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Quasi-unimolecular Reactions. The Decomposition of Diethyl Ether in the Gaseous State.

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Introduction.

During the last few years we have made in Oxford an investigation of a number of gaseous reactions with the chief object of applying the principles of the kinetic theory and discovering the mechanism of "activation." In order to make clear the bearing of the fresh experiments described in this paper it will be convenient first to give a brief summary of the general development of the enquiry.

1. At first the only homogeneous reactions which could be discovered were bimolecular reactions. The rate of these could be expressed by the equation—
 number of molecules reacting = number entering into collision $\times e^{-E/RT}$ —
 which had been applied by W. C. M. Lewis to the decomposition of hydrogen iodide. E is the "energy of activation." The conditions under which this equation is rigidly applicable are—(a) the two molecules participating in the reaction require independent activation to the extents E_1 and E_2 respectively, where $E_1 + E_2 = E$, though the separate values need not be known; (b) the energy of activation in each molecule is confined to two degrees of freedom, and (c) nearly all the collisions where (a) is satisfied are fruitful. Assumption (a) is very general and a highly probable one; assumption (b) is approximate only, but the equation remains very nearly true for any small number, one, two or three degrees of freedom. Since it is found to agree with experiment we may conclude that in most bimolecular reactions activation of the two colliding molecules in some simple manner in a few degrees of freedom is a necessary and sufficient condition for chemical change.

2. The decomposition of acetone* at about 500° C. now proved to be a unimolecular reaction, and the number of molecules reacting in unit time appeared to be about 10^5 times greater than the number which could be activated by collision in a manner at all similar to that characteristic of a bimolecular reaction. Analogous results had been found by Daniels and Johnston for nitrogen pentoxide.† It thus seemed that there must be some fundamental difference between the mechanisms of bimolecular and unimolecular reactions. This was brought out more sharply by the observation that the decomposition of acetaldehyde—a bimolecular reaction—although chemically similar to that of acetone, fell into line completely with other bimolecular reactions.

3. It was natural to turn at first to some form of radiation theory for unimolecular reactions, since, in spite of all its difficulties, this theory is not completely excluded from the realm of possibility. It must be emphasised that the difficulty does not lie in explaining how a unimolecular reaction can be determined by collisions—the theory of Lindemann provides for this—but in the apparent insufficiency of collisions. In the course of a discussion Prof. Lindemann suggested to me that the best plan would be to extend the idea of energy of activation to include not merely energy of some specific kind but energy of all kinds in every possible distribution in a large number of degrees of freedom, the only condition being that the total should exceed E . Plenty of collisions might be available to produce this kind of activated molecule. Some of the consequences of this suggestion were worked out in a recent paper‡ and may be summarised as follows.

The chance that a molecule contains in n degrees of freedom energy greater than E is no longer $e^{-E/RT}$ but

$$\frac{e^{-E/RT} (E/RT)^{\frac{1}{2}n-1}}{\frac{1}{2}n-1}.$$

A correction $(\frac{1}{2}n - 1) RT$ has, however, to be added to the value of E which is derived in the usual way from the Arrhenius equation.

In a unimolecular reaction it is only necessary that one of the molecules in a collision should be activated. We might assume that under favourable conditions all the energy of two molecules in collision could pass into one, but this is very unlikely. To calculate the number of collisions from which a molecule emerges with energy greater than E it is best to proceed as follows.

* 'Roy. Soc. Proc.,' A, vol. 111, p. 245 (1926). 'J. Amer. Chem. Soc.,' vol. 43, p. 53 (1921). Cf. Tolman, *ibid.*, vol. 47, p. 1524 (1925).

† 'Roy. Soc. Proc.,' A, vol. 113, p. 230 (1926).

