paraffin hydrocarbons do not absorb light in a conveniently accessible region, their photolysis has been little studied.

Rice and Herzfeld showed that mechanisms could be devised on a free radical basis which would lead to a first order rate for the over-all reaction even though it was the summation of a complex series of steps. Further, by a suitable choice of the activation energies of the steps in a chain mechanism, the activation energy of the over-all reaction could be made to agree with the experimental value. The details and particular examples are fully discussed by Steacie.⁶ The essential features of the Rice-Herzfeld type of mechanism are:

1. In the primary step, molecule M_1 is assumed to decompose into a radical R_1 and a molecule or radical M_2 .
2. The radical R_1 then attacks a fresh molecule of M_1 , abstracts an H atom, and forms a stable substance R_1H and the radical R_2 .
3. R_2 then decomposes into the radical R_1 and a molecule or radical M_3 . We thus have a chain process, since Steps 2 and 3 can repeat over and over again. There are also various opportunities for branching of the chains.
4. The chain is broken finally by a process which removes free radicals. By choosing different processes for terminating the chains, the mechanism can be made to yield $1/2$, 1 , or $3/2$ order kinetics, but these probably would not be distinguishable from first order on the basis of the present experimental data.

The falling-off of the observed rate with decreasing pressure is not surprising, since some of the mechanism steps depend on the total pressure. For example, the unimolecular decomposition of the ethyl radical, the prevention of wall recombination by diffusion of chain carriers to the wall, and the mechanisms of chain termination vary with pressure. The Rice-Herzfeld mechanisms have had some success in predicting the products as well as kinetics.

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Related to this is the work of Hinshelwood (Ref. 1, p. 170), who estimates the probability of an n-paraffin chain breaking at C - C bonds from the products of the reactions. He concludes that rupture to split off a CH_3 or C_2H_5 is by far the most probable. However, as emphasized by Steacie,⁶ later work has shown that the Rice-Herzfeld mechanisms are oversimplified, although verifying their qualitative correctness.

In the thermal decomposition of methane, Steacie concludes that the initial step is $\text{CH}_4 \rightarrow \text{CH}_3 + \text{H}$ with an activation energy of 102 kcal, equal to the bond dissociation energy of $\text{CH}_3 - \text{H}$. The over-all reaction has an activation energy of 79 kcal. Kassel, over the region 735 to 800°C and 15 to 300 mm, found the rate constants

$$k = 1.0 \times 10^{12} \exp(-79,400/RT) \text{ sec}^{-1}$$

If this is simply extrapolated to 2800°K, it gives

$$\tau = \frac{0.693}{k} \cong 10^{-6} \text{ sec}$$

However, this extrapolation may be meaningless (see first paragraph of Section 2). The final products appeared to be C_2H_2 , C_2H_4 , C_2H_6 , and H_2 , which would give only $\bar{m} = 16 \text{ g mole}^{-1}$, assuming 100% decomposition.

Gordon⁷ has studied the pyrolysis of methane flowing through a porcelain tube in the region 1000 to 1100°C and 1 atm. In a typical run, he found that with a contact time of 0.288 sec, 1.27% of the methane decomposed, yielding the following percentages of products: C_2H_2 , 0.04%; C_2H_4 , 0.11%; C_2H_6 , 0.09%; C_3H_6 , 0.02%; $\text{CH}_3\text{C} \equiv \text{CH}$, 0.02%; H_2 , 0.91%; CH_4 , 98.7%. If his rate constants are extrapolated to 2800°K, we get $\tau = 7 \times 10^{-7}$. If we consider the effect of increasing the pressure, this number would probably decrease to less than 10^{-7} at 100 atm.

McCarthy⁸ has made a study of free radicals produced in microwave fields. In a microwave glow discharge at 16 to 220 mm pressure, he found results such as the following:

	t, sec	% CH_4 reacted	% of reacted CH_4 as		
			C_2H_2	C_2H_4	C_2H_6
1.	0.02	26	72	16	9
2.	0.02	32	48	--	--

where t is the average time a molecule spends in the discharge zone. Experiment 1 differed from 2 in that the effluent stream from the discharge was allowed to impinge directly on a liquid nitrogen cooled wall. Only when this was done were significant amounts of ethane and ethylene produced. The remaining product was presumably hydrogen.

