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THE REGION OF EXISTENCE OF UNIMOLECULAR REACTIONS

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Rice and Ramsperger[2] and the author[3] have developed theories of unimolecular reactions based upon the assumptions of activated states, produced by collisions, and having specific reaction rates which are functions of their energy contents. If the rate of production of activated molecules is large compared to the rate of reaction, the fraction of the molecules present in the activated states will be very little affected by the reaction, and thus a first order reaction can be supported by a bimolecular activation process. But if the pressure is sufficiently decreased, a point will be reached at which the rate of production of activated molecules is no longer large compared to their rate of reaction, and the calculated first order constant for the reaction will begin to decrease, until eventually it will become proportional to the pressure and the reaction will have become of the second order.

Interpreted in terms of the collisions and the free paths occurring in the gas, this means that at high pressures in unimolecular reactions, where the mean free path is short, the time between an activating collision and a deactivating collision is seldom sufficient for the activated molecule to decompose; hence, when the pressure is decreased slightly, the rate of production of activated molecules is decreased, but the mean life of an activated molecule is increased in the same ratio, since this life is determined almost solely by the mean free path. Now at some pressure very much lower the mean free path will have become very long and most of the molecules which are activated will decompose before they suffer a collision. A decrease in the pressure will decrease the rate of production of activated molecules but it will have a very small effect on their average life, since this is determined chiefly by their specific reaction rates; and it will not increase very much the fraction of the activated molecules which decompose, since this fraction is already close to unity. Therefore the calculated unimolecular constant will decrease with the pressure and the reaction will no longer be first order. In the limit, when the time between collisions is so great that all of the activated molecules decompose, the reaction will, of course, be second order. The early stages of this transition have been observed by Hinshelwood and his students in the decomposition of propionaldehyde,[4] diethyl ether[5] and dimethyl

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[2] Rice and Ramsperger, THIS JOURNAL, **49**, 1617 (1927); **50**, 617 (1928).

[3] Kassel, *J. Phys. Chem.*, **32**, 225 (1928) and article in press.

[4] Hinshelwood and Thompson, *Proc. Roy. Soc.* (*London*), **113A**, 221 (1926).

[5] Hinshelwood, *ibid.*, **114A**, 84 (1927).

ether.[6] Ramsperger[7] has observed a somewhat larger portion of the change from first to second order in the decomposition of azomethane, and his results are in satisfactory agreement with the quantitative theories of Rice and Ramsperger and of the author.[3] The results obtained by Hinshelwood can also be explained by these theories but the test imposed here is not as severe as with azomethane. Nitrogen pentoxide does not exhibit a decrease in rate down to a pressure of at least 0.003 cm.[8] and it has not yet been possible to give a completely satisfactory explanation of this behavior. Ramsperger[9] has shown that azo*iso*propane does not decrease in rate down to a pressure of 0.025 cm.; at this same pressure, the rate of decomposition of azomethane has decreased to from 10 to 20% of its high pressure value, depending upon the temperature. Here, however, the results are in complete agreement with the author's theory. It had proved possible on the basis of this theory to account quantitatively for the results found with azomethane by assuming that of the 24 vibrational degrees of freedom of the molecule, six (one for each hydrogen atom) were of such high frequency that they were essentially frozen-in, and that the other eighteen had frequencies corresponding to 13.57μ. The value used for the diameter for collisional deactivation was 3.16×10^{-8} cm. If it is assumed that of the 60 vibrational degrees of freedom of azo*iso*propane, 14 (corresponding to the 14 hydrogen atoms) are essentially frozen-in, that the other 46 have the same frequency as in azomethane, and that the diameter is 4.47×10^{-8}, the rate will be about 95% maintained at 0.025 cm. and 300°, a temperature slightly greater than any Ramsperger used. This is almost certainly indistinguishable experimentally from complete maintenance, but there would be no difficulty in accounting for more than 95% by increasing the diameter slightly or decreasing the frequency assumed. Presumably, at still lower pressures, the reaction rate would begin to decrease noticeably.

Thus it appears that the theoretical prediction that at low pressures unimolecular reaction rates will decrease is borne out by most of the experimental data, and we may feel confident that the theory of these reactions is essentially correct. The theory of bimolecular reactions which is most generally accepted is that the energy of activation is supplied by the collision, and that the reaction occurs immediately. For these reactions it is an experimental fact that, within a factor of 2 or 3, we have

$$\text{number of molecules reacting} = \text{number entering into collision} \times e^{-E_0/RT}$$

This is frequently interpreted as meaning that when the available energy of the collision is at least E_0, both molecules will react. The author pre-

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[6] Hinshelwood and Askey, *Proc. Roy. Soc.* (*London*), **115A**, 215 (1927).