Suppose statistical equilibrium to be established in the gas, and let the chemical change be ignored. Then—number of molecules (N_1) of which the energy rises above the limit E in unit time = number (N_2) the energy of which falls below E . Since E is a very large amount, possessed by exceptional molecules only, the vast majority of activated molecules which suffer collisions will have their energy reduced below E . Thus N_2 is very nearly equal to number of collisions \times fraction of molecules with energy greater than E , *i.e.*, to

$$\frac{Z \cdot e^{-E/RT} (E/RT)^{\frac{1}{2}n-1}}{|\frac{1}{2}n - 1|}.$$

Hence from the condition for statistical equilibrium N_1 is also nearly equal to this. This argument was tacitly assumed in the former paper.

If n is large this expression is much greater than the simple exponential and the discrepancies of the order 10^5 which were mentioned above can be wiped out by assuming a sufficient number of degrees of freedom in the molecule.

Turning now to the experimental evidence, it is in fact observed that whereas bimolecular reactions which only require the simple exponential expression are usually transformations of comparatively simple molecules such as HI, Cl_2O and N_2O , unimolecular reactions seem to be characteristic of more complex molecules. The next step in the experimental investigation is therefore to test more thoroughly the definite hypothesis that unimolecular reactions are mainly confined to molecules with large numbers of internal degrees of freedom.

For these molecules, with the usual sort of values of E and the extended idea of energy of activation, there will be enough collisions for Lindemann's mechanism* to work. We must now consider this mechanism. Unlike the simple molecules such as HI, which probably react at once if at all, the more complex molecules have an appreciable time of relaxation, and having gained the total energy E in n degrees of freedom will not, on the average, react until after a small finite time, before the lapse of which they may lose their energy again in another collision. Thus at high pressures the rate of activation and de-activation may be great compared with the rate of chemical change. Under these circumstances the removal of molecules by chemical transformation does not seriously affect the Maxwell distribution. The number of molecules reacting in unit time is then a small constant fraction of the number of activated molecules, which in turn is a small constant fraction of the total number. Hence the reaction satisfies the unimolecular law.

But it can only satisfy the law exactly at pressures above a certain limit:

* 'Trans. Faraday Soc.,' vol. 17, p. 598 (1922).

at some pressure sufficiently low the law must begin to fail and give place to one approximating more closely to a bimolecular law the lower the pressure. Attempts to detect this phenomenon in the decomposition of nitrogen pentoxide* have given negative results so far, but the unimolecular velocity constant of the decomposition of propionic aldehyde† appears to fall sharply at pressures below about 80 mms. If it is assumed that at this point there are just enough collisions to activate the molecules it can be calculated that 12 to 14 degrees of freedom in the molecule are necessary. This is a very plausible result, but standing alone can hardly be considered conclusive. There is always the possibility of some undiscovered complication, and although the existence of any factor which would make the results of the experiments with propionic aldehyde unreliable was shown to be exceedingly unlikely, it is none the less desirable to examine as many examples as possible. If a whole series of substances appear to react by the Lindemann mechanism it is very improbable that all the results can be due to a deceiving coincidence.

To study the behaviour of molecules with large numbers of degrees of freedom we have to rely chiefly on organic compounds in the gaseous state. The present paper deals with the decomposition of diethyl ether. The decomposition of dimethyl ether is also being investigated and an account of the experiments will be published later.

The diethyl ether reaction proves to be simple kinetically. It is unimolecular over a wide range of pressures, but falls off in its specific rate at lower pressures. This falling off does not occur, however, in presence of an excess of hydrogen, which appears to be able to keep the number of activating collisions above the critical limit. The chemical result of the decomposition is not quite a simple one, though reasons are given in one of the following sections for believing that this fact does not affect the simplicity of the reaction kinetics. It was satisfactory, however, to find that the decomposition of dimethyl ether proceeds in accordance with the simple equation $\text{CH}_3\text{OCH}_3 = \text{CH}_4 + \text{CO} + \text{H}_2$, where there is less room for complications which might produce an illusory effect of simplicity. None the less the reaction of the dimethyl ether is exactly analogous kinetically to that of the diethyl ether. This fact is mentioned in anticipation because it strengthens very much the conclusions of this paper about the nature of the diethyl ether reaction.