In the few photochemical studies of the methane decomposition, C_2H_2 , C_2H_4 , C_2H_6 , and higher hydrocarbons have been detected. The primary step is probably $\text{CH}_4 \xrightarrow{h\nu} \text{CH}_3 + \text{H}$, although the data do not exclude $\text{CH}_4 \xrightarrow{h\nu} \text{CH}_2 + \text{H}_2$. However, Ref. 5, p. 330 states: "Usually

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elimination of a whole molecule is not expected. Aside from steric considerations, an electronic rearrangement is involved for reactions of this type."

The thermal decomposition of propane has been studied by Steacie. His rate measurements near 850°K and 50 to 600 mm gave, on extrapolation to the limiting high pressure rate

$$k_{\infty} = 3 \times 10^{13} \exp(-63,300/RT) \text{ sec}^{-1}$$

If we make the doubtful extrapolation to 2800°K, we get

$$\tau = 2 \times 10^{-9} \text{ sec}$$

The products of the reaction varied greatly with the percentage conversion. By extrapolation to zero conversion, Steacie concluded that the initial products were H_2 , CH_4 , C_2H_4 , and C_3H_6 in almost exactly equal quantities, independent of temperature or pressure. These have $\bar{m} = 22$, but this refers to zero conversion. Since the C-C bonds in hydrocarbons are much weaker than the C-H bonds, it is assumed that the initial step is $\text{C}_3\text{H}_8 \longrightarrow \text{CH}_3 + \text{C}_2\text{H}_5$ with $E = 84 \text{ kcal}$, corresponding to the bond dissociation energy.

Only one experiment⁶ has been made on the direct photolysis of propane, using 1650 Å. Hydrogen and unsaturated hydrocarbons were formed in equal amounts.

3. Estimation of Activation Energies

References 6 and 9 give pertinent discussions and data on estimation of activation energies.

If only one bond is broken in a reaction, the bond dissociation energy is related to energies of activation by

$$D = E(\text{decomposition}) - E(\text{recombination})$$

The reactions of Table 2 give only free radicals, and radical recombinations have been shown to have very small energies of activation, quite possibly equal to zero or even slightly negative. Thus to a good approximation, we take $D = E(\text{decomposition})$. Several experimental methods have led to fairly concordant values for bond dissociation energies, such as those listed in Table 3.

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TABLE 3

BOND DISSOCIATION ENERGIES
(kcal mole⁻¹)

CH ₃ - H	101-102
C ₂ H ₅ - H	98
CH ₃ - CH ₃	83-87
CH ₃ - C ₂ H ₅	84
n-C ₃ H ₇ - H	94-100
i-C ₃ H ₇ - H	89-94
NH ₂ - H	102-104
NH ₂ - NH ₂	54
H - H	103

4. Unimolecular Reactions and Slater Theory

A unimolecular reaction, $A \rightarrow \text{products}$, follows a first order rate law, $-d[A]/dt = k[A]$, which gives $\tau = \ln 2/k = 0.693/k$.

The necessary energy of activation for the unimolecular decomposition comes from kinetic energy of translation which is transferred to internal degrees of freedom during collisions. The Lindemann mechanism postulates a time lag before decomposition, during which an activated molecule can be deactivated by further collisions, and thus shows how it is possible to obtain (at sufficiently high pressures) a first order rate even though the energy supply process is second order (since a collision involves two molecules). The mechanism is¹⁰

	Process	Rate
$A + M \xrightarrow{a_i} A_i^* + M$	Activation	$a_i(A)(M)$
$A_i^* + M \xrightarrow{b_i} A + M$	Deactivation	$b_i(A_i^*)(M)$
$A_i \xrightarrow{c_i} \text{products}$	Decomposition	$c_i(A_i^*)$