[7] Ramsperger, This Journal, **49**, 912, 1495 (1927).

[8] Hibben, *Proc. Nat. Acad. Sci.*, **13**, 626 (1927).

[9] Ramsperger, *ibid.*, **13**, 849 (1927).

fers in some cases to regard it as an expression of the fact that the condition for reaction is the acquisition of the energy E_0 by a single bond in the molecule. For, whether the molecule is composed of two atoms or of more than two, the chance that in a collision, selected at random, the particular bond will acquire energy E_0 is $e^{-E_0/RT}$. It would thus seem as if every decomposition should have a bimolecular part, since this mechanism should be operative in the decomposition of azomethane as well as in that of nitrous oxide. Hence the typical decomposition of a polyatomic molecule will be bimolecular at high pressures, with a unimolecular part which is negligible; as the pressure is lowered the unimolecular part will gain in importance, and finally will dominate and then obscure the bimolecular part; as the pressure is still further decreased the rate of this unimolecular part will begin to decrease, until it will finally degrade from a first order reaction to a second order one. The constant for this low pressure second order reaction will, however, be greater than for the high pressure one, and may in the case of complex molecules exceed it by a factor of millions. The values of this constant should in general be sufficient data upon which to classify a second order reaction as the high or low pressure type, in the absence of other information. It is not to be expected that this entire sequence will fall within the range of realizable pressures for every reaction; for some substances the high pressure second order rate will be unobtainable, for others the low pressure one; for simple molecules, especially triatomic ones, even the first order phase may not be reached, and it is possible that in some cases the two second order rates will succeed each other too closely to permit the existence of an interval in which the reaction follows closely a first order law. In the special case of diatomic substances it seems reasonable to suppose that only the high pressure second order rate will exist, and that the reaction will therefore be bimolecular over the entire range of pressures. All of these considerations are to a large extent independent of the detailed theories which have been advanced by Rice and Ramsperger and by the author.[2,3]

It has just been shown that there are theoretical reasons for expecting unimolecular reactions to have a bimolecular part which is dominant at high pressures. This part has hitherto escaped experimental detection and it therefore becomes necessary to calculate the actual bimolecular rates which might be expected. The following list gives all of the unimolecular reactions which are generally accepted, and approximate expressions for their rates.

Acetone[10]	$\ln K = 34.95 - 68{,}500/RT$
Propionaldehyde[4]	$\ln K = 27.93 - 54{,}000/RT$
Diethyl ether[5]	$\ln K = 26.47 - 53{,}000/RT$
Dimethyl ether[6]	$\ln K = 30.36 - 58{,}500/RT$

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[10] Hinshelwood and Hutchinson, *Proc. Roy. Soc.* (*London*), **111A**, 245 (1926).

Pinene[11] $\ln K = 33.21 - 43{,}710/RT$
Azomethane[7] $\ln K = 36.73 - 51{,}200/RT$
Azo*iso*propane[9] $\ln K = 31.36 - 40{,}900/RT$
Nitrogen pentoxide[12] $\ln K = 31.45 - 24{,}700/RT$

It is very easy to see by a short calculation that except for diethyl ether and propionaldehyde the bimolecular mechanism suggested could not contribute appreciably to the total rate; for the contribution to a first order constant would be

$$\ln\text{ (contribution)} = \ln 4\sqrt{\frac{\pi RT}{M}}\,N\sigma^2 - E_0/RT$$

If we take $M = 25$, which is less than its actual value in any of the preceding reactions, $T = 1000°$ K., which is greater than any actual value used, $\sigma = 10^{-7}$ cm., and N, the number of molecules per cc., as 2×10^{19}, which corresponds to a pressure of nearly an atmosphere even at room temperature, we find the contribution is given by

$$\ln\text{ (contribution)} = 25.12 - E_0/RT$$

This is a greater contribution than is actually made in any of these reactions. If we repeat the calculation for diethyl ether, using the rather large molecular diameter $\sigma = 10^{-7}$ cm., we find that

$$\ln\text{ (contribution)} = 23.61 - E_0/RT$$

This is only about $^1/_{17}$ of the observed unimolecular rate; this is at a pressure of one atmosphere, where the effect would be greater than in any actual experiment. Actually, the unimolecular constant is still increasing somewhat at 500 mm., beyond which the measurements have not been made, but it is impossible to tell whether this is due to the approach of the unimolecular part of the reaction to its full value, or to the bimolecular part. For all of the other reactions listed, the bimolecular part would be entirely inappreciable at pressures of an atmosphere or less.