* Hunt and Daniels, 'J. Amer. Chem. Soc.,' vol. 47, p. 1602 (1925); Hirst and Rideal, 'Roy. Soc. Proc.,' A, vol. 109, p. 526 (1925).

† Hinshelwood and Thompson, 'Roy. Soc. Proc.,' A, vol. 113, p. 221 (1926).

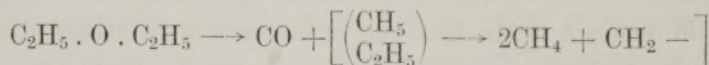
The following table shows the influence of the complexity of the molecule upon the type of reaction mechanism by which it decomposes thermally :—

Bimolecular.	Unimolecular.
HI N_2O Cl_2O O_3 <hr/> CH_3CHO	N_2O_5 (SO_2Cl_2) CH_3COCH_3 $\text{C}_2\text{H}_5\text{CHO}$ $\text{C}_2\text{H}_5 \cdot \text{O} \cdot \text{C}_2\text{H}_5$ $\text{CH}_3 \cdot \text{O} \cdot \text{CH}_3$ <div style="display: flex; justify-content: space-between; margin-top: 10px;"> <div>constant has normal value at 0.01 mm. data incomplete. no observations on falling of constant. constant falls off below 80 mm.</div> <div> ,, ,, ,, 150 ,, ,, ,, ,, 350 ,, </div> </div>

We have also made experiments with methyl acetate and with methyl alcohol, but the reactions of each were too much influenced by the surface of the silica vessel to allow the isolation and measurement of the true gas reaction.

The nature of the products of decomposition of diethyl ether.

The decomposition of ether in the gas phase does not yield ethylene and water according to the equation $\text{C}_2\text{H}_5 \cdot \text{O} \cdot \text{C}_2\text{H}_5 = 2\text{C}_2\text{H}_4 + \text{H}_2\text{O}$, but consists in the separation of carbon monoxide from the molecule. The hydrocarbon residue, of the empirical composition C_3H_{10} , is relatively somewhat richer in carbon than methane, the most stable hydrocarbon, and re-arranges itself to give mainly methane, a little ethylene, and a certain amount of a higher hydrocarbon which is probably ethane. The process of decomposition seems to take place more or less thus—



with a rapid combination of the CH_2- residues to give ethylene.

The net result is thus $\text{CO} + 2\text{CH}_4 + \frac{1}{2}\text{C}_2\text{H}_4$. According to this equation there would be about twice as much methane as carbon monoxide and about four times as much methane as ethylene. Actually the amount of ethylene is slightly less, and there is a little ethane. The following are the analyses of the products of complete decomposition at temperatures towards the extremes of the range over which the velocity measurements were made

	587°	477°
	Per cent.	Per cent.
CO	28.7	27.9
CH_4	55.3	54.4
C_2H_4	7.8	8.9
C_2H_6	8.2	8.8
CO_2	0.0	0.0

It is to be noted that the character of the decomposition does not alter over this range of temperature.

It has long been recognised that a rather complex set of products may be formed from one molecule in a single act of decomposition. There may be a rapid re-arrangement of the residual fragments after a part of the molecule has been split off, and it is not necessary to suppose a complicated series of consecutive reactions. Bone observed,* for example, that acetaldehyde, which decomposes at 500° C. into carbon monoxide and methane, could at higher temperatures yield free carbon and hydrogen. These were not formed by the subsequent decomposition of methane first produced, since at the temperatures in question methane was still quite stable. Sabatier also supposes the rapid re-arrangement of the residual fragments from a simple decomposition to be responsible for the large variety of products which are formed in certain pyrogenic reactions.

In making the measurements of reaction velocity the method employed was exactly similar to that described in previous papers, and depended upon observing the rate of increase of the total pressure as the decomposition proceeded. This can be regarded as a measure of the rate of reaction of the ether itself as long as any subsequent re-arrangements are rapid compared with the primary breaking up of the ether molecules. Apart from the general probability of the assumption that this condition is fulfilled, the following direct observations are evidence that it is. First, the reaction obeys a unimolecular law in a way which would be unlikely if the rate of pressure increase were determined by a series of consecutive changes of comparable rates. Secondly, the approach to the "end-point" of the reaction is quite definite as may be seen by reference to the figures in the next section.