Here A_i^* represents a molecule excited to state i above the critical energy, and M is any molecule present which may serve to transfer energy to A (the states of A and M are already averaged over in the detailed rate constants a_i and b_i). In terms of the mechanism

$$\frac{-d[A]}{dt} = \sum_i a_i [A][M] - \sum_i b_i [A_i^*][M] = k[A]$$

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We assume

$$0 = \frac{d[A_i^*]}{dt} = a_i [A] [M] - b_i [A_i^*] [M] - c_i [A_i^*]$$

for each state i , which is the steady-state assumption for the concentration of activated molecules. Thus, we get the empirical first order rate constant,

$$k = \sum_i \frac{a_i c_i [M]}{b_i [M] + c_i}$$

which is seen to depend on the total pressure. At high values of $[M]$, the rate of activation and deactivation is much greater than that of decomposition, $b_i [M] \gg c_i$ for all important i , and k approaches a limit

$$k_\infty = \sum \frac{a_i c_i}{b_i}$$

which is independent of $[M]$, so the over-all rate is first order. At the low concentration limit, $b_i [M] \ll c_i$, and

$$k_0 = \sum a_i [M]$$

Thus the over-all rate becomes proportional to $[A] [M]$ and so is second order.

There is thus an experimental test for determining whether a reaction following a first order rate law is truly unimolecular: The rate constant should show a falling-off with decrease in pressure. If then a high pressure of inert gas is added, the rate should be restored. Experimentally, the pressures at which the high concentration limit are attained are found to be strongly correlated with the complexity of the reactant molecule. The simpler the molecule, the greater is the pressure needed before the high concentration limit can be attained. It is only for molecules of complex internal structure, with several simultaneous vibrations, that complicated phase relations might be expected, leading to a time lag between activation and decomposition. Whenever the activated molecule has so long a lifetime that it is usually deactivated by collision before it has a chance to break apart, a first order rate law will hold.

All the features of a unimolecular reaction discussed in this section find expression in the Slater theory.¹¹⁻¹³ The gas molecule is treated as a system of classically vibrating point-atoms, subject to linear elastic restoring forces, i. e., a quadratic potential energy.

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A vibrational analysis of the molecule is carried out and the normal modes are found. These are special motions of the system in which all atoms move with the same frequency and initial phase, and oscillate about their equilibrium positions with simple harmonic motion. Any general vibrational motion of the system can be described by a combination of the normal modes. It is now assumed that the molecule dissociates when one particular internal coordinate, referred to as the reaction coordinate, reaches a critically large value, p_0 , which will be related to the energy of activation E of the reaction. The harmonic motion is assumed to persist up to the moment of rupture. Now p is a function of the time t from the last collision, and can be expressed in terms of the normal modes

$$p = \sum_{i=1}^n \alpha_i \sqrt{\epsilon_i} \cos 2\pi (\nu_i t + \phi_i)$$

where the α_i 's are the weights of the various normal modes as they contribute to p , and are evaluated from the geometry, atomic masses, and force constants of the molecule. Characterizing each normal mode there is a frequency ν_i (the fundamental vibrational frequencies observed in the infrared or Raman spectrum), an energy ϵ_i , and an initial phase ϕ_i . The ϵ_i 's and ϕ_i 's in this classical model are constant in a free molecule and can change only at molecular collisions. If the last collision leaves the molecule with an energy $E = \sum \epsilon_i$ distributed so that

$$\sum_i |\alpha_i| \sqrt{\epsilon_i} > p_0$$

then the molecule is activated, i. e., capable of dissociation, since it is then possible for p to reach p_0 . The minimum energy necessary to fulfill this requirement is found to be

$$E = \frac{p_0^2}{\alpha^2}$$

where

$$\alpha^2 = \sum_i \alpha_i^2$$

and E is interpreted as the activation energy for the reaction. It cannot be calculated within the context of the theory, since there is no way to predict p_0 . Even if activated, however, the molecule will not dissociate until the various normal modes contributing to p come sufficiently

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into phase for p to reach p_0 . Thus reaction occurs only if this happens before a new collision removes the high internal energy or spoils the necessary distribution. The frequency of dissociation, $L = \sum c_i$, therefore depends both on p as a function of t and on the collision frequency w , and L is evaluated as an average for all possible initial phases ϕ_i .