In a diatomic molecule there is only one bond, and unless we admit the possibility of electronic activation all of the internal energy is stored in the same place. Hence it would seem that decomposition is constrained to occur at collision, and that the reaction must be quite exactly bimolecular. But if the molecule is triatomic or still more complex, the reaction should contain a unimolecular portion. Although there is no basis for making precise predictions, it would be expected that this unimolecular portion would be relatively less important in the simpler molecules, and in agreement with this it is found that the decompositions of such substances as nitrous oxide[13] and ozone[14] are definitely bimolecular. The

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[11] Smith, This Journal, **49**, 43 (1927).

[12] Daniels and Johnston, *ibid.*, **43**, 53 (1921).

[13] Hinshelwood and Burk, *Proc. Roy. Soc.* (*London*), **106A**, 284 (1924).

[14] Warburg, *Ann. Physik*, 9, 1286 (1902); Clement, *ibid.*, **14**, 341 (1904); Perman and Greaves, *Proc. Roy. Soc.* (*London*), **80A**, 353 (1908); Jahn, *Z. anorg. Chem.*, **48**, 260 (1906); Clarke and Chapman, *J. Chem. Soc.*, **93**, 1638 (1908); Chapman and Jones, *ibid.*, 97, 2463 (1910); Wulf and Tolman, This Journal, **49**, 1183 (1927).

most complex molecule known to the author to decompose according to a second order law is acetaldehyde.[15] If it is attempted to regard this reaction as being the low pressure phase of a unimolecular reaction, difficulties are encountered. Unless the frequencies of all the oscillators are made extremely high, the total number of oscillators must be kept very small, and the diameter of the molecule less than is usually necessary to make the reaction bimolecular at a pressure of one atmosphere. Then, to account for the results with propionaldehyde, where the reaction is unimolecular at high pressures, it is necessary to make unreasonably great increases either in the number of oscillators, the associated wave length or the molecular diameter. Even if this is done, there are two remaining difficulties; the first is that the effect of hydrogen in maintaining the unimolecular rate, which was found for propionaldehyde, just as for the ethers, is absent in the case of acetaldehyde;[16] the other is that the reaction is not quite bimolecular; the plot of the reciprocal of the "half-life" against the pressure gives a straight line, as it should, but this line does not pass through the origin; instead it has a positive intercept on the half-life axis.[17]

All of these difficulties are overcome by regarding the decomposition of acetaldehyde as being composed of a unimolecular contribution, produced by the same sort of mechanism as in the case of propionaldehyde, and a bimolecular contribution, produced by the immediate reaction of molecules at collisions, the latter being of greater importance at pressures above 100 mm. We may then write

$$-\frac{\mathrm{d}n}{\mathrm{d}t} = an^2 + bn$$

The integral of this is

$$t = \frac{1}{b}\ln\frac{(an + b)\, n_0}{(an_0 + b)\, n}$$

and hence the half-life is given by

$$t_{1/2} = \frac{1}{b}\ln\frac{an_0 + 2b}{an_0 + b}$$

When an_0 is large compared to b (that is, when the bimolecular contribution is dominant), this may be written

$$t_{1/2} = \frac{1}{b}\left[\frac{b}{an_0 + b} - \frac{1}{2}\left(\frac{b}{an_0 + b}\right)^2 + \ldots\right] \cong \frac{1}{an_0 + b}$$

and hence

$$1/t_{1/2} \cong an_0 + b$$

It is found that the plot of $1/t_{1/2}$ against n_0 actually deviates but slightly from a straight line over its entire course. In the accompanying figure

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[15] Hinshelwood and Hutchison, *Proc. Roy. Soc.* (*London*), **111A**, 380 (1926).

[16] Hinshelwood and Askey, *ibid.*, **116A**, 163 (1927).