There is, however, another possible source of disturbance to which careful attention must be given. If hydrocarbon residues such as CH_2 — exist momentarily in the free state, then their fate may be influenced by pressure and by temperature in a way which makes the rate of pressure increase at one temperature or pressure bear a relation to the actual rate of ether decomposition different from that which it bears at another temperature or pressure. However, the table already given shows the products to be the same at different

* 'J. Chem. Soc.,' vol. 87, p. 910 (1905). In this paper Bone and Smith describe the thermal decomposition of acetaldehyde and of formaldehyde—though not from the kinetic standpoint. Reference to this very important work should have been made in the introduction to the paper by Hinshelwood and Hutchison on the kinetics of the former reaction.

temperatures. The total pressure increase is also constant, as the following figures show.

Temp. ° C.	Initial Pressure.	Total increase of Pressure.	Ratio.
525	199	384	1.93
555	194	357	1.84
588	218	407	1.86

In all calculations the increase will be taken as 188 per cent. of the initial pressure.

If pressure influenced the course of the re-arrangement, more condensed products would probably be formed at higher pressures. The total pressure increase, if it varied at all, would therefore be expected to be smaller for high than for low initial pressures of the ether. At 32 mm. the total increase was about 2.1 instead of 1.9 times the initial pressure. This is not a very accurate result but such deviation as there is agrees with expectation. When, therefore, the initial rate of reaction is measured by the actual rate of pressure increase the values obtained for the lower pressures will be slightly too high relatively to those for the higher pressures. Such small error as this introduces makes the unimolecular velocity constants appear to rise at lower pressures. Since the real fact is that they fall markedly, in the manner predicted by Lindemann's theory, it does not appear that this error can be appreciable.

The decomposition of dimethyl ether, $\text{CH}_3 \cdot \text{O} \cdot \text{CH}_3 = \text{CH}_4 + \text{CO} + \text{H}_2$, in which no unstable residues need be supposed to play a part, is kinetically similar in every respect to that of diethyl ether. This gives further reason for believing that the diethyl ether results are not in any way illusory.

As far as can be seen, therefore, there is no reason to suppose that what is measured is anything but the actual rate of decomposition of ether.

The Kinetics of the Reaction.

The reaction taking place in a silica bulb is predominantly homogeneous. Half-filling the bulb with powdered silica, which had increased the rate of decomposition of methyl formate sixteen times, caused little acceleration of the reaction.

Average value of k .

	594° C.	554°	525°	476°	434°
Bulb empty	0.0115	0.00247	0.00071	0.000088	0.0000090
Bulb and powdered silica	0.0097	0.00249	(0.00122)	0.000096	0.000025

The bracketed value is probably too high as it includes the first two experiments of the series, which showed an abnormal behaviour probably attributable to adsorbed air not completely pumped off from the finely powdered silica. There is therefore very little surface reaction in the empty bulb, except at the lowest temperatures, where it may amount to about 10 per cent. of the total.

In these experiments a wide necked bulb had to be used in order that the powdered silica might be introduced easily. This leads to a certain inaccuracy. In all the other experiments, therefore, bulbs with capillary connections were used. Two samples of ether, one specially purified in the laboratory, the other obtained from Kahlbaum, were used. The former was kept over sodium in a bulb sealed to the apparatus throughout the course of the experiments. Two different capillary-necked bulbs were used. The various results were concordant as the following examples show.

Temperature 525° C. The times are those required for the initial pressure to increase by 50 per cent., that is, for 26.6 per cent. of the reaction to take place. The initial pressure was about 200 mm. in all the experiments.

Bulb.	Ether Sample.	Time.
1	1	5' 53''
1	2	5' 36''
2	2	5' 47''

When the initial pressure of the ether is fairly high the reaction is kinetically unimolecular. One of the simplest criteria of a unimolecular reaction is that the time required for three-quarters of the change is exactly double that required for one half.