At the high concentration limit, the final result is

$$k_{\infty} = g\nu \exp(-E_0/RT)$$

where g is the degeneracy of the reaction coordinate (for example, in NH_3 , g is 3 if p is taken as the N - H distance), and ν is a root mean square average of the fundamental frequencies ν_i of the contributing normal modes of vibration weighted by the α_i

$$\nu^2 = \sum_{i=1}^n \frac{\alpha_i^2}{\alpha^2} \nu_i^2$$

Thus ν is in the range of molecular vibration frequencies. Consider the particular case when the reaction coordinate is chosen to be the elongation of the bond between two atoms of masses m_1 and m_2 . If in the potential energy there are no cross terms between p and other internal coordinates, then

$$\nu = \frac{1}{2} f p^2 + \sum \sum \text{other coordinates}$$

where f is the force constant for stretching of p . From this

$$\nu = \frac{1}{2\pi} \sqrt{\frac{f}{m_r}}$$

where m_r is the reduced mass $m_r = m_1 m_2 / (m_1 + m_2)$ and here $E = 1/2 f p_0^2$. Thus, in this case, ν is the frequency of an imaginary diatomic molecule with masses m_1 and m_2 , and force constant f . E is its energy at extension p_0 .

In extending the theory to give the decline of rate with pressure, it is necessary to assume deactivation on collision of every activated molecule. With this assumption and the use of classical statistical mechanical results in the Lindemann mechanism, Slater obtains the formula

$$\frac{k}{k_{\infty}} = I_n(\theta) = \frac{1}{\Gamma(n/2 + 1/2)} \int_0^{\infty} \frac{X^{(n-1)/2} e^{-X} dX}{1 + X^{(n-1)/2} \theta^{-1}}$$

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Here n is the effective number of normal modes which enter into the reaction coordinate. It is at most equal to the total number of normal modes of vibration with degenerate modes counted only once, and n may be less than this for a particular p . The parameter θ is proportional to the ratio of the collision frequency per molecule, w , to the characteristic reaction coordinate frequency, ν .

$$\theta = \frac{w}{\nu} b^{(n-1)/2} f_n$$

$$w = [M] 4\sigma^2 \sqrt{\frac{\pi RT}{m}}$$

$$b = \frac{E}{RT}$$

$$f_n = (4\pi)^{(n-1)/2} \Gamma(n/2 + 1/2) \prod_{i=1}^n \frac{|\alpha_i|}{\alpha}$$

Thus θ is proportional to the total pressure, but also is strongly dependent on the temperature and the structure of the molecule. In addition to assuming E , one must assume a collision diameter σ in order to evaluate θ . The function $I_n(\theta)$ is plotted for several values of n in Fig. 1.

As n increases, the pressure at which k/k_∞ becomes essentially unity decreases. The theory predicts, as is confirmed by experiment, that the high concentration limit is not attained until very high pressures for simple molecules of small n , whereas complicated molecules may attain first order rates at normal pressures.

Two important assumptions made in the Slater theory both tend to give low values of k , and thus to predict a high value of τ . Only the use of a strictly quadratic potential function leads to normal modes and strictly harmonic vibrations. The normal modes are excited independently of one another, and no energy is transferred between them. However, actually there are always anharmonic cubic or quartic terms in the potential energy, whose contribution becomes important with large amplitudes of vibration. If p_0 is calculated from E and α^2 , it is found to be relatively large, typically about 1/2 to 1/4 of the equilibrium bond lengths. If the anharmonic terms are taken into account (which would greatly complicate the calculations), the separation of the modes is not strict, and energy will be transferred between them slowly, which would lead to faster reaction rates. The assumption of deactivation on every collision also tends to underestimate the decomposition rates, since actually an activated molecule requires on the average several collisions before it is deactivated, as shown by studies of vibrational relaxation times in gases⁹ and of the relative efficiency of inert gases in maintaining unimolecular rates.¹⁴

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Fig. 1 Plot of $I_n(\theta)$ for several values of n , with pressure = 100 atm.