[17] Hinshelwood and Hutchison, *ibid.*, **111A**, 382 (1926).

the points represent Hinshelwood and Hutchison's measurements at 518°, and the line is the calculated curve for $a = 5.1 \times 10^{-6}$, and $b = 4.2 \times 10^{-4}$, the time being measured in seconds and the pressure in mm. This value for the bimolecular constant is only slightly less than that which Hinshelwood and Hutchison reported from their uncorrected measurements. If it is assumed that the unimolecular reaction has the same temperature coefficient (except for the omission of the factor $T^{1/2}$, which is proportional to the number of collisions) as the bimolecular reaction, then the unimolecular part is given by

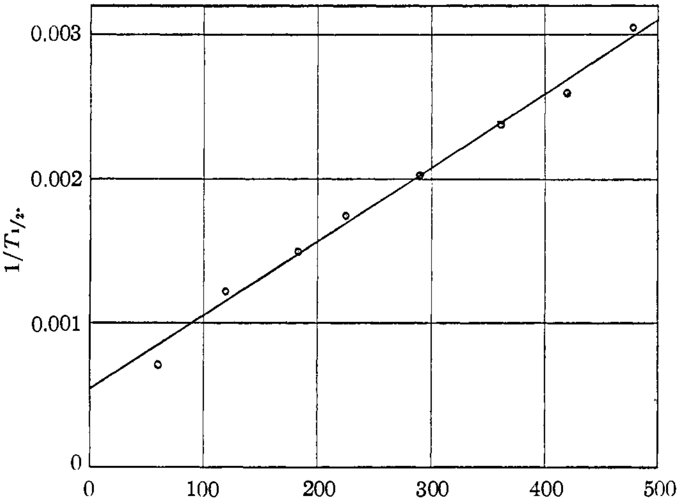

Fig. 1.

$$\ln K = 21.18 - 45500/RT$$

On the mechanism presented the temperature coefficients would be the same, but this cannot be regarded as certain in the absence of experimental evidence. For the two other cases in which pairs of similar substances have been studied (dimethyl ether–diethyl ether and azomethane–azo*iso*-propane) the simpler molecule has given larger values of E_0 and of A, in $K = Ae^{-E_0/RT}$; here, when it is assumed that the two temperature coefficients are the same, E_0 and A for the unimolecular phase of the acetaldehyde decomposition are both less than for propionaldehyde. There is no reason apparent why this should not be the case, but the matter can only be settled by experiments over a range of pressures and temperatures.

If it is assumed that the unimolecular part of the decomposition is actually given by

$$\ln K = 21.18 - 45500/RT$$

it is possible to make calculations on the maintenance of this reaction rate, with various numbers of oscillators, of various frequencies. It is thus easy to show that down to pressures of about 50 mm. at least the rate would be maintained. It would be possible to account for maintenance at much lower pressures if the need arose.

It is not intended to imply that in all bimolecular reactions the reaction occurs entirely, or even chiefly, through collisions which cause one of the colliding molecules to dissociate; this process should always occur, but it may contribute very little to the total reaction rate in special cases; thus the heat of dissociation of hydrogen iodide is certainly greater than 60,000 cal., while the critical energy, calculated from the temperature coefficient of the decomposition, is but 44,000 cal. It thus seems likely that in this case the reaction which actually occurs at collision is

$$\mathrm{HI} + \mathrm{HI} = \mathrm{H_2} + \mathrm{I_2} \tag{1}$$

and that the parallel reaction

$$\mathrm{HI} + \mathrm{HI} = \mathrm{H} + \mathrm{I} + \mathrm{HI} \tag{2}$$

does not contribute much to the total rate. If the necessary condition for the first reaction is that the collision shall exceed a certain critical "violence," then the rate due to reaction (1) will be approximately $N_c e^{-44,000/RT}$, while that due to reaction (2) will be about $N_c e^{-60,000/RT}$, where N_c is the number of collisions. It is evident that the first rate would be extremely large compared to the second. Indeed, it may actually be found that with most simple chemical substances the dominant portion of the reaction is of the type (1). In fact, it has been recently suggested by Kornfeld[18] that the explanation of the tendency of simple substances to decompose according to bimolecular laws and of more complex molecules to exhibit unimolecular decompositions is to be found, not in the numerous degrees of freedom of the latter molecules, but in the fact that the critical energy in processes which produce free atoms is much greater than in those which do not, and that reactions of type (2) are thus handicapped.

In any actual gaseous decomposition all of these mechanisms and possibly others should be operative at the same time and it is in general impossible to predict which of them will be dominant under given conditions. On the other hand, when any single reaction has been studied over a great enough range of temperatures and pressures, it may be found possible to decide, with a considerable degree of certainty, what processes are chiefly responsible for the reaction. Thus, in the case of acetaldehyde, if it is found that the unimolecular reaction has the same temperature coefficient as the bimolecular one, it would seem reasonable to conclude that the dominant bimolecular process is of type (2), while if the unimolecular part of the reaction has a larger temperature coefficient, then the dominant

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[18] Kornfeld, *Z. physik. Chem.*, **131**, 97 (1927).

bimolecular process must be of a different type, and (1) would be a reasonable guess. In no case, however, are any of these mechanisms to be considered as more than tentative hypotheses, since it is impossible to determine molecular processes from a study of the kinetics of a reaction.