Temperature °C.	Initial Pressure of Ether.	"Half-life."	"Three-quarter life."	Ratio.
525°	199	14' 10''	29' 10''	2.06
555°	194	4' 20''	9' 3''	2.09
588°	218	59''	127''	2.15

The complete course of these experiments is shown in the table below.

a is the total increase in pressure at the end of the reaction.

x is the increase at time t ; $k_{10} = \frac{1}{t} \log_{10} \frac{a}{a-x}$.

525° C.			555° C.		
$a = 384.$			$a = 357.$		
t (seconds).	x (mm.).	k_{10}	t	x	k_{10}
158	43	0.000326	67	53	0.00104
273	73	0.000335	106	83	0.00118
390	103	0.000350	176	133	0.00115
616	153	0.000358	270	183	0.00116
951	210	0.000362	340	213	0.00116
1,210	243	0.000360	523	263	0.00111
1,666	283	0.000348	900	313	0.00101
2,390	318	0.000320	1,680	343	
∞	384		2,350	353	
			3,360	357	

588° C.		
$a = 407.$		
t	x	k_{10}
22	80	0.00432
30	110	0.00456
40.5	150	0.00493
54	190	0.00505
82	250	0.00505
103	280	0.00491
147	320	0.00456
245	360	0.00383
600	395	
1,920	407	} The sharp end point is to be noted.
2,760	407	

At lower pressures the rate of reaction falls much below that required by the unimolecular law; this is shown to some extent by the falling in the values of k during the later stages, but is made more evident by plotting against the initial pressure of the ether the time required for a given fraction of the total reaction to complete itself. In fig. 1 the time required for 26.6 per cent. is plotted. In a truly unimolecular reaction the graph would be a straight line parallel to the pressure axis. Above 200 mm. this is nearly realised; the increase in the time at lower initial pressures corresponds to a fall in the velocity constant.

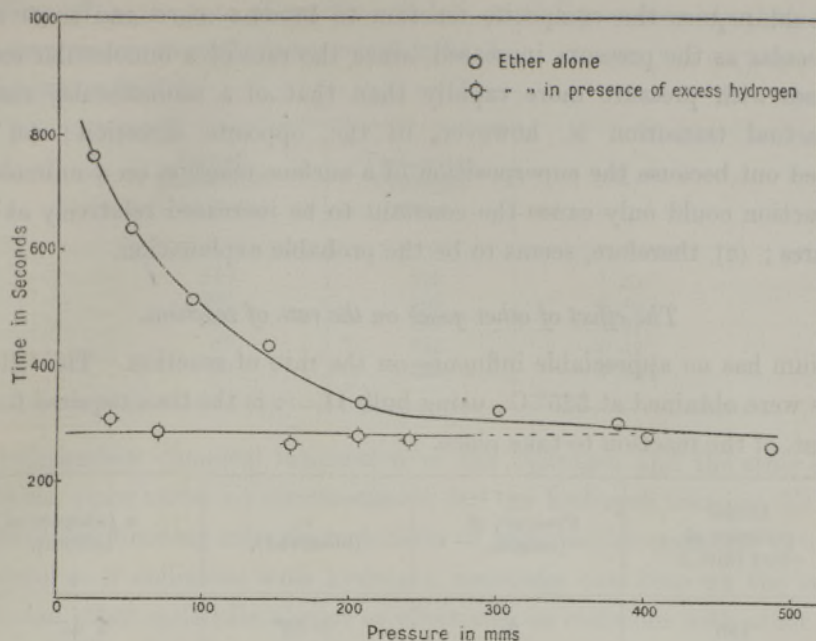


FIG. 1.

The curve is plotted from the values tabulated below, which were obtained in a random order. Bulb 1 was used.

Temperature 525° C.