Molecule	n	θ
x - NH_3	4	0.209
+ - H_2	1	3.6×10^{-4}
o - CH_4	4	0.194
diamond - C_3H_8	3	0.175

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5. Details of the Calculations

5.1 Ammonia

W. H. Jones of LASL Group CMR-4 has also made an estimate of the probable rate of $\text{NH}_3 \rightarrow \text{NH}_2 + \text{H}$, using a different approach. He calculates the equilibrium constant for the reaction as written, and then estimates the rate for the recombination rate

From these he finds a value for the decomposition rate and a rough value for τ of about 10^{-4} sec at 100 atm and 2800°K .

Much of the vibrational analysis required in applying the Slater theory to NH_3 could be taken from the formulas of Ref. 15. The notation is that of Refs. 13 and 15. In order to take full advantage of the molecular symmetry to simplify the calculations, symmetry coordinates were employed (Ref. 15, pp. 145, 155).

Geometrical factors

$$\frac{m_{\text{H}}}{m_{\text{N}}} = 0.07196 \quad p = 1.1882$$

$$\beta = 69^\circ \text{ (Ref. 15, p. 164)} \quad r = 1.0139$$

$$\cos^2 \frac{\alpha}{2} = 0.9037 \quad s = 0.0722$$

Vibration frequencies in cm^{-1}

i	1	2	3a, b	4a, b
ν_i	3337	950	3414	1628

Force constants in 10^5 dynes cm^{-1} (Ref. 15, p. 177)

$$b_1 = 6.37$$

$$b_2 = 0.51$$

Reaction coordinate (three-fold degenerate), the N-H bond, in terms of symmetry coordinates

$$p = \sum A_r S_r$$

r	1	2	3a	4a	3b, 4b
A_r	1.1882	-0.0722	-2.0278	0.3584	0

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Force constants in valence bond potential energy

$$V = \frac{1}{2} \sum_{rs} C_{rs} S_r S_s$$

rs	11	12	21	33	34	44
C _{rs}	27.003	-1.671	6.056	39.290	-6.932	3.447

Normal modes ξ_i in terms of symmetry coordinates but not normalized (Ref. 15, p. 177)

$$\xi_i = \sum_r a_{ir} S_r$$

a_{12}/a_{11}	a_{22}/a_{21}	a_{34}/a_{33}	a_{44}/a_{43}
-0.0066	1.98	0.027	2.54

After inverting the matrix of the a_{ir} , with

$$S_r = \sum_i U_{ri} \xi_i$$

r _i	11	12	21	22
U _{ri}	0.9967	0.00333	-0.5034	0.5034
ri	33	34	43	44
U _{ri}	1.0107	-0.0107	-0.3979	0.3979

Now introducing Slater's energy normalization in $10^{-4} \text{ erg}^{-1/2} \text{ cm}$

$$S_r = \sum_i \gamma_{ri} Q_i,$$

$$Q_i = \sqrt{\epsilon_i} \xi_i$$

ri	11	12	21	22
γ_{ri}	8.143	0.120	-4.113	18.146
ri	33	34	43	44
γ_{ri}	6.650	-0.615	-2.618	22.780

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Expressing the reaction coordinate in terms of the normal modes in $10^{-3} \text{ erg}^{-1/2} \text{ cm}$

$$p = \sum \alpha_i \phi_i$$

$$\alpha_i = \sum A_r \gamma_{ri}$$

i	1	2	3	4
α_i	0.9993	-0.1258	-1.4423	1.0411

Hence

$$\alpha^2 = \sum \alpha_i^2 = 4.179 \times 10^{-6} \text{ erg}^{-1} \text{ cm}^2$$

$$\prod |\alpha_i| / \alpha = 1.0805 \times 10^{-2}$$

$$\nu = \left(\sum \frac{\alpha_i^2}{\alpha^2} \nu_i^2 \right)^{1/2} = 9.10 \times 10^{13} \text{ sec}^{-1}$$

As expected, ν is close to the stretching frequencies, ν_1 and ν_3 .