The most important problem in the field of homogeneous gas reactions has been, not to unravel the precise mechanism of any single reaction, but to account for the order of magnitude of the rates of unimolecular reactions and to interpret both unimolecular and bimolecular reactions by means of a single, coherent scheme. Some few minor difficulties, chiefly associated with nitrogen pentoxide, still remain, but the method of solution of the problem has been indicated, and the solution itself, at least in its main features, has been given by the work of Lindemann, Christiansen, Hinshelwood, Rice, Ramsperger, and others.[3]

It may be pointed out that the table of reaction rates presented above is in disagreement with the formula first presented by Dushman[19]

$$K = \nu e^{-\frac{Nh\nu}{RT}}$$

In the following table the values of ln A calculated from this formula are compared with those found experimentally.

	ln A (calcd.)	ln A (obs.)		ln A (calcd.)	ln A (obs.)
Acetone	34.22	34.95	Pinene	33.77	33.21
Propionaldehyde	33.98	27.93	Azomethane	33.93	36.73
Diethyl ether	33.96	26.47	Azo*iso*propane	33.70	31.36
Dimethyl ether	34.06	30.36	Nitrogen pentoxide	33.20	31.45

The fair agreement obtained in the cases of acetone, pinene and nitrogen pentoxide loses any significance it might have had when the wide range of variation of the observed values is compared with the relatively constant computed values. Also, the statement made by Hinshelwood[10,5,6] that at temperatures at which E_0/RT is the same, all unimolecular reactions have about the same rates is seen to be only very roughly correct; for this is equivalent to saying that ln A is a constant for all reactions, while actually it is greater by 10 units for azomethane than it is for diethyl ether, corresponding to a difference in reaction rates at corresponding temperatures of more than 20,000-fold.

Summary

The typical homogeneous gaseous decomposition passes through three stages: at high pressures it is second order, due to reaction occurring at collisions; at lower pressures the rate becomes first order, the dominant factor being spontaneous decomposition of activated molecules, which are produced by collisions rapidly enough to maintain essentially the Maxwell-Boltzmann quota; at rather low pressures the reaction is again second order, though the rate constant is greater than for the high pressure stage;

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[19] Dushman, This Journal, 43, 397 (1921).

in this stage of the reaction nearly all of the activated molecules decompose, since collisions, which could cause deactivation, have now become infrequent. The decomposition of acetaldehyde is an example of a reaction in the process of transition from the high pressure bimolecular stage to the unimolecular stage; the decomposition of azomethane indicates the transition from unimolecular to low pressure bimolecular.

There are several possible types of bimolecular reactions and in some cases it may be found possible to decide, by methods which have been indicated, to which of them any particular reaction belongs; of course, in general, all of the types proceed together, but one of them may account for all but a negligible fraction of the total reaction.

The formula for the velocity of unimolecular reactions proposed by Dushman is not in agreement with experimental data; indeed, the rates of these reactions have a much greater range of variation than is permitted by this formula.

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[CONTRIBUTION FROM THE PHYSICAL CHEMICAL LABORATORY OF McGILL UNIVERSITY]

SULFUR DIOXIDE AND ITS AQUEOUS SOLUTIONS. I. ANALYTICAL METHODS, VAPOR DENSITY AND VAPOR PRESSURE OF SULFUR DIOXIDE. VAPOR PRESSURE AND CONCENTRATIONS OF THE SOLUTIONS

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The following is the first of two papers dealing with some of the physical properties of various phases of the two component system sulfur dioxide–water. The investigation had its beginning in an attempt to measure the conductivities of concentrated aqueous solutions of sulfur dioxide.

It was soon found, however, that other properties of sulfur dioxide had to be investigated before the conductivity could be measured. From some of the results obtained, these preliminary investigations proved to be of at least as great an interest as the main one and consequently the present paper is devoted solely to these. This work may be conveniently divided into the following topics: Purification of Sulfur Dioxide, Analysis of Sulfurous Acid, Vapor Density Determinations, Vapor Pressures of Pure Sulfur Dioxide and its Aqueous Solutions, Concentrations in the Two Liquid Phase System, Sulfur Dioxide–Water.

A second paper, dealing with the conductivities and containing a theoretical discussion of the equilibria involved, will follow.

Purification of Sulfur Dioxide

It was found that particularly pure liquid sulfur dioxide could be obtained commercially. In order to test the gas for sulfur trioxide, it was