Initial pressure of ether (millimetres).	Time required for 26·6 per cent. change, i.e., for pressure to increase by 50 per cent.
487	4' 22"
403	4' 40"
382	5' 6"
302	5' 26"
210	5' 33"
145	7' 14"
93	8' 32"
51	10' 36"
25	12' 45"

In seeking an explanation of this curve the following possibilities have to be considered: (a) the falling in the value of the velocity constant is due to the effect predicted by Lindemann's theory—(b) a unimolecular and a bimolecular reaction take place simultaneously—(c) a surface reaction comes in to a relatively much greater extent at low pressures. Neither (b) nor (c) is admissible.

(b) would require the composite reaction to become more and more nearly bimolecular as the pressure increased, since the rate of a bimolecular reaction increases with pressure more rapidly than that of a unimolecular reaction. The actual transition is, however, in the opposite direction; (c) must be ruled out because the superposition of a surface reaction on a unimolecular gas reaction could only cause the constant to be increased relatively at lower pressures; (a), therefore, seems to be the probable explanation.

The effect of other gases on the rate of reaction.

Helium has no appreciable influence on the rate of reaction. The following results were obtained at 525° C., using bulb II. τ is the time required for 26·6 per cent. of the reaction to take place.

Initial pressure of ether (mm.).	Pressure of helium.	τ (observed).	τ (absence of helium).
195	0	5' 52''	5' 45''
293	0	5' 42''	5' 15''
108	200	7' 44''	8' 5''
135	300	7' 35''	7' 12''

Nitrogen has little influence.

Initial pressure of ether.	Pressure of nitrogen.	τ (observed).	τ (absence of nitrogen).
190	292	6' 41''	5' 53''
109	287	7' 45''	8' 3''
71	288	8' 56''	9' 36''

The products of reaction in excess have a slight but definite retarding influence at all pressures of ether.

Initial pressure of ether.	Pressure of reaction products present initially.	τ observed.	τ (no products added).
209	0	5' 50''	5' 35''
237	290	6' 51''	5' 26''
94	290	10' 24''	8' 40''
60	290	14' 10''	10' 10''

None of these effects are very marked. The influence of hydrogen on the reaction is, however, very remarkable. A sufficient excess completely prevents

the falling off in the rate of reaction at low partial pressures of ether. This can be seen clearly from the lower curve in fig. 1.

Temperature 525° C.

Initial pressure of ether (mm.).	Pressure of hydrogen (mm.).	τ .
240	292	4' 31''
206	293	4' 40''
164	287	4' 21''
69	292	4' 47''
39	295	5' 10''

An independent chemical interaction of the hydrogen and the ether seems improbable, since under no circumstances can the hydrogen increase the total rate above the limiting rate characteristic of high partial pressures of ether.

It seems as if collisions with hydrogen molecules can keep up the supply of activated ether molecules almost as effectively as collisions with other ether molecules. Why the effect of hydrogen should be so specific is not evident.

Temperature Coefficient, Heat of Activation.

The following table contains all the important data :—

T (abs.)	τ (seconds).	k_{observed}	$k_{\text{calculated}}$
861°	30	0.0103	0.0099
828.5°	118	0.00262	0.00291
798°	347	0.000892	0.000851
747°	3,634	0.0000852	0.0000861
699°	42,050	0.0000074	0.00000736

τ is the time in seconds required for the initial pressure to increase by 50 per cent. Each value is the average result of at least two determinations at pressures in the steady region. k_{observed} is found from τ by the relation

$k = \frac{1}{\tau} \log_e \frac{188}{188 - 50}$, the total pressure increase being 188 per cent. $k_{\text{calculated}}$

is obtained from the formula

$$\ln k = 26.47 - \frac{53,000}{RT},$$

The heat of activation, 53,000 calories, is not very different from that of propionic aldehyde 55,000 calories. The absolute rates of the two decom-

positions are nearly the same. At 800° abs. k for propionic aldehyde is 2.1×10^{-3} while k for diethyl ether is 0.92×10^{-3} .

In the diethyl ether decomposition the value of k begins to fall at about $1/5$ atmosphere.