The high concentration limiting rate is, when $T = 2800^\circ\text{K}$, $E = 105 \text{ kcal}$, and $b = E/RT = 18.75$

$$\begin{aligned} k_\infty &= 3\nu e^{-b} \\ &= 1.2 \times 10^6 \text{ sec}^{-1} \end{aligned}$$

The rate at any concentration is given by

$$k = k_\infty I_n(\theta)$$

Here $n = 4$, since two of the six vibrational modes are degenerate,¹² and for $\sigma = 4A$, $E = 105 \text{ kcal}$, and $T = 2800^\circ\text{K}$

$$\theta = 2.09 \times 10^{-3} P \text{ atm}^{-1}$$

In this case θ is proportional to $PT^{-n/2}$, so if it is desired to change the values of P and T to P' and T' , the new θ' is given by

$$\theta' = \left(\frac{P'}{P} \right) \left(\frac{T}{T'} \right)^{n/2} \theta$$

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Similarly, if new assumptions for E and/or σ are used,

$$\theta' = \left(\frac{\sigma'}{\sigma}\right)^2 \left(\frac{E'}{E}\right)^{1/2(n-1)} \theta$$

The function $I_4(\theta)$ has been computed by numerical integration and is plotted in Fig. 1, along with $I_n(\theta)$ for other values of n taken from Ref. 12.

At $p = 100$ atm and $\theta = 0.209$

$$I_4(0.21) = 0.10$$

Hence

$$k = 1.2 \times 10^5 \text{ sec}^{-1}$$

$$\tau = \frac{0.693}{k_{\infty} I_4(\theta)} = 5.8 \times 10^{-6} \text{ sec}$$

A rough comparative estimate can be made for the rate of the reaction $\text{NH}_3 \longrightarrow \text{NH} + \text{H}_2$. There is considerably more uncertainty in predicting the activation energy. Since two N-H bonds are broken and one H-H bond is formed, the reaction should be endothermic by about 100 kcal, and hence E is at least 100 kcal. Since reactions of free radicals with molecules often have energies of activation less than 20 kcal, it is probable that $100 < E < 120$ kcal. The pre-exponential factor from the Slater theory at the high concentration limit, $g\nu$, will be somewhat smaller. Again $g = 3$, but ν will be less because the reaction coordinate will involve predominantly the bending modes. Again, n should be 4, and $\prod |\alpha_i|/\alpha$ is not likely to be much different. Thus θ will be roughly the same, and we expect that k will therefore probably be not more than a factor of 10 different if E is near 100 kcal, or a factor of 100 if E is near 120 kcal.

5.2 Hydrogen

In the case of hydrogen, $n = 1$ and $\nu = 4395 \text{ cm}^{-1} = 1.32 \times 10^{14} \text{ sec}^{-1}$.

For $E = 103$ kcal and $T = 5000^\circ\text{K}$

$$k_{\infty} = \nu e^{-b} = 4.07 \times 10^9 \text{ sec}^{-1}$$

$$k = k_{\infty} I_1(\theta)$$

Now we have simply

$$I_1(\theta) = \frac{1}{[1 + (\nu/w)]}$$

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Assuming $\sigma = 1 \text{ \AA}$, $T = 5000^\circ\text{K}$ and $P = 100 \text{ atm}$

$$\frac{\nu}{w} = \frac{1}{\theta} = 2770$$

and

$$\tau = \left(\frac{0.693}{k_\infty} \right) \left(1 + \frac{\nu}{w} \right) = 4.7 \times 10^{-7} \text{ sec}$$