At 800° abs. and this pressure the number of molecules, N , which react per second in 1 c.c. is 1.7×10^{15} . The total number of collisions, Z , is $\sqrt{2} \pi \sigma^2 \bar{u} n^2$, where σ , the molecular diameter, is taken as 5×10^{-8} cm., \bar{u} , the root mean square velocity, is 5.19×10^4 cm. per sec., n , the number of molecules per c.c. is 9.23×10^{18} at 800° and 760 mm.

At $1/5$ atmosphere $Z = 2.0 \times 10^{27}$.

If $E = 53,000$ calories, $Ze^{-E/RT} = 6.0 \times 10^{12}$. N , the number reacting, is 1.7×10^{15} or 280 times greater than $Ze^{-E/RT}$.

Introducing the expression for n degrees of freedom, and assuming that at $1/5$ atmosphere there are just enough collisions to account for the number of molecules which react

$$N = \frac{Z \cdot e^{-\frac{53,000 + (\frac{1}{2}n-1)RT}{RT}} \left(\frac{53,000 + (\frac{1}{2}n-1)}{RT} \right)^{\frac{1}{2}n-1}}{\left| \frac{1}{2}n - 1 \right|}$$

$$\frac{N}{Z \cdot e^{-53,000/(1.98 \times 800)}} = \frac{e^{-(\frac{1}{2}n-1)\{33.46 + (\frac{1}{2}n-1)\}} \left(\frac{1}{2}n - 1 \right)^{\frac{1}{2}n-1}}{\left| \frac{1}{2}n - 1 \right|}.$$

If $n = 6$, the right hand side is 85, while if $n = 8$, the right hand side is 402. The experimental value of the left hand side is 280, whence we may conclude that the participation of about 8 degrees of freedom will allow activation by Lindemann's mechanism.

General conclusions.

Whatever views may be held about the interpretation of the results described in this paper, the experimental fact is certain that three reactions—namely, the decomposition of propionic aldehyde, of diethyl ether and of dimethyl ether—appear to be unimolecular at high pressures and assume a bimolecular character at lower pressures.

It will probably be conceded that this proves collisions to be responsible for the activation of the molecules, and since the reactions are not in a strict sense transformations of isolated molecules they might be called quasi-unimolecular at the higher pressures.

These quasi-unimolecular reactions can be explained most simply by assuming that Lindemann's mechanism is operative, an assumption which is supported

by the observations on the influence of hydrogen, but can hardly be regarded as proved.

It is premature to say whether all reactions which obey the unimolecular law are of this kind. The decomposition of acetone is probably quasi-unimolecular, but the decomposition of nitrogen pentoxide still betrays no evidence of dependence on collisions at very low pressures. This can probably be accounted for by assuming that enough degrees of freedom are involved; but also it is true to say that nowhere must more care be exercised than in making inductions about the mechanism of chemical reactions. At the moment it is better to make reactions which are shown to be quasi-unimolecular into a separate class, in which the nitrogen pentoxide decomposition may or may not turn out to be included.

All the effects of foreign gases on the decomposition of diethyl ether can be explained in terms of the suggested mechanism, which allows for the most specific influences, without, however, providing the means by which these may be predicted.

Summary.

The decomposition of gaseous diethyl ether is a reaction which follows the unimolecular law at high pressures, but becomes more nearly bimolecular at lower pressures. The velocity is represented by the equation

$$\ln k = 26.47 - \frac{53,000}{RT}.$$

A sufficient amount of hydrogen completely stops the falling-off in the unimolecular velocity constant at low pressures; helium and nitrogen have little or no influence, while the reaction products in considerable excess have a slight retarding influence.

There are enough collisions to activate the molecules if the energy of activation is assumed to be distributed among about eight degrees of freedom.

These and other "quasi-unimolecular" reactions are most simply explained on Lindemann's theory; further evidence is needed however to confirm this interpretation.

A table is given showing the relation between the complexity of a molecule and the type of mechanism by which it decomposes. Simple molecules usually decompose bimolecularly; more complex ones in a quasi-unimolecular way, as might be expected on theoretical grounds.