If assumptions or conditions are changed, the new θ is calculated as explained in Section 5.1. It should be emphasized that the Slater theory is probably inherently much less satisfactory in the oversimple case $n = 1$. Here the dissociation frequency is simply $L = \nu$ or zero, according as the energy is greater than or less than E , and the resulting formula for $I_1(\theta)$ shows the characteristic linear relation between $1/k$ and $1/w$ (or $1/P$) which is obtained when the dissociation probability is taken independent of the excess of energy above E . The half-life of decomposition is then practically proportional to the time spent in collisions. Since the high concentration limit is so high for diatomic molecules (e. g., we have $k/k_\infty = 4 \times 10^{-4}$ at 100 atm for H_2 , and $k/k_\infty \rightarrow 1$ would require about $4 \times 10^5 \text{ atm}$), they are never observed to follow first order kinetics.

5.3 Methane

Take the C-H distance as the reaction coordinate (four-fold degenerate), and apply the special formula mentioned in Section 4

$$\nu = \left(\frac{1}{2\pi} \right) \sqrt{\frac{f}{m_r}} = 0.390 \sqrt{10^{-5} \frac{f}{m_r}} \times 10^{14} \text{ sec}^{-1}$$

when the units of the stretching force constant f are dynes cm^{-1} and the reduced mass m_r is in g mole^{-1} .

Here (Ref. 15, p. 182)

$$f = 5.04 \times 10^5 \text{ dynes cm}^{-1}$$

$$m_r = 0.922 \text{ g mole}^{-1}$$

$$\nu = 9.15 \times 10^{13} \text{ sec}^{-1}$$

For $E = 102 \text{ kcal}$ and $T = 2800^\circ\text{K}$

$$k_\infty = 4\nu e^{-b} = 5 \times 10^6 \text{ sec}^{-1}$$

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A complete vibrational analysis will not be carried out, as was done for ammonia, to find n and the α_i needed to calculate θ and obtain the general rate. Instead reasonable estimates will be used based on the ammonia results and those of Ref. 12.

Probably $n = 4$ here also and $\prod |\alpha_i|/\alpha \cong 10^{-2}$ again.

Since the maximum of $\prod$ occurs for each $\alpha_i = n^{-1/2} \alpha$, for $n = 4$

$$\prod \leq n^{-n/2} = \frac{1}{16} = 0.0625$$

Now, if $n = 4$, $\prod = 0.01$, $\sigma = 4$ A, $E = 102$ kcal, $T = 2800^\circ\text{K}$,

$$\theta = 1.94 \times 10^{-3} \text{ P atm}^{-1}$$

At 100 atm

$$I_4(0.19) \cong 0.097$$

$$\tau = 1.4 \times 10^{-6} \text{ sec}$$

5.4 Propane

We take the C-C bond distance as the (doubly-degenerate) reaction coordinate. Then (Ref. 15, p. 192) with

$$f = 4.50 \times 10^5 \text{ dynes cm}^{-1}$$

$$m_r = 6 \text{ g mole}^{-1}$$

we have

$$\nu = 3.36 \times 10^{13} \text{ sec}^{-1}$$

For $E = 84$ kcal and $T = 2800^\circ\text{K}$

$$k_\infty = 2 \nu e^{-b} = 2.1 \times 10^7 \text{ sec}^{-1}$$

Again, only estimates of n and $\prod$ will be used. Since essentially only vibrational modes of the carbon skeleton will contribute to the reaction coordinate chosen, take $n = 3$. Using a larger n would give a bigger k and a smaller t .

We have the bound

$$\prod |\alpha_i|/\alpha \leq 3^{-3/2} = 0.192$$

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We shall take $\Pi \cong 0.06$ (see Ref. 12). Then for $\sigma = 6A$, $E = 84$ kcal and $T = 2800^{\circ}K$

$$\theta = 1.75 \times 10^{-3} P \text{ atm}^{-1}$$

and at $P = 100$ atm

$$I_3(0.175) = 0.11$$

so

$$\tau = 3.2 \times 10^{-7} \text{ sec}$$

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